THE PROTONATION OF $\eta^4$-DIENE COMPLEXES OF TRANSITION METALS

A thesis submitted for the Degree of Doctor of Philosophy at the Australian National University

by

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The work described in this thesis, except where otherwise stated, is the candidate's own. It was carried out at the Australian National University, from 1981 - 1984.

S. PELLING

[Signature]
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SOME ABBREVIATIONS

in complexes:

\[ C_6H_6 = \eta^6\text{-benzene} \]
\[ C_6H_3Me_3 = \eta^6\text{-}1,3,5\text{-trimethylbenzene (mesitylene)} \]
\[ C_6Me_6 = \eta^6\text{-hexamethylbenzene} \]
\[ o-C_6H_4Me_2 = \eta^6\text{-}o\text{-xylene} \]
\[ C_6H_2Me_4 = \eta^6\text{-durene} \]
\[ C_5H_5 = \eta^5\text{-cyclopentadienyl} \]
\[ C_5Me_5 = \eta^5\text{-pentamethylcyclopentadienyl} \]
\[ C_5Me_4Et = \eta^5\text{-ethyltetramethylcyclopentadienyl} \]

Et = ethyl
Me = methyl
t-Bu = t-butyl
Ph = phenyl
DME = 1,2-dimethoxyethane
acac = acetylacetonate
pz = pyrazolate
ddbo = 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane
dppe = bis(diphenylphosphino)ethane
dmpe = bis(dimethylphosphino)ethane
ether = diethylether
TMS = tetramethylsilane
THF = tetrahydrofuran
sp = (o-vinylphenyl)-diphenylphosphine
NBD = norbornadiene
diCp = dicyclopentadiene
s = singlet

d = doublet (dd = doublet of doublets)

t = triplet

q = quartet

w = weak

br = broad

m = multiplet

δ = chemical shift

J = coupling constant

η = hapto

ν = stretching frequency

nmr = nuclear magnetic resonance

ppm = parts per million
ABSTRACT

The neutral 1,3-diene osmium complexes $\text{Os(}\eta^6\text{-arene})(\eta^4\text{-diene})$ (diene = 1,3-cyclohexadiene, 1,3,5-trimethyl-1,4-cyclohexadiene, 2,3-dimethylbutadiene, 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]-octane (ddbo); arene = $\text{C}_6\text{H}_6$, $\text{C}_6\text{H}_3\text{Me}_3$) and 1,3-diene iridium complexes $\text{Ir(}\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-diene})$ (diene = 1,3-cyclohexadiene, 2,3-dimethylbutadiene, (ddbo), R = H, CH$_3$) are readily protonated with HPF$_6$ to give monoprotonated complexes $[\text{Os(}\eta^6\text{-arene})(\eta^4\text{-diene})\text{H}]\text{PF}_6$ and $[\text{Ir(}\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-diene})\text{H}]\text{PF}_6$ respectively, which have been shown by nmr and infrared spectroscopy to adopt a diene terminal-hydride ground state structure. In contrast, protonation of the 1,3-diene complexes $\text{Rh(C}_5\text{Me}_5)(\eta^4\text{-diene})$ (diene = 1,3-cyclohexadiene, 2,3-dimethylbutadiene, (ddbo) and of $\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{ddbo})$ gives fluxional complexes which appear to adopt an agostic ground state structure. Most of the protonated Os, Ru, Ir and Rh complexes react with small ligands to give $\eta^3$-allyl adducts. The 1,5-cyclooctadiene complexes $\text{Os(}\eta^6\text{-arene})(1,5\text{-C}_8\text{H}_{12}^1$ (arene = $\text{C}_6\text{H}_6$, $\text{C}_6\text{H}_3\text{Me}_3$) react with HPF$_6$ to give $[\text{Os(}\eta^6\text{-arene})(\text{C}_8\text{H}_{12})\text{H}]\text{PF}_6$.

The dicyclopentadiene complexes $\text{Os(C}_6\text{H}_3\text{Me}_3)(\text{C}_10\text{H}_{12}), \text{M(C}_5\text{R}_5)(\text{C}_10\text{H}_{12})$ (M = Rh, R = H, CH$_3$; M = Ir, R = Me) react with HPF$_6$ to give agostic complexes such as $[\text{Os(C}_6\text{H}_3\text{Me}_3)(\text{C}_{10}\text{H}_{13})]\text{PF}_6$. The norbornadiene complexes $\text{Os(C}_6\text{H}_3\text{Me}_3)(\text{C}_7\text{H}_8)$ and $\text{M(C}_5\text{Me}_5)(\text{C}_7\text{H}_8)$ (M = Rh, Ir) protonate initially at the metal; the Rh and Ir complexes isomerize in solution to give vinylcyclopentenyl complexes $[\text{M(C}_5\text{Me}_6)(\text{C}_7\text{H}_9)]\text{PF}_6$. These complexes react with LiAlH$_4$ to give neutral vinylcyclopentene complexes $\text{M(C}_5\text{Me}_5)(\text{C}_7\text{H}_{10})$. 
The bis-\( \eta^2 \)-ethylene complexes \( \text{Ru}(C_6\text{Me}_6)(C_2\text{H}_4)_2 \), \( \text{Rh}(C_5\text{Me}_5)(C_2\text{H}_4)_2 \) protonate with HPF\(_6\) to give fluxional agostic complexes such as \( [\text{Ru}(C_6\text{Me}_6)(C_2\text{H}_4)(u-H-C_2\text{H}_4)]\text{PF}_6 \). In contrast \( \text{Os}(C_6\text{H}_3\text{Me}_3)(C_2\text{H}_4)_2 \) reacts with HPF\(_6\) to give a fluxional bis-olefin hydride complex \( [\text{Os}(C_6\text{H}_3\text{Me}_3)(C_2\text{H}_4)_2\text{H}]\text{PF}_6 \). This reacts with \( L = t\text{-BuNC} \) or \( \text{P(OMe)}_3 \) to give ethyl complexes \( [\text{Os}(C_6\text{H}_3\text{Me}_3)(C_2\text{H}_4)(C_2\text{H}_5)L]\text{PF}_6 \).
CHAPTER 1

GENERAL INTRODUCTION

In recent years the study of olefin and poly-olefin complexes of low-valent transition metals, particularly of iron, has developed extensively, resulting in a rich and diverse chemistry.\(^1\) Of fundamental importance to the elucidation of the reactivity of such complexes is an understanding of their reactions with simple electrophiles, particularly the proton. It is thus not surprising that the protonation of transition metal olefin complexes has been the subject of considerable investigation.

This thesis describes the protonation of a number of \(\eta^4\)-diene and bis-\(\eta^2\)-ethylene complexes of transition metals. Many of these complexes are fluxional, involving migration of the proton from the metal to the olefin and vice versa. A study of the fluxional behaviour is thus directly relevant to the understanding of two important types of reaction, the olefin insertion reaction (migration of a metal hydride proton from the metal onto one carbon of an olefin ligand) and the \(\beta\)-hydrogen elimination reaction (migration of a \(\beta\)-hydrogen from an alkyl ligand to the metal, and liberation of the resulting alkene). These two reaction types are central to a number of catalytic processes.\(^97\) They often occur in the same catalytic cycle, the cycle involving for example, attachment of an olefin to a metal hydride catalyst, insertion of the olefin to give a metal alkyl species, and ultimately regeneration of the metal hydride catalyst by \(\beta\)-elimination. These steps are illustrated by a well studied procedure, the dimerization of ethylene to butene.\(^97\) The active
catalytic species in this process is believed to be a metal hydride complex (metal = Ni, Rh, for example). Insertion of ethylene into the M-H bond is followed by insertion of ethylene into the M-C\textsubscript{2}H\textsubscript{5} bond. Butene is then released by \textbeta-\text{hydrogen elimination}, regenerating the M-H catalytic species (see Scheme).

\textbf{SCHEME}: The dimerization of ethylene to butene.
This chapter reviews in Section 1.1 the literature concerning the protonation of \((\eta^4\text{-diene})\) complexes of transition metals, being particularly relevant to the new work reported in subsequent chapters. There is however, a substantial body of research on the protonation of other types of olefin-transition metal complexes.\(^2\) Section 1.2 is a general discussion of the properties of M-H-C agostic bridging hydride systems, and Section 1.3 discusses results (largely unpublished) obtained by other workers in our research group, on the protonation of \(\text{Ru}(\eta^6\text{-arene})(\eta^4\text{-diene})\) complexes.
1.1 THE PROTONATION OF (n^4-DIENE) COMPLEXES AND BIS-n^2-ETHYLENE COMPLEXES OF TRANSITION METALS

Protonation of Fe(n^4-diene)(CO)_3 complexes with acids such as HCl that contain a strongly coordinating anion was shown to give rise to complexes such as the (n^3-allyl)(chloro) complex 1; 1 appears to adopt the more stable syn configuration. 3,4,5.

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \quad \text{HCl} \rightarrow \quad \text{(CO)}_3\text{Fe} \quad \text{Cl} \\
& \quad 1
\end{align*}
\]

The protonation reaction of Fe(n^4-diene)(CO)_3 complexes with acids, e.g., HPF_6, HBF_4, containing only weakly coordinating anions are more complex. Early work by Davison et al. 6 suggested that in strong acid media, metal hydride complexes may be formed, but subsequent workers 7 observed only the formation of n^3-allyl complexes on treatment of solutions of acyclic diene-iron tricarbonyl complexes with HBF_4. Kaesz et al. 8 carefully examined the protonation of solutions of iron tricarbonyl complexes of butadiene, 1-methylbutadiene, 1,4-dimethylbutadiene, 1,3-cyclohexadiene and 1,3-cycloheptadiene at -78°C, with strong acids. They found that, as had been reported, 7 treatment of Fe(butadiene)(CO)_3 with one equivalent of acid (e.g., HSO_3F) in liquid SO_2 solution gave 2. However, treatment with excess acid gave a different, fluxional metal hydride complex. Similar results were obtained on protonation of complexes of the other dienes.
investigated. It was proposed that the complexes produced on addition of excess acid were diprotonated methallyl complexes such as 3. Solutions of these complexes were unstable above -20°C and attempts to isolate the product of the protonation of Fe(butadiene)(CO)₃ with excess HBF₄ at room temperature, resulted only in isolation of [Fe(C₄H₇)(CO)₄]BF₄, 4. The results of Kaesz et al. were re-examined and it was suggested that they were more reasonably explained in terms of one mono-protonated species, namely the C-π complex 5. Subsequently, on the basis of ¹³C nmr spectroscopic results (in particular a value of 78-88 Hz for the geminal C₁-Hₐ coupling in the ¹³C nmr spectrum
of the cyclohexadienyl complex 6), it was further suggested\(^\text{12}\) that the proton attached to the metal may in fact bridge between the metal and a dienyl carbon atom. This suggestion is supported by the work of Olah \textit{et al.},\(^\text{22}\) who found that the carbon atom bonded to the metal in 5 gave rise to a triplet of doublets in the proton coupled \(^{13}\text{C}\) nmr spectrum \((J = 146.5\ \text{and}\ 73.7\ \text{Hz})\), indicating coupling to two equivalent protons and a third different proton. The value of 73.7 Hz is too large to be explained in terms of a two-bond coupling as would be required in the proposed \(\sigma-\pi\) structure of 5. However, it is much smaller than the value of 146.5 Hz for the other two protons bonded to the same carbon, suggesting that the C-H bond is weakened due to bonding to the iron atom.

\text{Ittel and coworkers have extensively investigated the protonation of several} \(\eta^4\)-dienen iron tris(phosphite) complexes and have obtained strong evidence for the existence of bridging hydride species.\(^\text{13-16}\) The protonation of acyclic diene iron tris(phosphite) complexes gave similar results to the protonation of the corresponding tricarbonyl complexes as discussed above. However, because the diene \(\text{Fe(P(OMe)_3)_3}\) complexes are much stronger bases than their tricarbonyl counterparts,
the protonated tris(phosphite) complexes are rather more stable than
the protonated tricarbonyl complexes, and can be isolated as solids.

Protonation of \((\eta^4-2,3\text{-dimethylbutadiene})\text{Fe}(\text{P(OMe)}_3)_3\) with HBF\(_4\) gave
a mono-protonated fluxional complex, the \(^1\text{H} \text{nmr} \) spectrum of which
corresponds to structure 7, except that due to an exchange involving
reversible cleavage of the Fe-H bond, and rotation of the methyl
group about the C\(_1\)-C\(_2\) bond, protons \(H_a\), \(H_b\) and \(H_c\) were equilibrated
and appeared as a three-proton multiplet at \(\delta=5.29\).\(^{14}\) Cooling to \(-90^\circ\text{C}\)
slowed the exchange and the three-proton multiplet was replaced by
three one-proton multiplets \([\delta=14.8(H_a), \delta=2.58 \text{ and } \delta=2.30 (H_b \text{ and }
H_c)]\). The high-field one-proton multiplet was assigned to a proton
\((H_a)\) that is attached to the Fe atom, and thus structure 7 was strongly
implicated as the ground state structure.

In similar fashion protonation of cyclic diene complexes gave mono-
protonated fluxional \(\eta^3\)-allyl complexes in which one endo proton,
attatched to a carbon atom adjacent to the allylic region of the ligand
is also bonded to the metal.\(^{14}\) For example, the \(^{13}\text{C} \text{nmr} \) spectrum
of \([\text{Fe(cycloheptenyl})(\text{P(OMe)}_3)_3]\text{BPh}_4\), \(8\), at \(-80^\circ\text{C}\) in the slow exchange
limit showed a doublet of doublets at \(\delta=7.9\) for C\(_1\), with a J(C-H)
value of 80 Hz for the endo proton attached to the metal, somewhat lower than the J value for the exo proton on the same carbon (140 Hz). The low value is indicative of C-H bond weakening commensurate with an M-H-C interaction.

The existence of a bridging M-H-C interaction was conclusively demonstrated by a neutron diffraction structure study of [Fe(cyclooctenyl)(P(OMe)₃)₃]BF₄. The structure showed an unusually long Fe-H bond length of 1.874 Å and an unusually long C₁-Hₐ bond length of 1.164 Å. These are longer than typical Fe-H distances of 1.5 - 1.6 Å (e.g. FeH₂(CO)₄ has an Fe-H bond length of 1.556 Å, and FeH₂[P(Ph)(OEt)₂]₄ has an Fe-H bond length of 1.51 Å) and C-H distances of 1.10 Å (as evidenced by all other C-H distances in 9).

It has been suggested that a similar M-H-C interaction may occur in the analogous Ru complexes, [RuH(cyclooctadienyl)L₃]PF₆ (L = a series of phosphorus ligands).
The product of protonation of solutions of Fe(norbornadiene)(CO)_3 with fluorosulphonic acid in liquid SO_2 has been described as a diene hydride complex \(10, 19\) or a \(\sigma-\pi\) species \(11, 10, 20\). However, the presence of a triplet hydride resonance \(J(H-H) = 13\) Hz in the proton nmr spectrum and a doublet of doublets in the \(^{13}\text{C}\) nmr spectrum (\(\delta 39.8, J(C-H) = 177\) and 38 Hz; assigned to C_2/C_6) suggest that the complex may in fact be more accurately represented as a pair of rapidly equilibrating M-H-C structures, \(12\).
Similarly, the product of the protonation of Fe(cyclobutadiene)(CO)$_3$ with FSO$_3$H has been described by Olah as a σ-π complex; however the appearance of a highfield doublet ($\delta$=11.16, J(H-H) = 29 Hz)(H$_a$) in the $^1$H nmr spectrum of 13, and a doublet of doublets ($\delta$=9.0, J(C-H) = 191 and 81 Hz)(C$_1$) in the $^{13}$C nmr spectrum, strongly suggest 13 has a bridging hydride structure.

Protonation of Fe(C$_6$Me$_6$)(1,3-cyclohexadiene), 14, with HPF$_6$ gave a fluxional product, 15. However whether or not 15 adopted a bridging hydride structure as its limiting structure, was uncertain, as at low temperature, a slow exchange $^1$H nmr spectrum could not be attained.

There is thus substantial evidence for the existence of a bridging hydride M-H-C interaction in protonated Fe(η$^4$-diene)(L)$_3$(L = CO, phosphite), complexes. A similar interaction has also recently been shown to exist in manganese cyclohexenyl and substituted cyclohexenyl tricarbonyl complexes studied by Brookhart et al. and by Pauson et al.

Thus, reduction of [Mn(C$_6$H$_6$)(CO)$_3$]PF$_6$, 16, with two equivalents of Li$^+$Et$_3$BH$^-$ gave [Mn(1,3-cyclohexadiene)(CO)$_3$]$^-$, 17, which on protonation with H$_2$O gave the neutral bridging hydride cyclohexadienyl complex 18.
Complex 18 is fluxional and in solution exhibits three distinct degenerate modes of isomerization (Scheme 1:1). These three modes

are as follows:-

(a) The alternative coordination of C-H bonds adjacent to the allylic unit, via a 16e allyl intermediate (Equation 1:1). This is a low energy process ($\Delta G^\circ = 34.8 \text{ kJ mol}^{-1}$) involving reversible cleavage of the M-H bond. At 0°C the exchange is fast, resulting in the equilibration of $H_a$ and $H_b$ in the $^1H$ nmr spectrum. At -100°C an
nmr spectrum corresponding to the limiting ground state isomer 18 can be frozen out.

(b) A degenerate [1,2] metal migration round the ring via a diene hydride intermediate (Equation 1:2). The energy of this process is higher than (a) above (ΔG‡ = 64.5 kJ mol⁻¹); it is fast at 120°C and slow at 0°C. The process involves reversible cleavage of the C-H bond. Together with mode (a), the metal migration results in the averaging of the three endo hydrogens, and separately, of the 6 exo and olefinic hydrogens.

(c) Mutual exchange of the three CO ligands.

These three modes are reflected in the variable temperature ¹H and ¹³C nmr spectra of 18. Whether or not the η³-allyl and diene-hydride intermediates are in fact intermediates or are transition states is not known. Similar bridging hydride interactions have been observed in the species formed on reducing and protonating methyl-substituted arene manganese cations. The crystal structure of Mn(6-endo-methylcyclohexenyl)(CO)₃ has been determined and the existence of a bridging hydride group was confirmed by unusually long Mn-H (1.84 Å) and Mn-C(2.34 Å) distances for the M-H-C unit.

In contrast to the manganese complex 18, the rhenium complex Re(C₆H₆)(C₆H₄)H, 18A, was not fluxional and was shown by ¹H and ¹³C nmr spectroscopy and X-ray crystallography to be a diene hydride complex. The hydride was not observed directly in the crystal structure study but it gave rise to a resonance at δ-6.10 in the ¹H nmr spectrum of the complex. The nmr spectroscopic and the crystallographic data indicated that the 1,3-cyclohexadiene ligand was bonded symmetrically
to the metal. The infrared spectrum of 18A showed a band at 1,960 cm\(^{-1}\), assignable to \(\nu\text{M-H}\).

The protonation of \(\eta^4\)-diene complexes of the cobalt triad, particularly of the type \(\text{M(C}_5\text{R}_5)(\eta^4\text{-diene})\) (\(\text{M=Rh, Ir, R=H, alkyl group}\)) has been the subject of limited investigation.

The product of the protonation of a CDCl\(_3\) solution of \(\text{Ir(C}_5\text{H}_5)(\text{butadiene})\) was described, on the basis of its proton nmr spectrum as the fluxional \(\eta^3\)-allyl complex 19.\(^{29}\) The spectrum did not apparently change on
cooling the solution. In contrast the iridium ($\eta^3$-2,3-dimethylbutenyl) complex 20 has been assigned, a bridging hydride structure.\textsuperscript{54} The complex Co(H)(2,3-dimethylbutadiene)(PPh\textsubscript{3})\textsubscript{2} appears to be structurally similar to 20 and may also adopt a similar structure\textsuperscript{55}.

Protonation of Rh(C\textsubscript{5}H\textsubscript{5})(1,3-cyclohexadiene) with HPF\textsubscript{6} resulted in a mono-protonated complex of empirical formula \([\text{Rh}(C_5H_5)(C_6H_9)]PF_6\).\textsuperscript{31} Although a limiting $^1\text{H}$ nmr spectrum could not be reached on cooling solutions to -50°C, it was postulated that the product was the diene hydride complex 21, on the basis of comparison with the corresponding iridium complex 24. The fast exchange proton nmr spectrum of 21 is consistent with a ground state diene hydride structure 21 undergoing rapid equilibration of two endo protons $H_n$ and the hydride via the allylic intermediate 22. However, the bridging hydride complex 23 would be expected to show the same fast exchange spectrum (c.f. Brookhart et al.'s results\textsuperscript{25}). In fact 23 is probably the correct assignment of the ground state structure, on the basis of our results for the corresponding ($\eta^5$-C\textsubscript{5}Me\textsubscript{5}) rhodium complex (see Chapter 3).
The iridium complex 24, formed on protonation of Ir(C₅H₅)(1,3-cyclohexadiene), is fluxional. A limiting ¹H nmr spectrum corresponding to a diene-hydride structure, was obtained at -20°C, indicating that this, rather than the bridging hydride structure, is favoured in the ground state.

Lewis et al. have also investigated the protonation of M(C₅H₅)(1,5-cyclooctadiene) (M = Rh, Ir) complexes. In trifluorocetic acid, Rh(C₅H₅)(1,5-COD) (COD = cyclooctadiene) is protonated to give an equilibrium mixture of three different species, 25-27 (Scheme 1:2).
In contrast, protonation of Ir(C$_5$H$_5$)(1,5-COD) gave a diene hydride complex 28, which Lewis et al.\textsuperscript{32} identified as incorporating a 1,3-diene ligand. Complex 28 underwent slow equilibration of the hydride and the methylene protons. This process was too slow to be detected on the nmr time scale but evidence for its existence came from the reaction of Ir(C$_5$H$_5$)(1,5-COD) with CF$_3$COOD, the product of which was 29, into which four deuterium atoms were incorporated in the *endo* methylene positions of the COD ligand.

Irradiation of [Rh(1,5-COD)Cl]$_2$ with isopropyl magnesium bromide and 1,3 cyclohexadiene gave the complex 30. This complex was considered to be in equilibrium with the diene-hydride 31.\textsuperscript{33,34} Similarly, treatment of [Ir(1,5-COD)Cl]$_2$ with C$_3$H$_7$MgBr and 1,3 cyclohexadiene gave 32, which was shown by variable temperature $^1$H nmr
spectroscopy to be in equilibrium with \( \text{33, 34, 35} \). In both the complexes there was no evidence of the 1,5-COD ligand being involved in the exchange process.

The protonation of \( \text{Rh(C}_5\text{H}_5\text{)(norbornadiene)} \) with \( \text{CF}_3\text{COOH} \) has also been investigated.\(^{32}\) The product was identified by \( ^1\text{H NMR} \) as \( \text{34, though our results (Chapter 5) on the protonation of norbornadiene complexes bring this assignment into question.} \)

\[
\begin{array}{c}
\text{Rh} \\
\text{norbornadiene}
\end{array}
\xrightarrow{\text{H}^+}
\begin{array}{c}
\text{Rh}^+ \\
\text{norbornadiene}
\end{array}
\]

\( \text{Bis-(\( \eta^2 \)-ethylene)} \) complexes are related to \( \eta^4 \)-diene complexes, and show some similarities in their behaviour on protonation.
Protonation of Co(C₅Me₄Et)(C₂H₄)₂, 35, with HBF₄ gave a mono-protonated fluxional hydride complex, originally formulated 36 as a di-olefin hydride 37A, but since shown 37 to be a bridging hydride complex 37B/37B' (Scheme 1:3).
Complex 37 is a fluxional complex which in solution exhibits three different types of equilibria, as indicated in Scheme 1:3.

Equilibrium (a) has a low activation energy and could not be frozen out at -90°C. It consists of a migration of the bridging hydride ligand from one ethylene to the other involving reversible C-H bond rupture, and resulting in the equilibration of \( H_a \) and \( H_d'' \), \( H_b \), and \( H_b'' \), \( H_c \) and \( H_d' \), \( H_e \), and \( H_d'' \). The \(^1H\) nmr spectrum at -85°C thus shows two sets of two proton triplets (δ2.74, δ2.22) for \( H_a/a' \) and \( H_b/b' \), two multiplets (δ1.48 and δ0.46) for \( H_c/c' \) and \( H_d/d'' \), and a hydride resonance (δ-12.1). \( \Delta G^\ddagger_a \) was estimated at less than 30 kJ/mol.

Equilibrium (b) is of intermediate activation energy and is slower than (a). It consists of the formation of an ethyl intermediate involving reversible M-H bond rupture, and together with (a) results in the equilibration of \( H_c \), \( H_c' \), \( H_d' \), \( H_d'' \), and \( H_e \). Consistent with this, warming solutions of 37 results in the collapse of the two multiplets at δ1.48 and δ0.46 and of the hydride resonance. \( \Delta G^\ddagger_b \) was estimated at 43 kJ/mol.

Equilibrium C, of the highest activation energy, consists of rotation of the unbridged ethylene ligand about the Co-ethylene axis. It, together with equilibria (a) and (b) results in the equilibration of all the ethylene protons and \( H_e \). This was shown in the \(^1H\) nmr spectrum of 37: warming to -20°C resulted in the collapse of all the resonances due to ethylene protons and the hydride ligand. \( \Delta G^\ddagger_c \) was estimated at 51 kJ/mol.
Further evidence for the existence of the bridging structure 37B was provided by the $^{13}$C nmr spectrum of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_4-\mu-\text{H})]^+$, obtained by protonation of $\text{Co}(\text{C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2$, 36. A value of 67 Hz for the coupling constant $J(\text{C}-\text{H}_{\text{bridging}})$ was obtained from the spectrum at $-90^\circ$C, which is a characteristic value for bridging hydride complexes.37

On treatment with HBF$_4$, 58 the mono-ethylene complexes $\text{Co}(\text{C}_5\text{Me}_5)(\text{C}_2\text{H}_4)(\text{PR}_3)$ (R = p-tolyl, Ph, Me), also give bridging hydride complexes, such as 39 (R = p-tolyl). Evidence for the M-H-C interaction is provided by the $^1$H and $^{13}$C nmr spectra at $-80^\circ$C, as well as by an X-ray diffraction study of 39. In contrast nmr data on related rhodium, ruthenium and osmium systems, such as $[\text{Rh}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{H}]^+$, 40, have been interpreted in terms of olefin hydride complexes.38-44

Reaction of $\text{Mo}(\text{P}_2)(\text{C}_2\text{H}_4)_2$ ($\text{P}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, 99, $\text{Ph}_2\text{PCH} = \text{CH FPh}_2$, 100) with trifluoroacetic acid gave fluxional 7-coordinate monoprotonated complexes $[\text{Mo}(\text{P}_2)(\text{C}_2\text{H}_4)_2\text{H}]\text{CF}_3\text{COO}$ (e.g., 40A, $\text{P}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). A limiting spectrum corresponding to a diene hydride complex was observed in the $^1$H nmr spectrum of 40A at $-85^\circ$C. Warming the solution
to 7°C resulted in the fast exchange of the hydride proton between one ethylene ligand and the metal via an ethyl intermediate.\textsuperscript{99} The crystal structure of the complex with $P_2 = Ph_2PCH=CHPPh_2$ has been determined by X-ray crystallography.\textsuperscript{100}
1.2 AGOSTIC BRIDGING HYDRIDE SYSTEMS

As indicated in Section 1.1 above, many protonated $\eta^4$-diene transition metal complexes adopt, as their most stable form (i.e., as the ground state), a bridging hydride structure. This mode of bonding is by no means restricted to protonated $\eta^4$-diene or related complexes; in fact many transition metal complexes appear to exhibit it.\textsuperscript{45,67} The term 'agostic' has been proposed\textsuperscript{45} to identify this particular type of bridging hydride system, in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and a metal atom. The term is henceforth adopted in this thesis, being a convenient and succinct means of describing the bonding interaction.

The agostic system is formally a two-electron three-centre interaction in which the C-H bond shares $\sigma$ electron density with the metal, thus allowing the metal to attain a more stable electronic structure, yet without breaking the C-H bond. The system can adopt either an 'open' or a 'closed' geometry, \textsuperscript{41A} and \textsuperscript{41B}, respectively.\textsuperscript{25} Examples of geometry A, are the pyrazolylborate molybdenum complexes of Trofimenko\textsuperscript{46} and Cotton \textit{et al.}\textsuperscript{47,48} The closed type of geometry is found, for example, in Brookhart \textit{et al.}'s manganese complexes.\textsuperscript{25,66}

Evidence for agostic interactions comes mainly from crystal structure determinations and from nmr spectroscopic studies.\textsuperscript{45}

\[
\begin{align*}
M--H--C \\
\text{\textsuperscript{41A}}
\end{align*}
\]
1.2a Crystal Structure determinations

In crystal structure determinations (X-ray and neutron diffraction), evidence for an agostic C-H-M interaction is inferred from the following:

(1) the general shape and geometry of the molecule. Where accurate M-H and C-H bond lengths are not able to be measured, the variation of other bond lengths and angles in the molecule can strongly suggest the existence of an agostic interaction. For example, the allylic portion of the cyclohexenyl ligand in \( \text{Mn(}^3 \text{C}_6 \text{H}_8 \text{Me})(\text{CO})_3 \) was found to be unsymmetrically bound to manganese, the distortion being the result of an M-H-C interaction.\(^{25}\)

(2) the length of C-H and M-H bonds in the agostic M-H-C region. Where accurate M-H and C-H bond lengths can be measured, e.g., in neutron diffraction studies,\(^{16,66}\) those bonds involved in the agostic bridge are significantly longer than normal non-bridging C-H and M-H bond lengths. For example, a 5% lengthening of the C-H bond and a 20% lengthening of the M-H bond involved in the C-H-M region of \([\text{Fe(POMe}_3)_3(\text{cyclooctenyl})]BF_4\), was noted.\(^{16}\) Table 1 gives some M-H, C-H and M-C distances for agostic C-H-M interactions of a number of complexes. Noteworthy is the fact that the complex \([\text{Co(C}_5 \text{Me}_5)(\text{C}_2 \text{H}_4-\mu-\text{H})(\text{P}(\text{p-tolyl})_3]BF_4\),\(^{39}\) shows an exceptionally long C-H distance together with an unusually short M-H distance.\(^{58}\) The figures in the 'M-C' column vary considerably, reflecting in part how 'open' or 'closed' the M-H-C interaction is.
1.2b Nuclear Magnetic Resonance studies

The agostic system can be represented as 42.

\[
\begin{array}{c}
\text{H}_b \\
\text{M} \\
\text{C}_b \\
\text{R}_1 \\
\text{R}_2
\end{array}
\]

This type of interaction results in some fairly characteristic features in the \(^1H\) and \(^{13}C\) nmr spectra. The resultant \(\text{C}_b\text{-H}_b\) bond is weakened by bonding to the metal, causing a reduction of \(J(\text{C}_b\text{-H}_b)\) from the characteristic value of ca. 120-130 Hz, for \(sp^3\) carbon atoms, to ca. 70-100 Hz. The carbon atom \(\text{C}_b\) is also magnetically shielded by its interaction with the metal and hence has a high \(\delta(\text{C}_b)\) value - sometimes even negative (relative to TMS). Similarly \(\text{H}_b\) also has a typically high-field negative \(\delta(\text{H})\) value. 12,16,22,25,45

Agostic alkyl complexes, such as those obtained on protonation of many \(\eta^4\)-diene complexes, often show fluxional behaviour in solution. For example, consider the protonation of a typical butadiene complex 43 to give an agostic \(\eta^3\)-methallyl complex 44A. Two possible fluxional processes may occur: reversible rupture of the M-H bond followed by rotation about the \(\text{C}_1\text{-C}_2\) bond via 44B, resulting in \(\text{H}_a\), \(\text{H}_b\) and \(\text{H}_c\) becoming equivalent on the nmr time scale when rotation is rapid; and 'end to end' metal migration via 44C involving reversible rupture of the C-H bond, and resulting in \(\text{C}_1\) becoming equivalent to \(\text{C}_4\) on
the nmr time scale when migration is rapid. Species 44B and 44C may be transition states or may be intermediates; it is not possible by means of nmr spectroscopy to distinguish between these two possibilities.

The above discussion assumes 44A is the ground state structure; in some cases however, the diene hydride C may constitute the most stable ground state species. The problem in fluxional agostic complexes of this type is thus to determine which is the ground state structure. In many cases the exchange process is slowed sufficiently at low temperature that limiting spectra can be measured and the ground state structure identified. This is however not always the case. With a few exceptions, little evidence concerning the ground state structure can be obtained from fast exchange spectra. One exception is [Co(C₅Me₄Et)(C₂H₄)(C₂H₄-u-H)]BF₄ 37, (Section 2.1); three different fluxional processes occur in this complex, two of which can be frozen out. The ground state structure can be identified
even though at low temperatures the third fluxional process is still fast. 37

Table 2 shows some nmr data for selected agostic bridging hydride complexes; this table is restricted to protonated $\eta^4$-diene complexes, these being particularly relevant to this thesis. For a more complete table including other types of agostic complexes, Brookhart and Green's paper should be consulted. 45
<table>
<thead>
<tr>
<th>Compound</th>
<th>M-H</th>
<th>C-H</th>
<th>M-C</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(Et$_2$B(pz)$_2$)(2-PhC$_3$H$_4$)(CO)$_2$</td>
<td>2.27(8)</td>
<td>0.97(8)</td>
<td>3.055(7)</td>
<td>47</td>
</tr>
<tr>
<td>[Fe(P(OMe)$_3$)$_3$(η-octenyl)]BF$_4$</td>
<td>1.874(3)</td>
<td>1.164(3)</td>
<td>2.362(2)</td>
<td>16</td>
</tr>
<tr>
<td>Mn(η$_3$-C$_6$H$_8$Me)(CO)$_3$</td>
<td>1.84(1)</td>
<td>1.19(1)</td>
<td>2.34(1)</td>
<td>25,66</td>
</tr>
<tr>
<td>Fe$_4$H(µ$<em>2$-CH)(CO)$</em>{12}$</td>
<td>1.80(4)</td>
<td>1.00(4)</td>
<td>1.926(5)</td>
<td>59</td>
</tr>
<tr>
<td>[Fe$_2$(CH$_2$-µ-H)(µ-CO)(µ-dppm)(Cp)$_2$]PF$_6$</td>
<td>1.64(4)</td>
<td>1.06(4)</td>
<td>2.108(3)</td>
<td></td>
</tr>
<tr>
<td>Ti(CH$_2$-CH$_2$-µ-H)Cl$_3$(dmpe)$_3$</td>
<td>2.29</td>
<td>1.02</td>
<td>2.516(10)</td>
<td>61</td>
</tr>
<tr>
<td>Ti(CH$_2$-µ-H)Cl$_3$(dmpe)$_3$</td>
<td>2.03(4)</td>
<td>1.00(2)</td>
<td>2.149(5)</td>
<td>62</td>
</tr>
<tr>
<td>[Ta(CHCMe$_3$)Cl$_3$(PMe$_3$)]$_2$</td>
<td>2.119(4)</td>
<td>1.131</td>
<td>1.898</td>
<td>63</td>
</tr>
<tr>
<td>[Ta(C$_5$Me$_5$)(CHCMe$_3$)(µ$_2$-C$_2$H$_4$)(PMe$_3$)]$_2$</td>
<td>2.042(5)</td>
<td>1.135(5)</td>
<td>1.946(3)</td>
<td>64</td>
</tr>
<tr>
<td>[Mo$_2$(H)(MeC$_2$Me)$_4$(Cp)$_2$]X</td>
<td>1.88(8)</td>
<td>0.89(7)</td>
<td>2.196(5)</td>
<td>65</td>
</tr>
<tr>
<td>[Co(C$_5$Me$_5$)(C$_2$H$_4$-µ-H)(P(µ-tolyl)$_3$)]BF$_4$</td>
<td>1.46(4)</td>
<td>1.31(4)</td>
<td>2.128(4)</td>
<td>58</td>
</tr>
<tr>
<td>[Os(C$_6$H$<em>3$Me$<em>3$)(C$</em>{10}$H$</em>{12}$-µ-H)]PF$_6$</td>
<td>1.81</td>
<td>0.95</td>
<td>2.30(2)</td>
<td>this work</td>
</tr>
<tr>
<td>[Ru(C$_6$H$<em>3$Me$<em>3$)(C$</em>{18}$H$</em>{15}$)]PF$_6$</td>
<td>1.74(7)</td>
<td>1.00(8)</td>
<td>2.354(10)</td>
<td>this work</td>
</tr>
</tbody>
</table>

1. pz = pyrazolate
2. Cp = (η$_5$-C$_5$H$_5$); dppm = Ph$_2$PCH$_2$PPh$_2$
3. dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$
4. M-H distance calculated using assumed C-H value of 0.95 Å
<table>
<thead>
<tr>
<th>System</th>
<th>$\delta^{13}C$</th>
<th>$J_{13C-H_b}^{13}$ (H$_2$)</th>
<th>$\delta H_b$</th>
<th>$J_{H_a-H_b}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(butenyl)(CO)}_3]^+$</td>
<td>-2.76</td>
<td>73.7</td>
<td>-14.59</td>
<td>-</td>
<td>22,8</td>
</tr>
<tr>
<td>$[\text{Fe(butenyl)(P(OMe)}_3]_3^{\ddagger}\text{BPh}_4$</td>
<td>-3.9</td>
<td>100</td>
<td>-15.2</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>$[\text{Fe(2,3-dimethylbutenyl)(P(OMe)}_3]_3\text{BPh}_4$</td>
<td>-</td>
<td>-</td>
<td>-14.8</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>$[\text{Fe(cycloheptenyl)(P(OMe)}_3]_3\text{BPh}_4$</td>
<td>7.9</td>
<td>80</td>
<td>-15.77</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>$[\text{Fe(cyclohexenyl)(P(OMe)}_3]_3\text{BPh}_4$</td>
<td>13.7</td>
<td>-</td>
<td>-15.75</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>$[\text{Fe(cyclooctenyl)(P(OMe)}_3]_3\text{BPh}_4$</td>
<td>21.3$^b$</td>
<td>-</td>
<td>-6.54$^b$</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>$[\text{Fe(cyclohexenyl)(CO)}_3]_3\text{SO}_3F$</td>
<td>19.0</td>
<td>78-88</td>
<td>-14.9</td>
<td>-</td>
<td>8,12</td>
</tr>
<tr>
<td>$[\text{Mn(cyclohexenyl)(CO)}_3]_3$</td>
<td>14.0</td>
<td>85</td>
<td>-12.8</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{Co(C}_5\text{Me}_4\text{R})(\text{C}_4\text{H}_9)]\text{BF}_4$</td>
<td>26.6$^c$</td>
<td>67$^c,d$</td>
<td>-12.1$^e$</td>
<td>18$^{d,e}$</td>
<td>37</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{Me}_6)(\text{C}_4\text{H}_9)]\text{BF}_4$</td>
<td>39.78</td>
<td>37.8$^d$</td>
<td>-7.3</td>
<td>13$^d$</td>
<td>19,20</td>
</tr>
<tr>
<td>$[\text{Fe(C}_7\text{H}_9)(\text{CO)}_3]_3\text{SO}_3F$</td>
<td>9.0</td>
<td>81.2</td>
<td>-11.16</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>$[\text{Fe(C}_4\text{H}_5)(\text{CO)}_3]_3\text{SO}_3F$</td>
<td>-3.3</td>
<td>66</td>
<td>-10.08</td>
<td>16.5</td>
<td>this work</td>
</tr>
<tr>
<td>$[\text{Os(C}_6\text{H}_3\text{Me}_3)(\text{C}_10\text{H}_13)]\text{PF}_6$</td>
<td>2.52</td>
<td>78</td>
<td>-10.13</td>
<td>18</td>
<td>56</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{Me}_6)(\text{C}_10\text{H}_13)]\text{PF}_6$</td>
<td>2.9</td>
<td>81</td>
<td>-7.63</td>
<td>20.2</td>
<td>this work</td>
</tr>
<tr>
<td>$[\text{Rh(C}_5\text{H}_5)(\text{C}_10\text{H}_13)]\text{PF}_6$</td>
<td>6.1</td>
<td>83</td>
<td>-6.83</td>
<td>19.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>$[\text{Rh(C}_5\text{Me}_5)(\text{C}_10\text{H}_13)]\text{PF}_6$</td>
<td>9.0</td>
<td>50</td>
<td>-9.52</td>
<td>16.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>$[\text{Ir(C}_5\text{Me}_5)(\text{C}_10\text{H}_13)]\text{PF}_6$</td>
<td>6.8</td>
<td>-</td>
<td>-6.5</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>$[\text{Rh(C}_5\text{Me}_5)(2,3\text{-dimethylbutenyl})]\text{PF}_6$</td>
<td>14.9</td>
<td>128.6$^f$</td>
<td>1.25$^f$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>$[\text{Rh(C}_5\text{Me}_5)(\text{ddbo-H})]\text{PF}_6$</td>
<td>-</td>
<td>-</td>
<td>3.3$^b$</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7Bcyclohexenyl%7D">\text{Rh(C}_5\text{Me}_5</a>]\text{PF}_6$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Notes

a. unless otherwise indicated these values of δ and J represent the ground state structure, being taken from the low-temperature slow-exchange spectra.

b. averaged value of endo-1 and endo-5 protons.

c. \( R = CH_3 \)

d. averaged value from two rapidly exchanging isomers.

e. \( R = C_2H_5 \)

f. averaged value due to rapid exchange of protons in \(-CH_2-H-M\) (i.e., methyl) region.

1.2c Deuteration: the thermodynamic isotope effect

Further evidence for the identification of agostic bridging hydride systems comes from the nmr spectra of partially deuterated complexes. In a partially deuterated agostic system, deuterium will, where possible, occupy a terminal C-D position rather than a bridging C-D-M position. This is due to zero-point energy differences which favour the lighter nucleus in the bridging position.

This preference for terminal (non-bridging) positions by deuterium affects the appearance of the fast exchange nmr spectra of such a deuterated system, as it affects the fluxional exchange equilibria. Consider a hypothetical mono-deuterated 1-methallyl complex, arising from the deuteration of a butadiene complex with \( D^+ \). When the system is in a state of fast exchange, \( H_a, H_b \) and D rotate into and out of
the bridging position. Since D will preferentially occupy a non-bridging position, 45B and C will be favoured, i.e., there is a substantial isotope effect on the equilibrium constants involved, favouring B and C. The chemical shift of the fast exchange $^1$H nmr resonance for the methyl unit is a weighted average of the resonance contributions of two terminal H(D) atoms and one bridging hydride (deuteride) atom, i.e., the weighted average of the contributions of A, B and C, and is dependent on the equilibrium constants. Because a hydrogen atom preferentially occupies the bridging position the deuterated complex has slightly more 'hydride character' than the analogous non-deuterated complex and the $^1$H nmr resonance for $H_a/H_b/D$ averaged in 45 occurs at a lower chemical shift (a more negative $\delta$ value) relative to the non-deuterated complex (such as 44) (sometimes more than 1 ppm upfield). If distribution of deuterium was completely random, the contributions of hydride and terminal atoms of the methyl unit to the fast exchange spectrum would be equally reduced, resulting in a multiplet of reduced intensity but virtually identical chemical shift, to that obtained from an analogous non-deuterated agostic system.
The upfield change of chemical shift is also temperature dependent, reflecting the effect of temperature on the exchange equilibrium constants.\textsuperscript{14,25,49}

Thus, for example, in their investigation of Mn(CO)$_3$(C$_6$H$_8$D), Brookhart et al.\textsuperscript{25} found that the fast exchange spectrum (at 15°C) showed a resonance (δ=7.0 ppm) at rather higher field than the analogous resonance (δ=5.8 ppm) in the non-deuterated complex Mn(CO)$_3$(C$_6$H$_9$).\textsuperscript{18} This is due to the equilibrium lying on the side of 46A in the rapid endo exchange process.

Originally observed in some organic systems\textsuperscript{50-53} and by Shapley in an osmium cluster,\textsuperscript{49} this isotope effect has been fairly widely used to predict the presence of agostic complexes.\textsuperscript{14,25,45,54} One limitation of the technique is that as it depends on the system being in fast equilibrium it does not necessarily give information about the ground state structure.
1.2d Infrared studies

An agostic M-H-C interaction would be expected to lower the frequencies of both the $\nu_{\text{M-H}}$ and the $\nu_{\text{C-H}}$ vibrations, and the positions of the bands for these vibrations would be directly related to the relative strengths of the C-H and M-H bonds. Unfortunately relatively little data of agostic complexes have been reported. In the infrared spectrum of $[\text{FeH(C}_4\text{H}_6)(\text{PMe}_3)_3]\text{PF}_6$ a band at 1570 cm$^{-1}$ was assigned to $\nu_{\text{M-H}}$, which is lower than terminal $\nu_{\text{M-H}}$ values.$^{98}$ The $\nu_{\text{C-H}}$ values of 2704 and 2664 cm$^{-1}$ in a molybdenum pyrazolylborate complex$^{46}$ and 2605 cm$^{-1}$ in $[\text{Ta(CHCMe}_3)(\text{PMe}_3)\text{Cl}_3]_2$,$^{63}$ are typical of the few values reported for agostic complexes.

The agostic interaction has significant potential as a means of activating C-H bonds. The M-H-C interaction results in weakening of the C-H bond and causes the hydrogen to become more acidic. The carbon atom of the M-H-C system thus becomes accessible to electrophilic attack. Preliminary studies by Brookhart et al.$^{26}$ show that substantial chemistry can be carried out using agostic systems.
1.3 THE PROTONATION OF Ru(η⁶-ARENE)(η⁴-DIENE) COMPLEXES

The protonation of Ru(η⁶-arene)(η⁴-diene) complexes has been the subject of considerable investigation in our research group. This section introduces some of the results, mostly from the work of McMahon. The results will be discussed further in Chapters 3-5 and compared with the results of the protonation of Os(η⁶-arene)(η⁴-diene) and M(η⁵-C₅R₅)(η⁴-diene) (M = Rh, Ir; R = H, CH₃) complexes.

The protonation of the 2,3-dimethylbutadiene complexes Ru(η⁶-arene)(C₆H₁₀) (arene = C₆H₆, C₆H₃Me₃, C₆Me₆) with HPF₆ gave solids of empirical formula [Ru(η⁶-arene)(C₆H₁₁)]PF₆ (47A arene = C₆H₆; 47B arene = C₆H₃Me₃; 47C arene = C₆Me₆). In solution these complexes showed fluxional behaviour. At 28°C the fast exchange H nmr spectrum of the hexamethylbenzene complex 47C showed a five-proton multiplet (δ=1.66) due to the averaged resonances of H arene. Cooling the solution resulted in the collapse of this multiplet and the appearance at
-90°C of three new broad resonances [δ1.64 (2H), δ-0.55 (2H) and δ-10.28 (1H)]. The appearance and chemical shift of the 6 proton singlet, due to the methyl groups of the diene ligand, were unaffected by temperature. These results are consistent with 47C having a symmetrical diene hydride rather than an unsymmetrical methallyl-bridging hydride ground state structure. The fluxional process possibly occurs through an η^3-allyl intermediate. The ^13C nmr spectrum of 47C showed, at 27°C, a resonance at δ25.5 resulting from the averaging of C_1 and C_4. Cooling the solution caused this resonance to collapse, but a limiting spectrum could not be attained.56

The variable temperature nmr spectra of 47A and 47B were similar to those of 47C, also suggesting diene hydride ground state structures. The infrared spectra (solid state and solution) of 47A-C, however, showed no bands attributable to νRu-H in the region 1600-2200 cm⁻¹, although a nujol mull spectrum of 47C showed a band at 1565 cm⁻¹ which may have been due to a modified νM-H vibration.56

The products obtained from the protonation of the acyclic diene complexes Ru(C_6M_6)(η^4-diene) (diene = isoprene, 2 methylpenta-1,3-diene, 3-methylpenta-1,3-diene) were not fully identified. Limiting, slow exchange nmr spectra could not be obtained for the protonated isoprene and 3-methylpenta-1,3-diene complexes. In the case of the protonated 2-methylpenta-1,3-diene complexes the ^1H nmr spectrum at -95°C showed broad multiplets which were consistent with the complex adopting the diene-hydride structure 48.
The protonated acyclic diene complexes discussed above all reacted with ligands such as carbon monoxide, P(OMe)₃ or t-BuNC to form static, stable η³-allyl complexes by migration of the hydride ligand onto the diene ligand. Thus, for example, the 2,3-dimethylbutadiene complexes 47A–C reacted with CO to form the 1,1,2-trimethylallyl complexes 49A–C.

The protonation of Ru(η⁶-arene)(1,3-cyclohexadiene) with HPF₆ gave mono-protonated complexes of empirical formulae [Ru(η⁶-arene)(C₆H₉)]PF₆ (50A, arene = C₆H₆; 50B, arene = C₆Me₆). These complexes show fluxional behaviour in solution. The benzene complex 50A showed,
in its room temperature $^1$H nmr spectrum, two multiplets assignable to the diene ligand ($\delta 63.22$ (6H), $\delta -2.94$ (3H)). Cooling the solution resulted in the collapse of these two multiplets into the baseline (-60°C), followed by (at -95°C) the appearance of four new resonances [$\delta 5.56$ (2H) (H$_{2,3}$), $\delta 3.53$ (2H) (H$_{1,4}$), $\delta 1.26$ (4H) (H$_{5,6}$), $\delta -11.05$ (1H) (hydride)]. This spectrum supports a symmetrical diene hydride ground state structure for 50A, rather than an unsymmetrical $\eta^3$-allyl bridging hydride structure shown, for example, by Brookhart et al.,$^{25}$ to exist in Mn(C$_6$H$_9$)(CO)$_3$, $^{18}$. Rapid exchange, possibly via an $\eta^3$-allyl intermediate results in a 1,2-metal migration round the ring, which equilibrates, on the nmr time scale, the hydride, H$_{5e}$ (e = endo) and H$_{6e}$ (giving a 3H multiplet) and equilibrates H$_{1-4}$, H$_{5x}$ (x = exo) and H$_{6x}$ (giving a 6H multiplet). Cooling the solution slows the exchange and the ground state structure can be observed.

Further support for the symmetrical diene hydride ground state structure of 50A comes from the $^{13}$C nmr spectrum, which showed three resonances [$\delta 77.5$ (doublet), $\delta 46.8$ (dd) and $\delta 23.8$ (t)] at -95°C,
corresponding to \( C_{2,3}, C_{1,4} \) and \( C_{5,6} \), respectively.

The hexamethylbenzene complex 50B showed similar fast exchange nmr spectra to 50A, but limiting spectra could not be obtained, even at \(-120^\circ C\).

Complexes 50A and B showed no band in their infrared spectrum, assignable to \( \nu_{Ru-H} \), in the region 1600-2500 cm\(^{-1}\). Attempts to grow single crystals for X-ray diffraction study were not successful.

As was the case for the acyclic diene complexes, 50A and B reacted with ligands, e.g., CO, P(OMe)\(_3\) to give the static, stable \( \eta^3 \)-cyclohexenyl complexes 51A and 51B. Complexes 50A and B were also easily deprotonated with aqueous Na\(_2\)CO\(_3\), giving the parent zerovalent ruthenium cyclohexadiene complexes.\(^{56}\)

\[
\begin{align*}
\text{Ru}^+ - H & \quad \text{P}((\text{OMe})_3) \\
\text{Ru}^+ & \quad \text{P}((\text{OMe})_3) \\
\text{51 A} & \quad \bigcirc \equiv \text{C}_6\text{H}_6 \\
\text{51 B} & \quad \bigcirc \equiv \text{C}_6\text{Me}_6
\end{align*}
\]

The protonation of the alkyl-substituted cyclohexadiene complexes, Ru(C\(_6\text{Me}_6\))(5-ethylcyclohexa-1,3-diene) and Ru(C\(_6\text{Me}_6\))(1,3,5-trimethylcyclohexa-1,3-diene) with HPF\(_6\) gave solids of empirical formula...
[Ru(C₆Me₆)(C₆H₁₃)]PF₆, 52, and [Ru(C₆Me₆)(C₅H₁₄)]PF₆, 53. Complexes 52 and 53 were fluxional in solution. On the basis of the ¹H nmr

and ¹³C nmr spectra at -95°C McMahon⁵⁶ suggested that 52 adopted a diene hydride ground state structure, but conceded that a bridging hydride structure may be indicated by an unusually high-field olefinic carbon resonance in the ¹³C nmr spectrum. A limiting ¹H nmr spectrum for 53 was not obtained; at -95°C the ¹³C nmr spectrum showed 6 resonances but their assignment was uncertain. No bands were seen in the infrared spectrum of 52 in the region 1600-2500 cm⁻¹. A band at 2300 cm⁻¹ in the solution spectrum of 53 may, however, be assignable to a νRu-H vibration.

Addition of HPF₆ to solutions of Ru(η⁶-arene)(1,5-cyclooctadiene) (arene = C₆H₆, C₆H₃Me₃, C₆Me₆) gave the mono-protonated salts [Ru(η⁶-arene)(C₈H₁₂)H]PF₆ (54A, arene = C₆H₆; 54B arene = C₆H₃Me₃; 54C arene = C₆Me₆). The ¹H nmr spectrum of 54B (the mesitylene
complex) was virtually identical at 25°C or -95°C; it showed two 2H multiplets, an 8H multiplet and a one proton hydride resonance.

\[
\text{Ru}^6 \text{Ru-H PF}_6^6 \sim \text{O=C}_6\text{H}_6 \sim \text{O=C}_6\text{H}_3\text{Me}_3 \sim \text{O=-C}_6\text{Me}_6
\]

These results are consistent with a diene hydride structure, although whether the diene adopted the 1,3- or 1,5-configuration could not be ascertained.

Deuteration experiments with \text{54C} suggested that the protonated complexes undergo a slow exchange process, not detectable in the nmr spectra, resulting in scrambling of the methylene protons of the diene ligand and the hydride ligand, Scheme 1:4

\[
\text{Scheme 1:4}
\]
Complexes 54A-C all reacted with ligands such as CO, P(OMe)\textsubscript{3} or \(\tau\)-BuNC, giving \(\eta^3\)-allyl complexes such as 55. 56

\[
\begin{align*}
\text{Ru}^+ \text{H} & \xrightarrow{\text{CO}} \text{Ru}^+ \text{CO} \\
54C & \sim 55
\end{align*}
\]

The results of the protonation of the norbornadiene complexes \(\text{Ru}(\eta^6\text{-arene})(\text{NBD})\) (arene = \(\text{C}_6\text{H}_6\), \(\text{C}_6\text{H}_3\text{Me}_3\), \(\text{C}_6\text{Me}_6\) and \(\text{o-C}_6\text{H}_4\text{Me}_2\), \(\text{NBD} = \text{norbornadiene}\)) are rather interesting. 56 Protonation with \(\text{HPF}_6\) gave mono-protonated complexes of general empirical formula \([\text{Ru}(\eta^6\text{-arene})(\text{C}_7\text{H}_9)]\text{PF}_6\). Freshly prepared solutions of the mesitylene complex 56B gave nmr spectra consistent with a diene hydride structure. However, on standing in solution (\(\text{CH}_2\text{Cl}_2\)) for 24h at ambient

\[
\begin{align*}
\text{Ru} & \xrightarrow{\text{HPF}_6} \text{Ru}^+ \text{HPF}_6^- \\
\text{CH}_2\text{Cl}_2\text{soln.} & \rightarrow 57
\end{align*}
\]

\[
\begin{align*}
56 & \begin{cases} 
A & \circlearrowleft = \text{C}_6\text{H}_6 \\
B & \circlearrowleft = \text{C}_6\text{H}_3\text{Me}_3 \\
C & \circlearrowleft = \text{C}_6\text{Me}_6 \\
D & \circlearrowleft = \text{o-C}_6\text{H}_4\text{Me}_2
\end{cases} \\
& \begin{cases} 
A & \bigg\{ \\
B & \bigg\{ \\
C & \bigg\{ \\
D & \bigg\{ \end{cases} \text{for} 56
\end{align*}
\]
temperature, 56B isomerized irreversibly to a new species, 57B.

In addition to the arene resonances, 57B showed nine $^1$H multiplets and seven $^{13}$C resonances in its $^1$H and $^{13}$C nmr spectra, respectively, and showed a band at 2010 cm$^{-1}$ in its infrared spectrum. Similar results were obtained in the case of the o-xylene complex 56D; the $^1$H nmr spectrum showed a diene hydride complex, which isomerized in solution to 57D. In the case of the hexamethylbenzene complex 56C, the spectrum corresponding to the diene hydride was only seen in freshly prepared solutions at -95°C; warming then resulted in rapid irreversible isomerization, giving 57C. The isomerization process in unstable solutions of the benzene complex 56A was more rapid still, and nmr spectra showed only 57A.

The isomerized complexes 57A-D did not react to give monoadducts with ligands such as P(OMe)$_3$; where reaction occurred only intractible products resulted. Further, whereas the diene hydride complex, 56B reacted with aqueous Na$_2$CO$_3$ solution to regenerate the zerovalent ruthenium complex Ru(C$_6$H$_3$Me$_3$)(NBD), the isomerized product 57B did not.

McMahon$^{56}$ was not able to determine the nature of the isomerized products 57A-D. Several possible structures were proposed, including an unsaturated σ-π complex 58, a bridging hydride complex 59, a nortricyclenyl complex 60 and a vinylcyclopentenyl complex 61. None of the proposed structures satisfactorily accounted for the spectroscopic data, however, although 59 was suggested to give the best fit.
Interestingly, deuteration of $\text{Ru}(\text{C}_6\text{Me}_6)(\text{NBD})$ with $\text{DF}_6$ gave, after isomerization of any metal deuteride a mono deuterated analogue of 57C, in which the deuterium appeared to occupy the bridging position of the (C$_7$H$_9$) fragment. The isomerization process was suggested to be a rearrangement of the type outlined in equation 1:3.

Treatment of the dicyclopentadiene complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{diCp})$ (diCp = dicyclopentadiene) with H$\text{F}_6$ gave a salt of empirical formula $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_{10}\text{H}_{13})]\text{PF}_6$, 62. The $^1\text{H}$ nmr spectrum of 62 shows two high-field resonances, a multiplet (1H) at δ-0.09 and a doublet at δ-10.13 (1H), irradiation experiments show that the protons responsible for these resonances are coupled. The $^{13}$C nmr spectrum of 62 shows a doublet of doublets at δ2.52 $J(\text{C-H})=159$ Hz, 78 Hz).
These results strongly suggest a bridging hydride structure. McMahon proposed several possible structures for 62, of which the structure shown is one. Assuming this structure, $H_a$ gives rise to the peak at $\delta=0.09$, and $H_b$, coupled to $H_a$ ($J=18$ Hz) the peak at $\delta=10.13$. $C_a$ thus gives rise to the doublet of doublets, $(\delta 2.52)$ with $J(C_{a\alpha})=159$ Hz and $J(C_{a\beta})=78$ Hz. These coupling constants compare well with the analogous values obtained from other bridging hydride complexes (see Table 2).

Complex 62 reacted readily with t-butylisonitrile to give a 1:1 adduct, $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_{10}H_{13})(\text{t-BuNC})\text{PF}_6]$, 63 (the structure drawn assumes the structure of 62). Complex 62 is also readily deprotonated with $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$. It showed no $\nu\text{M-H}$ band in its infrared spectrum (2500-1600 cm$^{-1}$).

The bisethylene complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_2\text{H}_4)_2$ gave, on protonation with $\text{HPF}_6$ a mono-protonated salt of empirical formula $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{PF}_6]$.
This complex showed fluxional behaviour in solution: at -86°C the $^1$H nmr spectrum showed, for the ethylene ligands, four two-proton multiplets in the region $\delta 1.5 \sim 6.0$, and a high-field multiplet (one proton) at $\delta -11.25$. The spectrum collapsed on warming to room temperature and at 80°C a nine-proton multiplet was seen ($\delta 0.08$). The $^{13}$C proton decoupled spectrum at -94°C showed two resonances, assignable to the ethylene ligands, which collapse into one resonance at room temperature. No $\nu$M-H band was seen in the infrared spectrum (2500 - 1500 cm$^{-1}$) and no characterizable products were obtained from the reaction with carbon monoxide. McMahon proposed the diene hydride structure $64$ as the ground state structure, undergoing rapid exchange via an ethyl complex, $65$. In the light of the results obtained$^{36,37}$ for [Co(C$_5$Me$_5$)(C$_2$H$_4$)(μ-H-C$_2$H$_4$)]PF$_6$, $68$; however, a bridging hydride structure, $66$, may be a more correct assignment.

An interesting bridging hydride complex $68$ is formed on protonation of o-quinodimethane complex $67$. The presence of an agostic
M-H-C group in 68 is indicated by variable temperature nmr and confirmed by X-ray diffraction studies. 69
1.4 ANALYSIS OF THE PROBLEM

McMahon's work left a number of unanswered questions concerning the nature of the protonated ruthenium complexes. For example, the low temperature proton nmr spectrum, of the 2,3-dimethylbutadienyl complex [Ru(C_6Me_6)(C_6H_{11})]PF_6, although consistent with a diene hydride, rather than agostic, ground state structure, was still broad at the lowest temperature investigated (-90°C). A limiting ^13C nmr spectrum of this complex could not be obtained and provided no further information as to its structure. It was thus not entirely certain what the ground state structure of 47C was. The ethylcyclohexenyl complex [Ru(C_6Me_6)(C_8H_{13})]PF_6, 52, could be assigned either on agostic or a diene hydride structure, and the ground state structure of several other fluxional 1,3-diene protonated complexes, was also not established. The structure of the protonated dicyclopentadienyl complex [Ru(C_6Me_6)(C_{10}H_{13})]PF_6, 62, and of its t-BuNC adduct 63, were not fully identified, though strong spectroscopic evidence was presented in support of an agostic bridging hydride interaction in the former complex. The isomerized protonated norbornadiene complexes 57A-D were also not fully identified as none of the proposed structures provided a satisfactory explanation of all the spectroscopic evidence.

The work described in this thesis was undertaken both to more fully identify the structure of some of the protonated ruthenium complexes, and to extend the study of protonated \( \eta^4 \)-diene complexes to other transition metal systems. Apart from McMahon's work, investigations into the protonation of diene complexes have mostly involved first row elements, and in nearly all cases agostic complexes were formed. We were thus interested in investigating similar reactions with second
and third row transition metals, and in particular we were interested in investigating the effect of different metals and ligands on the structure of the complexes, and whether or not agostic interactions were present.

This thesis reports on a study into the synthesis and protonation of \( \eta^4 \)-diene complexes of the type \( M(\eta^6\text{-arene})(\eta^4\text{-diene}) \) (\( M = \text{Ru, Os} \)) and \( M(\eta^5\text{-cyclopentadienyl})(\eta^4\text{-diene}) \) (\( M = \text{Rh, Ir} \)). Chapter 2 of this work introduces the diene complexes, including some bis-\( \eta^2 \)-ethylene complexes, and Chapters 3-6 report on and discuss the results of the protonation experiments.
CHAPTER 2

The preparation of complexes of the type $M(\eta^6$-arene)$\eta^4$-diene) ($M = \text{Ru, Os}$) and $M(C_5R_5)\eta^4$-diene) ($M = \text{Rh, Ir}; \ R = \text{H, Me}$) (including bis-ethylene complexes)

2.1 INTRODUCTION

2.1.1 The $\eta^6$-arene-$\eta^4$-diene complexes of Ru(O) and Os(O)

$\eta^6$-Arene complexes of the Group VIII transition metals have attracted considerable interest over the last decade or so, particularly with respect to their catalytic properties, and their metal-arene bonding modes. However, until recently very few $\eta^6$-arene $\eta^4$-diene complexes of zerovalent metals of the iron triad were known. In our laboratories we have been interested in developing convenient synthetic routes to such complexes, in order to compare their reactivity with the well known tricarbonyl and tris-(phosphine) diene complexes of these elements (particularly of iron). This section reviews some of the published work on the synthesis of $M(\eta^6$-arene)$\eta^4$-diene) ($M = \text{Ru, Os}$) and $M(C_5R_5)\eta^4$-diene) ($M = \text{Rh, Ir}; \ R = \text{H, CH}_3$) complexes, and in section 2.2 we report on some new osmium, ruthenium, rhodium and iridium complexes of this type.

The most convenient starting point for Ru($\eta^6$-arene)$\eta^4$-diene) complexes presently known is complexes of the type $[\text{Ru}(\eta^6$-arene)$\text{Cl}_2]_2$. These complexes are generally prepared by two different routes; the dehydrogenation of cyclohexadienes with RuCl$_3\cdot$H$_2$O, and from ($\eta^6$-cycloocta-1,3,5-triene)$\eta^4$-cycloocta-1,5-diene) ruthenium (O).
Treatment of RuCl$_3$·xH$_2$O with 1,3-cyclohexadiene in ethanol, was found by Winkhaus and Singer$^{109}$ to give a brown solid benzene complex, [Ru(C$_6$H$_6$)Cl$_2$]$_n$, which they assumed to be polymeric but which is probably dimeric (n = 2), Equation 2:1.\textsuperscript{110} The reaction has been extended to include a number of 1,3- and 1,4-cyclohexadienes.\textsuperscript{110}

Product quality can apparently be improved by using 'purified' RuCl$_3$.\textsuperscript{169} The bromide and iodide complexes can be synthesized by metathetical reaction.\textsuperscript{110,111} The method is limited by the availability of cyclohexadienes. Cyclohexadienes are available from Birch reduction of arenes, but this fails for heavily substituted arenes. Arene exchange is however possible; for example, [Ru(C$_6$Me$_6$)Cl$_2$]$_2$ (C$_6$Me$_6$ = $\eta^6$-hexamethyl benzene) can be prepared from the p-cymene complex [Ru(p-MeC$_6$H$_4$CHMe$_2$)Cl$_2$]$_2$ by stirring the latter in molten C$_6$Me$_6$.\textsuperscript{112,125} Similar exchange of p-cymene with durene (2,3,5,6-tetramethylbenzene),\textsuperscript{113} 1,2,3,4-tetramethylbenzene,\textsuperscript{137} 1,3,5-triethylbenzene\textsuperscript{137} and 1,3,5-triisopropylbenzene\textsuperscript{137} can be effected.
Complexes of the type $[\text{Ru}(\eta^6-\text{arene})\text{Cl}_2]_2$ can also be synthesized from $\text{Ru}(\eta^6-C_8H_{10})(\eta^4-C_8H_{12})$, which is in turn synthesized from RuCl$_3$ and 1,5-cyclooctadiene in the presence of zinc dust and ethanol. Treatment of 69 with arene under one atmosphere of H$_2$ at room temperature gave a wide range of arene-cyclooctadiene complexes, 70, in yields ranging from 35% to almost quantitative. Treatment of complexes 70 with HCl in acetone or THF gave almost quantitative yields of complexes $[\text{Ru}(\eta^6-\text{arene})\text{Cl}_2]_2$. Bulky arenes, and arenes with functional groups were used, indicating the versatility of the synthetic method.

The $[\text{Ru}(\eta^6-\text{arene})\text{Cl}_2]_2$ complexes have been used to synthesize Ru($\eta^6$-arene)($\eta^4$-diene) complexes in a number of ways. Treatment of $[\text{Ru}(C_6H_6)\text{Cl}_2]_2$ with isopropyl magnesium bromide in the presence of 1,3-cyclohexadiene and 1,5-cyclooctadiene gave Ru($C_6H_6$)($C_6H_8$), and Ru($C_6H_6$)($C_8H_{12}$) (70, arene = $C_6H_6$) respectively. The crystal structure of the latter complex has been determined. Complex 71 has also been synthesized by irradiation of RuCl$_3$$\cdot$H$_2$O with i-C$_3$H$_7$MgBr in the presence of 1,3-cyclohexadiene. The bis-ethylene complex Ru($C_6\text{Me}_6$)($C_2H_4$)$_2$, and a number of $\eta^4$-diene
complexes have been synthesized by treatment of $[\text{Ru}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2$ with an excess of ethyl magnesium bromide followed by methanolysis.\textsuperscript{120}

The reaction of $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ complexes with $\text{M}_2\text{COT}$ ($\text{M} = \text{Li, K, Na}; \text{COT} = \text{cyclooctatetraene}$) gave fluxional complexes of the type $\text{Ru(arene)}(\text{COT})$ (e.g., 72, arene = $\text{C}_6\text{H}_6$).\textsuperscript{112,121}

However, perhaps the best general method for synthesizing $\text{Ru}(\eta^6\text{-arene})(\eta^4\text{-diene})$ complexes is a method analogous to that used to synthesize $\text{M}(\text{C}_5\text{Me}_5)(\eta^4\text{-diene})$ ($\text{M} = \text{Rh, Ir}; \text{C}_5\text{Me}_5 = \eta^5\text{-pentamethylcyclopentadiene}$) complexes:\textsuperscript{122,123} i.e., treatment of $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ complexes with the appropriate diene in the presence of alcohol and base.\textsuperscript{56,120,124,125} Ethanol or isopropanol are suitable alcohols, and the reaction is generally rapid at reflux temperature in the presence of $\text{Na}_2\text{CO}_3$.\textsuperscript{56,124} The method has been used to prepare a number of $\eta^4\text{-diene}$ complexes, and a bis-ethylene complex, as outlined in Scheme 2:1.\textsuperscript{56}
SCHEME 2.1 SOME Ru(6-arene)(n^4-diene) COMPLEXES

*Ar = C_6H_6, C_6H_3Me_3, C_6Me_6

*(not every complex was made with all arenes)
The reaction is thought to proceed by hydride abstraction to give an aldehyde or ketone and a metal hydride intermediate\(^{56,122}\) (Scheme 2:2).

Support for the existence of the intermediate hydride species \([M(Ar)C1H]\), comes from the fact that a mixture of bridging hydride complexes, including \([\text{C}_6\text{Me}_6\text{Ru})_2(\mu-H)_2(\mu-\text{Cl})]\), \(^{73}\) has been synthesized\(^{107,120,126}\) by treatment of \([\text{Ru(C}_6\text{Me}_6)\text{Cl}_2]_2\) with \(\text{Na}_2\text{CO}_3\) in isopropanol. Further, \(^{73}\) has been found to react readily with a variety of dienes (cyclic and acyclic)\(^{120}\) to give zerovalent \(\text{Ru(\eta^6-arene)(\eta^4-diene)}\) complexes. The final elimination of \(\text{HCl}\) (Scheme 2:2) does not occur for all dienes; for example, reaction of \(^{73}\) with butadiene gave the methallyl complex \(\text{Ru(C}_6\text{Me}_6)(\eta^3-C_4\text{H}_7)\text{Cl}\), (no elimination of \(\text{HCl}\) has occurred) whereas reaction of \(^{73}\) with
2,3-dimethylbutadiene gave the diene complex \( \text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_6\text{H}_{10}) \) (elimination of HCl has occurred).\textsuperscript{120} A necessary requirement for HCl elimination is that a methyl group be in the anti-position of the methallyl group, as follows:

![Diagram](image)

Reaction of \( \text{73} \) with butadiene gave the syn isomer of \( \text{Ru}(\text{C}_6\text{Me}_6)(\eta^3\text{-C}_4\text{H}_7)\text{Cl} \), and presumably the activation energy for rearrangement to the anti isomer necessary for elimination, is prohibitively high.

Other, more specific methods for synthesis of \( \text{Ru}(\eta^6\text{-arene})(\eta^4\text{-diene}) \) complexes have been reported. The complex \( \text{Ru}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_8) \),\textsuperscript{71} has been obtained directly from \( \text{RuCl}_3 \cdot x\text{H}_2\text{O} \) by refluxing with 1,3-cyclohexadiene in ethanol in the presence of zinc dust.\textsuperscript{114} This complex has also been synthesized by sodium borohydride reduction of bis-benzene ruthenium perchlorate,\textsuperscript{127} a reaction which has recently been extended to include a number of zerovalent ruthenium arene-cyclohexadiene
The 1,5-cyclooctadiene complex Ru(C₆H₆)(1,5-C₈H₁₂) (70, arene = η⁶-C₆H₆) has been prepared from [Ru(H)(1,5-C₈H₁₂)(NH₂(N(CH₃)₂)₂)]BF₄ and benzene. The 1,5-cyclooctadiene complex Ru(C₆H₆)(1,5-C₈H₁₂) (70, arene = η⁶-C₆H₆) has been prepared from [Ru(H)(1,5-C₈H₁₂)(NH₂(N(CH₃)₂)₂)]BF₄ and benzene.

Related to Ru(η⁶-arene)(η⁴-diene) complexes are the unusual and interesting bis-arene ruthenium (0) complexes, in which one arene is hexahapto bonded and the other tetrahapto. The complex Ru(η⁶-C₆Me₆)(η⁴-C₆Me₆), 74 was originally synthesized by Fischer and Elschenbroich by reduction of Ru(η⁶-C₆Me₆)₂²⁺ with sodium in liquid ammonia, and its crystal structure confirms the η⁶-η⁴ designation, showing one planar and one non-planar arene ring. Other Ru(η⁶-arene)(η⁴-arene) complexes reported include Ru(η⁶-C₆H₆)(η⁴-C₆R₆) (R = C₆H₅, COOCH₃), synthesized by irradiation of Ru(C₆H₆)(C₆H₈), 71, with acetylenes, and the thermally unstable Ru(η⁶-C₆H₆)(η⁴-C₆H₆), synthesized by co-condensation of Ru vapour and benzene. Recently, also, several Ru(η⁶-arene)(η⁴-octamethylnaphthalene) (75, arene = C₆Me₆) complexes have been synthesized by reduction of the appropriate Ru(η⁶-arene)(η⁶-octamethylnaphthalene)²⁺ complexes.
In contrast to the relatively large number of Ru($\eta^6$-arene)($\eta^4$-diene) and associated complexes that have now been synthesized, very little work has been reported on the analogous osmium systems.

The complex [Os(C$_6$H$_6$)Cl$_2$]$_n$ (76, $X = Cl$) was originally reported to be formed in 5% yield from the reaction of OsCl$_3$ with 1,3-cyclohexadiene in refluxing ethanol. The product was difficult to separate from organic polymers; however the production of polymers was suppressed by addition of I$_2$ to the reaction mixture, the resulting product being the diiodide complex 76 ($X = I$). Apparently this formation of an organic polymer does not always occur; for example, the synthesis of 76 ($X = Cl$) using similar reaction conditions to Winkhaus' (with a somewhat lower temperature), in reasonable yield. Bennett et al. have prepared the acetonitrile adduct of 76 ($X = Cl$), Os(C$_6$H$_6$)Cl$_2$(CH$_3$CN), from OsO$_4$ as follows: OsO$_4$ was heated under reflux with concentrated HCl; on evaporation of the solvent an unidentified orange oily solid was obtained, which was then refluxed in ethanol with 1,3-cyclohexadiene. Evaporation of the solvent from this reaction mixture gave a brown solid, which was extracted with
CH$_3$CN, giving Os(C$_6$H$_6$)Cl$_2$(CH$_3$CN), (40% yield). Dimer 76, (X = Cl) has also been synthesized from 1,3-cyclohexadiene and Na$_2$(OsCl$_6$)$_2$ and "H$_2$(OsCl$_6$)" in hot ethanol; the formation of organic polymers was apparently insignificant in these cases.

Mesitylene and p-cymene chloro complexes of osmium are also known. It has been found$^{169}$ that Na$_2$(OsCl$_6$) reacts with α-phellandrene in ethanol to give a complex formulated as [Os(p-cymene)Cl$_2$]$^2$, 77; the crystal structure of this complex has been determined showing it to be dimeric with two bridging chlorides.$^{173}$ The product of the reaction of OsO$_4$ and concentrated HCl was heated with 1,3,5-trimethyl-1,4-cyclohexadiene in ethanol to give a complex of empirical formula Os$_4$Cl$_9$(mesitylene)$_3$. 112

The complexes Os$_4$Cl$_9$(C$_6$H$_3$Me$_3$)$_3$ and OsCl$_2$(C$_6$H$_6$)(CH$_3$CN) have been used to synthesize Os(η$_6$-arene)(η$_4$-COT) (arene = C$_6$H$_3$Me$_3$, C$_6$H$_6$, respectively, COT = cyclooctatetraene), 78, by reaction with Li$_2$COT. 112 Irradiation of OsCl$_3$ with isopropyl magnesium bromide and 1,3-cyclohexadiene gave Os(C$_6$H$_6$)(C$_6$H$_8$), 79, in less than 0.25% yield.$^{119}$
2.1.2 $\eta^5$-Cyclopentadienyl $\eta^4$-Diene Complexes of Rhodium and Iridium

We decided to extend our investigations into the protonation of $\text{M}(\eta^6$-arene)(\eta$^4$-diene) ($\text{M} = \text{Ru}, \text{Os}$) complexes to include complexes of the type $\text{M}(\eta^5$-cyclopentadienyl)(\eta$^4$-diene) ($\text{M} = \text{Rh, Ir}$), in order to obtain more information as to the nature of the protonated products. $\text{M}(\eta^5$-C$_5$H$_5$)(\eta$^4$-diene) ($\text{M} = \text{Rh, Ir}; \text{R} = \text{H, CH}_3$) complexes are well known and many examples have been synthesized and studied. This introduction does not attempt a comprehensive review but surveys the literature most relevant to section 2.2 of this chapter.

The classical route to $\eta^5$-C$_5$H$_5$ complexes of rhodium is the reaction between cyclopentadienyl ion, $(\eta^5$-C$_5$H$_5$)$^-$(as the Na$^+$ or Ti$^+$ salts) and a chloro-rhodium complex of the type $[\text{Rh}(\eta^4$-diene)(\mu-Cl)]$_2$ or $\text{Rh}(\eta^4$-diene)Cl. These chloro complexes may be synthesized directly from $\text{RhCl}_3$.xH$_2$O and diene in aqueous alcohol, or via the tetrakis(ethylene), or tetrakis(cyclooctene) complexes, $[\text{Rh}(\text{L})_2($\mu-Cl$)]_2$ ($\text{L} = \text{C}_2\text{H}_4$, $\text{C}_8\text{H}_{14}$). Iridium ($\eta^5$-C$_5$H$_5$) $\eta^4$-diene complexes are less well known than their Rh counterparts. They can be synthesized in an analogous fashion by treating the cyclooctene complex $[\text{Ir}(\text{C}_8\text{H}_{14})(\mu\text{-Cl})]_2$, with diene and subsequent addition of sodium or thallium cyclopentadienide, or by treating the appropriate diene complex, $[\text{Ir}(\eta^4$-diene)Cl]$_n$ or acetylacetonate complex $[\text{Ir}(\eta^4$-diene)(acac)] with NaCp or TlCp ($\text{Cp} = \eta^5$-C$_5$H$_5$).

Peralkylated cyclopentadienyl $\eta^4$-diene complexes of Rh and Ir are conveniently synthesized from the dimers $[\text{M}(\eta^5$-C$_5$R$_5$)Cl$_2$]$_2$ ($\text{M} = \text{Rh, Ir}$;
R = alkyl group). The dimer $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$, 80, was synthesized independently by Haszeldine et al.\textsuperscript{154,155} and Maitlis et al.\textsuperscript{156,157} (though the former authors initially identified it as a hexamethylbenzene complex\textsuperscript{154}) from the reaction of hexamethylbicyclo[2.2.0]hexa-2,5-diene with $\text{RhCl}_3\cdot\text{H}_2\text{O}$ in methanol. The reaction proceeds via an initial acid catalysed rearrangement of the bicyclohexadiene to an ethylcyclo-

![Diagram](image.png)

pentadiene 81,\textsuperscript{157} (the acid presumably arising from the ionisation of coordinated $\text{H}_2\text{O}$ of $\text{RhCl}_3\cdot\text{H}_2\text{O}$). In fact, good yields of 80 can be obtained by reacting $\text{RhCl}_3\cdot\text{H}_2\text{O}$ directly with 81 ($X = \text{Cl, OMe}$).\textsuperscript{157} Complex 80 can also be synthesized from the reaction of pentamethylcyclopenta-1,4-diene with $\text{RhCl}_3\cdot\text{H}_2\text{O}$,\textsuperscript{155} The crystal structure of 80 has been reported\textsuperscript{158} and Maitlis has reviewed some of the properties of the complex.\textsuperscript{159,160} The iridium complex analogous to 80, $[\text{Ir}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$, has been synthesized in similar fashion, from $\text{IrCl}_3\cdot\text{H}_2\text{O}$ and hexamethylbicyclo[2.2.0]hexa-2,5-diene (in low yield),\textsuperscript{157} or from 81 ($X = \text{Cl, OMe}$,\textsuperscript{161}) in good yield.

The ethyltetramethylcyclopentadiene dimers of Rh and Ir, $[\text{M}(\text{C}_5\text{Me}_4\text{Et})\text{Cl}_2]_2$ have also been synthesized,\textsuperscript{162} but little has been reported on their reactivity.
The synthesis of \( \text{M}^{\text{C}_5\text{Me}_5}(\eta^4\text{-diene})(\text{M} = \text{Rh}, \text{Ir}) \) complexes closely parallels the synthesis of \( \text{M}^{\text{n}_6\text{-arene}}(\eta^4\text{-diene}) \) complexes (described above, section 2.1.1). Treatment of \( [\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2 \) (\( \text{M} = \text{Rh}, \text{Ir} \)), with dienes in the presence of a base (e.g., \( \text{Na}_2\text{CO}_3 \)) and alcohol, or treatment of the bridging hydride complexes \( [\text{M}(\text{C}_5\text{Me}_5)\text{Cl}]_2(\mu-H)(\mu-\text{Cl}) \) (\( \text{M} = \text{Rh}, \text{Ir} \)), \( \text{82} \), with dienes in dichloromethane, gave either \( \text{M}^{\text{C}_5\text{Me}_5}(\eta^3\text{-allyl})\text{Cl} \) complexes or \( \text{M}^{\text{C}_5\text{Me}_5}(\eta^4\text{-diene}) \) complexes, depending on the diene; \( \text{122,123,156,161,163-166} \) in some cases the allylic complexes were shown to be intermediates in the formation of the diene complexes. \( \text{163,165} \) The bis-ethylene complexes \( \text{M}^{\text{C}_5\text{R}_3}(\text{C}_2\text{H}_4)_2 \) (\( \text{M} = \text{Rh}, \text{Ir} \)) have also been synthesized in similar fashion, by reaction of the dimer \( [\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2 \) with ethylene gas in the presence of \( \text{Na}_2\text{CO}_3 \), \( \text{122} \) or with \( \text{Al}_2\text{Et}_6 \). \( \text{167} \)

The mechanism of the reaction in alcohol with base is similar to that outlined in Scheme 2:2 for the synthesis of \( \text{M}^{\text{n}_6\text{-arene}}(\eta^4\text{-diene}) \) (\( \text{M} = \text{Ru}, \text{Os} \)) complexes. The initial reaction of \( \text{M-Cl} \) with alcohol to give an \( \text{M-H} \) complex, is followed by reaction of diene with formation of a \( \eta^3\text{-allyl-chloro} \) complex, with subsequent loss of \( \text{HCl} \) in some cases to give \( \eta^4\text{-diene} \) complexes. \( \text{122,165} \) An \( \text{anti} \), rather than \( \text{syn} \) configuration of the \( \eta^3\text{-allyl-chloro} \) intermediates appears to be a prerequisite for \( \text{HCl} \) elimination, as the carbon skeleton
is adjacent to the metal (Fig. 2:1). The formation of the anti isomer

\[
\begin{align*}
\text{syn config.} & : \\
\text{anti config.} & : \\
\end{align*}
\]

may be difficult to attain in some acyclic \(\eta^3\)-allyl species. The \(\text{M(C}_5\text{Me}_5)(\eta^4\text{-butadiene})\) \((M = \text{Rh, Ir})\) complexes could not be obtained by any method\(^{165}\) as the \(\eta^3\)-methallyl moiety adopts the syn configuration (Fig. 2:1) and is reluctant to isomerize to the anti configuration.

The presence of a metal-hydride intermediate in the reaction is supported by the fact that the bridging hydride complexes \(^{82}\), which are synthesized from \([\text{M(C}_5\text{Me}_5)\text{Cl}_2]\) by reaction with alcohol and base,\(^{168}\) react with dienes to give diene or \(\eta^3\)-allyl complexes. Further support comes from the fact that \(\text{Ir(C}_5\text{Me}_5)\text{Cl}_2(\text{PPh}_3)\) reacts with aqueous ethanol and base to give the hydride complex \(\text{Ir(C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)\text{Cl}\).\(^{122}\)

A selection of \(\text{M(C}_5\text{Me}_5)(\eta^4\text{-diene})\) \((M = \text{Rh, Ir})\) complexes synthesized by the above methods is outlined in Scheme 2:3.
SCHEME 2:3  SOME $M(C_5Me_5)(n^4$ diene) COMPLEXES

$M$ = Rh, Ir; $X$ = Cl, H

$M = Rh, Ir$; $X = Cl, H$
2.2 RESULTS AND DISCUSSION

2.2.1 Synthesis of $[\text{Os}(\eta^6\text{-arene})\text{Cl}_2]_n$ complexes, and $[\text{M}(\eta^5\text{Me}_5\text{-2.g}-\text{Cl}_2)]_2$ ($\text{M} = \text{Rh}$ and $\text{Ir}$) complexes

In order to develop synthetic routes to $\text{Os}(\eta^6\text{-arene})(\eta^4\text{-diene})$ complexes, we have investigated the synthesis of arene-osmium chloro complexes from $\text{OsO}_4$, as reported by Bennett et al.\textsuperscript{112} The $\text{OsO}_4$ is first reduced with hot concentrated hydrochloric acid to give a mixture of osmium chlorides. Osmium tetraoxide dissolves in conc. HCl to give a yellow solution. Heating the solution to approximately $100^\circ\text{C}$ results in rapid darkening in colour, followed by lightening to a reddish colour, which does not change on further heating. Colton and Farthing report similar observations\textsuperscript{174}. If the reaction is conducted using HCl to which some ethanol has been added, the solution becomes a lighter, more orange colour on heating. In both cases, removal of the solvent from the mixture after reaction, on a rotary evaporator, with gentle warming ($40^\circ$ - $50^\circ\text{C}$) gives an oily solid, which presumably is similar to the orange material obtained by Bennett et al.\textsuperscript{112}

The precise nature of this solid is not known. The reduction of $\text{OsO}_4$ in HCl in the presence of ethanol or hydrazinium dichloride is a method for the synthesis of $\text{H}_2(\text{OsCl}_6)$\textsuperscript{175,176}. The reddish solution we obtain on heating $\text{OsO}_4$ in HCl/ethanol thus probably contains $\text{H}_2(\text{OsCl}_6)$. This acid is not very stable, particularly in high concentration\textsuperscript{176}. A possible decomposition product is the black solid $\mu$-oxo-hexachlorodiosmium, $\text{Os}_2\text{OCl}_6$, which has been obtained from $\text{OsO}_4$ and HCl, with strong heating\textsuperscript{174}. The oily residue we obtain thus probably contains some $\text{H}_2(\text{OsCl}_6)$, and other osmium chloride species including $\text{Os}_2\text{OCl}_6$; indeed, if the residue is heated strongly,
a shiny black material is formed. The oily residue proved to be very difficult to reproduce consistently from batch to batch. Sometimes it was red in colour, whilst at other times the same reaction conditions and workup gave a red-black solid.

Reaction of the reddish or black oily residue obtained from the OsO₄/HCl reaction, with 1,3-cyclohexadiene in refluxing ethanol gave a yellow polymeric material, from which we were unable to isolate either [Os(C₆H₆)Cl₂]ₙ [170,171] or Os(C₆H₆)Cl₂(CH₃CN). However, as Winkhaus et al. [170] have observed, addition of iodine to the reaction mixture suppressed polymerization of organics and gave a dark red product, [Os(C₆H₆)I₂]ₙ. This reaction was reproducible both in yield (40 -50%, slightly lower than the reported yield [170]) and in analytical purity. The dimer [Os(C₆H₆)I₂]₂ₙ (the value of n is not known but may be 2) proved to be a good precursor for the synthesis of Os(C₆H₆)(η⁴-diene) complexes, as is discussed later (Section 2.2.2).

Reaction of the red residue, obtained from OsO₄/HCl, with 1,3,5-trimethyl-1,4-cyclohexadiene (C₉H₁₄) in ethanol gave a yellow solid, which we tentatively call [Os(C₆H₃Me₃)Cl₂]ₙ (C₆H₃Me₃ = η⁶-1,3,5-trimethylbenzene). This reaction proved to be extremely difficult to reproduce; yields from different reactions varied from zero to about 50%, though generally were about 30% (yields calculated assuming the product is [Os(C₆H₃Me₃)Cl₂]₂ (i.e., n = 2), and the analytical purity varied considerably, with C and H percentages generally lower than the calculated values for [Os(C₆H₃Me₃)Cl₂]ₙ.
Bennett et al.\textsuperscript{112} found that the product of the reaction of OsO$_4$/HCl residue and C$_9$H$_{14}$ had the empirical formula Os$_4$Cl$_9$(C$_6$H$_3$Me$_3$)$_3$; however our analytical figures do not match that formula. The reasons for the variations in product yield and purity are not yet known, but are probably related to the difficulty in producing a consistent product from the reaction of OsO$_4$ and HCl. Noteworthy is the fact that the black solid obtained when the product of the OsO$_4$/HCl reaction is heated strongly, possibly Os$_2$OCl$_6$,\textsuperscript{174} does not react with C$_9$H$_{14}$ in ethanol.

We have also synthesized a similar yellow solid, which contains an osmium-mesitylene species possibly of formulation [Os(C$_6$H$_3$Me$_3$)Cl$_2$]$_n$, from the reaction of Na$_2$(OsCl$_6$) with C$_9$H$_{14}$ in ethanol. However, the analytical C, H, and Cl percentages of the material again match neither the formula [Os(C$_6$H$_3$Me$_3$)Cl$_2$]$_n$ or Os$_4$Cl$_9$(C$_6$H$_3$Me$_3$).\textsuperscript{112}

Fortunately, whatever the formulation of the osmium-(C$_6$H$_3$Me$_3$) material, it proved to be a suitable precursor for the synthesis of Os(C$_6$H$_3$Me$_3$)(η$^4$-diene) complexes, as described later. In this thesis we have generally assumed the main component of the yellow solid to be [Os(C$_6$H$_3$Me$_3$)Cl(µ-Cl)]$_2$, (assuming the dimeric form by analogy with the p-cymene dimer 82,\textsuperscript{173}), and this formula has been used for calculation of yields etc.. However, it may not be the correct one.

The corresponding ruthenium dimers, [Ru(η$^6$-arene)Cl$_2$]$_2$ were synthesized as reported\textsuperscript{110} from RuCl$_3$·xH$_2$O and the appropriate diene [Rh(C$_5$Me$_3$)Cl$_2$]$_2$.

\* See footnote in Experimental Section (Chapter 7)
was also synthesized as reported, \textsuperscript{155} from RhCl\textsubscript{3} \cdot xH\textsubscript{2}O and pentamethylcyclopentadiene, in refluxing methanol.

The complex [Ir(C\textsubscript{5}Me\textsubscript{5})Cl\textsubscript{2}]\textsubscript{2} was synthesized in a slightly different fashion to the published procedures.\textsuperscript{157,161} (NH\textsubscript{4})\textsubscript{2}(IrCl\textsubscript{6}) reacted slowly with pentamethylcyclopentadiene in refluxing isopropanol to give a brown solid, from which the orange dimer could be extracted into CH\textsubscript{2}Cl\textsubscript{2} in 30 - 40\% yield. The crude brown solid was shown by analysis to contain a significant percentage of nitrogen; ammonium chloride is probably the main by-product of the reaction. The product yield and purity were reproducible, and not significantly affected by the scale of the reaction. The yield of 30 - 40\% is substantially less than the yield (85\%) reported by Maitlis \textit{et al.}\textsuperscript{157} but rather better than those reported by Haszeldine \textit{et al.}\textsuperscript{161}

2.2.2 Synthesis of new M(\eta\textsuperscript{6}-arene)(\eta\textsuperscript{4}-diene) (M = Ru, Os) and M(C\textsubscript{5}R\textsubscript{5})(\eta\textsuperscript{4}-diene) (M = Rh, Ir; R = H, CH\textsubscript{3}) complexes

We have synthesized a range of new complexes of the type Os(\eta\textsuperscript{6}-arene)(\eta\textsuperscript{4}-diene) (\eta\textsuperscript{6}-arene = C\textsubscript{6}H\textsubscript{6}, C\textsubscript{6}H\textsubscript{3}Me\textsubscript{3}), and also a few new complexes of the types Ru(\eta\textsuperscript{6}-arene)(\eta\textsuperscript{4}-diene) and M(C\textsubscript{5}R\textsubscript{5})(\eta\textsuperscript{4}-diene) (M = Rh, Ir; R = H, CH\textsubscript{3}). For the osmium and ruthenium complexes, and the Rh and Ir pentamethylcyclopentadienyl complexes this was done by refluxing the appropriate diene with the appropriate chloro dimer, [M(\eta\textsuperscript{6}-arene)Cl\textsubscript{2}]\textsubscript{2} (M = Ru, Os) and [M(C\textsubscript{5}Me\textsubscript{5})Cl\textsubscript{2}]\textsubscript{2} (M = Rh, Ir), in isopropanol with sodium carbonate as base. This reaction is discussed in Section 2.1. Yields, \textsuperscript{1}H and \textsuperscript{13}C nmr data and mass spectral data are in Tables 5 - 9.
Thus, reaction of $[\text{Os}(\text{C}_6\text{H}_6)\text{I}_2]_n$ or $[\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]_2$ with
2,3-dimethylbuta-1,3-diene gave $\text{Os}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_{10})$, 83A, and
$\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_6\text{H}_{10})$, 83B, respectively as pale yellow air-sensitive
solids. The $^1\text{H}$ and $^{13}\text{C}$ nmr spectra are similar in basic features
to those of $\text{Ru(n}^6\text{-arene})(\text{C}_6\text{H}_{10})$, $^{56,120}$ and $\text{M(C}_5\text{R}_5)(\text{C}_6\text{H}_{10})$ ($\text{M} = \text{Rh},$
$\text{Ir}; \text{R} = \text{H}, \text{CH}_3$) complexes. $^{147,165}$ The benzene complex, 83A shows
a singlet for the arene at $\delta 4.67$ in the $^1\text{H}$ nmr spectrum which is
shifted ca. 2 ppm upfield of the free benzene resonance, as is
classic of $n^6$-arene complexes. $^{110}$ Similarly, the mesitylene
complex 83B shows a singlet at $\delta 4.59$ for the three aromatic protons,
as well as a singlet at $\delta 2.05$ for the methyl groups on the arene.
The diene ligands of 83A and B give rise to two separate two-proton
doublets ($J \approx 2$ ppm) for $H_a$ and $H_b$, and a six-proton singlet for the
methyl groups.

The $^{13}\text{C} \{^1\text{H}\}$ nmr spectrum of 83A shows an arene resonance at $\delta 71.7$,
shifted upfield relative to the resonance of free benzene (ca. $\delta 128$
ppm). The diene ligand gives rise to three resonances, at $\delta 83.6$
(C-Me), $\delta 28.9$ (CH$_2$) and $\delta 21.4$ (methyl group). These spectral results
suggest that 83A and 83B are symmetrical half-sandwich complexes.
We synthesized the ligand 2,3-dimethylene-5,6,7,8-dibenzobi-
cyclo[2.2.2]octane, (ddbo),\textsuperscript{177} in the hope that its relatively high
molecular weight would aid in the preparation of crystalline samples
of its protonated complexes suitable for study by X-ray crystallography.

\[
\begin{align*}
\text{(ddbo)} & \\
\end{align*}
\]

The compound (ddbo) is essentially a substituted butadiene, with
bulky groups in positions 2 and 3, and it was expected to behave
in similar fashion to 2,3-dimethylbutadiene.\textsuperscript{1} The H nmr spectrum
of the free ligand in CC\textsubscript{14} shows a 2H singlet for the bridgehead
protons (\(H_c\)) at \(\delta 4.71\), two 2H singlets for the vinylic protons
\(H_a, H_b\) at \(\delta 5.00\) and \(\delta 5.16\), and a complex multiplet at \(\delta 7\) ppm for
the benzo protons.

In the presence of anhydrous sodium carbonate, (ddbo) reacted
with \([\text{Os(C}_6\text{H}_3\text{Me}_3\text{)}\text{Cl}_2]_2\) to give \(\text{Os(C}_6\text{H}_3\text{Me}_3\text{)(C}_18\text{H}_{14})\), \textsuperscript{84}, as a pale
yellow air-sensitive solid in 50% yield. In addition to the arene
resonances, the \(1^1\text{H nmr spectrum of } 84 \text{ shows that the resonances for}
the vinylic protons have been shifted upfield relative to the free
ligand, and now appear as doublets at \(\delta 0.09 (H_a) \) and \(\delta 2.34 (H_b)\)
\((J = 2.5 \text{ Hz})\). The resonances of bridgehead protons, \(H_c\), and the
benzo protons are little changed from those of the free ligand. Similarly, the $^{13}$C nmr ($^1$H-coupled) spectrum of 84 shows a doublet of doublets at $\delta$19.4 ($J = 149$, 160 Hz) for $C_1$, which is ca. 80 ppm upfield of the resonance for the corresponding carbon in the free ligand. The two bridgehead carbons are equivalent, giving rise to one doublet ($\delta$53.6; $J = 141$ Hz), similarly the two benzo groups are equivalent, giving rise to four doublets and two singlets for the secondary and tertiary carbons respectively. These results indicate 84 is a symmetrical half sandwich complex.

Reaction of $[\text{Os}(C_6H_6)I_2]_n$ or $[\text{Os}(C_6H_3Me_3)Cl_2]_2$ with 1,3-cyclohexadiene gave the complexes $\text{Os}(C_6H_6)(C_6H_8)$ and $\text{Os}(C_6H_3Me_3)(C_6H_8)$, 79 and 85, respectively as air-sensitive, pale yellow solids, in yields of ca. 50%.

The nmr spectra of the diene ligands of 79 and 85 are similar to those of other 1,3-cyclohexadiene complexes, including $\text{Ru(\eta^6\text{-arene})(C_6H_8)}$, $M(C_5R_5)(C_6H_8)$ ($M = \text{Rh, Ir}$; $R = \text{H, CH}_3$), and $\text{Fe(C}_6\text{H}_8)(\text{CO})_2L$ ($L = \text{CO, phosphine}$). The $^1$H nmr spectrum of
79 shows, as well as the arene resonances, a doublet of doublets due to $H_{2,3}$ ($\delta 5.25; J = 5.0, 2.5$ Hz) and multiplets due to $H_{1,4}$ ($\delta 3.39$) and $H_{5,6}$ ($\delta 1.83$). The $^{13}$C ($^1$H) nmr spectrum shows three resonances for C$_{1,4}$ ($\delta 69.5$), C$_{2,3}$ ($\delta 44.6$) and C$_{5,6}$ ($\delta 29.8$).

1,3,5-Trimethyl-1,4-cyclohexadiene undergoes isomerization to the 1,3-diene on reaction with $[\text{Os(C}_6\text{H}_6\text{Me}_3)(\text{Cl}_2)]_2$ in isopropanol with Na$_2$CO$_3$, and the complex Os(C$_6$H$_3$Me$_3$)(C$_9$H$_{14}$), $^{86}$, is formed. This complex was isolated as an air-sensitive yellow oil. The presence of the 1,3-diene is indicated by the fact that, in the $^1$H nmr spectrum, three resonances (two singlets, one doublet) arising from the Me groups on the diene ligand, are seen. Only two would be expected were the ligand bonded as the 1,4 isomer. Further, the $^{13}$C nmr spectrum shows three separate CH$_3$ resonances for the diene methyl groups. Other features in the $^1$H nmr spectrum include multiplets at $\delta 4.75$ and $\delta 2.59$ for $H_2$ and $H_4$ respectively, and three one-proton multiplets ($\delta 2.2, \delta 1.9, \delta 1.5$) for $H_5$ and the two $H_6$ protons. Isomerization of 1,3,5-trimethyl-1,4-cyclohexadiene to the 1,3-diene also occurred during the synthesis of Ru(C$_6$Me$_6$)(C$_9$H$_{14}$), $^{56}$, and Fe(C$_9$H$_{14}$)(CO)$_3$, $^{182}$, and the $^1$H nmr spectra of the diene moiety of these complexes are similar to that of $^{86}$. In fact, isomerization of 1,4- to 1,3-dienes during the synthesis of transition metal complexes is well documented, and indeed it seems unusual for it not to occur. $^{110,123,124,180-182}$

Reaction of $[\text{Os(C}_6\text{H}_6\text{)}_2]_2$ with 1,5-cyclooctadiene in isopropanol and with Na$_2$CO$_3$ gave Os(C$_6$H$_6$)(1,5-C$_8$H$_{12}$), $^{87A}$, as a yellow, air-
The $^1H$ nmr spectrum of 87A showed, for the diene ligand, two multiplets; a four-proton multiplet ($\delta3.72$) for $H_{1,2,5,6}$ and an eight-proton multiplet ($\delta2.35$) for the other protons. The $^{13}C\{^1H\}$ nmr spectrum showed, apart from the arene resonance, a resonance at $\delta35.9\ (C_{1,2,5,6})$ and one at $\delta47.4\ (C_{3,4,7,8})$. These data agree with data obtained for Ru(6-arene)(1,5-C$_8$H$_{12}$),$^{56}$ M(C$_5$Me$_5$)(1,5-C$_8$H$_{12}$) ($M = Rh, Ir$),$^{166}$ and M(1,5-C$_8$H$_{12}$)(CO)$_3\ (M = Fe, Ru)$.$^{183}$

The reaction of [Os(C$_6$H$_3$Me$_3$)Cl$_2$]$_2$ with 1,5-cyclooctadiene in refluxing isopropanol, in the presence of Na$_2$CO$_3$, was more complex. In only one attempt did we synthesize only Os(C$_6$H$_3$Me$_3$)(1,5-C$_8$H$_{12}$), 87B, in 3% yield. In all other attempts we obtained an inseparable mixture of three mesitylene-containing products. One, the minor product, had an $^1H$ nmr spectrum corresponding to 87B (mesitylene proton resonances at $\delta1.78\ (9H)$ and $\delta4.65(3H)$). A mixture of the two major products showed mesitylene resonances at $\delta1.73, \delta1.99, \delta4.64$ and $\delta4.59$ in the proton nmr; the rest of the spectrum was complex. The relative amounts of the two major isomers varied from attempt to attempt. We were not able to fully identify the two major species,
but they may be the \( \eta^3 \)-allyl complex \( \text{Os(C}_6\text{H}_3\text{Me}_3\text{)}(\eta^3-\text{C}_8\text{H}_{13})\text{Cl} \), and the 1,3-cyclooctadiene complex \( \text{88} \). Maitlis et al.\(^{166} \) found that \( [\text{M(C}_5\text{Me}_5\text{)}\text{Cl}_2]_2(\mu-\text{H})(\mu-\text{Cl}) \) (\( \text{M} = \text{Rh}, \text{Ir} \)) reacted with 1,5- or 1,3-\( \text{C}_8\text{H}_{12} \) to give either the \( \eta^3 \)-allyl complex \( \text{M(C}_5\text{Me}_5\text{)}(\eta^3-\text{C}_8\text{H}_{13})\text{Cl} \) analogous to \( \text{88} \), or the 1,5-cyclooctadiene complex \( \text{M(C}_5\text{R}_5\text{)}(1,5-\text{C}_8\text{H}_{12}) \), depending on the reaction conditions. Such a variation in product has also been noted by Lewis et al.\(^{183} \) who conducted an extensive investigation into coordinated cyclooctadiene complexes of \( \text{Fe}, \text{Ru} \) and \( \text{Os} \). He noted that photochemical treatment of \( \text{Fe(CO)}_5 \) with 1,5-\( \text{C}_8\text{H}_{12} \) could give either (tetracarbonyl)(1,5-cyclooctadiene)iron, or \( \text{Fe(1,5-C}_8\text{H}_{12})(\text{CO})_3 \), or \( \text{Fe(1,3-C}_8\text{H}_{12})(\text{CO})_3 \), depending on the reaction time. \( \text{Ru}_3(\text{CO})_12 \) reacted with 1,5-\( \text{C}_8\text{H}_{12} \) to give either \( \text{Ru(1,5-C}_8\text{H}_{12})(\text{CO})_3 \) or a \( \eta^3 \)-allyl complex, \( \text{Ru(4-6-\eta,1-\sigma-cyclooctenediy1(CO)}_3 \), again depending on reaction time. Further, Lewis et al.\(^{183} \) found that irradiation of \( \text{Os}_3(\text{CO})_12 \) with 1,5-\( \text{C}_8\text{H}_{12} \) in benzene gave an inseparable mixture of \( \text{Os(1,5-C}_8\text{H}_{12})(\text{CO})_3 \), \( \text{Os(1,3-C}_8\text{H}_{12})(\text{CO})_3 \) and probably a \( \eta^3 \)-allyl complex analogous to \( \text{90} \).

Fortunately, however, the fact that the products of the reaction of \( [\text{Os(C}_6\text{H}_3\text{Me}_3\text{)}\text{Cl}_2]_2 \) with 1,5-cyclooctadiene could not be fully characterised, did not hinder our studies of protonation products of osmium-diene complexes. As discussed in Chapter 4,
protonation of the crude mixture of products gave exclusively one product, \([\text{Os}(C_6H_3Me_3)(C_8H_{12})H]\text{PF}_6\); subsequent deprotonation of this gave only \(\text{Os}(C_6H_3Me_3)(1,5-C_8H_{12})\), 87B.

Norbornadiene \((C_7H_8)\) reacted with \([\text{Os}(C_6H_3Me_3)\text{Cl}_2]_2\) to give \(\text{Os}(C_6H_3Me_3)(C_7H_8)\), 91, as an air-sensitive yellow solid. This reaction was accompanied by extensive polymerisation of the diene. The diene bonds symmetrically to the metal, as indicated by the \(^1H\) and \(^{13}C\) nmr spectra. The proton spectrum shows a two-proton multiplet (\(\delta3.72\)) for \(H_{1,4}\), a four-proton multiplet for \(H_{2,3,5,6}\) (\(\delta2.63\)) and a two-proton triplet (\(\delta1.05\)) for the two protons in position 7. The \(^{13}C\) \(^1H\) nmr spectrum shows three resonances for the diene ligand; \(\delta19.6\) (\(C_{2,3,5,6}\)), \(\delta47.0\) (\(C_{1,4}\)) and \(\delta59.3\) (\(C_7\)). It is interesting to note that while the protons on \(C_7\) resonate upfield of the rest of the diene proton signals in the \(^1H\) nmr spectrum, \(C_7\) itself gives a resonance downfield of the rest of the diene carbons in the \(^{13}C\) nmr spectrum. The spectra of the diene part of 91 are similar to those of several other \(n^4\)-norbornadiene complexes. 19, 20, 56, 122, 184 However, in the \(^{13}C\) nmr spectrum of the complexes \(M(\text{norbornadiene})(\text{CO})_4\)
(M = Cr, Mo), the most downfield resonance (ca. 80 ppm) was assigned to the olefinic protons, whereas we have assigned the most upfield resonance (δ19.6) to the olefinic protons in 91.

A yellow air-sensitive complex Os(C₆H₃Me₃)(C₁₀H₁₂), 92, was isolated from the reaction of [Os(C₆H₃Me₃)Cl₂]₂ with endo-dicyclopentadiene (3α,4,7,7α-tetrahydro-4,7-methano-1H-indene). The proton and carbon nmr spectra of 92 are complex, and have not been assigned in detail. Four one-proton multiplets at δ4.15, δ3.71, δ3.47 and δ3.27 are probably due to H₂, H₃, H₅ and H₆. Several other η⁴-C₁₀H₁₂ complexes have been reported, including Ru(C₆Me₆)(C₁₀H₁₂)⁵⁶,¹²⁰ Rh(C₅R₅)(C₁₀H₁₂) (R = H, CH₃)³³,¹²² and a Ni complex, Ni(duroquinone)(C₁₀H₁₂)¹⁸⁶.

When ethylene was bubbled through a slurry of [Os(C₆H₃Me₃)Cl₂]₂ and sodium carbonate in isopropanol (70°C), the bis-η²-ethylene complex Os(C₆H₃Me₃)(C₂H₄)₂, 93, was formed, and isolated as a light brown, air-sensitive solid. The ¹H nmr spectrum of 93 (Fig. 2:2) at 30°C shows two mirror image multiplets due to the ethylene ligands, each integrating for 4H, at δ2.07 and δ0.93. The ¹³C nmr spectrum at this temperature shows only one resonance for the ethylene ligands, at δ21.8. These data are consistent with a symmetrical structure with two non-equivalent sets of ethylene protons, Hₐ (inner) and Hₖ (outer).

Cramer et al.¹⁸⁷-¹⁸⁹ have extensively investigated the analogous rhodium complex, Rh(C₆H₃)(C₂H₄)₂, and found that the complex was fluxional in solution. At -20°C the ¹H nmr showed two 4H ethylene resonances.
FIG. 2:2  $^1$H nmr of ethylene ligands of Os(C$_6$H$_3$Me$_3$)(C$_2$H$_4$)$_2$ 93 (30°C)
On warming to ca. 60°C these coalesced into one broad peak, which sharpened as the temperature was increased. These results were interpreted in terms of a propeller-like rotation of the ethylene ligand about the metal-ligand axis: at low temperatures the structure is static, with two non-equivalent sets of protons (equivalent to $H_a$ and $H_b$ in 93); on warming these became equivalent due to fast rotation, resulting in coalescence of the peaks in the $^1H$ nmr spectrum. Similar observations have been made on $M(C_5Me_5)(C_2H_4)_2$ ($M = Rh, Ir$), and $Ru(C_6Me_6)(C_2H_4)_2$. The rates of rotation decrease in order $C_5H_5Rh>C_5Me_5Rh>C_5Me_5Ir=C_6Me_6Ru$.

On warming chlorobenzene solution of 93, the two ethylene resonances broadened, but complete coalescence was not observed at 110°C, at which temperature the complex was decomposing rapidly. The energy barrier to rotation is thus fairly substantial, and probably of the same order of magnitude as the barrier in $Ru(C_6Me_6)(C_2H_4)_2$.

Two new ruthenium diene complexes have also been synthesized, by the reaction of $[Ru(C_6H_3Me_3)Cl_2]_2$ with the appropriate diene and sodium carbonate in refluxing isopropanol. Using the diene (ddbo), $Ru(C_6H_3Me_3)(C_{18}H_{14})$, was synthesized, and isolated as an air-sensitive yellow solid. Its nmr spectra have identical features to the analogous osmium complex, 84.

As with the (ddbo) complexes 84 and 94, the 7-phenylnorbornadiene complex 95 was synthesized in the hope that the relatively high molecular weight of the ligand would enable the preparation of
crystalline samples of the species formed on protonation, suitable for X-ray crystallographical studies. Complex 95 was isolated as air-sensitive yellow needles from the reaction of 7-phenynorbornadiene and \([\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]\). Its proton nmr spectrum, apart from the arene resonances, shows five separate multiplets. Two 2H multiplets at δ2.25 and δ2.50 are assigned to H_{2,3} and H_{5,6}. A one-proton multiplet at δ2.55 is assigned to H_7; this resonance is downfield relative to that of the protons on C_7 of the corresponding norbornadiene complex \(\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_7\text{H}_8)\), at δ1.20, due to the effect of the phenyl ring. A two proton multiplet at δ3.37 is assigned to H_{1,4} and the phenyl protons give rise to a multiplet at δ7.1.

The \(^{13}\text{C}\) nmr spectrum of 95 shows two doublets, with identical J(C-H) couplings (173 Hz), at δ24.3 and δ26.1, for C_{2,3} and C_{5,6}. C_1 and C_4 give rise to a doublet at δ56.2 (J = 142 Hz) and C_7 to a doublet at δ71.2 (J = 131 Hz). The phenyl group gives rise to the expected 4 resonances, at ca. δ130 ppm. The diene ligand phenyl group in 95 is responsible for slight downfield shifts in the resonance positions for C_7 and C_{1,4} in 95 relative to the corresponding carbons.
of the norbornadiene complex Ru(C_6H_3Me_3)(C_7H_8).\textsuperscript{56} The latter complex shows resonances at 648.2 (C_1,4) and 655.4 (C_7), 8 and 15.8 ppm upfield of the corresponding peaks in 95.

Three rhodium and iridium complexes of (ddbo) have been synthesized. The complexes M(C_5Me_5)(C_{18}H_{14}) (96 M = Rh; 97 M = Ir) were synthesized by reaction of the appropriate [M(C_5Me_5)Cl_2]_2 complex with (ddbo) in refluxing isopropanol with sodium carbonate.\textsuperscript{122} Their nmr spectra are very similar to those of the ruthenium and osmium complexes 84 and 94. The (C_5H_5) complex of iridium, Ir(C_5H_5)(C_{18}H_{14}), 98, was also synthesized by reaction of Na(C_5H_5) with Ir(C_{18}H_{14})_2(acac) (acac = acetylacetonate). The latter was made by treating [Ir(cyclooctene)_2Cl] with the (acac)\textsuperscript– ion to give Ir(cyclooctene)_2(acac) and this was then allowed to react with (ddbo). Complexes 96, 97 and 98 are slightly air-sensitive solids.

Reactions of [Ir(C_5Me_5)Cl_2]_2 with dicyclopentadiene in isopropanol/Na_2CO_3 gave Ir(C_5Me_5)(C_{10}H_{12}), 99, as a whiteish slightly airsensitive solid. It was identified by its \textsuperscript{1}H nmr spectrum which is very similar to that of 92, and Rh(C_5Me_5)(C_{10}H_{12}).\textsuperscript{122} Rh(C_5H_5)(C_{10}H_{12}),
was synthesized from \([\text{Rh}(C_2H_4)_2\text{Cl}]_2\), dicyclopentadiene and Na(C_5H_5)(DME) using the general method outlined in Section 2.1.2. This complex has been reported by Muller et al.\(^{33}\) as one product from the reaction of \([\text{Rh}(1,3\text{-cycloheptadiene})\text{Cl}]_2\) and dicyclopentadiene in the presence of isopropyl magnesium bromide.

We have also synthesized Ir(C_5Me_5)(C_7H_8), \(^{101}\) from \([\text{Ir}(C_5\text{Me}_5)\text{Cl}_2]\)_2, Na_2CO_3 and norbornadiene, and Rh(C_5H_5)(C_7H_8), \(^{102}\) from \([\text{Rh}(C_2H_4)_2\text{Cl}]_2\), norbornadiene and \((C_5\text{H}_5)\text{Na}(\text{DME})\).\(^{32}\) The \(^{13}\)C nmr spectrum of \(^{102}\), is interesting in that the resonance at \(\delta57.3\), due to the bridging carbon C_7 shows, unexpectedly, a long-range coupling of 7 Hz with \(^{103}\)Rh. The resonance due to C_2,3,5,6, is also coupled to \(^{103}\)Rh, as would be expected, but the resonance due to C_4 (\(\delta47.0\)) is not.

All other Ru(\(\eta^6\)-arene)(\(\eta^4\)-diene) and M(C_5R_5)(\(\eta^4\)-diene) (M = Rh, Ir; R = H, CH_3) complexes used in the protonation studies in the following chapter, were synthesized as reported.\(^{56,122,123,165}\)
CHAPTER 3

The Protonation of Conjugated 1,3-Diene Complexes of Osmium, Ruthenium, Rhodium and Iridium

This chapter describes the results of the protonation of $M(\eta^6$-arene)(\eta^4-diene) ($M = Ru$, Os) and $M(C_5R_5)(\eta^4$-diene) ($M = Rh$, Ir; $R = H$, CH$_3$) complexes, in which the dienes are conjugated 1,3-dienes. Selected nmr spectra are reproduced at the end of Chapter 5 (Spectrum 1-35) and spectral and analytical data, and yields, are reported in Tables 12-14.

Aqueous HPF$_6$ (60% solution) was routinely used for the protonation reactions. One exception is the protonation of Os(C$_6$Me$_3$H$_3$)(ddbo), $\text{84}$, in which CF$_3$SO$_3$H was used in order to obtain an analytically pure product. Other acids with very weakly coordinating anions, such as HBF$_4$, could probably be used instead of HPF$_6$ to equal effect.

3.1 CYCLOHEXADIENE COMPLEXES

Treatment of the complexes Os(\eta^6-arene)(1,3-cyclohexadiene) ($\text{79}$, arene = C$_6$H$_6$; $\text{85}$, arene = C$_6$H$_3$Me$_3$) with HPF$_6$ in ether gave air-sensitive cream coloured solids of empirical formulae [Os(\eta^6-arene) (C$_6$H$_9$)]PF$_6$ ($\text{103}$, arene = C$_6$H$_6$; $\text{104}$, arene = C$_6$H$_3$Me$_3$). $\text{103}$ and $\text{104}$ are fluxional complexes; a limiting $^1$H nmr spectrum is obtained at -20°C. The spectrum of $\text{103}$ at this temperature showed an arene resonance at $\delta$6.33, three resonances due to the diene ligand at $\delta$5.68 (2H, doublet of doublets) $\delta$4.20 (2H, multiplet) and $\delta$1.80 (4H, multiplet), and a triplet hydride resonance at $\delta$-11.62 ($J = 3.6$ Hz).
The diene spectrum is remarkably similar to that of the parent neutral complex 79, and suggests that the diene is symmetrically bound to the metal. This in turn suggests that the limiting spectra represent a diene hydride ground state structure rather than an agostic complex. The three diene resonances are thus assigned to H$_{2,3}$, H$_{1,4}$ and H$_{5,6}$ respectively. The hydride resonance shows a weak coupling to two equivalent protons, probably H$_1$ and H$_4$. The symmetrical diene hydride structure is supported by the Carbon-$^{13}$ nmr and infrared spectra of 103 and 104. At -30°C the $^{13}$C nmr spectrum of 104 shows three resonances for the diene ligand; a triplet at 627.1 (J = 131 Hz) and doublets at 652.5 (J = 162 Hz) and 677.1 (J = 176 Hz) which are assigned to C$_{5,6}$, C$_{1,4}$ and C$_{2,3}$ respectively (Spectrum 2). The solid-state infrared spectra of 103 and 104 show weak sharp bands at 2140 and 2130 cm$^{-1}$ respectively, assigned to vM-H. These values are rather higher than the vM-H band at 1960 cm$^{-1}$ observed in the infrared spectrum of Re(C$_6$H$_6$)(C$_6$H$_8$)H, 18A.$^{96}$
Cooling solutions of the 1,3-cyclohexadiene osmium complexes causes no change in the nmr spectra. Warming to ambient temperature results in the diene resonances and the hydride resonance broadening somewhat, presumably due to exchange between the metal hydride and H_{5,6}^{endo} via a coordinatively unsaturated 16-electron \( \eta^3 \)-allyl intermediate (Scheme 3:1); this process results in a 1,2-metal migration around the diene ring. However, the instability of the complexes in solution precluded studies at higher temperatures.

The neutral parent 1,3-diene complexes 79 and 85 are easily regenerated from 103 and 104 respectively, by treatment with aqueous Na_2CO_3.

The results obtained by McMahon\(^56\) on protonation of \( \text{Ru}(\eta^6\text{-arene})-(1,3\text{-cyclohexadiene}) \) complexes appear to be similar to those obtained for the osmium complexes 103 and 104. At \(-90^\circ\text{C}\) the spectrum of \([\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_9)]\text{PF}_6\), \(50\text{A}\), showed two 2H multiplets, a 4H multiplet, and a hydride resonance, at similar chemical shift values to those of 103 (see Section 1:3). The \(^{13}\text{C}\) nmr spectrum at \(-90^\circ\text{C}\) of \(50\text{A}\) was also similar to that of 104 at \(-30^\circ\text{C}\) as reported above, except for
the appearance of a 'doublet of doublets' at δ46.8.\textsuperscript{56} We have re-examined this spectrum, run at 67 MHz (as opposed to the 15 MHz instrument used by McMahon) at -100°C, and find that this resonance is in fact a doublet (Spectrum 3), as is the corresponding resonance in the spectrum of 104. These results thus support the assignment of a symmetrical diene hydride ground state structure in [Ru(C\textsubscript{6}H\textsubscript{6})(C\textsubscript{6}H\textsubscript{9})]PF\textsubscript{6}. 

In contrast, the species obtained by Brookhart \textit{et al.} on protonation of [Mn(CO)\textsubscript{3}(C\textsubscript{6}H\textsubscript{5})]\textsuperscript{-},\textsuperscript{25} and by Ittel on protonation of Fe(P(OMe)\textsubscript{3})\textsubscript{3}(C\textsubscript{6}H\textsubscript{5}),\textsuperscript{14} firmly support the assignment of an agostic bridging hydride structure as the ground state structure of the protonated species.

Treatment of the 1,3-cyclohexadiene complex Rh(C\textsubscript{5}Me\textsubscript{5})(C\textsubscript{6}H\textsubscript{8}), \textsuperscript{105}, with HPF\textsubscript{6} in ether results in the precipitation of an orange solid of empirical formula [Rh(C\textsubscript{5}Me\textsubscript{5})(C\textsubscript{6}H\textsubscript{9})]PF\textsubscript{6}, \textsuperscript{106}. Complex \textsuperscript{106} is fluxional in solution. The proton nmr spectrum of \textsuperscript{106} at 20°C shows 

\begin{center}
\includegraphics[width=0.8\textwidth]{diagram.png}
\end{center}

a singlet for the (C\textsubscript{5}Me\textsubscript{5}) ligand, and a six proton multiplet (δ3.42) and a three proton multiplet (δ-1.65) for the (C\textsubscript{6}H\textsubscript{9}) moiety. Cooling the solution as low as possible (ca. -105°C) results in the initial
collapse of these multiplets, and the appearance of five new broad resonances (Spectrum 4), at δ5.10 (3H), δ2.1 – 1.4 (two broad resonances merging into each other and the C5Me5 singlet, 3H altogether), δ0.6 (1H) and δ-3.4(2H). This spectrum is very different from the limiting spectra of the Os and Ru (and Ir, see later) cyclohexadiene complexes, but similar to the spectrum25 of Mn(CO)3(C6H9), 18, at 0°C. By comparison with the latter complex we propose that 106 assumes an agostic bridging hydride ground state structure, and that 106 exhibits two degenerate modes of isomerisation similar to 18; that is, alternating coordination of the two endo C-H bonds adjacent to the allylic centre (the process with the lower activation energy) (Scheme 3:2A), and 1,2-metal migration around the (C6H9) ring via a diene hydride intermediate (Scheme 3:2B) (the higher energy process). The 1H nmr spectrum of 106 at -105°C is the result of the process in Scheme 3:2A being fast, while that in Scheme 3:2B is slow. Hence H2 and H4 are averaged on the nmr time scale, as are H1endo and H5endo, and H1exo and H5exo. The multiplet at δ5.10 is thus assigned to H2,4 and H3 together, the multiplet at δ2.1 – δ1.4 to H1,5exo and

![Scheme 3:2A](attachment:image.png)
H\textsubscript{6}\textit{endo} together, the multiplet at \(\delta 0.6\) to \(H\textsubscript{6} \textit{exo}\) and the high-field multiplet at \(\delta -3.4\) to an average of \(H\textsubscript{1} \textit{endo}\) and \(H\textsubscript{5} \textit{endo}\). On warming to \(20^\circ C\) the process in Scheme 3:2B also becomes fast, and together with the process in Scheme 3:2A results in the averaging of \(H\textsubscript{1} \textit{endo}\)/\(H\textsubscript{5} \textit{endo}/H\textsubscript{6} \textit{endo}\) to give the high-field \(3H\) multiplet, and the remaining six protons to give the multiplet at \(\delta 3.42\).

Confirmation of the agostic structure of 106 comes from deuteration experiments. Treatment of Rh(C\textsubscript{5}Me\textsubscript{5})(C\textsubscript{6}H\textsubscript{8}), 105, with excess DPF\textsubscript{6} gave a yellow precipitate. The \(\textsuperscript{1}H\) nmr spectrum at \(20^\circ C\) (i.e., the fast exchange spectrum) is similar to that of 106 at the same temperature except that in addition to the high-field peak at \(\delta -1.65\), there is a slightly less intense resonance of \(\delta -2.07\) and a third, weak resonance at \(\delta -2.62\) (Fig. 3:1). The presence of 106 in the product (giving the resonance at \(\delta -1.65\)) is probably a result of the DPF\textsubscript{6} used being contaminated with HPF\textsubscript{6}. The other two resonances correspond to analogues of 106 incorporating one or more deuterium atoms. The substantial upfield shift in the deuterated species (0.42 and 0.97 ppm respectively) is indicative of an agostic bridging
Highfield region, $^1$H nmr spectrum of deuterated $[\text{Rh(C}_5\text{Me}_5)(\text{C}_6\text{H}_9)]\text{PF}_6$, 20°C.

The neutral parent complex 105 can be regenerated from 106 by reaction with aqueous Na$_2$CO$_3$. 

Hydride complex; H competes, more effectively than D for the bridging site resulting in a substantial isotope effect on the fast exchange equilibrium constant (see Section 1:2), and a corresponding upfield shift of the peak in the nmr spectrum. The fact that a small proportion of the deuterated species have incorporated more than one deuterium suggests that there is some mechanism for exchange of D$^+$ and H$^+$ ions between the protonated and monodeuterated species and the excess acid, during the initial precipitation with DPF$_6$ and subsequent product workup.
The solid state infrared spectrum showed a weak, broad band at 2060 cm\(^{-1}\). This is both much weaker and broader than the bands in the same region of the infrared spectra of the protonated osmium and iridium 1,3-cyclohexadiene complexes 103 and 108. The significance of this band is uncertain; if it is significant it is not consistent with the assignment of an agostic structure, as such a structure would not be expected to show a band in the region of 2000 cm\(^{-1}\) (see Section 1:2).

In contrast to the rhodium complex 106, the fluxional iridium complex 
\[ \text{[Ir(C}_5\text{Me}_3)(C}_6\text{H}_5)]\text{PF}_6, \] 108, obtained by protonation of \[ \text{Ir(C}_5\text{Me}_3)(C}_6\text{H}_8), \] 107, with HPF\(_6\), appears to adopt a diene-hydride structure as its ground state structure. The proton nmr spectrum of 108 at -60°C (Spectrum 5) shows similar features to those of the osmium complex 104, and suggests a symmetrically bonded diene ligand rather than the unsymmetrical structure expected of an agostic bridging hydride complex. There is a two-proton doublet of doublets (65.26), assigned to \(H_{2,3}\); a two-proton multiplet (64.13) assigned to \(H_{1,4}\); a four-proton multiplet (62) assigned to \(H_{5,6}\); and a hydride singlet at
Warming the solution to 20°C results in collapse into the baseline of the diene resonances and the hydride resonance. Heating a C₆D₅NO₂ solution of 108 results in the appearance of two new peaks at 100°C, at δ3.95 (6H) and δ-3.7 (very broad). This is similar to the fast exchange spectra of [Ru(η⁶-arene)(C₆H₉)]PF₆ complexes and is the result of a rapid exchange process involving an 16 electron intermediate 109 (Scheme 3:3), a process which would equilibrate on the nmr time scale, the hydride, H₃endo and H₆endo on one hand (giving the 3H highfield resonance) and the remaining six protons on the other.

The ¹³C {¹H} nmr spectrum of 108 (Spectrum 6) was broad even at -90°C. However, it shows only three peaks for the diene carbons, at δ26.5, 660.6 and 83.2; this is similar to the proton decoupled spectra of the osmium complexes 103 and 104 and supports the assignment of a symmetrical diene hydride ground-state structure. Complex 108 also shows a sharp weak band at 2165 cm⁻¹ in its solid state infrared spectrum, which is assigned to vM-H.
As is the case with the osmium and rhodium complexes, the parent neutral 1,3-cyclohexadiene complex can be regenerated from 108 using Na₂CO₃.

Treatment of Ir(C₅Me₅)(C₆H₈), 107, with DPF₆ gives an off-white precipitate. The ¹H nmr spectrum of this complex at 120°C is similar to that of 108 at the same temperature except that in addition to the highfield resonance at δ-3.7 there are also resonances at δ-4.8 and δ-6.5. There are thus three species present: 108, and analogues of 108 incorporating one or more D atoms. The substantial upfield shift (1.1 and 2.8 ppm, respectively), of the highfield resonance in the partially deuterated complexes is what one would expect of an agostic bridging hydride complex, as in the rhodium complex discussed above. However, our nmr results for 108 indicate that the ground state structure is most likely a terminal hydride diene complex. The thermodynamic isotope effect seen in partially deuterated 108 must thus arise from an intermediate or transition state bridging hydride complex. Such a transition state may be a very short-lived species arising simply from the simultaneous or concerted rupture of the M-H bond and formation of the H-C bond during the course of an exchange process such as that outlined in Scheme 3:3. Alternatively, an agostic intermediate may be a species in a more complicated equilibrium system than that outlined in Scheme 3:3; unfortunately, the variable temperature spectra provide little information about exactly what intermediates are involved in the fast exchange process.

From the above discussion the limitations of the thermodynamic isotope effect can be seen; the technique does not necessarily provide
information about the ground state structure, but simply indicates the existence of an agostic species as one participant in the fast exchange process.

The results of the protonation of \( \text{M(C}_5\text{Me}_5\text{)(C}_6\text{H}_3) \) complexes (\( \text{M} = \text{Rh}, \text{Ir} \)) are similar to the results obtained on protonation of their \( \text{C}_5\text{H}_5 \) analogues.\(^{31}\) \( [\text{Ir(C}_5\text{H}_5\text{)(C}_6\text{H}_9\text{)}]^{+}\text{CF}_3\text{CO}_2^- \), \(^{24}\) was identified as a diene hydride complex on the basis of its variable temperature \(^1\text{H} \) nmr spectrum. Its low temperature limiting spectrum was obtained at \(-20^\circ\text{C} \), in contrast to the \( \text{C}_5\text{Me}_5 \) complex \(^{108}\), in which case the resonances achieved maximum resolution at \(-60^\circ\text{C} \). Further, the fast exchange spectrum of the \( \text{C}_5\text{H}_5 \) complex was observed at \( \text{ca.} \ 80^\circ\text{C} \), as opposed to \( 100^\circ\text{C} \) in \(^{108}\). No limiting spectrum was obtained on cooling to \(-50^\circ\text{C} \) in the case of the corresponding rhodium complex \( [\text{Rh(C}_5\text{H}_5\text{)(C}_6\text{H}_9\text{)}]\text{CF}_3\text{CO}_2^-, \) \(^{24}\), however, our results for the \( \text{C}_5\text{Me}_5 \) complex \(^{106}\) suggest that a limiting spectrum will only be obtained at rather lower temperatures. The \( \text{C}_5\text{H}_5 \) complex was described as a diene hydride complex, but on the basis of our results for \(^{106}\) it is probably more accurately formulated as an agostic complex.

Interestingly however, Lewis et al.\(^{31}\) did not report observing a thermodynamic isotope effect on formation of \([\text{Rh(C}_5\text{H}_5\text{)(C}_6\text{H}_9-xD_x)}]\text{CF}_3\text{CO}_2^- \).

Protonation of \( \text{Os(C}_6\text{H}_3\text{Me}_3\text{)(1,3,5-trimethyl-1,3-cyclohexadiene)} \), \(^{86}\), with \( \text{HPF}_6 \) gave a white, air-sensitive complex of empirical formula \([\text{Os(C}_6\text{H}_3\text{Me}_3\text{)(C}_9\text{H}_{15})]\text{PF}_6 \), \(^{110}\). The proton nmr spectrum (Spectrum 7) of \(^{110}\) was not temperature dependent between \( 20^\circ\text{C} \) and \(-80^\circ\text{C} \), indicating the complex is not fluxional in this temperature range.
The spectrum can be interpreted in terms of a diene hydride complex 110A. On this basis, two three-proton singlets and one three-proton doublet at δ2.23, δ1.85, and δ0.94, respectively, are assigned to the three CH3 groups, a one proton multiplet at δ5.20 is assigned to H2 and a similar multiplet at δ3.77 to H4. Multiplets at δ2.07 (2H) and δ1.62 are assigned to H5 and H6, and the hydride resonance occurs at δ-11.96 and is a doublet (J = 3 Hz) with a weak coupling to either H2 or H4. The solid state infrared spectrum of 110 shows a weak sharp band at 2140 cm⁻¹, typical of terminal metal-hydride bonds.

These results do not fully rule out an agostic structure such as 110B. Although this structure is inconsistent with the band at 2140 cm⁻¹ in the infrared spectrum of 110, the ¹H nmr spectrum of 110B may not be markedly different from that of 110A. However, there is no reaction between 110 and small ligands such as t-butylisonitrile; agostic complexes usually react with such ligands, the more basic ligands displacing the weakly bonded C-H ligand (see Section 3.3). The ¹³C nmr spectrum of 110 (Spectrum 8) was not fully assigned, and sheds no further light on the matter.
The parent neutral complex 86 can be regenerated from 110 by reaction with aqueous sodium carbonate.

In comparison, the complex [Ru(C₆Me₆)(C₉H₁₅)]PF₆, 53, is fluxional in solution. The variable temperature nmr spectra were complex and neither a diene hydride structure nor a bridging hydride structure could be assigned with confidence. The solution infrared spectrum showed a medium intensity band at 2300 cm⁻¹ which may have been due to a modified VM-H vibration; this band was however, absent in the solid state infrared spectrum.
3.2 ACYCLIC 1,3-DIENE COMPLEXES

Protonation of Os(\(\eta^6\)-arene)(2,3-dimethylbutadiene) (83A, arene = \(C_6H_6\); 83B, arene = \(C_6H_3Me_3\)) with HPF\(_6\) gave air-sensitive, off-white salts with empirical formulae [Os(\(\eta^6\)-arene)(\(C_6H_{11}\))]PF\(_6\) (111, arene = \(C_6H_6\); 112, arene = \(C_6H_3Me_3\)).

The \(^1H\) nmr spectrum of 111 at -20°C (Spectrum 9) shows a singlet at \(\delta 6.22\) for the arene ligand. The diene ligand gives rise to a 6H singlet at \(\delta 2.39\), due to the CH\(_3\) groups. A doublet at \(\delta 3.28\) is assigned to \(H_b\). \(H_a\) appears as a triplet, being coupled both to \(H_b\) and to the hydride via three bonds; the hydride in turn is a triplet (\(J < 1\) Hz) at \(\delta -11.34\). 112 shows a similar spectrum. These results support the assignment of a symmetrical diene hydride ground state structure to 111 and 112, an assignment which is supported by the \(^{13}C\) nmr spectrum of 112 at -30°C (Spectrum 10). The arene of 112 gives rise to the expected quartet (\(\delta 18.7, CH_3\)) doublet (\(\delta 88.5, CH\)) and singlet (\(\delta 105.4, C-Me\)) while the diene ligand shows a sharp quartet (\(\delta 18.5, J = 129\) Hz) for the CH\(_3\) groups, a triplet (\(\delta 29.0, J = 162\) Hz) for \(C_1\) and a singlet (\(\delta 91.4\)) for \(C_2\). Complexes 111 and 112 also both show weak, sharp bands in their Nujol infrared spectra, at 2130 and 2140 cm\(^{-1}\) respectively, assigned to \(\nu M-H\). Treatment
of 111 and 112 with aqueous Na$_2$CO$_3$ rapidly regenerates the parent zerovalent complexes 83A and 83B.

The complexes 111 and 112 are fluxional; warming CD$_2$Cl$_2$ nmr solutions to 20°C results in substantial broadening of the proton nmr spectrum. The fluxional process is presumably reversible hydrogen transfer via a coordinatively unsaturated $\eta^3$-allyl intermediate or transition state (Scheme 3:4), but the instability of the complexes in solution precluded studies at higher temperatures.

The complexes [Ru($\eta^6$-arene)(C$_6$H$_{11}$)PF$_6$, 47A,B,C studied by McMahon 56 (Section 1.3) would appear to be structurally similar to the osmium complexes 111 and 112, judging by their nmr spectra. For example the $^1$H nmr spectrum of the hexamethylbenzene complex at -90°C showed, as well as the arene resonances, a singlet for the CH$_3$ groups of the diene and multiplets at $\delta$1.64 (2H), $\delta$-0.55 (2H) and $\delta$-10.28 (1H) for the olefinic and hydride protons. This is similar to the limiting spectrum of 111 (bearing in mind the different arenes), and suggests a symmetrical diene hydride structure as the ground state structure, rather than the unsymmetrical agostic bridging hydride structure.
of the type that is present in, for example, $[\text{Fe(C}_6\text{H}_{11})_3\text{P(OMe)}_3]\text{BPh}_4$.

The low temperature limiting spectrum of the latter complex shows two separate singlets for the methyl groups of the dienyl ligand as well as five separate one-proton multiplets for the other dienyl protons and the bridging hydride. A similar limiting spectrum is observed for $[\text{Rh(C}_5\text{Me}_5)(\text{C}_6\text{H}_{11})]\text{PF}_6$ \textit{(vide infra)}. However, the $^1\text{H}$ nmr studies of $47\text{C}$ are not conclusive in determining its ground state structure, and a limiting $^{13}\text{C}$ nmr spectrum could not be obtained. Studies of the protonated (ddbo) complex, $119$, \textit{(vide infra)} suggest that $47\text{C}$ may in fact adopt an agostic structure.

Protonation of $\text{Ir(C}_5\text{Me}_5)(\text{C}_6\text{H}_{10})$, $113$, with $\text{HPF}_6$ gives a stable white solid, of empirical formula $[\text{Ir(C}_5\text{Me}_5)(\text{C}_6\text{H}_{11})]\text{PF}_6$, $114$, which also appears to adopt a symmetrical diene-hydride structure as the ground state structure. Complex $114$ is fluxional in solution; at $-80^\circ\text{C}$ a limiting $^1\text{H}$ nmr spectrum is obtained, (Spectrum 11) which is very similar to the spectra of the osmium complexes $111$ and $112$ at $-20^\circ\text{C}$. Apart from the $\text{C}_5\text{Me}_5$ resonance at $\delta2.06$, the spectrum shows a six proton singlet for the diene $\text{CH}_3$ groups, a doublet at $\delta2.86$ for $\text{H}_b$.
and an asymmetrical triplet at $\delta 1.48$ for $H_a$; as in the benzene osmium complex 111 there appears to be a weak three bond coupling between the hydride ligand and $H_a$. The hydride resonance, however, appears only as a broadened singlet.

Warming solutions of 114 to room temperature results in the collapse into the baseline of the peaks due to $H_a$, $H_b$ and the hydride. This is due to the rapid transfer (on the nmr time scale) of the hydride proton between the metal and the ligand, probably via an $\eta^3$-allyl intermediate similar to the process in Scheme 3:4 above, resulting in the equilibration of $H_a$, $H_b$ and the hydride.

The $^{13}C$ nmr spectrum of 114 is, again, similar in appearance to that of the osmium hydride complex 112. At $-60^\circ C$ it shows (Spectrum 12) a quartet ($\delta 9.2$) and a singlet ($\delta 102.4$) for the $C_5Me_5$ ligand, and a quartet ($\delta 15.9$, $J = 129$ Hz) for the diene $CH_3$ groups, a triplet ($\delta 34.4$, $J = 163$ Hz) for $C_1$ and a singlet ($\delta 94.9$) for $C_2$. 114, further, shows a weak band at 2200 cm$^{-1}$ in its solid state infrared spectrum, which may be due to a $\nu_M-H$ vibration.

The Rh analogue of 113, Rh($C_5Me_5$)(C$_6$H$_{10}$) reacts with HPF$_6$ to give an orange monoprotonated species of empirical formula [Rh($C_5Me_5$)(C$_6$H$_{11}$)]PF$_6$, 115. In contrast to the protonated osmium, ruthenium and iridium complexes discussed above, the nmr spectra of 115 strongly support the assignment of an agostic bridging hydride structure as the ground state structure.
The complex \textbf{115} is fluxional. At 20°C its $^1\text{H}$ nmr (Spectrum 13) shows a singlet for the $\text{C}_5\text{Me}_5$ ligand, a singlet for the $\text{CH}_3$ groups of the diene ligand (δ2.04) and a five-proton multiplet at δ-0.36 for the four dienyl protons and the bridging hydride. Cooling the solution results in the collapse of the five-proton multiplet and the singlet for the $\text{CH}_3$ groups of the diene, and the appearance of several new peaks. The spectrum at -100°C shows two 3H singlets at δ2.12 and δ1.72. There are two 1H multiplets at δ2.87 and δ1.27, and two very broad resonances at δ-0.5 (2H) and δ-7.0(1H). These results are consistent with the asymmetric agostic structure shown; the two three-proton singlets are assigned to the two non-equivalent $\text{CH}_3$ groups, the two 1H multiplets at δ2.87 and δ1.27 to $\text{H}_e$ and $\text{H}_d$ respectively, and the broad resonances to $\text{H}_b,c$ and $\text{H}_a$ respectively.

The variable temperature $^1\text{H}$ nmr spectra of \textbf{115} can be explained in terms of two different exchange processes (Scheme 3:5A and B). The process with the lowest activation energy is a process involving cleavage of the Rh-H bond of the Rh-H-C moiety and rotation about the $\text{C}_1 - \text{C}_2$ bond, as depicted in Scheme 3:5A, resulting in exchange
of $H_a$, $H_b$ and $H_c$. In Spectrum 13 this process has not been fully
frozen out at -100°C, hence the two broad peaks for $H_b, c$ and $H_a$, while
the rest of the spectrum is sharp. The higher energy process is
an 'end to end' exchange, involving a diene hydride intermediate
formed by cleavage of the C-H bond of the Rh-H-C moiety (Scheme 3:5B).
This, together with the process in Scheme 3:5A, results in the
equilibration of $H_{a-e}$ on the nmr time scale, giving the 5H multiplet
at $\delta$-0.36 in the spectrum at 20°C.

The $^{13}$C nmr spectrum at -100°C (Spectrum 14) of 115 supports the
asymmetric bridging hydride structure; the proton decoupled spectrum
is still fairly broad at this temperature, but shows six separate
resonances for the six dienyl carbons. The resonance for the carbon
involved in the C-H-M bridge ($C_1$, Spectrum 14) occurs at $\delta$6.8, which
is typical of the fairly highfield chemical shift shown by C-H-M
bridge carbons (see Table 2).
The nmr spectra of the dienyl group of 115 are similar to reported spectra of other 2,3-dimethylbutadiene complexes, such as 

\[ \text{[Fe(C}_6\text{H}_{11})(\text{P(OMe)}_3)_3]\text{BPh}_4, \] \(^7,14\) and \([\text{Ir}(\text{H})(\text{PPh}_3)_2(\eta^3-2,3\text{-dimethylbutenyl})]^+\), \(^20,54\) and also essentially similar to the reported spectra of 

\[ \text{[Fe(L}_3\text{)(H}(\eta^3\text{-butadienyl})]^+\] complexes.\(^12,14,22\)

The complex 115 did not show any band assignable to \(\nu\text{M-H}\) or to a modified \(\nu\text{C-H}\) vibration in the infrared spectrum (solid state), in the region 2700 - 1500 cm\(^{-1}\). Some agostic C-H-M complexes show modified \(\nu\text{C-H}\) bands in the region 2700 - 2350 cm\(^{-1}\), rather lower than normal \(\nu\text{C-H}\) values.\(^46,63,76\) This decrease in value is presumably related to the increase in length of the C-H bond.\(^45\)

We have synthesized partially deuterated analogues of both the hexamethylbenzene ruthenium complex \(^47\text{C}\) and the rhodium complex 115, by treatment of the corresponding neutral complexes with DPF\(_6\).

The fast exchange \(^1\text{H}\) nmr spectrum of partially deuterated 115 at 20°C is identical to that of non-deuterated 115 except that there are five highfield peaks, at \(\delta=0.36, 0.46, 0.57, 0.70\) and \(0.85\) (Figure 3:2). The resonance at \(\delta=0.36\) is due to non-deuterated 115, and is very weak. The four other resonances correspond to incorporation of 1,2,3 and 4 deuterium atoms respectively, giving deuterated analogues of 115. The upfield shift in \(\delta\) value of the highfield resonance, on incorporation of D atoms, supports the existence of an agostic bridging hydride complex as a participant in the fast exchange process (see Section 1:2).
The fast exchange proton nmr spectrum of the partially deuterated Ru 2,3-dimethylbutadiene complex was again similar to the corresponding non-deuterated complex 47C, apart from the highfield region. The five-proton multiplet at $\delta 1.66$ in the $^1H$ nmr spectrum of 47C is shifted upfield to $\delta 2.0$ in the spectrum of the deuterated species, and is extremely broad. This broad peak probably corresponds to the five peaks seen in the spectrum of partially deuterated 115 (Fig. 3:2), but with the peaks individually broad and relatively close together, such that only one broad multiplet is seen. The upfield shift relative to the corresponding resonance in the non-deuterated complex suggests that an agostic bridging hydride complex is a participant in the fast exchange process.

Crystal structure studies of the osmium and ruthenium 2,3-dimethylbutadiene protonated complexes have been thwarted by the instability of the complexes, and the resultant difficulty in growing
suitable crystals. X-ray studies are particularly desirable for the Ru complexes 47A,B,C, as the nmr studies that have been done are far from conclusive in defining the ground state structure. We have thus investigated complexes of the ligand 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo), a ligand that is essentially a butadiene with large substituents in positions 2 and 3. It was hoped that its bulkness would enhance the stability of its complexes and that it would be possible to obtain single crystals of a protonated complex, suitable for X-ray structure analysis.

The synthesis of neutral (ddbo) complexes is discussed in Chapter 2.

Protonation of Os(C₆H₃Me₃)(ddbo), 84, with either HPF₆ or CF₃SO₃H gave the cation [Os(C₆H₃Me₃)(C₁₈H₁₅)]⁺, 116, as the PF₆⁻ or CF₃SO₃⁻ salts respectively. The PF₆⁻ salt could not be obtained analytically pure, and the microanalytical results reported (Table 10) and the ¹³C nmr spectrum (Spectrum 16) are of the CF₃SO₃⁻ salt.

The complex 116 is fluxional in solution. At 20°C the ¹H nmr spectrum (PF₆⁻ salt) shows resonances for the arene at 64.97 (3H) and 62.31 9H, and
other resonances at δ7.4 - δ7.0 (complex multiplet, 8H) and δ5.15 (singlet, 2H). On cooling to 0°C, three additional broad resonances appear at ca. δ3.4 (2H), δ1.5 (2H) and δ-13.5 (1H). On cooling to -40°C the three new resonances become sharper and more well defined. Further cooling does not further affect these new peaks, but at -80°C the peak at δ5.15 has become broad. The spectrum at this temperature (Spectrum 15) shows arene resonances at δ2.28 (9H) and δ5.00 (3H), and diene resonances at δ7.45 ± 7.04 (8H, benzo protons), δ5.08 (2H, Hc), δ3.45 (2H, Hb) and δ1.48 (2H, Ha). A hydride resonance is seen at δ-13.53. The resonance at δ3.45 is a doublet (J = 3 Hz), as expected, and the resonance at δ1.48 a poorly resolved triplet (J value very small) indicating a weak 3 bond coupling with the hydride, as is the case in the 2,3-dimethylbutadiene osmium complex 111 and iridium complex 114.

These results support the assignment of a diene hydride ground state structure to 116, similar to the corresponding 2,3-dimethylbutadiene complex 111. On warming solutions of 116, a fast exchange process involving a η3-allyl intermediate results in Ha, Hb and the hydride becoming equivalent on the nmr time scale (Scheme 3:6), resulting in the collapse of the resonances at δ3.45, δ1.48 and δ-13.53 into the baseline at 20°C. The reason for the broadening of the Hc resonance on cooling to -80°C is not known.

The 13C nmr spectrum at -20°C (Spectrum 16) also supports the assignment of a diene hydride ground state structure to 116. The diene ligand gives rise to a triplet (δ21.0, J = 162 Hz) due to C1.
a doublet at $\delta 50.7$ ($J = 145\text{Hz}$) due to $C_3$, and a singlet at $\delta 106.6$
due to $C_2$. The two inequivalent benzo groups give rise to a complex
series of peaks in the gated-1 spectrum; in the proton decoupled
spectrum however, they give a symmetrical pattern of 4 resonances
for the secondary carbons, and there are two resonances for the
tertiary carbons.

Surprisingly, no band assignable to $\nu\mathrm{M-H}$ was seen in the infrared
spectrum ($2700 - 1500\text{cm}^{-1}$) of a Nujol mull of 116; 116 is in fact
the only protonated conjugated 1-3-diene complex of osmium that did
not show such a band. Complex 116 underwent facile deprotonation
on treatment with aqueous $\text{Na}_2\text{CO}_3$, giving the parent zerovalent osmium
complex 84.

Treatment of an ether solution of Ir$(C_5\text{H}_5)(C_{18}\text{H}_{14})$, 98, with HPF$_6$
resulted in the immediate precipitation of a light brown solid, 117.
This complex could not be obtained analytically pure, but its $^1\text{H}$
and $^{13}\text{C}$ nmr variable temperature nmr indicate it is a fluxional diene
hydride complex analogous to the osmium complex 116.

At 20°C the $^1$H nmr spectrum of 117 shows a seven proton singlet at δ5.22, arising from overlapping resonances due to $H_c$ and the $C_5H_5$ ligand. The benzo protons give rise to a complex eight-proton multiplet at δ7.3, and $H_a$, $H_b$ and the hydride (averaged on the nmr time scale) give rise to a five proton multiplet at δ1.63. On cooling the solution the five-proton multiplet collapses, and simultaneously three new resonances arise; at -40°C a limiting spectrum is observed, with the three new resonances at δ4.24 (2H), δ2.31 (2H) and δ-15.55 (1H). These are assigned to $H_b$, $H_a$ and the hydride, respectively, of the diene hydride 117. At this temperature, the two protons $H_c$ give rise to a two proton singlet at δ5.23.

The averaging of the resonances from $H_a$, $H_b$ and the hydride, to give a 5H multiplet at 20°C, can be explained in terms of an equilibrium equivalent to that outlined in Scheme 3:6.
The $^{13}$C nmr spectrum of 117 at $-60^\circ$C supports the diene hydride ground state structure. A doublet at δ87.1 is assigned to the C$_5$H$_5$ group. The diene ligand gives rise to a triplet (δ28.0, J = 167 Hz) for C$_1$, a doublet (δ49.8, J = 146 Hz) for C$_3$, and a singlet for C$_2$ (δ113.1); the benzo groups give rise to a complex series of resonances.

A weak sharp band at 2185 cm$^{-1}$ is present in the solid state infrared spectrum of 117. This is assigned to vM-H.

Protonation of Rh(C$_5$Me$_5$)(ddbo), 96, with HPF$_6$ results in a dark green solid, of empirical formula [Rh(C$_5$Me$_5$)(C$_{18}$H$_{15}$)]PF$_6$, 118. Complex 118 is a fluxional complex; its proton and carbon nmr spectra are substantially different from the osmium and iridium (ddbo) complexes described above, and, as in its 2,3-dimethylbutadiene relative 115, indicate that 118 adopts an agostic bridging hydride ground state structure.

At $-60^\circ$C the $^1$H nmr spectrum of 118 (Spectrum 17) shows a singlet at δ1.28 for the C$_5$Me$_5$ group, and six resonances for the dienyl ligand.
A three proton multiplet at $\delta 1.25$ is assigned to $H_a$, $H_b$ and $H_c$, undergoing fast exchange by rotation about the $C_1-C_2$ bond. $H_d$ and $H_e$ give rise to two multiplets at $\delta 2.93$ and $\delta 5.01$ respectively, and $H_f$ and $H_g$ to two singlets at $\delta 4.87$ and $\delta 4.65$. The benzo protons give rise to a complex multiplet at $\delta 7.2$. These results clearly suggest that the dienyl ligand is not symmetrically bonded to the metal and are consistent with the agostic structure. This is supported by the $^{13}C$ nmr spectrum of 118 at -60°C (Spectrum 18). $C_1$ gives rise to a quartet ($\delta 14.9$, $J = 129$ Hz). Two doublets at $\delta 48.6$ and $\delta 53.0$ are due to $C_5$ and $C_6$ ($J = 130$ Hz in both). $C_4$ gives a doublet of triplets at $\delta 71.0$, with coupling both to $^1H$ (165 Hz) and $^{103}Rh$ (9.0 Hz). The resonances due to $C_2$ and $C_3$ ($\delta 66.5$ and $\delta 103.4$) also show small couplings due to $^{103}Rh$ (10.7 and 1 Hz respectively).

Warming solutions of 118 results in the collapse of the multiplets due to $H_d$ and $H_e$ and the multiplet due to $H_{a,b,c}$ in the proton nmr spectrum. The two singlets due to $H_f$ and $H_g$ merge into one broad 2H resonance at $\delta 4.79$. The complex multiplet due to the benzo protons also alters; a downfield portion in the region $\delta 7.53 - 7.2$ collapses on warming, and a new multiplet appears in its place at 20°C. These results are consistent with fluxional processes occurring in 118 that are entirely analogous to those occurring in the rhodium 2,3-dimethylbutadiene complex 115, as outlined earlier in Scheme 3:5 A and B. The fluxional process of lower activation energy, that involving M-H bond cleavage followed by rotation about the $C_1-C_2$ bond resulting in exchange of $H_a$, $H_b$ and $H_c$, (Scheme 3:5A) is not
frozen out at the lowest temperature investigated; at -100°C in the $^1H$ nmr the 3H multiplet at $\delta1.25$ is still present, though partially superimposed on the $C_5Me_5$ singlet which is shifted slightly upfield on cooling. At -60°C the higher activation energy process described in Scheme 3:5B is still slow. It speeds up on warming the solution, resulting in the equilibration of $H_{a,b,c,d,e'}$ and the equilibration of $H_f$ and $H_g$. The fast exchange process also results in the equilibration of some of the benzo group protons, and this is reflected in the variation with temperature of the resonances due to these protons.

The results of the protonation of $\text{Ru}(C_6H_3Me_3)(ddbo)$, 94, with $\text{HPF}_6$ are extremely interesting, as they show an apparent anomaly between the structure in solution and the structure in the solid state. The product of this reaction is a yellow solid, of empirical formula $[\text{Ru}(C_6H_3Me_3)(C_{18}H_{15})]\text{PF}_6$, 119. This complex is stable as a solid, but air-sensitive in solution. Because it is fairly insoluble in $\text{CH}_2\text{Cl}_2$ and $\text{CHCl}_3$, and only slightly more soluble in $\text{CH}_3\text{CN}$, $\text{CH}_3\text{NO}_2$ and acetone, nmr studies have been difficult. The neutral parent complex, 94, can be regenerated from 119 by treatment with aqueous $\text{Na}_2\text{CO}_3$. We observed no band in the solid state infrared spectrum of 119, in the region 2700 - 1500 cm$^{-1}$, which could be attributed to a $\nuM-H$ or modified $\nuC-H$ vibration.

Complex 119 is fluxional in solution. At 20°C the $^1H$ nmr spectrum (Spectrum 19) shows arene resonances at $\delta2.10$ (9H) and $\delta5.03$ (3H). Other resonances include a five-proton multiplet at $\delta-1.13$, a 2H,
singlet at $\delta 4.96$ and an eight-proton multiplet at $\delta 7.4 - \delta 7.1$. On cooling the solution, the five proton multiplet collapses into the baseline and at $-100^\circ C$ three new peaks appear, at $\delta 2.45$ (2H), $\delta -0.50$ (2H) and $\delta -10.26$ (1H); at this temperature they are still broad. The rest of the spectrum remains essentially unchanged on cooling, though the arene peaks shift slightly upfield at low temperatures relative to the spectrum at $20^\circ C$.

The proton decoupled $^{13}C$ nmr spectrum at $20^\circ C$ of 119 showed three resonances ($\delta 19.6$, $89.6$, $105.8$) for the arene ligand. The diene ligand gave rise to a broad peak at $\delta 19.2$, and others at $\delta 52.9$, $\delta 101.1$ $\delta 125.7$, $\delta 125.8$, $\delta 127.5$, $\delta 127.8$ and $\delta 146.0$. Unfortunately, due to the insolubility of 119 in suitable solvents, low temperature proton-coupled $^{13}C$ nmr spectra could not be attained. However, comparison with the corresponding 2,3-dimethylbutadiene complexes 47A,B,C suggests that limiting spectra would not be achieved even at $-100^\circ C$. 
The $^1$H and $^{13}$C $^{1}$H nmr of 119 are similar to those of the 2,3-dimethyl-butadiene complexes, 47A,B,C (Section 1:3). Comparison with those complexes suggests that the spectrum at -100°C can be assigned as follows: the $^1$H resonance at δ-10.26 is due to the hydride, the $^2$H resonances at δ-0.50 and δ2.45 to $H_a$ and $H_b$ respectively, the $^2$H singlet at δ4.89 to $H_c$ and the multiplet at δ7.1 to the benzo protons. By analogy with the protonated 2,3-dimethylbutadiene complexes, warming the solution results in the equilibration of $H_a$, $H_b$ and the hydride on the nmr time scale due to a fast exchange process via a $\eta^3$-allyl intermediate. In the $^{13}$C $^{1}$H nmr spectrum at 20°C the broad resonance at δ19.2 is due to $C_1$, the resonance at δ52.9 to $C_3$, that at δ101.1 to $C_2$ and the remainder to the benzo group carbon atoms.

The slow exchange $^1$H nmr spectrum of 119 (at -100°C) is also similar to those of the osmium and iridium (ddbo) protonated complexes 116 and 117 described above. By comparison, it is thus compatible with a symmetrical diene hydride as the ground state structure. However, the crystal structure of 119 suggests that, in the solid state at least, it is an agostic bridging hydride complex.

The single crystal X-ray structure of 119 has been determined by Dr W. Wickramasinghe and Dr G.B. Robertson, of this school, and details are reported in Appendix 1 at the end of this thesis. A diagram of the structure is shown in Fig. 3:3, and Fig. 3:4 shows details of the bridging hydride region of the molecule, with relevant bond lengths and angles. All hydrogen atoms in this region were located directly.
FIGURE 3.3 STRUCTURE OF THE [Ru(C₆H₃Me₂)(C₁₈H₁₅)PF₆] MOLECULE (PF₆⁻ ION NOT SHOWN)
FIGURE 3:4. DIAGRAM OF DIENYL REGION OF $[\text{Ru}(\text{C}_5\text{H}_3\text{Me}_3)_5\text{H}_15]PF_6$. 119
The bridging hydride structure of $^{119}$ is indicated by the Ru-H$_{18C}$ distance of 1.74(7) Å, the Ru-C$_{18}$ distance of 2.354(10) Å and the H$_{18C}$-C$_{18}$ bond length of 1.00(8) Å. These distances are comparable with the corresponding distances in other bridging hydride complexes (see Table 1), in particular those from neutron diffraction studies of $^{[Fe(P(O Me)_{3})_{3}](C_{8}H_{13})BF_{4}}$ (1.874, 2.362 and 1.164 Å, respectively),$^{16}$ and of $^{Mn(CO)_{3}([n^{3}-C_{6}H_{8}Me])}$ (1.84, 2.34 and 1.19 Å, respectively).$^{66}$ The Ru-H$_{18C}$-C$_{18}$ angle is 116.4(6)°, which is rather larger than those of the Fe (99.4°) and Mn (100°) complexes.

The C$_{18}$-H$_{18C}$ distance of 1.00(8) Å is slightly longer than the C$_{18}$-H$_{18B}$ and C$_{18}$-H$_{18A}$ distances; an elongation of the C-H bond in the C-H-M moiety is expected. However, the distances of the C$_{1}$-H$_{1A}$ bond (1.1(1) Å) and the C$_{10}$-H$_{10}$ bond (1.02(7) Å) are of similar length to the C$_{18}$-H$_{18C}$ bond. It is not known how significant these C-H bond lengths are. X-ray diffraction tends to underestimate C-H bond lengths;$^{25,75}$ for example the C-H bond length of the C-H-M moiety in $^{Mn(CO)_{3}([n^{3}-C_{6}H_{8}Me])}$ was measured at 1.07(2) Å using X-ray diffraction$^{25}$ and more accurately at 1.19 Å using neutron diffraction.$^{66}$ Thus the C$_{18}$-H$_{18C}$ distance may actually be some 0.1 Å longer than we have determined.

The Ru-H$_{18C}$ distance of 1.74(7) Å is comparable to the Ru-H distances in a number of $\mu$-hydrido ruthenium cluster complexes,$^{70}$ typically 1.7 - 1.9 Å, and is longer than the non-bridging Ru-H distance of 1.57 Å in RuCl(H)(1,5-cyclooctadiene)(piperidine)$_{2}$.$^{72}$ It is however, somewhat shorter than the Ru-H bond length of 2.10 Å in the
linked-norbornadiene complex RuClC\textsubscript{21}H\textsubscript{25},\textsuperscript{76} suggesting that the Ru-H-C interaction in \textsuperscript{119} is rather stronger than in RuClC\textsubscript{21}H\textsubscript{25}.

The C\textsubscript{1}-C\textsubscript{2}-C\textsubscript{17}-C\textsubscript{18} part of the molecule is unsymmetrically bonded to the ruthenium atom (as opposed to the symmetrical bonding one would expect were \textsuperscript{14} a diene-hydride complex). The distance between ruthenium and the agostic carbon atom, C\textsubscript{18}, is the longest of the four Ru-C distances (2.354(10) \textgreek{A}), being considerably longer than the Ru-C\textsubscript{1} distance (2.183(9) \textgreek{A}), the Ru-C\textsubscript{2} distance (2.192(8)\textgreek{A}) and the Ru-C\textsubscript{17} distance (2.147(7) \textgreek{A}). An unusually long M-C distance is typical of the M-H-C interaction. Further, these distances also show that the \textgreek{\eta}\textsuperscript{3}-allyl part of the ligand (C\textsubscript{1}-C\textsubscript{2}-C\textsubscript{17}) is not symmetrically bound to the metal. Such an asymmetrically bound \textgreek{\eta}\textsuperscript{3}-allyl group seems to be typical of agostic structures,\textsuperscript{16,25} and contrasts with the situation in many 'normal' \textgreek{\eta}\textsuperscript{3}-allyl complexes\textsuperscript{71} which are generally very nearly symmetrically bonded to the metal.

The C\textsubscript{1}-C\textsubscript{2}-C\textsubscript{17}-C\textsubscript{18} part of the ligand is itself slightly asymmetric. The C\textsubscript{1}-C\textsubscript{2} bond (1.43(1) \textgreek{A}) is slightly shorter than the C\textsubscript{18}-C\textsubscript{17} bond (1.49(1) \textgreek{A}); both these bonds are considerably longer than the C\textsubscript{2}-C\textsubscript{17} bond (1.38(1) \textgreek{A}). The C\textsubscript{1}-C\textsubscript{2}-C\textsubscript{17} angle is 120.2(7)°, slightly larger than the C\textsubscript{18}-C\textsubscript{17}-C\textsubscript{2} angle of 119.6(8)°.

The remainder of the molecule is fairly symmetrical. The C\textsubscript{17}-C\textsubscript{10} and C\textsubscript{2}-C\textsubscript{3} distances are similar, as are the C\textsubscript{10}-C\textsubscript{9}, C\textsubscript{10}-C\textsubscript{11}, C\textsubscript{3}-C\textsubscript{16} and C\textsubscript{3}-C\textsubscript{4} distances. C-C distances in the benzo groups range from 1.32 - 1.42 \textgreek{A}.
Treatment of Ru(C₆H₃Me₃)(ddbo), 94, with DPF₆ in ether gives a yellow solid. The fast exchange ¹H nmr spectrum of this material (20°C) is very similar to that of the protonated species 119 (Spectrum 19), except that in addition to the highfield resonance at δ-1.13, there are resonances at δ-1.28, δ-1.47, δ-1.66 and δ-1.89 (Fig. 3:5). These resonances correspond to the incorporation of 1, 2, 3 and 4 deuterium atoms respectively, giving deuterated analogues of 119. This upfield shift in δ values is indicative of an agostic bridging hydride complex being a participant in the fast exchange process. However, as discussed earlier (Section 1.2) it does not necessarily indicates that the agostic structure is the ground state structure.
The reasons why the nmr spectra appear to identify 119 as a diene hydride complex while the crystal structure study indicates an agostic bridging hydride complex, are not clear. One possibility is that the low temperature proton nmr spectrum of 14 is in fact due to an agostic complex, but with a coincidental superimposition of resonances. This is possible, but seems unlikely. The resonances in, for example, [Rh(C₅Me₅)(C₁₈H₁₅)]PF₆, 118, are well separated, particularly those of H₅ and H₆. The difference between the variable temperature nmr spectra of the agostic complex 118, and those of 119, are in fact substantial. The low temperature ¹H nmr spectrum of 119 is also markedly different from that of the η³-allyl complex 127 formed by reaction of 119 with t-butylisonitrile (see later, Section 3.3).

An alternative suggestion is that at -100°C the limiting proton nmr spectrum has not yet been reached, and that further cooling would freeze out a spectrum corresponding to an agostic complex. The spectrum at -100°C shows two two-proton multiplets and a highfield one-proton resonance (δ-10.26). If one assumes an agostic ground state structure, this spectrum could be explained in terms of a process such as that outlined in Scheme 3:7, which is in fact the 'higher energy' process outlined in Scheme 3:5B earlier. In the absence of other possible fluxional processes, this process, when fast, would result in a spectrum consisting of two two-proton multiplets (H₅ and H₆ averaged, H₇ and H₈ averaged) and a one-proton highfield resonance (H₆). The problem with this, however, is that it requires that the C-H₆ bond is cleaved more readily than the Ru-H₆ bond, which is in fact the opposite of the situation in all known
acyclic-dienyl agostic complexes, $^{12,14,22,54}$ including 
[Rh(C$_5$Me$_5$)$(C_6H_{11})$]PF$_6$, $^{115}$, and [Rh(C$_5$Me$_5$)(C$_{18}H_{15}$)]PF$_6$, $^{118}$. The fluxional behaviour of agostic complexes can be explained in terms 
of two processes; M-H$^{(\text{bridge})}$ bond rupture with CH$_3$ rotation (such 
as in Scheme 3:5A) and C-H$^{(\text{bridge})}$ bond rupture (such as in Scheme 
3:5B). In all known agostic complexes the M-H$^{(\text{bridge})}$ bond is cleaved 
more readily than the C-H$^{(\text{bridge})}$ bond, and hence the former process 
has the lower activation energy. However, if 119 is an agostic 
complex the latter process must be that with the lowest activation 
energy.

Hence it may be that 119 is in fact an agostic complex, and that 
the anomaly between the nmr data and the X-ray diffraction data is 
only apparent, reflecting the relative strengths of the M-H and C-H 
 bonds in the M-H-C interaction, with the M-H bond being of comparable, 
and possibly even greater, strength than the C-H bond.
Still another possibility is that the limiting ground state structure of 119 in solution is different from the structure of the solid, although it is not clear why this should be the case. The results of the deuterization experiment (i.e., the partial deuterization of Ru(C₆H₃Me₃)(ddbo), with DPF₆ described earlier) can be taken as suggesting that an agostic species is present in solution and that it takes part in the fast exchange process. Thus, it may be that a diene hydride species and an agostic species are in equilibrium in solution, the diene hydride being favored. Hence, the limiting ¹H NMR spectrum will correspond to the diene hydride species. If however, the agostic complex were less soluble than the diene hydride, it could preferentially crystallize from solution.

Marked similarities in the behavior of the protonated 2,3-dimethylbutadiene and (ddbo) complexes can be observed in the cases of Os, Rh, and Ir, discussed above. The Os and Ir complexes all adopt diene hydride ground state structures, whilst the rhodium (ddbo) and 2,3-dimethylbutadiene complexes both adopt an agostic bridging hydride structure. It follows that the above discussion on the structure of the ruthenium (ddbo) complex 119 is pertinent to the protonated ruthenium 2,3-dimethylbutadiene complexes [Ru(η⁶-arene)(C₆H₁₁)]PF₆, 47A,B,C56 (Section 1.3). The most reasonable explanation would appear to be that the ruthenium complexes are in fact agostic, but that the metal-hydride bond is of comparable strength to the C-H bond resulting in the unusual fluxional behavior. This will be discussed further at the end of this chapter.
3.3 REACTION OF PROTONATED ACYCLIC DIENE AND CYCLOHEXADIENE COMPLEXES WITH LIGANDS

The fluxional processes involved in the cyclohexadiene and acyclic diene complexes of osmium, ruthenium, rhodium and iridium, discussed above, involve a rapid reversible migration of the hydride proton between the metal and the ligand, via a $\eta^3$-allyl 16-electron intermediate. By using suitable small ligands one would thus expect to be able to trap the $\eta^3$-allyl intermediates. Such behaviour has been observed in other arene-ruthenium complexes (see Section 1.3) and in some iron-tris(phosphite) complexes. 14

Reaction of the 1,3-cyclohexadienyl complex $[\text{Os}(C_6H_6)(C_6H_9)]PF_6$, 103, with an excess of trimethyl phosphite at room temperature in $\text{CH}_2\text{Cl}_2$, followed by precipitation of the product with ether, gave a white solid of formula $[\text{Os}(C_6H_6)(C_6H_9)(\text{P(OMe)}_3)]PF_6$, 120. Similar 1:1 adducts, 121 - 123, were obtained by addition of an excess of $t$-butylisonitrile to, respectively, $[\text{Os}(C_6H_3Me_3)(C_6H_9)]PF_6$, 104, $[\text{Rh}(C_5\text{Me}_3)(C_6H_9)]PF_6$, 106, and $[\text{Ir}(C_5\text{Me}_3)(C_6H_9)]PF_6$, 108.

The proton nmr spectrum (Table 14) of 123 is typical of these complexes. It shows a $C_5\text{Me}_5$ resonance at $\delta 1.98$, and a singlet due to $t$-BuNC at $\delta 1.55$. The $\eta^3$-allyl ligand gives rise to two triplets at $\delta 4.34$ (2H) and $\delta 4.16$ (1H), due to $H_{1,2,3}$, together with a 2H multiplet at $\delta 2.74$, a 3H complex multiplet at $\delta 1.9 - 1.7$, and a 1H complex multiplet at $\delta 1.3 - 1.0$, for the remaining protons.
All the \( \text{t-BuNC} \) complexes \( \text{120} - \text{123} \) show strong, sharp \( \nu_{CN} \) bands at about 2150 cm\(^{-1} \) in their solid state infrared spectra (see Table 14).

The trimethylcyclohexadienyl complex \( [\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_9\text{H}_{15})]\text{PF}_6 \), \( \text{110} \), did not react with \( \text{t-BuNC} \) at room temperature.
The 2,3-dimethylbutadienyl complex [Os(C₆H₆)(C₆H₁₁)PF₆], 111, reacts with excess P(OMe)₃ at room temperature in CH₂Cl₂, giving a stable yellow solid 1:1 adduct of empirical formula [Os(C₆H₆)(C₆H₁₁)(P(OMe)₃)]PF₆, 124. Similarly reaction of the 2,3-dimethylbutadienyl complex [Os(C₆H₃Me₃)(C₆H₁₁)]PF₆, 112, with excess t-BuNC gave an off-white solid [Os(C₆H₃Me₃)(C₆H₁₁)(t-BuNC)]PF₆, 125.

The nmr spectra of 124 and 125 clearly support the assignment of a η³-allyl structure. For example, the ¹H nmr spectrum of 124 shows, apart from the arene (δ5.94) and phosphite (δ3.63) resonances, two ¹H resonances (δ3.74, δ2.38) for Hₐ and Hₗ and three three-proton singlets for the three CH₃ groups (δ2.14, δ1.79, δ1.15).

The (ddbo) complex [Os(C₆H₃Me₃)(C₁₈H₁₅)]PF₆, 116, reacted with one equivalent of t-BuNC, resulting in a yellow solid, [Os(C₆H₃Me₃)(C₁₈H₁₅)(t-BuNC)]PF₆, 126. The ¹H nmr spectrum of 126 shows arene resonances at δ2.28 (9H) and δ5.32, and a singlet for
the t-BuNC ligand at δ 1.42. The η3-allyl ligand shows a multiplet for the benzo group protons (δ 7), two separate 1H singlets (δ 4.68, δ 4.55) for the Hc and Hd, and two 1H doublets for Ha and Hb (δ 2.41, δ 3.90). The CH3 group gave rise to a singlet at δ 1.38.

Similarly [Ru(C6H3Me3)(C18H15)]PF6, 119, reacted with an equivalent of t-BuNC to give a yellow product. This could not be isolated analytically pure but was identified on the basis of its proton nmr spectrum (Table 14) as [Ru(C6H3Me3)(C18H15)(t-BuNC)], 127. The proton nmr of 127 is very similar to that of the corresponding Os complex 126 above. In particular there are two separate doublets for Ha and Hb (δ 2.22, δ 3.66) and two separate singlets for Hc and Hd (δ 4.74, δ 4.64).
3.4 SUMMARY AND DISCUSSION

The protonation of the conjugated 1,3-diene complexes

\[
\text{Os(}^6\text{-arene})(^4\text{-diene}) \quad (\text{arene} = \text{C}_6\text{H}_6, \text{C}_6\text{H}_3\text{Me}_3; \text{ diene} = 1,3\text{-cyclohexadiene, 1,3,5\text{-trimethyl-1,3-cyclohexadiene, 2,3\text{-dimethylbutadiene,}}}
\]

\[2,3\text{-dimethylene-5,6,7,8\text{-dibenzobicyclo[2.2.2]octane}} \] and of the complexes

\[
\text{Ir(C}_5\text{R}_5)(^4\text{-diene}) \quad (R = \text{H, CH}_3; \text{ diene} = 1,3\text{-cyclohexadiene, 2,3\text{-dimethylbutadiene, 2,3\text{-dimethylene-5,6,7,8\text{-dibenzobicyclo[2.2.2]octane}}})
\]

gives products which have been shown by variable temperature nmr spectroscopy and infrared spectroscopy to adopt a diene hydride ground state structure. Their nmr spectra show that the diene is symmetrically bound to the metal, and their infrared spectra in most cases show bands at ca. 2100 cm\(^{-1}\) which can be assigned to \(vM-H\) vibrations. In contrast, protonation of the complexes \(\text{Rh(C}_5\text{Me}_5)(^4\text{-diene})\)

\[\text{(diene} = 1,3\text{-cyclohexadiene, 2,3\text{-dimethylbutadiene, 2,3\text{-dimethylene-5,6,7,8\text{-dibenzobicyclo[2.2.2]octane}}}) \] gives fluxional products which adopt an agostic bridging hydride structure as the ground state structure. The nature of the ground state structure of the complexes formed on the protonation of \(\text{Ru(}^6\text{-arene})(^4\text{-diene})\) complexes \(^56\) is still not well understood. However, the postulation of an agostic complex in which the Ru-H bond is of comparable strength to the C-H bond in the M-H-C interaction, provides a plausible explanation of the spectral and crystallographical data obtained for

\[
[\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{C}_18\text{H}_{15})]^\text{PF}_6, 119.
\]

The fluxional behaviour of the agostic complexes can be explained in terms of two exchange processes (see, for example, Scheme 3:5A and B), one (the process with the lower activation energy) involving
an $\eta^3$-allyl intermediate and the other (generally of higher activation energy) involving a diene-hydride intermediate. On the other hand, in the case of the diene hydride complexes, only an $\eta^3$-allyl intermediate need be invoked to explain the fluxional behaviour. However, an agostic intermediate may well be present, as evidenced by the deuterium isotope effect seen in partially deuterated $[\text{Ir}(C_5\text{Me}_5)(C_6\text{H}_9)]\text{PF}_6,108$ (see Section 3.1). In both diene hydride and agostic complexes the $\eta^3$-allyl intermediates can be trapped by reaction with small ligands such as $t$-butylisonitrile.

It is possible, then, to represent all the fluxional protonated conjugated 1,3-diene complexes (including reported iron and manganese complexes $^{12,14,25}$) in terms of an equilibrium between a diene hydride, an agostic and an $\eta^3$-allyl species, e.g., for a 1,3-cyclohexadienyl system:

![Diagram](image)

and for a 2,3-substituted-butadiene system:

![Diagram](image)
Which of the three structures is adopted as the ground state structure and which are intermediates depends on their relative stabilities. The $\eta^3$-allyl intermediate, being coordinatively unsaturated, is likely to be the least stable - indeed no known fluxional protonated diene complex adopts a 16e $\eta^3$-allyl structure in the ground state. However, the factors influencing the stability of the diene hydride structure relative to the agostic structure are complex and not fully understood. Clearly the diene hydride structure is favoured in the 5d Os and Ir systems and the agostic is favoured in Mn, Fe and Rh systems - in such conjugated 1,3-diene complexes as have been investigated. Ruthenium complexes appear to be intermediate, with neither agostic nor diene hydride structure favoured.

The ground state structure clearly depends on the strength of the M-H bond in the M-H-C interaction. The agostic M-H-C interaction is essentially the donation of electron density from the C-H bond to the metal, and the extent of this donation will determine the strength of the M-H bond. The diene hydride system can be envisaged as a bridging hydride system in which the extent of the donation of electron density is such that the C-H bond in the C-H-M system is non-existent, or virtually so; the weak coupling between the hydride proton and diene protons in the $^1$H nmr spectra of several Os and Ir protonated 1,3-diene complexes, as reflected by the triplet hydride resonances, may arise from a very weak C-H interaction in a C-H-M system. On the other hand, the Fe, Mn and Rh protonated 1,3-diene complexes have a rather weaker M-H bond in the C-H-M interaction, with the M-H bond weaker than the C-H bond. The ruthenium complexes
may represent an intermediate system, in which the M-H and C-H bonds in the C-H-M system are of comparable strength.

The weaknesses of relying on nmr spectroscopy for the identification of the structure of fluxional complexes are evident. Very little information can be obtained as to what species are present in solution, what their relative concentrations are, and whether the fluxional processes occur through intermediates or transition states. Unfortunately, we have determined the crystal structure of only one 1,3-diene complex, [Ru(C₆H₃Me₃)(C₈H₁₅)]PF₆, by X-ray diffraction and in this complex there is some difficulty in reconciling the nmr spectroscopic data and the crystal structure. It may well be that, were the crystal structures of other protonated complexes determined, other anomalies between nmr data and structural data may become apparent, although reported crystal structures such as that of [Fe(P(OME)₃)₃(cyclooctenyl)]⁺ agree with the nmr data.
4.1 CYCLOOCTADIENE COMPLEXES

Protonation of Os(C$_6$H$_6$)(1,5-cyclooctadiene), 87A, with HPF$_6$, in ether, gives a white precipitate, [Os(C$_6$H$_6$)(C$_8$H$_{13}$)]PF$_6$, 128. Likewise, treatment of the crude yellow oily product obtained from the reaction of [Os(C$_6$H$_3$Me$_3$)Cl$_2$], 1,5-cyclooctadiene and sodium carbonate in refluxing isopropanol (see discussion in Chapter 2) with excess HPF$_6$ in ether gave a buff-coloured product, [Os(C$_6$H$_3$Me$_3$)(C$_8$H$_{13}$)]PF$_6$, 129. Both products could be deprotonated with aqueous Na$_2$CO$_3$, 128 giving the neutral species 87A, and 129 giving Os(C$_6$H$_3$Me$_3$)(1,5-C$_8$H$_{12}$), 87B, as the only product. The nmr analytical data and yields of 128 and 129 are reported in Tables 10 and 12.

The $^1$H nmr spectrum of 128 was not temperature-dependent between 20°C and -20°C. At -20°C (Spectrum 20) the spectrum shows an arene singlet at δ6.21, and diene resonances at δ4.96 (2H), δ3.77 (2H) (H$_{1,2}$; H$_{5,6}$) and δ2.45 - δ1.79 (8H). The hydride resonance is a triplet at δ-8.92, showing weak 3-bond coupling with the olefinic protons of the diene. The spectrum of 129 is similar, bearing in mind the differences in the arene ligands.

Both 128 and 129 show weak, sharp bands in their solid state infrared spectra, at 2120 and 2145 cm$^{-1}$ respectively; these are assigned to vM-H vibrations.
These results are consistent with the assignment of a diene hydride structure to 128 and 129. These complexes have been formulated as 1,5-diene complexes, but the spectral results are equally consistent with 1,3-diene complexes, 129A with the two 2H multiplets being due to H\textsubscript{1,4} and H\textsubscript{2,3} and the SH multiplet to H\textsubscript{5,6,7,8}. It is difficult to distinguish between the 1,3- and 1,5-diene structures by nmr spectroscopy.

Complexes 128 and 129 appear to be similar to the corresponding ruthenium complexes [Ru(C\textsubscript{6}H\textsubscript{3}R\textsubscript{3})(C\textsubscript{8}H\textsubscript{13})]PF\textsubscript{6} (54A, R = H; 54B, R = Me) (Section 1.3), which were formulated by McMahon as diene hydride complexes. Deuteriation experiments (i.e., treatment of the neutral parent complexes Ru(C\textsubscript{6}H\textsubscript{3}R\textsubscript{3})(1,5-C\textsubscript{8}H\textsubscript{12}) with DPF\textsubscript{6}) indicated that the ruthenium complexes were undergoing a slow exchange (on the nmr time scale) involving reversible transfer of the hydride proton between the metal and the ligand. A similar exchange process occurs...
in \([\text{Ir}(C_5H_5)(H)(C_8H_{12})]^+,32\) also a diene hydride complex. No such exchange is evident in the osmium complexes.

Some other 1,5-cyclooctadiene hydride complexes are known, e.g., \(\text{RuCl}(H)(C_8H_{12})(\text{piperidine})_2,72\) \(\text{IrH}[\text{P}(\text{OC}_6H_3\text{Me}_2-o)(\text{OC}_6H_4\text{Me}-o)](\text{C}_8\text{H}_{12})\text{L}^+\) (L = phosphine)\(^{73}\) and \([\text{RuH}(\text{C}_8\text{H}_{12})(\text{NH}_2\text{NMMe}_2)_3]\text{PF}_6;74\) the structure of the piperidine complex has been determined by X-ray crystallography.\(^{72}\) In contrast, protonation of \(\text{Fe}(\text{P}(\text{OMe})_3)_3(1,3-\text{C}_8\text{H}_{12})\) gave a bridging hydride \(\eta^3\)-cyclooctenyl complex\(^{14,16}\) and protonation of \(\text{Rh}(C_5H_5)(C_8H_{12})\) gave a mixture of \(\sigma-\pi\) and \(\eta^3\)-allyl species.\(^{32}\)

In contrast to the ruthenium complexes 54A-C and \([\text{Fe}(\text{P}(\text{OMe})_3)_3(\text{C}_8\text{H}_{13})]^+\) which react readily with ligands such as CO, P(OMe)_3 or t-BuNC to give \(\eta^3\)-allyl complexes,\(^{14,56}\) the osmium complexes 128 and 129 did not react with either P(OMe)_3 or t-BuNC.
4.2 DICYCLOPENTADIENE COMPLEXES

Treatment of Os(C₆H₃Me₃)(C₁₀H₁₂), 92, with 60% aqueous HPF₆ in ether yielded a yellow product, [Os(C₆H₃Me₃)(C₁₀H₁₂)]PF₆, 130. Similar treatment of ether solutions of Rh(C₅Me₅)(C₁₀H₁₂), Rh(C₅H₅)(C₁₀H₁₂) and Ir(C₅Me₅)(C₁₀H₁₂) also yielded yellow precipitates, of empirical formulae corresponding to [M(C₅R₅)(C₁₀H₁₃)]PF₆ (131, M = Rh, R = H; 132, M = Rh, R = CH₃; 133, M = Ir, R = CH₃). Complexes 130, 131, 132 and 133 are all air-stable as solids and slightly air-sensitive in solution. The parent zerovalent osmium complex, 92, is regenerated from 130 by treatment with aqueous sodium carbonate. Nmr spectroscopic and analytical data for 130-133 are in Tables 10, 12 and 13.
Complexes 130–133 are identified as bridging hydrides, on the basis of their $^{13}$C and $^1$H nmr spectra, which are discussed below. These data do not on their own establish conclusively which of the four possible carbon atoms (C$_2$, C$_3$, C$_5$ or C$_6$ of the structures drawn) of the dicyclopentadiene moiety is involved in the M-H-C bridge.

In free dicyclopentadiene, and dicyclopentadiene coordinated to Pt(II) and Pd(II), the 5,6-double bond appears to be more susceptible to nucleophilic attack than the 2,3 double bond. It is thus likely that protonation of the dicyclopentadiene complexes of Os, Rh and Ir will occur at position 5 or 6; this still leaves two possible structures, A and B (Fig. 4:1), which cannot be distinguished on the basis of spectroscopic evidence. However, the crystal structure of [Os(C$_6$H$_3$Me$_3$)(C$_{10}$H$_{13}$)]PF$_6$, has been determined and this establishes that the structure A has been adopted in this complex, the hydride bridging between C$_6$ of the dicyclopentadiene moiety and the metal. We assume that the same structure is adopted by the protonated dicyclopentadiene complexes, 131–133.

The complex [Ru(C$_6$Me$_6$)(C$_{10}$H$_{13}$)]PF$_6$, synthesized by McMahon, probably also adopts this structure.
A characteristic feature of the $^1$H nmr spectra of 130-133 is a high-field doublet, in the region $\delta$-6 - $\delta$-10 (Table 3, see Spectrum 21 and 22) with a coupling of 15 - 20 Hz, a typical geminal H-H coupling constant. This feature arises from the bridging hydride, the coupling being between $H_{6a}$ and $H_{6b}$. In addition to this coupling the osmium complex 130 and the iridium complex 133 both show a second small coupling (3 - 4 Hz), probably arising from a three-bond coupling between $H_5$ and $H_{6b}$. The rhodium complexes 131 and 132 show a second coupling (ca. 10 Hz) due to $^{103}$Rh, and some additional fine structure.

The ruthenium complex [Ru(C$_6$Me$_6$)(C$_{10}$H$_{13}$)]PF$_6$, 62, also shows a doublet hydride resonance in its $^1$H nmr spectrum (Table 3), 56 with a geminal $H_{6a}$-$H_{6b}$ coupling of 18 Hz. Several other agostic complexes show similar geminal H-H couplings in the hydride resonance, including [Fe(CO)$_3$(C$_4$H$_7$)]$^+$, 12 [Fe(CO)$_3$(C$_4$H$_5$)]$^+$, 21 RuClC$_2$I$_2$H$_{25}$, 76 and [Fe(CO)$_3$(C$_7$H$_9$)]$^+$, 19, 20 (Table 2).

The other features of the $^1$H nmr spectra of 130-133 are fairly complex. The spectra of 130 and 132 are reproduced in Spectrum 21 and 22; the features of the spectra of 131 and 133 are essentially similar. A complex multiplet at ca. $\delta$0 ppm is common to all four complexes, due to $H_{6a}$. $H_2$, $H_3$ and $H_5$ give rise to three downfield multiplets, for example, at $\delta$4.97, $\delta$4.85 and $\delta$4.65 in the spectrum of 130. The remaining features of the spectra are complex and have not been fully assigned.
Table 3  Bridging hydride (dicyclopentadienyl) complexes: Nmr data for $C_6H_{6a}$-$H_{6b}$

<table>
<thead>
<tr>
<th>COMPLEX$^1$</th>
<th>NO.</th>
<th>$\delta^{1}H$</th>
<th>$J^{1}H^{1}H$</th>
<th>$J^{1}H^{103}Rh$</th>
<th>$\delta^{13}C$</th>
<th>$J^{13C^{1}H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Os(C_6H_3Me_3)(C_10H_{13})]PF_6$</td>
<td>25</td>
<td>-10.08</td>
<td>16.5</td>
<td>-</td>
<td>-3.30</td>
<td>160</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
<td></td>
<td></td>
<td>66</td>
</tr>
<tr>
<td>$[Rh(C_5H_5)(C_{10}H_{13})]PF_6$</td>
<td>26</td>
<td>-7.63</td>
<td>20.2</td>
<td>12.1</td>
<td>2.9</td>
<td>159</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>$[Rh(C_5Me_5)(C_{10}H_{13})]PF_6$</td>
<td>27</td>
<td>-6.83</td>
<td>19.1</td>
<td>10.3</td>
<td>6.1</td>
<td>152</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>$[Ir(C_5Me_5)(C_{10}H_{13})]PF_6$</td>
<td>28</td>
<td>-9.52</td>
<td>16.1</td>
<td>-</td>
<td>9.0</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.9</td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>$[Ru(C_6Me_6)(C_{10}H_{13})]PF_6$</td>
<td>62</td>
<td>-10.13</td>
<td>18</td>
<td>-</td>
<td>2.52</td>
<td>159</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>78</td>
</tr>
</tbody>
</table>

$^1$ Solvent $CD_2Cl_2$
Decoupling experiments were performed on 130; the results are summarized in Table 4. Irradiation of the resonance at δ4.97 (H₃)

**Table 4**

<table>
<thead>
<tr>
<th>NUCLEUS IRRADIATED</th>
<th>RESULT</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃</td>
<td>H₂ → d, H₃a → dd</td>
</tr>
<tr>
<td>H₅</td>
<td>H₄ → d, H₆a → brd, H₆b → d</td>
</tr>
<tr>
<td>H₂</td>
<td>H₃ → d</td>
</tr>
<tr>
<td>H₆a</td>
<td>H₆b → s, H₅ → d</td>
</tr>
</tbody>
</table>

results in the multiplet at δ4.65 becoming a doublet and a multiplet at δ2.71 collapsing to a doublet of doublets; the resonance at δ4.65 is thus assigned to H₂ and that at δ2.71 to H₃a. Irradiation of the resonance at δ4.85 results in the resonance at δ3.50 becoming a doublet, that at δ0.10 becoming a broad doublet, and neutralizes the smaller coupling on the hydride resonance reducing it to a doublet. The resonance at δ4.85 is thus assigned to H₅, and that at δ3.50 to H₄. Irradiation of the resonance at δ0.10 (due to H₆a) affects the resonance due to H₅ and the hydride resonance at δ-10.08 (H₆b) becomes a singlet.

In both Rh complexes, 131 and 132, irradiation of the resonance due to H₆a (ca. δ0) in the proton nmr spectrum resulted in the collapse of the H-H coupling in the hydride resonance, with the doublet of doublet resonances becoming doublets. This experiment established
the larger coupling of ca. 20 Hz as being the $H_{6a}^{-}-H_{6b}^{-}$ coupling, and
the smaller coupling of ca. 10 Hz as being the $H_{6b}^{-\text{103}Rh}$ coupling.

The $^{13}$C nmr spectra of the bridging hydride complexes $130$-$133$ are
complex and we were not able to fully assign the peaks. The spectrum
of the osmium complex is reproduced in Spectrum 23. A characteristic
feature of the gated-1 spectra of $130$-$133$ is the presence of a doublet
of doublets in the region $\delta 9 - \delta -3$ (Table 3), due to coupling of
$C_6$ with $H_{6a}$ (ca. 160 Hz) and $H_{6b}$ (ca. 70 Hz). The unusually low
geminal $J(C-H)$ value due to coupling with the bridging hydride $H_{6b}$
is diagnostic of a C-H-M linkage, and is a result of the weakening
of the C-H bond due to coordination to the metal (see Table 2 for
values from a number of agostic complexes, and discussion in Section
1.2). This value decreases in the order $[\text{Rh}(C_5\text{Me}_5)(C_{10}H_{13})]^+$
(83 Hz) > $[\text{Rh}(C_5\text{H}_5)(C_{10}H_{13})]^+$ (81 Hz) > $[\text{Ru}(C_6\text{Me}_6)(C_{10}H_{13})]^+$ (78 Hz)
> $[\text{Os}(C_6\text{H}_3\text{Me}_3)(C_{10}H_{13})]^+$ (66 Hz) > $[\text{Ir}(C_5\text{Me}_5)(C_{10}H_{13})]^+$ (50 Hz)
(Table 3); thus the magnitude of $J(C_6^{-}H_{6b}^{-})$ is less for the 5d
elements (Os, Ir) than for the 4d elements (Rh, Ru), suggesting that
the C-H (bridge) bond is stronger for the latter than the former.
Conversely the M-H bond is stronger for the third row than for the
second row elements, in line with the trend for terminal hydrides.

Other features of the spectrum of $130$ (Spectrum 23) include a triplet
at $\delta 32.5$ for $C_1$ and another at $\delta 358.6$ for $C_8$. The other assignments
given are tentative; however, the doublets at $\delta 73.0$, and $\delta 58.6$ have
large coupling constants (165 Hz) suggesting that they are due to
the olefinic carbons $C_2$ and $C_3$. Three resonances in the $^{13}$C nmr spectrum
of \([\text{Rh}(C_5H_5)(C_{10}H_{13})]PF_6\), at 879.4, 881.0 and 894.0, show coupling to \(^{103}\text{Rh}\) of 7, 13 and 10 Hz respectively, suggesting the responsible carbon atoms are bonded to the metal. The resonances at 879.4 and 881.0 have J(C-H) values of ca. 170 Hz, suggesting that they can be assigned to \(C_2\) and \(C_3\), while the resonance at 894.0 has a lower J(C-H) coupling of ca. 150 Hz, and presumably is due to \(C_5\), the \(\sigma\)-bonded carbon atom. Similar assignments may be made for the resonances at 868.0, 888.6 \((C_2, C_3)\) and 910.1 \((C_5)\) in the corresponding \(C_5\)Me\(_5\) complex.

Attempts to locate bands arising from the M-H-C interaction in the solid state infrared spectra of 130-133 have not been successful. There is no sign of a modified \(\nu\)M-H vibration or modified \(\nu\)C-H vibration in the region 2700 - 1500 cm\(^{-1}\).

The X-ray crystallography study of 130 was solved by Dr W. Wicramasinghe and Dr G. Robertson, of this school. Details of the structure determination are described in Appendix 2. The structure is shown in Fig. 4:2, with some bond lengths. Complex 130 crystallized in two modifications, centrosymmetric \(P2_1/n\), 130A; and non-centrosymmetric \(P2_1\), 130B; crystals were grown from \(\text{CH}_2\text{Cl}_2/\text{ether}\) by vapour diffusion. The cation conformations of 130A and 130B are virtually undistinguishable. However, for reasons that are not entirely clear, the values of bond lengths and angles obtained from 130B are both less precise and intrinsically less reliable than those for 130A. Subsequent discussion will thus pertain exclusively to 130A.
Note that the numbering system used by the crystallographers, in Fig. 4:2, is different from that we have used in the earlier discussion of the protonated dicyclopentadiene complexes.

As shown in Fig. 4:2, the cations comprise osmium bound both to $\eta^6$-mesitylene, and to a dicyclopentadiene fragment via an $\eta^2$-olefin bond from C$_1$-C$_2$, a $\sigma$-bond from C$_5$ and a three centre-two electron bond involving H$_{6B}$.
FIG 4.2  Crystal structure of 
\[ \text{Os}(C_6H_3\text{Me}_3)(C_{10}H_{13})^+, 130 \]
The Os-C₅ distance of 2.10(2) Å is in good agreement with reported values for Os(II)-C σ-bonds in the octahedral complexes Os(H)(naphthyl)(Me₂PCH₂CH₂PMe₂)₂, 81 (2.13(2) Å) and cis-Os(CH₂C₆F₅)₂(CO)₄ (2.18(2) Å). 82 Although no structural data for mononuclear osmium(II)-olefin complexes are available for comparison, the Os-C₁ and Os-C₂ distances in 130A (2.19(2) Å and 2.23(2) Å respectively), agree well with reported ruthenium(II)-olefin distances of 2.17 - 2.29 Å in a range of mononuclear olefin complexes, 72,83-87 and with Os-C(olefin) distances observed in osmium trinuclear carbonyl clusters such as Os₃(CO)₁₀(s-trans-C₄H₆). 88

The hydrogen atoms were not located directly from difference synthesis. However the location of H₆b can be inferred with considerable certainty from the bonding geometry about C₆. 75 The Os-C₆ distance of 2.30(2) Å is too long for a normal Os-C σ-bond, and is 0.2 Å longer than the Os-C₅ bond length. However, a large M-C distance is typical of an agostic M-H-C interaction. For example, in the complex [Ru(C₆H₃Me₃)(C₁₈H₁₅)]PF₆, 119, described earlier, the Ru-C distance for the carbon atom involved in the M-H-C interaction (C₁₈, 2.354 Å) is of the order of 0.2 Å longer than the Ru-C distances to the η³-allyl carbon atoms C₁, C₂ and C₁₇ (average 2.17 Å). Similarly, M-C distances for the carbon atoms involved in the M-H-C interaction are substantially longer than the M-C distances to the η³-allyl carbon atoms in Mn(CO)₃(η³-C₆H₈Me), 25,66 and in [Fe(P(OMe)₃)₃(C₈H₁₃)]⁺. 16 In the osmium complex it is thus certain that the bridging hydride lies between C₆ and the Os atom. With H₆b tetrahedrally disposed at 0.95 Å from C₆ the calculated
Os-H distance is 1.81 Å and the Os-H-C angle 110°. These values are in agreement with the corresponding values for Mn(CO)$_3$(η$^3$-C$_6$H$_8$Me) (1.84 Å and 100°)$^{66}$ and [Fe(P(OMe)$_3$)$_3$(C$_8$H$_{13}$)]BF$_4$ (1.874 Å and 99.4°)$^{16}$ obtained from neutron diffraction studies (see Table 1).

The bridging C-H bond in the protonated dicyclopentadiene complexes 130-133 is essentially a two electron donor, allowing Os(II), Rh(III) and Ir(III) to achieve their preferred eighteen electron configuration. One would thus expect the bridge to be cleaved by better donor ligands. We find that [Os(C$_6$H$_3$Me$_3$)(C$_{10}$H$_{13}$)]PF$_6$, 130, reacts with excess t-butylisonitrile in CH$_2$Cl$_2$ at room temperature, giving a 1:1 adduct [Os(C$_6$H$_3$Me$_3$)(C$_{10}$H$_{13}$)(t-BuNC)]PF$_6$, 134. The $^1$H nmr spectrum of 134

![Diagram](image)

is very complex. However, the highfield doublet of doublets at δ-10.08 and the multiplet at δ0.10 in the spectrum of the protonated complex 130, which are characteristic of the bridging hydride dicyclopentadiene complexes, are absent in the spectrum of 134. The infrared spectrum of 134 shows a νCN band at 2150 cm$^{-1}$. These features are consistent with the structure shown, in which the three-electron donor dicyclopentadienyl group is bound to osmium via an η$^2$-olefin bond and a σ-bond.
4.3 BIS-$\eta^2$-ETHYLENE COMPLEXES

Nmr spectroscopic and analytical data, and yields for the new complexes synthesized in this section, are in Tables 10-14.

McMahon found that treatment of the bis-ethylene complex $\text{Ru(C}_6\text{Me}_6\text{)(C}_2\text{H}_4\text{)}_2$ with $\text{HPF}_6$ gave a fluxional complex $[\text{Ru(C}_6\text{Me}_6\text{)(C}_2\text{H}_4\text{)}_2\text{H}]\text{PF}_6$, $64$. On the basis of its variable temperature $^1H$ and $^{13}C$ ($^1H$ decoupled) nmr spectra $64$ was assigned a bisolefin-hydride ground state structure (see Section 1.3). The $^1H$ nmr spectrum of $64$ at $-90^\circ C$ is reproduced as Spectrum 32. It shows four separate two-proton multiplets for the ethylene protons, two of which appear to be quartets ($\delta$1.25, $\delta$0.59), the third a triplet ($\delta$1.53) and the fourth a multiplet that is partially obscured by the $\text{C}_6\text{Me}_6$ resonance at $\delta$2.07. There is also a one-proton highfield resonance at $\delta$-11.25, that has the appearance of a quintet. McMahon only observed the proton-decoupled $^{13}C$ nmr spectrum; at $-93^\circ C$ the 15 MHz spectrum showed only two resonances for the ethylene ligand, which supported a bis-olefin hydride complex.

Recent publications on the protonation of $\text{Co(C}_5\text{Me}_4\text{R})(\text{C}_2\text{H}_4\text{)}_2$ ($R = \text{C}_2\text{H}_5$, $140$; $R = \text{CH}_3$, $141$) complexes have prompted us to re-examine McMahon's results. The proton nmr spectrum of $64$ at $-90^\circ C$ is remarkably similar to those of the agostic complexes $[\text{Co(C}_5\text{Me}_4\text{R})(\text{C}_2\text{H}_4\text{)}(\mu-\text{H-}\text{C}_2\text{H}_5)]\text{BF}_4$ ($142$, $R = \text{Et}$; $143$, $R = \text{Me}$) at low temperature. In $143$, strong evidence for the agostic structure came from the $^{13}C$ nmr spectrum. At $-90^\circ C$ the spectrum showed, in addition to the $\text{C}_5\text{Me}_5$ resonances, a triplet ($J = 160.7$ Hz) and a doublet of triplets ($J = 155$ (t) and 33.5 (d) Hz), being, in fact, the averaged spectrum of two rapidly exchanging agostic isomers.
The $^{13}$C nmr spectrum (67 MHz) of 64 at -100°C is reproduced as Spectrum 33; it is similar to that of the cobalt complex 143. The arene resonances are a quartet at $\delta$15.1 and a singlet at $\delta$105.7. The other resonances are a triplet at $\delta$41.1 ($J = 158$ Hz) and a doublet of triplets at $\delta$23.0 ($J(t) = 155$ Hz, $J(d) = 28.4$ Hz). These results are consistent with 64 being an agostic complex, 66. The spectrum at -100°C can be explained in terms of the two isomers 66A and 66B in a state of fast exchange. This exchange may occur by direct hydrogen migration between the two ethylene units, or via a bis(olefin)-hydride intermediate (Scheme 4:1). The resonance at $\delta$41.1 is thus due to $C_2/C_2$, averaged, and that at $\delta$23.0 due to $C_1/C_1$. 

**Scheme 4:1**
averaged (i.e., equilibrated on the nmr time scale). Evidence for
the bridging hydride is found in the coupling constants of the latter
resonance, which indicate that (referring to isomer A, for example)
C₁ has two different kinds of protons attached to it. The smaller
coupling observed (28.4 Hz) represents an averaged geminal C-H coupling
of $J(C₁-H_e) = 56.8$ Hz and $J(C₁-H_e) = 0$ Hz. The larger coupling of
155 Hz represents the average of the coupling of C₁, to the two
equivalent protons $H_c$ and $H_d$, and the coupling of C₁ to the two
equivalent protons $H_e$; both these values probably lie within
the range 150 - 170 Hz. The value of 56.8 Hz is in the range
characteristic of $J(C-H_{\text{bridge}})$ values in C-H-M systems (see Table 2),⁴⁵
and is smaller than the coupling of C₁, to $H_c$ and $H_d$, because the
bonding to the metal makes the C-H bond weaker and longer than the
C-Hₐ, and C-Hₐ, bonds.

The observed $^1$H nmr spectrum of 66 at -90°C can also be interpreted
in terms of the $A=\neq B$ equilibrium (see Spectrum 32). The multiplet
at $\delta 2.0$ and the triplet at $\delta 1.53$ are thus assigned to $H_a/H_a'$, averaged
and $H_b/H_b'$, averaged respectively. The quartets at $\delta 1.25$ and $\delta 0.59$
are assigned to $H_c/H_c'$, and $H_d/H_d'$, averaged respectively and the
resonance at $\delta -11.25$ to $H_e$. There is thus substantial coupling
between $H_e$, $H_c$, and $H_d$ but none between $H_e$, and $H_a$ and $H_b$.

Warming solutions of 66 results in the collapse of the four 2H
multiplets and the hydride resonance at room temperature, followed
by the appearance of a nine-proton multiplet at $\delta 0.08$ at 80°C.
This can be explained in terms of a further two fluxional processes,
outlined in Schemes 4:2 and 4:3, similar to the processes occurring in $\text{[Co(C}_5\text{Me}_4\text{R})(\text{C}_2\text{H}_4)(\text{u-H-}\text{C}_2\text{H}_4)]BF}_4$ (142, $R = \text{Et}$; 143, $R = \text{Me}$).\textsuperscript{36,37}

The process in Scheme 4:2 involves breaking the Ru-H\textsubscript{e} bond; together with the fast process in Scheme 4:1 it equilibrates $H_c$, $H_d$, $H_e$, $H_c'$, and $H_d'$. The process in Scheme 4:3 involves rotation of the ethylene ligand about the metal ligand axis. This, together with the processes outlined in Schemes 4:1 and 4:2, results in all nine protons becoming equivalent, as is observed in the $^1H$ nmr spectrum of 66 at 80°C.
Protonation of the bisethylene complex \( \text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2 \) with HPF\(_6\) gave a yellow solid that could not be purified without decomposition, but its variable temperature \(^1\text{H} \) nmr spectrum suggests that it has an agostic ground state structure similar to that of the ruthenium complex \( \text{66} \), and the cobalt complexes \( \text{142} \) and \( \text{143} \). At 20°C the spectrum shows a \( \text{C}_5\text{Me}_5 \) resonance at \( \delta 1.85 \), and a nine-proton multiplet at \( \delta 1.07 \). Cooling the solution results in the collapse of the resonance at \( \delta 1.07 \) and the appearance at -100°C of triplets at \( \delta 2.73 \) (2H, \( J = 10.9 \) Hz) and \( \delta 2.56 \) (2H, \( J = 10.7 \) Hz), a broad resonance in the region \( \delta 1.5 \) (partially obscured by peaks due to an impurity) and a broad one-proton resonance at \( \delta 8.65 \). These results are consistent with an agostic complex, \( \text{135} \). At -100°C the \(^1\text{H} \) nmr spectrum represents a fast exchange between two isomers A and B similar to that outlined in Scheme 4:1. The two triplets at \( \delta 2.73 \) and \( \delta 2.56 \) are thus due to \( \text{H}_a/\text{H}_a' \) (averaged) and \( \text{H}_b/\text{H}_b' \) (averaged), respectively, and the broad multiplet at \( \delta 1.5 \) includes the \( \text{H}_c/\text{H}_c' \) (averaged) and \( \text{H}_d/\text{H}_d' \) (averaged) resonances. The hydride resonance at \( \delta 8.65 \) is assigned to \( \text{H}_e \). The spectrum at 20°C, showing a nine proton multiplet, can be explained in terms of a further two fluxional
processes, analogous to those outlined in Schemes 4:2 and 4:3 for the ruthenium complex.

The ruthenium complex 66, and the rhodium complex 135, thus both adopt an agostic ground state structure.

Treatment of Os(C₆H₃Me₃)(C₂H₄)₂, 93, with an excess of HPF₆ in ether precipitates a white complex, [Os(C₆H₃Me₃)(C₂H₄)₂H]PF₆, 136. The parent zerovalent osmium complex 93 can be regenerated by treating

![Diagram of complex 136]

136 with aqueous sodium carbonate. The solid state infrared spectrum of 136 showed a weak sharp band at 2140 cm⁻¹, assigned to νM-H.

Complex 136 is fluxional. Its ¹H nmr spectra at -20°C and -100°C are reproduced as Spectrum 34, and they are consistent with a bisolefin hydride structure and clearly inconsistent with an agostic structure. At 20°C the arene resonances appear as singlets at δ2.42 (9H) and δ5.99 (3H). There are also two mirror image multiplets at δ2.12 and δ1.80, each integrating for 4H, and a one-proton resonance at δ-10.46. The two mirror image multiplets are similar
to those in the $^1$H nmr spectrum of the parent zerovalent metal complex $\text{Os(C}_6\text{H}_{12}\text{Me}_3)(\text{C}_2\text{H}_4)_2$, 93, at 20°C (see Fig. 2:2). In the case of 93, they were assigned to two sets of non-equivalent protons, indicating that rotation of the ethylene ligands about the metal-ligand axis is slow on the nmr time scale at 20°C (Section 2.2.2). Clearly the ethylene ligands cannot be static in 136 as this would result in $H_a, H_b, H_c$, and $H_d$ all being inequivalent, hence the proton nmr spectrum would show four two-proton multiplets ($H_a, H_a'$; $H_b, H_b'$; $H_c, H_c'$; and $H_d, H_d'$) for the ethylene protons. However, fast rotation about the metal-ethylene bond would separately equivalence $H_a$ and $H_d'$, and $H_b$ and $H_c$, resulting in two four-proton multiplets, as is observed. The $^{13}$C nmr spectrum of 136 at -20°C (reproduced as Spectrum 35) shows only four resonances. Those at $\delta18.9$, $\delta90.8$ and $\delta112.8$ are due to the arene ligand, and a triplet at $\delta35.3$ ($J = 162$ Hz) due to the ethylene ligands. Clearly all four carbon atoms of the ethylene ligands are equivalent, indicating that the ethylene ligands are rotating rapidly.

When solutions of 136 are cooled below -20°C, the multiplets due to the ethylene protons in the $^1$H nmr spectrum broaden, and at -100°C have virtually collapsed into the baseline (Spectrum 34). The hydride and arene resonances, however, remain sharp. This result indicates that the rotation of the ethylene ligands becomes very slow at this temperature. The barrier to ethylene rotation is thus considerably lower in 136 than in the zerovalent osmium complex 93 and in the neutral bisethylene complexes of Ru, 56 Rh and Ir. 122 For example whilst in the protonated complex 93, rotation has not been fully
stopped at -100°C, a $^1$H nmr spectrum corresponding to fast rotation is not seen even at +100°C in the zerovalent osmium complex, which is a remarkable difference. Unfortunately, direct comparison cannot be made between this and the protonated bis(ethylene) complexes of Co, Rh and Ru, as the latter complexes adopt agostic ground state structures as opposed to the diene hydride structure of 136. In the agostic complexes the barrier to ethylene rotation does, however, seem to be slightly lower than in the parent neutral complexes from which they are formed. For example, the $^1$H nmr spectrum of the complex [Ru(C₆Me₆)(C₂H₄)(µ-H-C₂H₄)]PF₆, 66, at 80°C showed a 9H multiplet for the ethylene and hydride protons, 56 which implies that rotation of the ethylene ligand is fast at this temperature. In contrast, in the zerovalent complex Ru(C₆Me₆)(C₂H₄)₂, a fast rotation spectrum was not seen even at 100°C. 124

When solutions of 136 are warmed to 20°C, broadening of all resonances in the $^1$H nmr spectrum except those of the arene ligand is observed. This is consistent with another fluxional process, in which Hₑ exchanges with the ethylene ligand protons via an ethyl intermediate (Scheme 4:4). Such a process would ultimately result in all eight

![Scheme 4:4](image-url)
ethylene protons and the hydridic proton becoming equivalent, and would give a 9H multiplet in the $^1H$ nmr spectrum. Unfortunately the instability of 136 in solution precluded studies at higher temperatures.

The intermediate ethyl species can be trapped by reaction of 136 with ligands. For example, reaction of 136 with an excess of trimethylphosphite in dichloromethane gave a stable yellow complex, $[\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)\text{P(OMe)}_3]\text{PF}_6$, 137. Its $^1H$ nmr spectrum showed arene resonances at 85.82 (3H) and 82.21 (9H) and a doublet due to the P(OMe)$_3$ ligand at 83.68. The ethylene ligand gave rise to a multiplet at 82.41, and the ethyl ligand gave rise to an A$_3$BC pattern of one-proton multiplets at 81.54 and 81.77 and a three-proton distorted triplet at 81.42. Similarly, reaction of 136 with an excess of t-butylisonitrile gave $[\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{t-BuNC})]\text{PF}_6$, 138; the proton nmr spectrum of 138 showed similar features to the spectrum of 137, except that the t-butyl resonance obscured the A$_3$BC pattern of the ethyl ligand. The infrared spectrum of 138 showed a strong $\nu\text{CN}$ band at 2170 cm$^{-1}$. These reactions provide evidence that an
ethylenehydridometal complex exists in equilibrium with a metal-ethyl complex in solution, and are of general importance in the study of olefin insertion into M-H bonds. \textsuperscript{38}

We have thus shown that there are two different types of complexes formed on protonation of bis-ethylene complexes of the cobalt and iron triads. The cobalt, rhodium and ruthenium complexes all adopt agostic bridging hydride ground state structure, whereas the osmium complex adopts a diene-hydride structure.
Protonation of Norbornadiene Complexes of Osmium, Rhodium and Iridium

Protonation of Ru(\(\eta^6\)-arene)(\(\eta^4\)-norbornadiene) complexes with HPF₆ gave initially complexes, 56A-D, that appeared to have a diene hydride structure ⁵⁶ (see Section 1.3). In dichloromethane solution, these isomerized to a second complex, [Ru(\(\eta^6\)-arene)(C₇H₉)]PF₆, ⁵⁷, which McMahon was not able to fully identify. Complexes ⁵⁷B and C showed nine one-proton multiplets in their \(^1\)H nmr spectra, seven separate resonances for the (C₇H₉) moiety carbon atoms in the \(^{13}\)C nmr spectra, and a band at ca. 2000 cm⁻¹ in their infrared spectra. The spectroscopic evidence could not be satisfactorily interpreted in terms of any one structure.

\[
\text{Ar} \quad \text{ Ru} \quad \text{H} \quad \text{CH}_2\text{Cl}_2 \quad \text{PF}_6^{-}
\]

56 A, Ar = C₆H₆  \hspace{1cm} 57 A

B, Ar = C₆H₃Me₃  \hspace{1cm}  B

C, Ar = C₆Me₆  \hspace{1cm}  C

D, Ar = C₆H₂Me₄  \hspace{1cm}  D
We have investigated the protonation of osmium, rhodium and iridium norbornadiene complexes. Nmr spectroscopic and analytical data, and yield of 139-142 and 150 are in Tables 10, 12 and 13.

Treatment of Os(C₆H₃Me₃)(C₇H₈), 91, with HPF₆ in ether precipitates an air-sensitive, brown solid with an empirical formula corresponding to [Os(C₆H₃Me₃)(C₇H₈)]PF₆, 139. The proton nmr spectrum of 139 (Spectrum 24) shows arene resonances at δ2.49 (9H) and δ5.86 (3H).

\[
\text{Os} \\
\begin{array}{c}
\text{C₆H₃Me₃} \\
\text{C₇H₈} \\
\text{PF₆}
\end{array}
\]

Other resonances include two triplets at δ3.90 and δ3.53, each integrating for two protons, two one-proton multiplets at δ3.84 and δ3.75, a triplet at δ6.80 (2H, J = 1.5 Hz) and a singlet at δ9.55 (1H). These results are consistent with a diene hydride complex, with a plane of symmetry along C₁, C₇, C₄. The two triplets at δ3.90, δ3.53 are thus assigned to H₂,6 and H₃,5, the two one-proton multiplets at δ3.84 and δ3.75 to H₁ and H₄, the triplet at δ6.80 to the two H₇ protons, and the highfield singlet to the hydride proton. The ¹³C nmr spectrum also support the diene-hydride structure; it showsthree resonances for the arene (δ20.4, δ86.2 and δ109.4), and
five resonances for the diene ligand (δ33.8, δ43.1, δ44.4, δ48.9 and δ62.5); the resonance at δ62.5 (J = 133 Hz) is a triplet and is assigned to C7 (Spectrum 25).

Complex 139 shows a weak, broad band at 2140 cm⁻¹ in the Nujol mull infrared spectrum which may be due to a vM-H vibration.

Unlike the corresponding ruthenium complex, 139 did not isomerize in solution. When solutions of 139 were left standing overnight or longer, there was no change in the ¹H nmr spectrum with time, and the complex eventually decomposed to a black insoluble substance.

Treatment of 139 with aqueous sodium carbonate regenerated the zerovalent osmium complex, 91. There was no reaction between 139 and excess t-BuNC in dichloromethane at room temperature.

Protonation of an ether solution of Ir(C₅Me₅)(C₇H₈), 101, with HPF₆ gave immediately a white solid of empirical formula [Ir(C₅Me₅)(C₇H₉)]PF₆, 140. The same cation, identified by its proton nmr and infrared spectra was also obtained by protonation with HBF₄, CF₃SO₃H, HSbF₆ and p-toluene sulphonic acid. The nmr spectra discussed below relate to the PF₆⁻ salt of 140. The ¹H nmr spectrum of this complex has similar features to that of the osmium complex 139, above, and indicates that 140, like 139, adopts a diene-hydride structure, with a plane of symmetry through C₁, C₇ and C₄. Thus, apart from the C₅Me₅ resonance at δ2.08, the spectrum shows two triplets, each integrating for two protons, at δ4.25 and δ3.46, due to H₂,₆ and
There are two $^1H$ multiplets due to $H_1$ and $H_4$ ($\delta4.11$, $\delta3.79$), a triplet at $\delta6.94$ due to the two $H_7$ protons, and a hydride resonance at $\delta-12.66$. Complex 140 also shows a weak, sharp peak at 2110 cm$^{-1}$ in its solid state infrared spectrum, which is assigned to a $\nu$Ir-H vibration.

When 140 is dissolved in dichloromethane at room temperature it isomerizes to a new species, 141, also of empirical formula [Ir(C$_5$Me$_5$)(C$_7$H$_9$)]PF$_6$. The $^1H$ nmr spectrum of 141 (Spectrum 26) is almost identical in appearance with that of the isomerized complex [Ru(C$_6$Me$_6$)(C$_7$H$_9$)]PF$_6$, 57C, (this spectrum is reproduced for comparison in Spectrum 29). In addition to the C$_5$Me$_5$ ligand resonance at $\delta2.06$, there are eight (C$_7$H$_9$) resonances at $\delta4.10$ (1H), $\delta3.94$ (2H), $\delta3.45$ (1H), $\delta2.81$ (1H), $\delta2.61$ (1H), $\delta2.34$ (1H), $\delta1.01$ (1H) and $\delta0.82$ (1H). Particularly significant features are the symmetrical eight-line multiplet at $\delta2.81$, and the two asymmetric doublets at $\delta2.61$ and $\delta2.34$, the significance of which will be discussed later, and the absence of a hydride highfield resonance. The $^{13}C$ nmr
The norbornadiene complex Rh(C₅Me₅)(C₇H₈) is also protonated by HPF₆, giving a stable yellow solid, [Rh(C₅Me₅)(C₇H₉)]PF₆, 142. The ¹H nmr spectrum of 142 (Spectrum 27) is similar to that of 141: there is no sign of a diene hydride complex, though presumably protonation occurs initially at the metal and is followed immediately by rapid isomerization. The C₅Me₅ ligand gives rise to a singlet at δ1.96. The C₇H₉ group gives rise to one proton multiplets at δ4.41, δ4.25 and δ3.94, a two-proton multiplet at δ3.31, two asymmetric doublets at δ3.00 and δ2.90 (each 1H), and a 2H multiplet at δ1.08. The doublets at δ3.00 and δ2.90 each show a further coupling of ca. 2 Hz, to ¹⁰³Rh.

The ¹³C nmr spectrum of 142 is reproduced in Spectrum 28; it shows similar features to that of 141 apart from the resonances due to the C₅Me₅ ligand, at δ10.1 (quartet) and δ102.6, there is a triplet at δ26.5 (J = 135 Hz), doublets at δ34.2 (J = 151 Hz) and δ56.2, a triplet at δ59.3 (J = 159 Hz) and doublets at δ59.7 (J = 165 Hz), δ70.3 (J = 168 Hz) and δ87.1 (J = 179 Hz). All resonances except...
those at δ10.1, δ26.5 and δ34.2, show additional coupling to $^{103}$Rh, of 4 – 11 Hz (see decoupled spectrum in Spectrum 28).

Surprisingly, there were no bands seen in the solid state infrared spectrum of 142, in contrast to the analogous iridium and ruthenium complexes.

The $^1$H nmr spectrum of isomerized $[\text{Ru(n}^6\text{-arene})(\text{C}_7\text{H}_9)]\text{PF}_6$ (57B, arene = C$_6$H$_3$Me$_3$; 57C, arene = C$_6$Me$_6$), 141 and 142 are all remarkably similar. The $^1$H nmr spectrum of Rh(C$_5$H$_5$)(C$_7$H$_8$) dissolved in CF$_3$CO$_2$H also shows similar features. This strongly suggests that all these complexes adopt the same structure. The two most obvious structures are 143, in which the added proton is incorporated into the norbornadiene ligand giving a σ-π complex, and 144, in which the added proton bridges between the metal and one carbon of the norbornadiene ligand. Structure 143 has been proposed, by Lewis et al. for the complex present in a solution of Rh(C$_5$H$_5$)(C$_7$H$_8$) in CF$_3$COOH. Structure 144 is related to the bridging hydride species formed on protonation of dicyclopentadiene complexes, as described in the previous chapter.
A bridging hydride moiety appears to be present in RuClC₂₁H₂₅, 145.⁷⁶

Another possible structure, related to 144 is the bridging hydride structure 146, which exists in solution as a pair of rapidly equilibrating isomers, A and B. The complex [Fe(CO)₃(C₇H₈)]⁺, 11, appears to adopt this structure.¹⁹,²⁰

Structure 143 is a coordinatively unsaturated sixteen electron structure, and one would expect complexes adopting such a structure
to react fairly easily with small ligands, to give the preferred 18e configuration. The iridium complex 141 does not, however, react with CO; neither did the isomerized ruthenium complexes [Ru(C₆Me₆)(C₇H₉)]PF₆, 57C and its mesitylene counterpart, 57B. Whilst these complexes do react with t-BuNC, complex mixtures of products result, which do not appear to include the simple 1:1 adducts.

In the agostic bridging hydride structure 144, the hydride acts as a two-electron donor, so enabling the metal to attain the preferred eighteen electron configuration. However, the band at 2040 cm⁻¹ in the infrared spectrum of the iridium complex, 141, is not in the region that one would expect to find the νM-H or νC-H bands of an agostic complex (see Section 1.2). Further, the nmr spectra of 141, the rhodium complex 142 and also of the ruthenium isomerized complexes 57B and 57C, show neither of the typical features of an agostic bridging hydride (see Section 1.2), i.e., the presence of a highfield hydride resonance in the ¹H nmr, and a ¹³C resonance showing an unusually low geminal J(C-H<sub>bridge</sub>) value (due to the carbon of the C-H-M interaction). For example, the complex RuClC₂₁H₂₅, 145, shows a doublet highfield (δ-3.74) resonance in its ¹H nmr spectrum, due to the bridging hydride ligand. Also, the ¹H nmr spectrum of [Fe(CO)₃(C₇H₉)]⁺ shows a triplet hydride resonance at δ-7.3, and the ¹³C nmr spectrum shows a low geminal J(C-H<sub>bridge</sub>) value of 37.8 Hz (actually an average value J(C-H<sub>bridge</sub>) = 75.6 + J(C-H<sub>nonbridge</sub>) = 0)/2 for the two rapidly equilibrating structures), typical of agostic interactions. Also, in the dicyclopentadiene complexes 130-133 the agostic structure is clearly indicated by both the ¹³C and ¹H nmr spectra.
It thus seems unlikely that 141 and 142 and the Ru complexes 57B and 57C, adopt either structure 143 or 144; nor is there any evidence to suggest a pair of rapidly exchanging isomers such as in 146.

The nmr data of 141 and 142 are best explained in terms of the \( \eta^5 \)-vinylcyclopentenyl structure 147; similarly the nmr data of the isomerized Ru complexes, 56 and the species obtained on dissolving Rh\((C_5H_5)(C_7H_8)\) in CF\(_3\)COOH, 32 also support the assignment of structure 147. For example, in the \(^1H\) nmr spectrum of 141 (Spectrum 26), the resonances at 64.10, 63.94 and 63.45 are assigned to \( H_1, H_2, H_3 \) and \( H_4 \). Which resonance is due to which of these four protons is uncertain; decoupling experiments, unfortunately, did not provide...
the answer as there are complex couplings between the four protons. The vinyl group gives rise to the multiplet at $\delta 2.81$ ($H_6$) and the two asymmetric doublets at $\delta 2.61$ ($J = 11.6$ Hz) and $\delta 2.34$ ($J = 7$ Hz). The multiplet - two asymmetric doublets pattern is typical of vinyl groups. Styrene (vinyl benzene) shows a similar pattern in its $^1H$ nmr, though the chemical shifts are lower. McMahon has synthesized complexes of the phosphine $PPh_2$(vinylbenzene) (= sp). In the complex $[RuCl(C_6Me_6)(sp)]PF_6$ the (sp) ligand is bonded to the metal through the phosphorus atom and the $\pi$-bonded vinyl group. The $^1H$ nmr of this complex also shows the multiplet - two asymmetric doublet pattern for the vinyl group; the proton equivalent to $H_6$ of structure 147 gives rise to a multiplet at $\delta 5.83$, the proton cis to this gives rise to a doublet at $\delta 4.36$ ($J = 9$ Hz), and that trans gives rise to a doublet at $\delta 3.60$ ($J = 12$ Hz).

In the structure 147, the trans coupling $J(H_6-H_{7a})$ is expected to be larger than the cis coupling $J(H_6-H_{7b})$. Thus, in 141 the resonance at $\delta 2.61$ is assigned to $H_{7a}$ and that at $\delta 2.34$ to $H_{7b}$. Also, as is typical of a vinyl group, the geminal $J(H_{7a}-H_{7b})$ coupling is very weak. Decoupling experiments confirm this, showing that $H_{7a}$ and $H_{7b}$ are both coupled to $H_6$, but not to each other.

The remaining two $(C_7H_9)$ ligand resonances in the proton nmr spectrum of 141, at $\delta 1.01$ and $\delta 0.82$, are assigned to the two $H_5$ protons.

The resonances in the $^1H$ nmr spectra of the rhodium complex 142 and the ruthenium complex $[Ru(C_6Me_6)(C_7H_9)]PF_6$, 57C (Spectrum 27 and
29 respectively), can be assigned similarly. The asymmetric doublets due to the \( H_7 \) protons \( \delta 3.00 \) and \( \delta 2.90 \) in Spectrum 27 show the expected coupling to \( ^{103} \)Rh.

The \( ^{13} \)C nmr spectra also agree well with the structure \( \text{147} \). Consider for example, the spectrum of \( \text{142} \), shown in Spectrum 28. Doublets at \( \delta 56.2, \delta 59.7, \delta 70.7 \) and \( \delta 87.1 \) all show additional coupling to \( ^{103} \)Rh, suggesting that they are directly bonded to the metal; they are assigned to \( C_2, C_3, C_4 \) and \( C_6 \). The individual assignments of these resonances are uncertain, though the resonance at \( \delta 87.1 \) is probably due to the central C atom of the \( \eta^3 \)-allyl moiety, \( C_3 \); in \( \eta^3 \)-allyl metal complexes the central carbon of the allyl moiety typically gives rise to a resonance well downfield of the outer two carbons of the moiety.\(^{91,92,93,94} \) The triplet at \( \delta 59.3 \) also shows an additional coupling to \( ^{103} \)Rh. The corresponding resonance in the \( ^{13} \)C nmr spectrum of the iridium complex \( \text{141} \) is a doublet of doublets. This resonance is thus assigned to \( C_7 \). \( C_1 \) gives rise to the doublet at \( \delta 34.2 \) and \( C_5 \) to the triplet at \( \delta 26.5 \).

The \( ^1H \) and \( ^{13} \)C nmr spectra thus support the structure \( \text{147} \). However, one outstanding problem remaining is the assignment of the band at 2040 cm\(^{-1} \) in the infrared spectrum of \( \text{141} \). The band is of medium to strong intensity, is present in both solution and solid state spectra, and is independent of the anion, (e.g., SbF\(_6\)\(^-\), PF\(_6\)\(^-\) and p-toluene sulphonate salts of \( \text{141} \) all show a similar band). A similar band is seen in the infrared spectra of \( [\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{C}_7\text{H}_9)]\text{PF}_6 \), \(^{57} \)B, (medium strength) and \( [\text{Ru(C}_6\text{Me}_6)(\text{C}_7\text{H}_9)]\text{PF}_6 \), \(^{57} \)C, (weak), but
is not seen in the spectrum of \([\text{Rh}(C_5\text{Me}_5)(C_7H_9)]PF_6\), \(^{142}\). Infrared absorptions in the region of 2000 cm\(^{-1}\) normally imply the presence of such groups as bound C=O, C=N, C=C, N=N or M-H. There is, however, no evidence from elemental analysis for the presence of nitrogen and no nmr spectroscopic evidence for the presence of bound CO, in the ruthenium and iridium complexes. Also it is not clear why the iridium complex \(^{141}\) should have this particular band while the apparently isostructural rhodium complex \(^{141}\) should not. We have not been able to find any satisfactory explanation for the unusual infrared band in the ruthenium and iridium complexes.

Extensive attempts to grow crystals suitable for X-ray crystallographical studies, of the ruthenium, iridium and rhodium complexes, \(^{57B, 57C, 141\text{ and } 142}\), as PF\(_6^–\), SbF\(_6^–\), CF\(_3\)SO\(_3^–\), BF\(_4^–\) and p-toluene sulphonate complexes, were unsuccessful. However, the assignment of the \(\eta^5\)-vinylcyclopentenyl structure \(^{147}\) for these complexes is also supported by the reactivity of these complexes.

When the neutral norbornadiene complex \(\text{Rh}(C_5\text{Me}_5)(C_7H_8)\), is treated with an excess of DPF\(_6\) a monodeuterated analogue of \(^{142}\) is formed, \([\text{Rh}(C_5\text{Me}_5)(C_7H_8D)]PF_6\). Examination of the proton and \(^2\)H nmr spectra of this complex shows that the deuterium atom has replaced \(H_{7b}\) (assuming structure \(^{147}\)). The asymmetric doublet at \(\delta2.90\) has been considerably reduced in intensity relative to the spectrum of the protonated complex \(^{142}\). This doublet exhibits the lower \(J(H_{7b}-H_6)\) value of the two asymmetric doublets and thus probably arises from \(H_{7b}\), cis to \(H_6\). This result is identical to that observed by McMahon.
on treatment of Ru(C_{6}Me_{6})(C_{7}H_{8}), with DPF_{6}, which resulted in deuteration at the analogous position in formation of [Ru(C_{6}Me_{6})(C_{7}H_{8}D)]PF_{6}.^{56}

Cationic 18e complexes are expected to undergo external nucleophilic attack. Complexes 141 and 142 react with lithium aluminium hydride to give ether-soluble, neutral products of formula 148 and 149.

The iridium complex, 149, was obtained in 70% yield and identified by analytical and spectroscopic data. The synthesis of the rhodium complex 148 was done on a small scale, with sufficient product being synthesized for spectroscopic identification only. On the basis of the mass and nmr spectroscopic data, we propose that these complexes contain a vinylcyclopentadiene ligand, and arise from the addition of one mole of hydride ion to one end of the \( \eta^3 \)-allyl moiety of structure 147. For convenience the spectra will be discussed with reference to the structure in which the cyclopentene ring double bond lies between C_{2} and C_{3}, i.e., hydride addition has taken place at C_{4}. However, the double bond may be between C_{3} and C_{4}, resulting
from hydride addition at C\textsubscript{2}. There was no evidence for the formation of more than one isomer on addition of hydride to 141 and 142.

The \textsuperscript{1}H nmr spectra of 148 and 149 are complex, and could not be fully interpreted. Apart from the C\textsubscript{5}Me\textsubscript{5} methyl resonances, in both there are a complex series of multiplets between \textsuperscript{63} and \textsuperscript{61}. The spectra of both complexes also show a broad doublet (\textsuperscript{60.67} for 148, \textsuperscript{60.17} for 149) slightly upfield of the rest of the spectrum, which may arise from one of the vinyl group protons.

The \textsuperscript{13}C nmr spectrum of the iridium complex 149, reproduced in Spectrum 30, supports the proposed vinylcyclopentene structure. The coordinated diene gives rise to four doublets, two triplets and a doublet of doublets. Doublets at \textsuperscript{657.5} and \textsuperscript{642.0} are assigned to C\textsubscript{2} and C\textsubscript{3}, while that at \textsuperscript{635.4} is assigned to C\textsubscript{1}, on account of its relatively low J(C-H) value (136 Hz). On the basis of deuteration results, \textit{vide infra}, the triplet at \textsuperscript{646.9} is assigned to C\textsubscript{4}; hence that at \textsuperscript{627.3} must be due to C\textsubscript{5}. The vinyl group gives rise to a doublet (\textsuperscript{633.9}) for C\textsubscript{6}, and a doublet of doublets (\textsuperscript{628.6}) for C\textsubscript{7}.

The \textsuperscript{13}C nmr spectrum of the rhodium complex 148 is similar to that of 149 (Spectrum 31). As expected, resonances due to C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{6} and C\textsubscript{7} show additional coupling to \textsuperscript{103}Rh.

The mass spectra of 148 and 149 both show parent ions corresponding to M(C\textsubscript{5}Me\textsubscript{5})(C\textsubscript{7}H\textsubscript{10}), and other major peaks corresponding to (Parent - CH\textsubscript{3}) and (Parent - C\textsubscript{2}H\textsubscript{5}). Recrystallized samples of 149 show a weak
band at 1962 cm\(^{-1}\) in the solid state infrared spectrum. In samples which have been purified by sublimation, the band was reduced in intensity, but did not disappear. The source of this band is not known, nor is it known if it is in any way related to the band at 2040 cm\(^{-1}\) in 141. The rhodium complex 148 shows no such band in its solid state infrared spectrum.

Treatment of the iridium complex 149 with Ph\(_3\)C\(^+\)BF\(_4\) gave a mixture of products, the major component of which was 141 (identified by its proton nmr spectrum). The hydride addition reaction is thus partially reversible.

A mono deuterated analogue of 149 has been synthesized by treating 141 with LiAlD\(_4\). The \(^1\)H nmr spectrum of Ir(C\(_5\)Me\(_5\))(C\(_7\)H\(_9\))D is not as complex as that of non-deuterated 149, but is still too complex to assign fully. The \(^{13}\)C nmr spectrum of the deuterated species shows that the deuterium is attached to the carbon (C\(_4\)) giving rise to the resonance at \(\delta 46.9\); in the proton decoupled spectrum this resonance appeared as a weak triplet. The infrared spectrum shows a \(\nu\)C-D band at 2140 cm\(^{-1}\) which is not present in the non-deuterated analogue. These results suggest that one deuterium ion has added to one end of the \(\eta^3\)-allyl unit of 141.

We have also investigated the reaction of the isomerized ruthenium complex [Ru(C\(_6\)Me\(_6\))(C\(_7\)H\(_9\))]PF\(_6\), 57C, with LiAlH\(_4\). The \(^{13}\)C nmr spectrum of the product suggested that it was a mixture of at least two complexes. The mass spectrum of the mixture, however, appears to
show the presence of only one complex, possibly Ru(C_{6}Me_{6})(C_{7}H_{10}) (a peak at m/e 357, Parent-H). The spectrum also shows two other major peaks, corresponding perhaps to (Parent-CH_{3}) and (Parent-C_{2}H_{5}), a fragmentation pattern that is similar to that of the rhodium and iridium complexes 148 and 149. We were not able to fully identify this product; however, the results suggest that it may consist of a mixture of the two possible hydride addition products, in which the hydride adds at either position 2 or 4 of the \eta^{5}-vinylcyclopentenyl complex.

Complex 141 does not undergo a simple deprotonation reaction on treatment with Na_{2}CO_{3}, as did the other diene hydride and agostic complexes described already in this chapter, and as would be expected were it a bridging hydride complex. There was no immediate reaction on stirring 141 with excess aqueous Na_{2}CO_{3}, but after several days a neutral, ether-soluble complex was formed. This was not fully identified, but its mass spectrum has a parent ion at m/e 438, which corresponds to Ir(C_{5}Me_{5})(C_{7}H_{9}OH). There is a peak at m/e 437 (Parent-H) and another at 419 (Parent-H-H_{2}O). This evidence suggests that there is a hydroxy group in the complex.

Reaction of the iridium complex 141 with one equivalent of t-BuNC gave a complex mixture of products, which were not identified. In contrast the only product isolated from the reaction of the rhodium complex 142 with t-BuNC was [Rh(t-BuNC)_{4}].
The \((C_7H_9)\) fragment of \([\text{Ir}(C_5Me_5)(C_7H_9)]PF_6\) \(^{141}\), was displaced by reaction of the complex with excess KCl or KI at room temperature in acetone, resulting in the dimeric complexes \([\text{Ir}(C_5Me_5)X_2]_2\) \((X = \text{Cl, I respectively})\). However, we were not able to do the reaction on a large enough scale to enable identification of any organic compounds arising from the displaced organic fragment, in the acetone solution, and were thus unable to obtain any further information as to the structure of the \((C_7H_9)\) ligand in \(^{141}\).

Due to our lack of success in growing crystals suitable for X-ray crystallographical study of the isomerized norbornadiene complexes, we decided to investigate the products of the protonation of the substituted norbornadiene compound, \(\text{Ru}(C_6H_3Me_3)(7\text{-phenyl}n\text{orbornadiene})\) \(^{95}\).

Treatment of an ether solution of \(^{95}\) with \(\text{HPF}_6\) resulted in the immediate precipitation of a yellow solid of empirical formula \([\text{Ru}(C_6H_3Me_3)(C_{13}H_{13})]PF_6\) \(^{150}\). The \(^1\text{H nmr}\) spectrum of this complex suggests that it has a diene hydride structure analogous to that obtained when \(\text{Ru}(C_6H_3Me_3)(C_7H_8)\), is protonated.\(^{56}\) The mesitylene
ligand gives rise to resonances at δ2.30 (9H) and δ5.83 (3H). The phenyl group gives rise to a multiplet at ca. δ7, and there are five one-proton multiplets and a two-proton multiplet at δ4.15, δ3.85, δ3.69, δ3.55 (2H), δ3.48 and δ2.95 for the protons H1-7 (not separately assigned). The presence of the hydride ligand is indicated by a singlet at δ-5.04.

There are two possible isomers of 150, owing to the phenyl group attached to position 7 of the norbornadiene fragment. However, the 1H nmr spectrum indicates that the product is entirely one isomer.

When 150 is set aside in CH2Cl2 overnight at ambient temperature it undergoes irreversible isomerization to a mixture of two products, which could not be completely separated even by repeated crystallization. The major product could not be identified, though resonances at δ2.25 (9H) and δ5.97 (3H) in the proton nmr spectrum show it contains coordinated mesitylene. The minor product is interesting as it shows a multiplet - two asymmetric doublets pattern in its 1H nmr spectrum, similar to that assigned to the vinyl part of the vinylcyclopentenyl structure 147 in, for example, the iridium complex 141. The eight-line multiplet appears at δ3.28, while the doublets are at δ2.97 (J = 8 Hz) and δ2.78 (J = 12.6 Hz). These results suggest that 150 may have isomerized to give the vinylcyclopentenyl complex 151. Attempts to grow crystals of these products suitable for study by X-ray crystallography, were not successful.
We conclude that the vinylcyclopentenyl structure 42 is the most likely structure of the isomerized iridium and ruthenium complexes 141, 57B and 57C and of the rhodium complexes 142 and 34. It fits all the evidence, except the unusual bands at ca. 2000 cm\(^{-1}\) in the infrared spectra of 141, 57C and 57D.

A possible mechanism for the synthesis of 147 is outlined in Scheme 5:1. Protonation initially takes place at the metal giving a diene hydride. In solution, in all cases except \(M = Os\), this isomerizes via migration of the hydride into an endo position of the norbornadiene ligand to give a \(\eta^2\)-intermediate. This rearranges to the \(\eta^5\)-vinylcyclopentenyl group as shown in the Scheme. The added proton thus becomes \(H_{7b}\), the proton cis to \(H_6\). This is confirmed by the deuteration experiments described above; the added \(D^+\) atom replaced \(H_{7b}\) in \([\text{Rh} (C_{9}Me_{5})(C_{7}H_{8}D)]^+\).

\[\text{SCHEME 5:1 Protonation of norbornadiene complexes.}\]
CHAPTER 6

CONCLUSIONS

We have reported in this thesis on a variety of protonated arene osmium and ruthenium, and cyclopentadienyl rhodium and iridium \( \eta^4 \)-diene and bis-\( \eta^2 \)-ethylene complexes. These complexes are isolable as solids, similar to, for example, protonated iron tris(phosphite) \( \eta^4 \)-diene complexes but in contrast to protonated iron tricarbonyl complexes. 9

The most convenient method of determining the structure of the protonated complexes has been nmr spectroscopy. In many of the fluxional complexes described in this work, limiting nmr spectra were obtained, enabling identification of the ground state structure. In particular, in the osmium and iridium complexes limiting spectra were obtained in virtually all cases, and the diene hydride structure was identified by the hydride resonance, and the fact that the spectra showed that the diene was symmetrically bonded to the metal in the ground state. Even in those complexes where limiting spectra were not observed, such as the agostic 1,3-cyclohexadienyl complex \([\text{Rh}(\text{C}_5\text{Me}_3)(\text{C}_6\text{H}_9)]\text{PF}_6\), 106, the ground state structure was suggested by the pattern of fluxional behaviour observed in the variable temperature nmr spectra. The exception was the (ddbo) complex \([\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_{18}\text{H}_{15})]\text{PF}_6\), 119, in which, as has been discussed, the nmr data were not easily reconciled with the structure determined by X-ray crystallography.
Unfortunately, in the case of most of the complexes synthesized in this work, we were not able to confirm the structure by X-ray crystallography due to the difficulty of growing suitable crystals. Elsewhere in the literature there are only a few reports of crystal structure determinations of protonated $\eta^4$-diene complexes, and this is clearly one area of study which must be extended to enable a greater understanding of the nature of the M-H-C interaction in these complexes.

Infrared spectra have proven to be of limited value in the identification of complexes. The diene hydride complexes of osmium and iridium show bands at ca. 2000 cm$^{-1}$ in their infrared spectra, and it seems reasonable to assign these to $v_{M-H}$ vibrations, in spite of the fact that the band in the same region of the infrared spectrum of the norbornadiene complex $[\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6$, 140, did not appear to be due to $v_{M-H}$. The rhenium 1,3-cyclohexadiene complex Re($\text{C}_6\text{H}_6$)($\text{C}_6\text{H}_8$)H showed a similar band in its infrared spectrum which was assigned to $v_{M-H}$. There was no significant evidence of modified $v_{M-H}$ or $v_{C-H}$ vibrations in the infrared spectra of any of the agostic complexes.

We now have information available on a wide range of protonated $\eta^4$-diene and bis-$\eta^2$-ethylene complexes of a variety of transition metal complexes including the metals Fe, Ru, Os, Co, Rh, Ir, Mn, Re and Mo, with a wide range of ligands. On examination of this information it becomes clear that a complex interplay of factors influences where the added proton is located in the protonated complex.
The most significant of these is the metal. As might be expected, the M-H bond is strongest in the third row 5d metal complexes. In the osmium, iridium and rhenium complexes (except the dicyclopentadiene complexes of Os and Ir, \( \text{Ir}^130 \) and \( \text{Ir}^133 \), and the norbornadiene Ir complex \( \text{Ir}^140 \)) the M-H bond is sufficiently strong to result in diene hydride complexes with no significant interaction between the diene ligand and the metal-hydride. These complexes show in most cases a vM-H band in the region that one would expect for terminal metal hydrides. The X-ray structure determination of \( \text{Re}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_8)\text{H} \), \( \text{Ir}^18A, \text{Ir}^96 \) shows the complex has no significant M-H-C interaction. The protonated dicyclopentadiene complexes of Ir and Os adopt a bridging hydride structure which shows that these metals can in fact form agostic complexes though the diene hydride structure is preferred. However, even in these complexes the greater strength of the Os-H and Ir-H bonds compared to their counterparts in the Ru and Rh dicyclopentadiene complexes, is shown by the relative values of the geminal \( J(\text{C-H}_{\text{bridge}}) \) coupling constants, as discussed in Chapter 4.

In contrast, \( \eta^4 \)-diene complexes of first row 3d transition elements Fe and Mn, and the bis-\( \eta^2 \)-ethylene complexes of Co, form complexes with an agostic structure on protonation. In the diene complexes the M-H bond is weaker than the C-H bond, as is indicated by the fact that it is preferentially ruptured in the fluxional exchange processes that the complexes undergo.

Of the second row 4d transition elements investigated, the rhodium protonated \( \eta^4 \)-diene and bis-\( \eta^2 \)-ethylene complexes (with the exception
of the norbornadiene complex \([\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6\), adopt an agostic bridging hydride structure in the ground state. The structure of ruthenium protonated complexes is less certain. The bis-\(\eta^2\)-ethylene complex is clearly agostic, as is the \(\sigma\)-xylylene complex \([\text{Ru}(\text{C}_{12}\text{H}_{17})(\text{PMe}_2\text{Ph})(\text{dppe})]\text{PF}_6\), \(68\), (dppe = bis(diphenylphosphino)ethane). In \(68\) the agostic structure is confirmed by an X-ray crystallographic study.\(^{69}\) The (ddbo) complex \([\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_{18}\text{H}_{15})]\text{PF}_6\), \(119\), adopts an agostic structure in the solid state at least, and probably also in solution. The dicyclopentadienyl complex \([\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_{10}\text{H}_{13})]\text{PF}_6\), \(119\), has a bridging hydride C-H-M interaction, but the cyclooctadiene complexes \([\text{Ru}(\eta^6\text{-arene})(\text{C}_8\text{H}_{13})]\text{PF}_6\), \(54\), are most likely diene hydride complexes.\(^{56}\) In other complexes, such as the ethylcyclohexenyl complex \([\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_8\text{H}_{13})]\text{PF}_6\), \(52\), the ground state structure has not been identified.\(^{56}\) The molybdenum bis-ethylene complexes \([\text{MoH(ddpe)}_2(\text{C}_2\text{H}_4)_2]^+\), \(40\), and \([\text{MoH(Ph}_2\text{CH=CHPPh}_2)_2(\text{C}_2\text{H}_4)_2]^+\), appear to adopt a diene hydride structure.\(^{99,100}\)

The types of ligand attached to the metal will also influence the position of the added proton in the protonated complexes. Of the \(\eta^4\)-diene ligands used, dicyclopentadiene and norbornadiene both give unusual protonated complexes. Dicyclopentadiene protonated complexes, even of the 5d elements investigated are agostic, and norbornadiene is unique among the \(\eta^4\)-diene ligands investigated because of the unusual irreversible rearrangement it undergoes, to a vinylcyclopentadienyl complex. Unfortunately there is little evidence available to enable comparison of the influence of arene or cyclopentadienyl vs. phosphite vs. carbonyl in the protonated species \(M(\eta^4\text{-diene})L_3\) (\(L_3 = \eta^6\text{-arene}\),
(P(OMe)$_3$)$_3$, (CO)$_3$) – except in the case of the protonated iron diene complexes, in which comparison can be made between the relative effects of phosphite vs. carbonyl ligand. The protonated iron complexes adopt the agostic structure, in which a C-H group donates 2e to the metal. One would thus expect that a change in the electron density of the metal would change the M-H, and consequently the C-H, bond strengths in the M-H-C linkage. The change in M-H bond strength is reflected, in the butadiene complex [Fe(L)$_3$(C$_4$H$_7$)]$^+$, by a change in the energy barrier to the fluxional process involving M-H bond rupture and subsequent rotation of the CH$_3$ group of the ligand, on changing L from CO to P(OMe)$_3$ to PMe$_3$. The relative values are CO 42.7, P(OMe)$_3$ 36.9, PMe$_3$ 35.6 kJ mol$^{-1}$, suggesting that the M-H bond strength decreases in the order CO > P(OMe)$_3$ > PMe$_3$ as the basicity of the ligand increases. The corresponding change in the C-H bond strength is reflected in the relative values of the $J$(C-H$_{\text{bridge}}$) coupling constant. For L = CO the value is $\approx 74$ Hz, compared to the value of $\approx 100$ Hz in the complex with L = P(OMe)$_3$.14
SPECTRUM 1

\(^1\)H nmr, -20°, CD\(_2\)Cl\(_2\)

Hydride

Ar

H\(_{2,3}\)

ref

H\(_{1,4}\)

H\(_{5,6}\)
SPECTRUM 2

$^{13}\text{C nmr}, -30^\circ, \text{CD}_2\text{Cl}_2$

(Gated-1)
$\text{SPECTRUM 3}$

$^{13}\text{C nmr, } -100^\circ, \text{ CD}_2\text{Cl}_2$
(Gated-1)

arene

solvent

$\text{Ru-H}$

$\text{PF}_6^-$

$\text{C}_{23}$

$\text{C}_{14}$

$\text{C}_{56}$
SPECTRUM 4

$^1\text{H nmr, } +20^\circ, \text{ CD}_2\text{Cl}_2$

$-105^\circ$

C$_5$Me$_5$

impurity

solv.

H$_{2,3,4}$

H$^\text{exo}$

H$^\text{endo}$

H$^\text{exo}$

H$^\text{endo}$

PF$_6^-$

Rh$^+$
SPECTRUM 5

$^1$H nmr -60°
CD$_2$Cl$_2$

Hydride

x = impurity

C$_5$Me$_5$
**SPECTRUM 6**

$^{13}$C nmr, $-90^\circ C$, CD$_2$Cl$_2$

($^1$H decoup.)
SPECTRUM 7

H nmr, 20°, CD$_2$Cl$_2$

[Chemical structure diagram with labels for arene, CH$_3$, H$_{2,4}$, H$_{5,6}$, solv, and hydride peaks]
SPECTRUM 8
$^{13}\text{C}(^1\text{H} \text{decoup.) nmr, 20°}}$
CD$_2$Cl$_2$

$^{13}\text{C}(^1\text{H} \text{decoup.) nmr, 20°}}$
CD$_2$Cl$_2$
SPECTRUM 9

$^1$H nmr, -20°, CD$_2$Cl$_2$

- Ref
- CH$_3$
- Ha
- Hydride

Chemical shifts:
- 6
- 5
- 4
- 3
- 2
- 1
- -11
- -12
SPECTRUM 10

$^{13}$C nmr, -30°, CD$_2$Cl$_2$

(Gated-1)

arene

diene

$\text{Os-H}$

PF$_6^-$

arene

C$_1$

C$_2$

solv.

delta
SPECTRUM 11

$^1$Hnmr, $-80^\circ$, CD$_2$Cl$_2$

Solv.

H$_b$

H$_a$

CH$_3$

C$_5$Me$_5$

Hydride

$\delta$

-14

-15
SPECTRUM 12
$^{13}$C nmr, -60°C, CD$_2$Cl$_2$
(Gated-1)

$\text{Ir}^{-}\text{HPF}_6$

$\text{C}_5\text{Me}_5$

$\text{C}_2$

$\text{solv.}$

$\text{C}_1$

$\text{C}_5\text{Me}_5$

$\text{diene CH}_3$

$\text{solvent}$
SPECTRUM 13
$^1$H nmr, CD$_2$Cl$_2$

+20°

-100°

H$_a$ - e

H$_b$,c

H$_a$

(amplified)
SPECTRUM 14
$^{13}$C ($^1$H decoup.) nmr, -100°C, CD$_2$Cl$_2$

C$_5$Me$_5$

$x =$ impurity

solv.

C$_2$, C$_3$

C$_{56}$

C$_1$

100 80 60 40 20 0
SPECTRUM 15

$^1$H nmr, $-80^\circ$, CD$_2$Cl$_2$

benzo H

arene

solv.

H$_c$

H$_b$

H$_a$

hydride

-13 -14 δ
$^{13}$C nmr; -20°C; CD$_2$Cl$_2$

(GATED-1)
SPECTRUM 17
$^1H$ nmr, 20°, CD$_2$Cl$_2$
$^{13}$C nmr, $-60^\circ$C, CD$_2$Cl$_2$

(Gated-1)

benzo C

![Chemical Structure](image)
SPECTRUM 19

$^1\text{H nmr. } \text{CD}_2\text{Cl}_2$

$+20^\circ$

benzo $\text{H}$

$-100^\circ$

$\text{H}_{a,b}, \text{hydride}$

$\text{H}_b$

$\text{H}_a$

$\text{solv.}$

$\text{arene}$

$\text{arene/ H}_c$

$\text{hydride} -10.26 \text{ppm}$

$\text{PF}_5$

$\text{Ru}^+$

$\text{arene}$

$\text{PF}_6$
SPECTRUM 20

$^1H$ nmr, $-20^\circ$, $CD_2Cl_2$

arene

solv.

$H_{1,2,5,6}$

$H_{3,4,7,8}$

hydride
SPECTRUM 21

$^1$H nmr, 20°, CD$_2$Cl$_2$

peak at $\delta$ 0.10 expanded.

arene

solv.

H$_3$, H$_2$

H$_4$

H$_5$

H$_{6a}$

H$_{6b}$

hydride peak expanded.

hydride H$_{6b}$
SPECTRUM 22
$^1$H nmr, 20°, CD$_2$Cl$_2$

1H
2H
1H
6H

C$_5$Me$_5$

hydride -6.83 ppm

(ampiified)
SPECTRUM 23

$^{13}$C nmr, 20°C, CDCl$_3$

(Gated-1)

[Diagram of a chemical structure with labeled carbon atoms and peaks corresponding to different chemical shifts.]
SPECTRUM 24

\(^1\)H nmr, 20°, CD\(_2\)Cl\(_2\)

- H\(_{2,3,5,6}\)
- H\(_{1,4}\)
- H\(_7\)

Chemical shifts:
- 6
- 5
- 4
- 3
- 2
- 1

Chemical structure:
- Arene
- Solvent
- Hydride

1H nmr decoup. nmr, 20°, CD\(_2\)Cl\(_2\)
SPECTRUM 25
$^{13}$C ($^1$H decoup.) nmr, 20°, CD$_2$Cl$_2$
SPECTRUM 26

$^1H$ nmr, $20^\circ$, $CD_2Cl_2$

$[\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6$
SPECTRUM 27

$^1\text{H nmr, } 20^\circ, \text{CD}_2\text{Cl}_2$

$[\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_4\text{H})]\text{PF}_6$

H1,2,4,3,6,

H7

$\text{C}_5\text{Me}_5$

$x =$ impurity

H5
\[ ^{13}C\ nmr,\ 20^\circ C,\ CD_2Cl_2 \]

[J values in Hz.]

\[ J(C-Rh) = 5.7 \]
\[ J(C-Rh) = 7.6 \]
\[ J(C-Rh) = 10.6 \]
\[ J(C-Rh) = 10.8 \]
\[ J(C-Rh) = 7.6 \]
\[ J(C-Rh) = 4 \]
\[ J(C-Rh) = 4.5 \]

\[ C_5Me_5 \]

\[ \text{solvent} \]
$^1$H nmr, 20°C, CD$_2$Cl$_2$. 

[Graph with peaks labeled H1,2,3,4, H6, H7, and H5, and a molecular structure showing Ru$^+$, PF$_6^-$, and arene highlighting.]
$^{13}$C nmr, 20°C, C$_6$D$_6$

($^1$H decoupled)

d=doublet
dd=doublet of doub.

in gated-1 spectrum.
t=triplet

C$_5$Me$_5$
$^{13}$C nmr, 20°C, C$_6$D$_6$

($^1$H decoupled)
SPECTRUM 32

$^1$H nmr, $-90^\circ$, CD$_2$Cl$_2$
SPECTRUM 33
$^{13}$C nmr, -100°, CD$_2$Cl$_2$
(Gated-1)

H$_2$C$^2$Ru-CH$_2$
H$_2$C$^1$H-CH$_2$

H$_2$C$^2'$Ru=CH$_2$
H$_2$C$^1'H=CH$_2$

$C^2, C^2'$

(J=155, 284 Hz)

arene

solvent

arene
$^1$H nmr, $-20^\circ$, CD$_2$Cl$_2$
SPECTRUM 35

$^{13}$C nmr, $-20^\circ$C, CD$_2$Cl$_2$

(Gated-1)
Table 5

Analytical and mass spectroscopy data and reaction yields for the complexes $M(\eta^6$-arene)(\eta^4-diene) ($M = Ru$, Os), $M(\eta^5-C_5R_5)(\eta^4$-diene) ($M = Rh$, Ir; $R=H$, CH$_3$), and Os(C$_6$H$_3Me_3$)(C$_2$H$_4$)$_2$

<table>
<thead>
<tr>
<th>Complex</th>
<th>No.</th>
<th>Mass Spectrum m/e of parent ion</th>
<th>Analysis (calc. in parenthesis)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(C$_6$H$_6$)(C$_6$H$_8$)</td>
<td>79</td>
<td>350</td>
<td>C,41.57(41.4) H,4.0(4.1)</td>
<td>50</td>
</tr>
<tr>
<td>Os(C$_6$H$_6$)(C$<em>8$H$</em>{12}$)</td>
<td>87A</td>
<td>378</td>
<td>C,44.3(44.7) H,5.0(4.8)</td>
<td>55</td>
</tr>
<tr>
<td>Os(C$_6$H$_6$)(C$<em>6$H$</em>{10}$)</td>
<td>83A</td>
<td>352</td>
<td>C,41.2(41.1) H,4.7(4.6)</td>
<td>80</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$_6$H$_8$)</td>
<td>85</td>
<td>392</td>
<td>C,46.3(46.1) H,5.2(5.2)</td>
<td>50</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$<em>6$H$</em>{10}$)</td>
<td>83B</td>
<td>394</td>
<td>C,45.3(45.9) H,5.5(5.7)</td>
<td>70</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$<em>8$H$</em>{12}$)</td>
<td>87B</td>
<td>420</td>
<td>C,48.8(48.8) H,5.7(5.8)</td>
<td>3</td>
</tr>
<tr>
<td>Os(C$<em>6$H$<em>3Me_3$)(C$</em>{18}$H$</em>{14}$)</td>
<td>84</td>
<td>542</td>
<td>C,60.1(60.9) H,5.2(4.9)</td>
<td>50</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$<em>9$H$</em>{14}$)</td>
<td>86</td>
<td>434</td>
<td>C,50.0(50.0) H,6.1(6.1)</td>
<td>50</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$_7$H$_8$)</td>
<td>91</td>
<td>404</td>
<td>C,47.6(47.7) H,5.0(5.0)</td>
<td>70</td>
</tr>
<tr>
<td>Os(C$<em>6$H$<em>3Me_3$)(C$</em>{10}$H$</em>{12}$)</td>
<td>92</td>
<td>444</td>
<td>C,51.1(51.6) H,5.4(5.5)</td>
<td>55</td>
</tr>
<tr>
<td>Os(C$_6$H$_3Me_3$)(C$_2$H$_4$)$_2$</td>
<td>93</td>
<td>368</td>
<td>C,42.1(42.6) H,5.4(5.5)</td>
<td>70</td>
</tr>
<tr>
<td>Ru(C$<em>6$H$<em>3Me_3$)(C$</em>{18}$H$</em>{14}$)</td>
<td>94</td>
<td>452</td>
<td>C,69.9(71.8) H,5.7(5.8)</td>
<td>65</td>
</tr>
<tr>
<td>Ru(C$<em>6$H$<em>3Me_3$)(C$</em>{13}$H$</em>{12}$)</td>
<td>95</td>
<td>390</td>
<td>C,68.0(67.8) H,6.4(6.2)</td>
<td>55</td>
</tr>
<tr>
<td>Rh(C$<em>5$H$<em>5$)(C$</em>{10}$H$</em>{12}$)</td>
<td>100</td>
<td>300</td>
<td>C,60.2(60.0) H,6.0(5.7)</td>
<td>80</td>
</tr>
<tr>
<td>Rh(C$_5$H$_5$)(C$_7$H$_8$)</td>
<td>102</td>
<td>260</td>
<td>C,55.4(55.4) H,5.0(5.0)</td>
<td>90</td>
</tr>
<tr>
<td>Ir(C$<em>5$H$<em>5$)(C$</em>{18}$H$</em>{14}$)</td>
<td>98</td>
<td>488</td>
<td>C,57.1(56.7) H,3.9(3.9)</td>
<td>50</td>
</tr>
<tr>
<td>Rh(C$<em>5$Me$<em>5$)(C$</em>{18}$H$</em>{14}$)</td>
<td>96</td>
<td>468</td>
<td>C,72.1(71.8) H,6.4(6.2)</td>
<td>20</td>
</tr>
<tr>
<td>Ir(C$<em>5$Me$<em>5$)(C$</em>{18}$H$</em>{14}$)</td>
<td>97</td>
<td>558</td>
<td>C,60.0(60.3) H,5.3(5.2)</td>
<td>30</td>
</tr>
<tr>
<td>Ir(C$_5$Me$_5$)(C$_7$H$_8$)</td>
<td>101</td>
<td>420</td>
<td>C,48.9(48.7) H,5.6(5.5)</td>
<td>95</td>
</tr>
<tr>
<td>Ir(C$<em>5$Me$<em>5$)(C$</em>{10}$H$</em>{12}$)</td>
<td>99</td>
<td>460</td>
<td>C,52.6(52.3) H,6.1(6.0)</td>
<td>90</td>
</tr>
</tbody>
</table>

1 Note that yields assume the formula [Os(C$_6$H$_3Me_3$)Cl$_2$]$_2$ for the starting material (see Section 2.2.1)

2 Best analysis after repeated crystallization
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT AND MHz</th>
<th>NO.</th>
<th>(ARENE)</th>
<th>6 (ppm), J(Hz)</th>
<th>(DIENE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(C₆H₆)(C₆H₁₀)</td>
<td>C₆D₆ 100</td>
<td>83A</td>
<td>4.67</td>
<td>2.38 (2H, d, J = 2.1), 2.15 (6H, s), 0.32 (2H, d, J = 2.1)</td>
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<tr>
<td>Os(C₆H₃Me₃)(C₆H₁₀)</td>
<td>C₆D₆ 100</td>
<td>83B</td>
<td>2.05 (9H, s), 4.59 (3H, s)</td>
<td>2.13 (6H, s), 1.91 (2H, d, J = 2), 0.51 (2H, d, J = 2)</td>
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</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₀)</td>
<td>C₆D₆ 100</td>
<td>79</td>
<td>4.87 (6H, s)</td>
<td>5.25 (2H, dd, J = 5.0, 2.5), 3.39 (2H, m), 1.83 (4H, m)</td>
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</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₆H₁₀)</td>
<td>C₆D₆ 100</td>
<td>85</td>
<td>2.07 (9H, s), 4.83 (3H, s)</td>
<td>5.09 (2H, dd, J = 4.5, 2.5), 2.76 (2H, m), 1.96 - 1.56 (4H, m)</td>
<td></td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₈)</td>
<td>C₆D₆ 100</td>
<td>87A</td>
<td>4.74 (6H, s), 4.65 (3H, s)</td>
<td>3.72 (4H, m), 2.35 (8H, m)</td>
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</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₆H₈)</td>
<td>C₆D₆ 100</td>
<td>87B</td>
<td>1.78 (9H, s), 4.65 (3H, s)</td>
<td>3.23 (4H, m), 2.36 (8H, m)</td>
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</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₆H₁₂)</td>
<td>C₆D₆ 100</td>
<td>84</td>
<td>4.43 (3H, s)</td>
<td>7.26 - 6.76 (8H, m), 4.40 (2H, s), 2.34 (2H, d, J = 2.5), 0.09 (2H, d, J = 2.5)</td>
<td></td>
</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₈H₁₄)</td>
<td>C₆D₆ 100</td>
<td>86</td>
<td>2.00 (9H, s), 4.61 (3H, s)</td>
<td>4.75 (1H, m), 2.59 (1H, m), 2.2 (1H, m), 2.05 (3H, s), 1.9 (1H, m), 1.5 (1H, m), 1.42 (3H, s), 1.21 (3H, d, J = 6)</td>
<td></td>
</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₉H₁₂)</td>
<td>C₆D₆ 100</td>
<td>91</td>
<td>1.90 (9H, s), 4.77 (3H, s)</td>
<td>3.72 (2H, m), 2.63 (4H, m), 1.05 (2H, t, J = 1.5)</td>
<td></td>
</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₁₀H₁₂)</td>
<td>C₆D₆ 100</td>
<td>92</td>
<td>1.71 (9H, s), 4.46 (3H, s)</td>
<td>4.15 (1H, m), 3.71 (1H, m), 3.47 (1H, m), 3.27 (1H, m), 2.75 - 1.95 (8H, m)</td>
<td></td>
</tr>
<tr>
<td>Os(C₆H₃Me₃)(C₁₂H₂₄)</td>
<td>C₆D₆ 100</td>
<td>93</td>
<td>1.74 (9H, s), 4.60 (3H, s)</td>
<td>2.07 (4H) and 0.93 (4H); mirror image multiplets</td>
<td></td>
</tr>
<tr>
<td>Ru(C₆H₃Me₃)(C₁₈H₁₄)</td>
<td>C₆D₆ 100</td>
<td>94</td>
<td>1.78 (9H, s), 4.54 (3H, s)</td>
<td>7.3 - 6.9 (8H, m), 4.46 (2H, s), 2.02 (2H, d, J = 1.8), 0.11 (2H, d, J = 2.0)</td>
<td></td>
</tr>
<tr>
<td>Ru(C₆H₃Me₃)(C₁₃H₁₂)</td>
<td>C₂D₂Cl₂ 200</td>
<td>95</td>
<td>2.02 (9H, s), 5.09 (3H, s)</td>
<td>7.10 (5H, m), 3.37 (2H, m), 2.55 (1H, m), 2.50 (2H, m), 2.25 (2H, m)</td>
<td></td>
</tr>
</tbody>
</table>
Table 7

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT AND MHz</th>
<th>NO.</th>
<th>$\delta$(PPM) AND J(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rh(C}_5\text{H}_5\text{)(C}<em>10\text{H}</em>{12})$</td>
<td>C$_6$D$_6$ 200</td>
<td>100</td>
<td>4.82 (5H, d, J = 0.7)</td>
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<tr>
<td>$\text{Ir(C}_5\text{H}_5\text{)(C}_7\text{H}_8)$</td>
<td>C$_6$D$_6$ 200</td>
<td>102</td>
<td>5.06 (5H, d, J = 0.9)</td>
</tr>
<tr>
<td>$\text{Rh(C}_5\text{Me}_3\text{)(C}<em>18\text{H}</em>{14})$</td>
<td>C$_6$D$_6$ 200</td>
<td>96</td>
<td>1.65 (15H, s)</td>
</tr>
<tr>
<td>$\text{Ir(C}_5\text{H}_5\text{)(C}<em>18\text{H}</em>{14})$</td>
<td>C$_6$D$_6$ 200</td>
<td>98</td>
<td>4.57 (5H, s)</td>
</tr>
<tr>
<td>$\text{Ir(C}_5\text{Me}_3\text{)(C}<em>18\text{H}</em>{14})$</td>
<td>C$_6$D$_6$ 200</td>
<td>97</td>
<td>1.67 (15H, s)</td>
</tr>
<tr>
<td>$\text{Ir(C}_5\text{Me}_3\text{)(C}_7\text{H}_8)$</td>
<td>C$_6$D$_6$ 200</td>
<td>101</td>
<td>1.84 (15H, s)</td>
</tr>
<tr>
<td>$\text{Ir(C}<em>5\text{Me}<em>3\text{)(C}</em>{10}H</em>{12})$</td>
<td>C$_6$D$_6$ 200</td>
<td>99</td>
<td>1.56 (15H, s)</td>
</tr>
<tr>
<td>COMPLEX</td>
<td>SOLVENT AND N°.</td>
<td>NO. (ARENE)</td>
<td>δ (PPM) AND J (Hz) (DIENE)</td>
</tr>
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<td>---------</td>
<td>----------------</td>
<td>-------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₅H₁₀)</td>
<td>C₆D₆ 15</td>
<td>83A 71.7</td>
<td>21.4(CH₃), 28.9(CH₂), 83.6</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₀)</td>
<td>C₆D₆ 15</td>
<td>83B 20.5(CH₃), 73.4(CH) 85.3</td>
<td>20.5(CH₃), 31.1(CH₂), 83.6</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₈)</td>
<td>C₆D₆ 15</td>
<td>79 71.0</td>
<td>29.8(CH₂), 44.6(CH), 69.5(CH)</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₅H₅)</td>
<td>C₆D₆ 15</td>
<td>85 20.7(CH₃), 73.2(CH)</td>
<td>29.9(CH₂), 47.4(CH), 70.6(CH)</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87A 79.3</td>
<td>35.9(CH₂), 47.4(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87B</td>
<td>18.1(CH₃), 82.4(CH), 91.2</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87C</td>
<td>19.4 (d, J = 149, 160), 53.6 (d, J = 141), 81.5 (s), 123.2, 123.8, 124.7, 125.1 (overlapping doublets), 145.6 (s), 147.0 (s)</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87D</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87E</td>
<td>36.0(CH₂), 50.8(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87F</td>
<td>36.0(CH₂), 50.8(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87G</td>
<td>44.4, 47.2, 56.5, 75.5, 82.4</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87H</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87I</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87J</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
</tr>
<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87K</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87L</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87M</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87N</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87O</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87P</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87Q</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87R</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87S</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87T</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87U</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87V</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87W</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87X</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87Y</td>
<td>23.3(CH₃), 24.4(CH₂), 27.8(CH₃), 39.4, 44.4, 47.2, 56.5, 75.5, 82.4</td>
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<tr>
<td>Os(C₆H₆)(C₆H₁₂)</td>
<td>C₆D₆ 15</td>
<td>87Z</td>
<td>19.6(CH), 47.0(CH), 59.3(CH)</td>
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</table>
Table 9  

\(^{13}\)C nmr data for selected M(C\(_5\)R\(_5\))(\(\eta^4\)-diene) complexes (M = Rh, Ir; R = H, CH\(_3\))

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT AND MHz</th>
<th>NO.</th>
<th>((C_5R_5))</th>
<th>(\delta)(PPM) AND J(Hz)</th>
<th>(DIENE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(C(_5)H(_5))(C(_7)H(_8))</td>
<td>C(_6)D(_6) 50</td>
<td>102</td>
<td>84.8 (J(C-Rh) = 3)</td>
<td>27.8 (J(C-Rh) = 10)(CH), 47.0(CH), 57.3 (J(C-Rh) = 7)(CH(_2))</td>
<td></td>
</tr>
<tr>
<td>Rh(C(_5)Me(_5))(C(_18)H(_14))</td>
<td>C(_6)D(_6) 50</td>
<td>96</td>
<td>11.1 (CH(_3)), 94.8 (J(C-Rh) = 5.9)</td>
<td>34.0 (J(C-Rh) = 16.1)(CH(_2)), 52.9(CH), 94.8(C), 123.2, 123.8, 125.2 (benzo CH), 144.8, 147.6 (benzo methine)</td>
<td></td>
</tr>
<tr>
<td>Ir(C(_5)H(_5))(C(_18)H(_14))</td>
<td>CD(_2)Cl(_2) 50</td>
<td>98</td>
<td>76.5</td>
<td>18.9(CH(_2)), 51.7(CH), 93.5(C), 122.6, 124.3 125.5, 125.7 (benzo CH) (benzo methine not distinguished from noise)</td>
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</tr>
<tr>
<td>Ir(C(_5)Me(_5))(C(_18)H(_14))</td>
<td>C(_6)D(_6) 50</td>
<td>97</td>
<td>11.0(CH(_3)), 88.9</td>
<td>22.0(CH(_2)), 52.3(CH), 88.9(C), 123.4, 123.7, 125.0, 125.1 (benzo CH), 144.5, 147.3 (benzo methine)</td>
<td></td>
</tr>
<tr>
<td>Ir(C(_5)Me(_5))(C(_7)H(_8))</td>
<td>C(_6)D(_6) 50</td>
<td>101</td>
<td>10.3 (q, J = 126), 90.9 (s)</td>
<td>13.1 (d, J = 173), 46.2 (d, J = 145), 60.3 (t, J = 130)</td>
<td></td>
</tr>
<tr>
<td>COMPLEX</td>
<td>NO.</td>
<td>ANALYSIS (Calculated)</td>
<td>Yield %</td>
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<td></td>
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<tr>
<td>----------------------------------------------</td>
<td>-----</td>
<td>-----------------------------------------------</td>
<td>---------</td>
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<tr>
<td>([\text{Os}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_9)]\text{PF}_6)</td>
<td>103</td>
<td>C, 29.0 (29.2); H, 3.0 (3.1); P, 6.4 (6.3)</td>
<td>80</td>
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<td></td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}_6)(\text{C}<em>9\text{H}</em>{13})]\text{PF}_6)</td>
<td>128</td>
<td>C, 32.3 (32.2); H, 3.7 (3.7); P, 6.1 (5.9)</td>
<td>50</td>
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<td></td>
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<tr>
<td>([\text{Os}(\text{C}_6\text{H}_6)(\text{C}<em>6\text{H}</em>{11})]\text{PF}_6)</td>
<td>111</td>
<td>C, 28.6 (29.0); H, 3.4 (3.5); P, 6.0 (6.2)</td>
<td>35</td>
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<td></td>
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<tr>
<td>(<a href="%5Ctext%7BC%7D_6%5Ctext%7BH%7D_9">\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})</a>\text{PF}_6)</td>
<td>104</td>
<td>C, 33.5 (33.6); H, 4.0 (4.0); P, 6.4 (5.8)</td>
<td>50</td>
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<td></td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BC%7D_8%5Ctext%7BH%7D_%7B13%7D">\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})</a>\text{PF}_6)</td>
<td>129</td>
<td>C, 36.3 (36.2); H, 4.4 (4.5); P, 5.6 (5.5)</td>
<td>70</td>
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</tr>
<tr>
<td>(<a href="%5Ctext%7BC%7D_6%5Ctext%7BH%7D_%7B11%7D">\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})</a>\text{PF}_6)</td>
<td>112</td>
<td>C, 32.9 (33.5); H, 4.3 (4.3); P, 5.9 (5.8)</td>
<td>50</td>
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</tr>
<tr>
<td>(<a href="%5Ctext%7BC%7D_8%5Ctext%7BH%7D_%7B15%7D">\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})</a>\text{PF}_6)</td>
<td>103</td>
<td>C, 33.5 (33.6); H, 4.0 (4.0); P, 6.4 (5.8)</td>
<td>50</td>
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<tr>
<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>18\text{H}</em>{15})]\text{PF}_6)</td>
<td>116</td>
<td>C, 49.0 (48.7); H, 4.2 (3.9)</td>
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<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>6\text{H}</em>{15})]\text{PF}_6)</td>
<td>110</td>
<td>C, 37.5 (37.4); H, 4.7 (4.5); P, 5.2 (5.4)</td>
<td>40</td>
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<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>7\text{H}</em>{9})]\text{PF}_6)</td>
<td>139</td>
<td>C, 34.7 (35.0); H, 4.0 (3.9); P, 6.0 (5.7)</td>
<td>75</td>
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<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>9\text{H}</em>{13})]\text{PF}_6)</td>
<td>130</td>
<td>C, 38.8 (38.8); H, 5.3 (5.3); P, 5.2 (5.3)</td>
<td>80</td>
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<tr>
<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>18\text{H}</em>{15})]\text{PF}_6)</td>
<td>136</td>
<td>C, 30.7 (30.5); H, 4.2 (4.1); P, 5.9 (6.0)</td>
<td>55</td>
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<td></td>
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<tr>
<td>([\text{Ru}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>6\text{H}</em>{15})]\text{PF}_6)</td>
<td>119</td>
<td>C, 54.4 (54.3); H, 4.6 (4.6); P, 5.2 (5.2)</td>
<td>65</td>
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<tr>
<td>([\text{Ru}(\text{C}_6\text{H}<em>3\text{Me}</em>{3})(\text{C}<em>9\text{H}</em>{15})]\text{PF}_6)</td>
<td>128</td>
<td>C, 49.1 (49.4); H, 4.6 (4.7); P, 5.8 (5.8)</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ir}(\text{C}<em>5\text{H}</em>{5})(\text{C}<em>18\text{H}</em>{15})]\text{PF}_6)</td>
<td>117</td>
<td>C, 46.8 (43.6); H, 3.4 (3.2)</td>
<td>85</td>
<td></td>
<td></td>
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<tr>
<td>([\text{Rh}(\text{C}<em>5\text{H}</em>{5})(\text{C}<em>6\text{H}</em>{11})]\text{PF}_6)</td>
<td>115</td>
<td>C, 41.2 (41.2); H, 5.7 (5.6); P, 6.8 (6.6)</td>
<td>50</td>
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<tr>
<td>([\text{Rh}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>6\text{H}</em>{9})]\text{PF}_6)</td>
<td>142</td>
<td>C, 41.3 (41.3); H, 4.5 (4.9); P, 6.3 (6.1)</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>10\text{H}</em>{13})]\text{PF}_6)</td>
<td>135</td>
<td>C, 30.1 (38.2); H, 4.0 (5.5)</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\text{C}<em>5\text{H}</em>{5})(\text{C}<em>{10}\text{H}</em>{15})]\text{PF}_6)</td>
<td>131</td>
<td>C, 40.7 (40.4); H, 4.0 (4.1); P, 7.3 (6.9)</td>
<td>40</td>
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<td></td>
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<tr>
<td>([\text{Rh}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>{10}\text{H}</em>{15})]\text{PF}_6)</td>
<td>132</td>
<td>C, 46.4 (46.5); H, 5.4 (5.5); P, 6.2 (6.0)</td>
<td>45</td>
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<td></td>
</tr>
<tr>
<td>([\text{Rh}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>6\text{H}</em>{9})]\text{PF}_6)</td>
<td>106</td>
<td>C, 41.5 (41.4); H, 5.2 (5.2); P, 6.8 (6.7)</td>
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<td></td>
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<tr>
<td>([\text{Rh}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>6\text{H}</em>{15})]\text{PF}_6)</td>
<td>118</td>
<td>C, 54.7 (54.7); H, 5.0 (4.9); P, 5.0 (5.0)</td>
<td>60</td>
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<tr>
<td>([\text{Ir}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>6\text{H}</em>{9})]\text{PF}_6)</td>
<td>108</td>
<td>C, 34.7 (34.7); H, 4.3 (4.4); P, 5.6 (5.6)</td>
<td>50</td>
<td></td>
<td></td>
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<tr>
<td>([\text{Ir}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>6\text{H}</em>{11})]\text{PF}_6)</td>
<td>114</td>
<td>C, 34.8 (34.6); H, 4.8 (4.7); P, 5.7 (5.6)</td>
<td>95</td>
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<tr>
<td>([\text{Ir}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>10\text{H}</em>{13})]\text{PF}_6)</td>
<td>133</td>
<td>C, 39.3 (39.7); H, 4.5 (4.7); P, 5.8 (5.1)</td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ir}(\text{C}<em>5\text{Me}</em>{5})(\text{C}<em>7\text{H}</em>{9})]\text{PF}_6)</td>
<td>141</td>
<td>C, 35.9 (36.1); H, 4.2 (4.3); P, 5.6 (5.5)</td>
<td>55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 The \text{PF}_6^- salt could not be obtained analytically pure.
2 Satisfactory analyses could not be obtained.
3 This complex could not be recrystallized without decomposition.
## Table 11

Analytical data and yields for P(OMe)\(_3\) and t-BuNC complexes

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>NO.</th>
<th>ANALYSIS (Calc)</th>
<th>YIELD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_9)(\text{P(OMe)}_3)]\text{PF}_6)</td>
<td>120</td>
<td>C, 29.4(29.1); H, 3.8(3.9); P, 9.9(10.1)</td>
<td>75</td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}_6)(\text{C}<em>6\text{H}</em>{11})(\text{P(OMe)}_3)]\text{PF}_6)</td>
<td>124</td>
<td>C, 29.1(29.0); H, 4.3(4.2); P, 10.1(10.0)</td>
<td>30</td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_6\text{H}_9)(\text{t-BuNC})]\text{PF}_6)</td>
<td>121</td>
<td>C, 39.2(38.8); H, 5.0(4.9); P, 4.9(5.0); N, 2.4(2.3)</td>
<td>60</td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}<em>6\text{H}</em>{11})(\text{t-BuNC})]\text{PF}_6)</td>
<td>125</td>
<td>C, 38.7(38.6); H, 5.4(5.2); P, 4.4(5.0); N, 2.0(2.3)</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}<em>3)(\text{C}</em>{10}\text{H}</em>{13})(\text{t-BuNC})]\text{PF}_6)</td>
<td>134</td>
<td>C, 43.1(42.9); H, 5.2(5.1); P, 2.3(2.1); N, 4.5(4.6)</td>
<td>70</td>
</tr>
<tr>
<td>([\text{Os}(\text{C}_6\text{H}<em>3\text{Me}<em>3)(\text{C}</em>{18}\text{H}</em>{15})(\text{t-BuNC})]\text{PF}_6)</td>
<td>126</td>
<td>C, 50.2(49.9); H, 4.9(4.7); N, 1.6(1.8)</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Ru}(\text{C}_6\text{H}<em>3\text{Me}<em>3)(\text{C}</em>{18}\text{H}</em>{15})(\text{t-BuNC})]\text{PF}_6) (^1)</td>
<td>127</td>
<td>C, 55.6(56.5); H, 5.4(5.3); N, 2.0(2.1)</td>
<td>65</td>
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<tr>
<td>([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{t-BuNC})]\text{PF}_6)</td>
<td>138</td>
<td>C, 32.2(32.3); H, 5.0(5.1); N, 2.5(2.4)</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_6\text{H}_9)(\text{t-BuNC})]\text{PF}_6)</td>
<td>122</td>
<td>C, 46.4(46.1); H, 6.2(6.1); N, 2.5(2.6)</td>
<td>60</td>
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<tr>
<td>([\text{Ir}(\text{C}_5\text{Me}_5)(\text{C}_6\text{H}_9)(\text{t-BuNC})]\text{PF}_6)</td>
<td>123</td>
<td>C, 39.4(39.6); H, 5.3(5.2); N, 2.6(2.2)</td>
<td>60</td>
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</tbody>
</table>

\(^1\) Satisfactory analysis not obtained.
<table>
<thead>
<tr>
<th>Code</th>
<th>Value</th>
<th>Type</th>
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</thead>
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<td>456</td>
<td>789</td>
</tr>
<tr>
<td>234</td>
<td>567</td>
<td>890</td>
</tr>
<tr>
<td>345</td>
<td>678</td>
<td>901</td>
</tr>
</tbody>
</table>

Table 1: Example Table

Table 2: Another Table
<table>
<thead>
<tr>
<th>Year</th>
<th>Category</th>
<th>Data1</th>
<th>Data2</th>
<th>Data3</th>
<th>Data4</th>
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</thead>
<tbody>
<tr>
<td>2020</td>
<td>Growth</td>
<td>123</td>
<td>456</td>
<td>789</td>
<td>123</td>
</tr>
<tr>
<td>2021</td>
<td>Revenue</td>
<td>234</td>
<td>567</td>
<td>890</td>
<td>234</td>
</tr>
<tr>
<td>2022</td>
<td>Expenses</td>
<td>345</td>
<td>678</td>
<td>901</td>
<td>345</td>
</tr>
</tbody>
</table>

*Note: Data represents hypothetical values.*
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>SOLVENT AND MHz</th>
<th>NO.</th>
<th>δ (PPM), J (Hz)</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)P(OMe)₃PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>120</td>
<td>0.02 (6H, s)</td>
<td>3.66 (9H, d, J = 12.5) (P(OMe)₃)₃, 4.95 (3H, m), 2.5-1.0 (m)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)P(OMe)₃PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>124</td>
<td>5.94 (6H, s)</td>
<td>3.63 (9H, d, J = 12) (P(OMe)₃)₃, 3.74 (1H, d, J = 2.5), 2.38 (1H, dd, J = 16, 11), 2.14 (3H, s), 1.79 (3H, s), 1.15 (3H, m)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>121</td>
<td>2.28 (9H, s)</td>
<td>4.75 (1H, t, J = 6), 4.09 (2H, t, J = 6.5), 2.63 (2H, m), 1.2-0.8 (4H, m)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>125</td>
<td>5.56 (3H, s)</td>
<td>5.3 (m, under solvent peak), 3.25 (1H, d, J = 2.3), 2.11 (3H, s), 1.68 (3H, s), 1.32 (3H, s), 1.45 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>124</td>
<td>2.33 (9H, s)</td>
<td>5.3 (m, under solvent peak), 3.25 (1H, d, J = 2.3), 2.11 (3H, s), 1.68 (3H, s), 1.32 (3H, s), 1.45 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>127</td>
<td>2.15 (9H, s)</td>
<td>7.4-6.9 (8H, m), 4.68 (1H, s), 5.32 (under solvent peak)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>126</td>
<td>2.28 (9H, s)</td>
<td>7.4-6.9 (8H, m), 4.68 (1H, s), 4.55 (1H, s), 3.90 (1H, d, J = 2.7), 2.41 (1H, d, J = 2.9), 1.38 (3H, s), 1.42 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>123</td>
<td>2.22 (9H, s)</td>
<td>2.65 (2H) and 2.48 (2H) (mirror image mult., ethylene), 1.87 (1H, m), 1.40 (4H, m), 1.47 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₆H₄)H(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>138</td>
<td>5.80 (3H, s)</td>
<td>2.22 (2H, m), 2.15 (9H, s), 2.65 (2H) and 2.48 (2H) (mirror image mult., ethylene), 1.87 (1H, m), 1.40 (4H, m), 1.47 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Os(C₆H₆)₆(C₂H₅)(C₆H₄)(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>137</td>
<td>5.82 (3H, s)</td>
<td>2.41 (4H, m) (ethylene), 1.77 (1H, m), 1.54 (1H, m), 1.42 (3H, distorted triplet), 3.66 (9H, d, J = 10.7) (P(OMe)₃)₃ (t-BuNC)</td>
</tr>
<tr>
<td>Rh(C₆H₆)₆(C₆H₄)(t-BuNC)PF6</td>
<td>CD₂Cl₂ 100</td>
<td>122</td>
<td>1.88 (15H, s)</td>
<td>4.56 (2H, t, J = 6.7), 4.26 (1H, t, J = 6.5), 2.41 (2H, m), 1.8-1.1 (4H, m), 1.53 (9H, s) (t-BuNC)</td>
</tr>
<tr>
<td>Ir(C₆H₆)₆(C₆H₄)(t-BuNC)PF₆</td>
<td>CD₂Cl₂ 100</td>
<td>123</td>
<td>1.98 (15H, s)</td>
<td>4.34 (2H, t, J = 6.6), 4.16 (1H, t, J = 6.2), 2.74 (2H, m), 1.9-1.7 (3H, m), 1.3-1.0 (1H, m), 1.55 (9H, s) (t-BuNC)</td>
</tr>
</tbody>
</table>
**CHAPTER 7**

**EXPERIMENTAL SECTION**

**General**

All reactions were performed under high-purity nitrogen or argon using standard Schlenk techniques, or in a Vacuum Atmospheres Dri-Train HE-193-1 glove box. Solvents were degassed prior to use by distillation under nitrogen or by several freeze-pump-thaw cycles.

Nuclear magnetic resonance spectra were recorded on several instruments (MHz quoted to nearest whole number): Varian HA100 (\(^1\text{H}, 100\) MHz), Bruker HFX270 (\(^1\text{H}, 270\) MHz; \(^{13}\text{C}, 68\) MHz), Bruker CXP200 (\(^1\text{H}, 200\) MHz; \(^{13}\text{C}, 50\) MHz), Jeol FX200 (\(^1\text{H}, 200\) MHz; \(^{13}\text{C}, 50\) MHz), and Jeol FX60 (\(^{13}\text{C}, 15\) MHz). The internal reference was either \(\text{Me}_4\text{Si}\), or the residual solvent peak relative to \(\text{Me}_4\text{Si} (\text{C}_6\text{D}_6, 57.15 (\text{H}), 5128.0 (\text{C}); \text{CD}_2\text{Cl}_2, 55.32 (\text{H}), 553.5 (\text{C}))\). Deuterium (\(^2\text{H}\)) nmr spectra were recorded on the Bruker CXP200. All \(^1\text{H}\) nmr spectra of the protonated complexes were recorded on 200 or 270 MHz instruments.

Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer, and mass spectra on a VG Micromass 7070F instrument at 70eV.

Microanalyses were performed in the analytical laboratories of the Research School of Chemistry.
Starting Materials

Osmium tetraoxide \((\text{OsO}_4)\) was obtained from Johnson and Matthey Co., England, and from Noah Chemicals, New York. \(\text{RuCl}_3(\text{xH}_2\text{O})\) and \(\text{RhCl}_3(\text{xH}_2\text{O})\) were obtained from Johnson and Matthey Co..

Sodium hexachloroosmate, \(\text{Na}_2\text{OsCl}_6\), was prepared as follows:-

\[(\text{NH}_4)_2\text{OsCl}_6\] (obtained from commercial sources) was reduced to metallic osmium by heating at 350°C in a stream of hydrogen, in a tube furnace. The osmium powder was then thoroughly mixed with sodium chloride (2 parts NaCl : 1 part osmium) and heated in a stream of chlorine, at 600°C for 45 minutes. The resulting brown material was extracted with an ethanol/conc. HCl mixture (ca. 5:1 ratio), giving an orange solution of \(\text{Na}_2\text{OsCl}_6\). The salt was not isolated, but the solution was reduced in volume in vacuo and used to synthesize \([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]\)_2, as described below.

Ammonium hexachloroiridate, \((\text{NH}_4)_2\text{IrCl}_6\) was synthesized in our laboratory from iridium residues, following the procedure of Kauffman and Myers.

1,3-Cyclohexadiene, 2,3-dimethyl-1,3-butadiene, bicyclo-[2.2.1]-2,5-heptadiene (norbornadiene), 1,5-cyclooctadiene and dicyclopentadiene were used as received from commercial suppliers, with the exception of norbornadiene, which was freed from yellow impurities by distillation or by chromatographing on neutral alumina (activity 1).

1,3,5-Trimethyl-1,4-cyclohexadiene was synthesized by reduction of mesitylene (1,3,5-trimethylbenzene) with lithium in liquid ammonia.
2,3-Dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo) was prepared via Diels-Alder reaction of anthracene and fumaryl chloride, following a literature procedure. 7-Phenynorbornadiene is available commercially (Frinton Laboratories, New Jersey), but the sample used was synthesized from norbornadiene following the method of Story et al..

Cyclopentadiene was obtained by cracking dicyclopentadiene, Cyclopentadienylsodium, NaCp (Cp = \( \eta^5 - C_5 H_5 \)) was prepared from cyclopentadiene and sodium, and stored as the 1,2-dimethoxyethane (DME) adduct. The initially white adduct decomposed over several months to a purple substance. 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene was used as received from commercial sources.

HPF₆ (60% aqueous solution), trifluoromethanesulphonic (triflic) acid, HSBF₆ (65% aqueous solution), HBF₄ (ether adduct), p-toluene-sulphonic acid, tert-butylisonitrile, trimethylphosphite were all used as received from commercial sources.

The following complexes were prepared following published procedures:

\[ [\text{Os}(C_6 H_6)I_2]_2 \], \( [\text{Ru}(C_6 H_6)Cl_2]_2 \), \( [\text{Ru}(C_6 H_3 Me_3)Cl_2]_2 \), \( [\text{Ru}(C_6 H_6)Cl_2]_2 \), \( [\text{Rh}(C_5 Me_5)Cl_2]_2 \), \( [\text{Rh}(C_5 Me_5)(C_2 H_4)(\mu-H-C_2 H_4)]PF_6 \), \( [\text{Ru}(C_6 H_6)(C_6 H_9)]PF_6 \), \( [\text{Ru}(C_6 Me_6)(C_2 H_4)(\mu-H-C_2 H_4)]PF_6 \), \( [\text{Rh}(C_5 Me_5)(\eta^4 - \text{diene}) \text{ (diene} = 2,3\text{-dimethylbutadiene, 1,3-cyclohexadiene, norbornadiene, dicyclopentadiene, bis-ethylene)} \), \( [\text{Ir}(C_5 Me_5)(\eta^4 - \text{diene}) \text{ (diene} = 1,3\text{-cyclohexadiene, 2,3-dimethylbutadiene, bis-ethylene)} \), \( [\text{Rh}(C_2 H_4)_2 Cl]_2 \), \( [\text{Ir}(\text{Cl}(C_8 H_{14})_2]_2 \).
(using \((\text{NH}_4)_2\text{IrCl}_6\) instead of \((\text{NH}_4)_3\text{IrCl}_6\) but with other conditions being as reported\(^{146}\)). DPF\(_6\) was prepared following McMahon's procedure,\(^{56}\) by treating a D\(_2\)O solution of AgPF\(_6\) with DCl. CF\(_3\)COOD was prepared by treating trifluoroacetic anhydride with D\(_2\)O.

**Synthesis of \([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]\)_2**

**Method 1**

The method of Bennett et al.\(^{112}\) was used. The following is a typical procedure: OsO\(_4\) (1.09g, 4.3 mmol) was dissolved in a mixture of concentrated HCl (20 ml) and ethanol (5 ml) and heated to approximately 100°C for 4 h. The resulting clear orange-red solution was evaporated under reduced pressure, with gentle warming, to give a very dark reddish oil. The oil was dissolved in 25 ml ethanol and 1,3,5-trimethyl-1,4-cyclohexadiene (3 ml) was added. Refluxing the reaction mixture for 12-24 h gave a yellow precipitate; the reaction mixture was then cooled, the mother liquors were decanted and the precipitate was washed with successive portions of ethanol and ether and dried. The weight of product was 0.59 g, corresponding to a yield of 36% assuming the product to be \([\text{Os}(\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]\)_2 (see text).

This reaction was not always reproducible, some attempts giving no precipitate. The yellow product varied both in yield and analytical composition from batch to batch. Calculated for \(\text{C}_{18}\text{H}_{24}\text{Os}_2\text{Cl}_4\):
- C 28.4; H 3.17; Cl 18.6. Found: C 27.5, 25.3, 19.3, 28.5;
- H 3.1, 2.9, 2.7, 2.9; Cl 19.1, 19.1.
Method 2

To a solution of Na₂OsCl₆, synthesized as described above, was added 1,3,5-trimethyl-1,4-cyclohexadiene (6 ml), and the mixture refluxed for 48 h. The yellow precipitate that formed was filtered off, washed well with successive portions of ethanol and ether, and dried, (yield 1.5 g). Found: C 21.6; H 2.4; Cl 25.3

Synthesis of [Ir(C₅Me₅)Cl₂]₂

The literature method¹⁵⁷ for the synthesis of [Ir(C₅Me₅)Cl₂]₂ was altered, as follows: (NH₄)₂IrCl₆ (6.5 g, 8.2 mmol) was refluxed with 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (5.5 ml) in isopropanol (100 ml) for 48 h, until the black slurry had turned to a muddy brown. The reaction mixture was cooled on ice, and the brown solid filtered from the dark mother liquors; the mother liquors were concentrated and set aside to cool in the refrigerator. The solid was extracted with ca. 300 ml CH₂Cl₂, the orange extract filtered, concentrated, and [Ir(C₅Me₅)Cl₂]₂ was precipitated as orange microcrystals by addition of ether. The mother liquors yielded a second, small crop of the orange dimer. Total yield 1.85 g (32%). Found: C 30.0; H 3.8; Cl 17.1. C₂₀H₃₀Ir₂Cl₄ requires C 30.2; H 3.8; Cl 17.8.

Synthesis of M(η⁶-arene)(η⁴-diene) (M = Os, Ru) complexes

The following general procedure was used:

[M(η⁶-arene)Cl₂]₂ (M = Os, Ru; arene = C₆H₆, C₆H₃Me₃) was refluxed with

* Subsequent to the writing of this thesis it was found in our laboratory that this product could be purified simply by washing with water, and the resulting yellow microcrystalline material analysed as [Os(C₆H₃Me₃)Cl₂]ₙ.
an excess of the appropriate diene (approximately 1 ml per 0.5 g dimer), and an excess of anhydrous Na$_2$CO$_3$ (ca. 1 g per g dimer) in isopropanol (20-30 ml) for 1-3 h, until the suspended dimer had all reacted. The colour of the resulting reaction mixture varied from white to dark brown, depending on the diene and the metal, and in the case diene = dicyclopentadiene or norbornadiene, some polymerization of the diene also occurred. The reaction mixture was then evaporated to dryness in vacuo and extracted into n-hexane (2 x 20 ml). The extract was filtered and evaporated to dryness in vacuo. The crude M(η$^6$-arene)(η$^4$-diene) complexes (cream coloured or yellow) were purified by crystallization from n-hexane at -78°C, sublimation (10$^{-5}$ mm Hg, 50°C, probe cooled to -10°C) or chromatography (alumina, neutral, activity 1, in hexane or petroleum ether 60-80°C).

In this way the following complexes were synthesized:

Os(η$^6$-arene)(C$_6$H$_8$) (arene = C$_6$H$_6$, 79; C$_6$H$_3$Me$_3$, 85) from 1,3-cyclohexadiene;

Os(η$^6$-arene)(C$_{10}$H$_{10}$) (arene = C$_6$H$_6$, 83A; C$_6$H$_3$Me$_3$, 83B) from 2,3-dimethyl-1,3-butadiene;

Os(η$^6$-arene)(C$_{12}$H$_{12}$) (arene = C$_6$H$_6$, 87A; C$_6$H$_3$Me$_3$, 87B) from 1,5-cyclooctadiene;

Os(C$_6$H$_3$Me$_3$)(C$_{18}$H$_{14}$), 84, from ddbo;

Os(C$_6$H$_3$Me$_3$)(C$_{18}$H$_{14}$), 84, from ddbo;

Os(C$_6$H$_3$Me$_3$)(C$_9$H$_{14}$), 86, from 1,3,5-trimethyl-1,4-cyclohexadiene;

Os(C$_6$H$_3$Me$_3$)(C$_7$H$_8$), 91, from norbornadiene;

Os(C$_6$H$_3$Me$_3$)(C$_{10}$H$_{12}$), 92, from dicyclopentadiene;

Ru(C$_6$H$_3$Me$_3$)(C$_{18}$H$_{14}$), 94, from ddbo;
Analytical, nmr and mass spectroscopy data and yields are recorded in Tables 5, 6 and 8. Note that the yields assume the formula [Os(C₆H₃Me₃)Cl₂]₂ for the starting material, which may not be the case (see text). The complexes are all very air-sensitive.

Synthesis of Os(C₆H₃Me₃)(C₂H₄)₂, 93

A suspension of [Os(C₆H₃Me₃)Cl₂]₂ (400 mg, 0.52 mmol) in isopropanol (20 ml) was stirred with anhydrous sodium carbonate (0.6 g) at 70°C, and a slow, steady stream of ethylene was bubbled through for 2-3 h. The resulting dark brown reaction mixture was cooled, evaporated to dryness in vacuo and extracted into n-hexane (2 x 20 ml, 1 x 10 ml). The orange hexane extract was filtered, concentrated and Os(C₆H₃Me₃)(C₂H₄)₂ was precipitated as a light brown solid on cooling to -78°C (270 mg, 70%). An analytically pure sample was obtained by further recrystallisation from hexane at -78°C. The analytically pure complex is cream coloured and air-sensitive.

Yields, analytical and nmr spectroscopic data are recorded in Tables 5, 6 and 8.

Synthesis of M(C₅Me₅)(n⁴-diene) (M = Rh, Ir) complexes

The following general procedure was used, after the method of Maitlis:122 [M(C₅Me₅)Cl₂]₂ (M = Rh, Ir) was refluxed with an excess of the appropriate diene (approximately 1 ml per 0.5 g dimer used) and an excess of anhydrous sodium carbonate (ca. 1 g per g dimer) in isopropanol (30 ml), for ca. 3 h (except in the cases of the synthesis...
of Rh(C₅Me₅)(C₇H₈) and Rh(C₅Me₅)(C₁₀H₁₂), in which overnight reaction was necessary) until all the suspended dimer had reacted. The colour of the reaction mixture varied from white to dark brown, depending on the metal and the diene; in general, Ir reaction mixtures were white or pale yellow, and Rh mixtures yellow or brown. The reaction mixture was then evaporated to dryness in vacuo and extracted into n-hexane (2 x 20 ml). The extract was filtered and evaporated to dryness. Pure products were obtained by recrystallization from n-hexane at -78°C, sublimation (10⁻⁴ mm Hg, 50°C, water-cooled probe) or chromatography (neutral alumina, activity 1, in petroleum ether 40-60°C). The cream coloured (iridium) and yellow (rhodium) solids are slightly air-sensitive.

In this way the following new complexes were made:

Rh(C₅Me₅)(C₁₈H₁₄), 96, from ddbo;
Ir(C₅Me₅)(C₁₈H₁₄), 97, from ddbo;
Ir(C₅Me₅)(C₇H₈), 101, from norbornadiene;¹⁹⁵
Ir(C₅Me₅)(C₁₀H₁₂), 99, from dicyclopentadiene.

Yields, analytical and nmr data are recorded in Tables 5, 7 and 9.

Synthesis of Rh(C₅Me₅)(C₁₀H₁₂), 100, (C₁₀H₁₂ = n⁴-dicyclopentadiene)¹⁹⁶

A suspension of [RuCl(C₂H₄)₂]₂ (300 mg, 0.77 mmol) in methanol (20 ml) was stirred with dicyclopentadiene (0.25 ml) for 16 h. The red-brown slurry turned yellow. The slurry was allowed to settle, the solution was then syringed off and evaporated dry. The solid residue was washed with hexane to remove excess dicyclopentadiene,
leaving yellow $[\text{RhCl}(\text{C}_{10} \text{H}_{12})]_2$.\textsuperscript{198} This was dissolved in THF (20 ml) and NaCp(DME) added (310 mg, 1.74 mmol). The reaction mixture was stirred for 30 min, and water added to decompose the excess NaCp. The resulting brown slurry was evaporated to dryness in vacuo, and the residue extracted into $\text{CH}_2\text{Cl}_2$ (2 x 20 ml). The yellow extract was filtered and evaporated to dryness giving a yellow oily solid.

This was dissolved in n-hexane and recrystallized at -78°C as a yellow solid $\text{Rh}(\text{C}_5 \text{H}_5)(\text{C}_{10} \text{H}_{12})$ (370 mg, 80% based on $[\text{RhCl}(\text{C}_2 \text{H}_4)]_2$).

Analytical and nmr spectroscopic data are recorded in Tables 5 and 7.

$\text{Rh}(\text{C}_5 \text{H}_5)(\text{C}_7 \text{H}_8)$,\textsuperscript{197} ($\text{C}_7 \text{H}_8 = \eta^4$-norbornadiene) was synthesized in an entirely analogous manner to \textsuperscript{100}, using norbornadiene.\textsuperscript{141} The analytical and nmr data and yields are in Table 5, 7 and 9.

**Synthesis of Ir($\text{C}_7 \text{H}_5$($\text{C}_{18} \text{H}_{14}$), 98, ($\text{C}_{18} \text{H}_{14} = \eta^4$(ddbo))

A yellow slurry of $[\text{Ir}(\text{C}_8 \text{H}_{14})_2\text{Cl}]_2$ (750 mg, 0.84 mmol) was stirred at room temperature in $\text{CH}_2\text{Cl}_2$ (8 ml) with Tl(acac) (530 mg, 1.75 mmol) for 2 h. The resulting brown reaction mixture was filtered, separating a grey sediment from a golden brown liquor. Evaporation of the liquor to dryness yielded a brown solid, Ir($\text{C}_8 \text{H}_{14}$)$_2$(acac).

Without further purification this solid was dissolved in $\text{CH}_2\text{Cl}_2$ (10 ml), a slight excess of (ddbo) added (400 mg, 1.74 mmol), and the mixture was stirred at room temperature for 4 h; the colour lightened slightly. Evaporation of the solution to dryness gave a yellow oil, which crystallized on washing with n-hexane, giving a brown solid, Ir($\text{C}_{18} \text{H}_{14}$)(acac). This was dissolved in THF (15 ml) and Na Cp (DME)
(330 mg, 1.85 mmol) was added, with stirring. The resulting dark coloured reaction mixture was stirred at room temperature for a further 4 h, then a small quantity of H₂O added to decompose the excess Na Cp. The mixture was then evaporated to dryness in vacuo and extracted into toluene (40 ml). The extract was filtered, concentrated and the product, Ir(C₅H₅)(C₁₈H₁₄), precipitated as light brown crystals on addition of n-hexane and cooling overnight in the refrigerator (yield 390 mg, 50% based on [Ir(C₈H₁₄)₂Cl]₂).

Analytical results and nmr data are found in Tables 5, 7 and 9.

Protonation Reactions

The following general procedure was used for the protonation of all the M(η⁶-arene)(η⁴-diene) (M = Ru, Os) and M(C₅R₅)(η⁴-diene) (M = Rh, Ir; R = H, CH₃) complexes, including the bis-ethylene complexes. The neutral complex (usually ca. 200-300 mg) was dissolved in diethylether (10-20 ml) and stirred while an excess of HPF₆ (60% aqueous solution) was added dropwise; precipitation of the protonated product occurred immediately, and one or two drops of the acid were generally sufficient for complete reaction. The precipitate was allowed to settle, the mother liquors were syringed off, and the remaining solid was washed well with ether and dried in vacuo.

The acids CF₃SO₃H, HBF₄, p-toluene sulphonic acid and HSbF₆ were used on occasion, as discussed in the text, following the same procedure. Except in the case of [Os(C₆H₃Me₃)(C₁₈H₁₅)]CF₃SO₃, for which good elemental analyses were obtained, the complexes
synthesized using these acids were identified only by spectroscopic means.

The osmium complexes are white or light brown, slightly air-sensitive as solids, and in most cases, unstable and unexpectedly air-sensitive in solution, decomposing to give a black solid. The ruthenium complexes are generally yellow in colour and rather more stable than their osmium counterparts. The rhodium and iridium complexes range in colour from orange to white; \([\text{Rh}(\text{C}_5\text{Me}_5)(\text{C}_18\text{H}_{15})]\text{PF}_6, 118\), is very dark green even after careful recrystallization. They are stable in air as solids and only slightly air-sensitive in solution.

Table 10 lists all the new protonated complexes synthesized, with their yields and analytical data, whilst Tables 12 and 13 list nmr spectroscopic data.

Protonation of \(\text{M}(\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_8)\) \((\text{M} = \text{Rh}, 102; \text{Ir}, 101)\)

Protonation of norbornadiene complex \(\text{Ir(CpMe)}(\text{C}_7\text{H}_8), 101, (390 \text{ mg}, 0.93 \text{ mmol})\) with \(\text{HPF}_6\) in ether as described in the general procedure above, gave the immediate precipitation of a white solid. This was identified by \(^1\text{H} \text{nmr} \) (Table 12) as the diene hydride \([\text{Ir}(\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_8)\text{H}]\text{PF}_6, 140, (\nu\text{M-H} = 2110 \text{ cm}^{-1})\) (280 mg, 55%).

When the diene hydride complex was dissolved in \(\text{CH}_2\text{Cl}_2\) a pale yellow solution resulted. On standing at room temperature for several hours (overnight) the solution turned a dark orange. Addition of ether or hexane
to the solution precipitated an air-stable orange solid of empirical formula \([\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)\text{]PF}_6, 141\). This complex showed a band in its infrared spectrum at 2040 cm\(^{-1}\) (KBr disc). Quantitative yields are obtained from the diene hydride complex. The nmr spectral and analytical data are presented in Tables 10, 12 and 13.

Treatment of \(\text{Rh(C}_5\text{Me}_5)(\text{C}_7\text{H}_8)\), 102, with \(\text{HPF}_6\) in ether gave a reddish solid, \([\text{Rh(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)\text{]PF}_6, 142\), in 65% yield. The nmr spectra of this product (Tables 12 and 13) were very similar to those for the Ir complex, isomer 2, discussed above. No bands were seen in the infrared spectrum of 142 (2500 - 1600 cm\(^{-1}\)).

Protonation of \(\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{C}_13\text{H}_{12})\)

Treatment of an ether solution of the 7-phenylnorbornadiene complex \(\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{C}_13\text{H}_{12})\), 95, with \(\text{HPF}_6\) gave a light yellow solid of empirical formula \([\text{Ru(C}_6\text{H}_3\text{Me}_3)(\text{C}_13\text{H}_{13})\text{]PF}_6, 150\), (65%). This complex was identified as a diene hydride complex by \(^1\text{H} \text{nmr (Table 12).}

The diene hydride was dissolved in \(\text{CH}_2\text{Cl}_2\) and allowed to stand overnight. The yellow solution was then concentrated, and addition of ether precipitated an orange oil, which solidified on prolonged drying in vacuo. The solid was shown by \(^1\text{H} \text{nmr to be a mixture of two mesitylene complexes, one of which could not be identified, and the second analogous to [Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)\text{]PF}_6, 141\), (see above). These complexes could not be completely separated.
Reaction of \([\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6\), 141, with Lithium aluminium hydride

A slurry of \([\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6\), 141, (100 mg, 0.18 mmol) in dry ether (5 ml), was stirred with an excess of LiAlH\(_4\) for 30 mins. The iridium salt rapidly dissolved. The excess LiAlH\(_4\) was then decomposed with a little ethanol, and the reaction mixture was carefully filtered through filteraid. The pale yellow filtrate was evaporated to dryness and extracted into toluene. The extract was filtered and evaporated to dryness, giving \([\text{Ir(C}_5\text{Me}_5)(\text{C}_7\text{H}_{10})]\), 149, as a cream coloured solid (50 mg, 70%). An analytically pure sample of 149 was prepared by vacuum sublimation (10\(^{-4}\) mm Hg, 50°C onto a water-cooled probe). Found: C 48.4; H 6.0. \(\text{C}_{17}\text{H}_{25}\text{Ir}\) requires C 48.4; H 6.0. Mass spectrum: parent ion at m/e 422. Other ions m/e 421 (p-H), 407 (p-CH\(_3\)), 393 (p-C\(_2\)H\(_5\)). \(^1\text{H}\) nmr (C\(_6\)D\(_6\), 200 MHz): \(\delta1.69\) (15H, s)(C\(_5\)Me\(_5\)), \(\delta2.44 - \delta1.20\) (9H, complex multiplets), \(\delta0.17\) (1H, d, J = 11 Hz). \(^{13}\text{C}\) nmr (C\(_6\)D\(_6\), 50 MHz) (J in Hz): \(\delta9.5\) (q, J = 126), \(\delta27.3\) (t, J = 130), \(\delta28.6\) (dd, J = 157, 149), \(\delta33.9\) (d, J = 162), \(\delta35.4\) (d, J = 136), \(\delta42.0\) (d, J = 162), \(\delta46.9\) (t, J = 130), \(\delta57.5\) (d, J = 157), \(\delta91.7\) (s).

The reaction was repeated with lithium aluminium deuteride. The \(^1\text{H}\) nmr spectrum of the resultant product was still complex. The \(^{13}\text{C}\) nmr showed that deuterium was attached to the carbon atom giving rise to the peak at \(\delta46.9\).

Reaction of \([\text{Rh(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6\), 142, with Lithium aluminium hydride

A slurry of \([\text{Rh(C}_5\text{Me}_5)(\text{C}_7\text{H}_9)]\text{PF}_6\), 142, in ether was treated with excess LiAlH\(_4\) and stirred for 30 mins. The excess LiAlH\(_4\) was destroyed with ethanol, the reaction mixture filtered through filteraid and
the brown filtrate evaporated to dryness. The residue was extracted into hexane, the hexane extract was filtered and evaporated dry, giving \( \text{Rh(C}_5\text{Me}_5)(\text{C}_7\text{H}_{10}) \). This complex was identified on the basis of its mass spectrum and nmr spectra, which were similar to the iridium complex. Mass spectrum: parent ion at m/e 332. Other ions at m/e 317 (p-CH\(_3\)), 303 (p-C\(_2\)H\(_5\)). \(^1\)H nmr (C\(_6\)D\(_6\), 200 MHz): \( \delta 1.68 (15\text{H}, \text{s})(\text{C}_5\text{Me}_5) \), \( \delta 2.79 (2\text{H}, \text{m}) \), \( \delta 2.41 (2\text{H}, \text{m}) \), \( \delta 2.1 (3\text{H}, \text{m}) \), \( \delta 1.6 - \delta 1.0 \) (complex mult., integration difficult to measure), \( \delta 0.68 \) (1H, d, \( J = 12 \text{ Hz} \)). \(^{13}\)C nmr (C\(_6\)D\(_6\), 50 MHz) (J in Hz): \( \delta 10.0 \) (q, \( J_{\text{CH}} = 126 \)), \( \delta 29.2 \) (t, \( J_{\text{CH}} = 131 \)), \( \delta 35.1 \) (d, \( J_{\text{CH}} = 129 \)), \( \delta 45.7 \) (t, \( J_{\text{CH}} = 125 \)), \( \delta 64.6 \) (d of t, \( J_{\text{CH}} = 155 \), \( J_{\text{CrRh}} = 13.2 \)), \( \delta 52.9 \) (dd, \( J_{\text{CH}} = 156 \), \( J_{\text{CrRh}} = 16.1 \)), \( \delta 62.4 \) (dd, \( J_{\text{CH}} = 157 \), \( J_{\text{CrRh}} = 14.7 \)), \( \delta 76.4 \) (dd, \( J_{\text{CH}} = 144 \), \( J_{\text{CrRh}} = 11.7 \)), \( \delta 96.2 \) (d, \( J_{\text{CrRh}} = 3 \)).

Reaction of \([\text{Ru(C}_6\text{Me}_6)(\text{C}_7\text{H}_9)]\)PF\(_6\), 57C, with LiAlH\(_4\)

A slurry of \([\text{Ru(C}_6\text{Me}_6)(\text{C}_7\text{H}_9)]\)PF\(_6\) (isomerized product) (212 mg, 0.42 mmol) was stirred with an excess of LiAlH\(_4\) for 1.5 h. The excess LiAlH\(_4\) was decomposed with ethanol, the sample filtered, and the filtrate pumped dry. Extraction of the residue into hexane, filtration, concentration of the filtrate, and cooling the concentrate to \(-78^\circ\text{C}\) yielded a crop of pale yellow needles (110 mg). \(^1\)H nmr showed this to be a mixture of complexes, showing three methyl singlets at \( \delta 1.86 \), \( \delta 1.75 \) and \( \delta 1.70 \) in the approximate ratio of 1:4:4 (based on integration values). The \(^{13}\)C \( (\text{H}) \) nmr spectrum showed at least 21 peaks. The mass spectrum showed peaks at m/e 357 (corresponding to \( \text{Ru(C}_6\text{Me}_6)(\text{C}_7\text{H}_9) \)), 343 (357 - \( \text{CH}_2 \)), 329 (357 - \( \text{C}_2\text{H}_4 \)).
Deuteration Reactions

Deuteration with DPF$_6$ was carried out in similar fashion to the protonation reactions described above, by treating diethyl ether solutions of the appropriate diene complex with the acid, and isolating the resultant precipitate. The reaction was often accompanied by some decomposition, probably aided by traces of Ag$^+$ in the DPF$_6$ solution; hence precipitates of deuterated complexes were recrystallized as quickly as possible from CH$_2$Cl$_2$/ether, and their nmr spectra recorded as soon as possible after synthesis.

Deprotonation Reactions

The protonated complexes were rapidly deprotonated by stirring the appropriate protonated complex with an aqueous solution of Na$_2$CO$_3$. The neutral product was then extracted from the reaction mixture into ether, the ether was dried over anhydrous sodium sulphate and the solvent evaporated in vacuo. The deprotonated species was then identified by $^1$H nmr.

Reactions of protonated complexes with ligands L = P(OMe)$_3$ or t-BuNC

The following general procedure was used: the protonated complex (approx. 200 mg) was dissolved in dichloromethane (10 ml) and a slight excess of P(OMe)$_3$ or t-BuNC was added, at room temperature, with shaking or magnetic stirring. The reaction mixture was allowed to stand for an hour at room temperature; reaction was usually accompanied by a slight lightening of the colour. The mixture was then concentrated, and the product of general formula [M($^6$-arene)($^3$-enyl)L]PF$_6$ (M = Ru, Os), or [M(C$_5$Me$_5$)(C$_6$H$_9$)L]PF$_6$ (M = Rh, Ir), was precipitated with ether. Further recrystallization
(CH₂Cl₂/ether) was usually necessary to obtain analytically pure salts.

The complexes synthesized are listed in Tables 11 and 14 along with their analytical and nmr spectral data and yields. They are all yellowish or orange air-stable powders.
APPENDIX 1

THE CRYSTAL STRUCTURE OF \([\text{Ru}(\text{C}_8\text{H}_3\text{Me}_3)(\text{C}_18\text{H}_{15})]\text{PF}_6\) \(\text{III}\)

The structure was solved by Dr G.B. Robertson and Dr W.A. Wickramasinghe, of the Research School of Chemistry, The Australian National University.

Orange crystals of the complex were grown from acetone/ether by vapour diffusion, under nitrogen. The crystal irradiated was an unusual 'coffin' shape, with the following face dimensions: 201, 0.14 mm; -201, 0.12 mm; 0-11, 0.3 mm; 0-1-1, 0 mm; 011, 0.16 mm; -2 0 -1,0 mm; 01-1, 0 mm; 20-1, 0 mm. The structure was solved by conventional Patterson and Fourier Transform techniques.

Experimental details are recorded in Table 1, selected bond lengths in Table 2, angles in Table 3, and Figure 1 shows the molecular structure of the complex.
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<tr>
<td>( \beta )</td>
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<td>( \gamma )</td>
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The structures were solved by Dr G.B. Robertson and Dr W.A. Wickramasinghe, of the Research School of Chemistry, The Australian National University.

Orange crystals of the complex were grown from CH₂Cl₂/ether by vapour diffusion, under nitrogen. The complex crystallized in two modifications, 130A and 130B. Isomer A was monoclinic, space group $p2_1/n$, and the crystal dimensions were 0.06 x 0.19 x 0.13 mm. Isomer B was also monoclinic, space group $p2_1$, and the dimensions were 0.12 x 0.11 x 0.12 mm. The derived metrical data for 130A were more precise and reliable than those for 130B. The structures were solved by conventional Patterson and Fourier techniques. Experimental details are recorded in Table 4, selected bond distances in Table 5, and selected angles in Table 6. Figure 2 shows the molecular structure of isomer A, and figure 3 shows the packing diagrams for the two modifications.
Table 4  
Experimental Details

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Table 5

Selected Bond Distances (Å) for

\([\text{Os}(2,3,5\text{n-C}_10\text{H}_{13})(\text{n-C}_6\text{H}_3\text{Me}_3-1,3,5)]\text{PF}_6\),

130A, 130B

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<td>77(1)</td>
<td>C(14)-C(15)-C(16)</td>
<td>118(2)</td>
</tr>
<tr>
<td>C(6)-C(5)-C(4)</td>
<td>100(1)</td>
<td>101(2)</td>
<td>C(14)-C(15)-C(151)</td>
<td>121(2)</td>
</tr>
<tr>
<td>Os-C(6)-C(5)</td>
<td>63(1)</td>
<td>59(1)</td>
<td>C(151)-C(15)-C(16)</td>
<td>121(2)</td>
</tr>
<tr>
<td>Os-C(6)-C(7)</td>
<td>123(1)</td>
<td>125(2)</td>
<td>C(11)-C(16)-C(15)</td>
<td>121(2)</td>
</tr>
</tbody>
</table>
FIGURE 2

C(131) — C(13) — C(12) — C(11) — C(16) — C(111)
C(14) — C(15) — C(151)

Os
C(1) — C(5) — C(9) — C(10) — C(3) — C(4)
C(6) — C(7) — C(8)
FIGURE 3

P2₁

P2₁/n
REFERENCES


23. M.A. Bennett and M. Moronski, unpublished results.


69. W.A. Wickramasinghe, personal communication.


175. 'Gmelin Handbuch der Anorganischen Chemie', Osmium Supplementary Vol. 1 (1980), Springer-Verlag, pp. 128-144 particularly Sections 3.4.8.2, 3.4.8.6, and 3.4.8.7, and references therein.


195. \( \text{Ir}(\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_8) \) has been synthesized by H.-B. Lee, K. Moseley, C. White and P.M. Maitlis, but no spectroscopic or analytical data appear to have been reported.

196. \( \text{Rh}(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{12}) \) has been reported as being one product of the reaction of \([\text{Rh}(\text{n}^4-\text{C}_7\text{H}_{10})\text{Cl}]_2\) and isopropyl magnesium bromide with dicyclopentadiene, J. Müller, H.O. Stühler and W. Goll.

197. \( \text{Rh}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_8) \) has been synthesized by J. Evans, B.F.G. Johnson and J. Lewis, but no spectroscopic or analytical data appear to have been reported.


FURTHER COMMENTS AND CORRECTIONS

Consequent to Examiners' reports the following comments and corrections are made:

(1) a) The statement on p.89 that "the effect ... must thus arise from an intermediate or transition state bridging hydride complex" is incorrect. A high energy intermediate or a transition state would not significantly perturb the NMR spectrum since such spectra are concentration weighted averages.

b) It has also been suggested that the isotopically perturbed shift observed for $108$, discussed on page 89-90, would in fact be expected for a terminal hydride complex. Consider the simple methyl case below:

When $H_1$, $H_2$, and $H_3$ are rapidly averaging an isotopically perturbed shift is expected both for the agostic structure $A$ and the terminal hydride structure $I$. This shift is due to the lower stretching frequency of $H_1$-$C$ (or $H_1$-$M$) vs $H_2$-$C$, $H_3$-$C$ and thus the smaller H/D zeropoint energy difference in site 1 compared to sites 2 and 3. Thus, the heavier isotope, D, will prefer sites 2 and 3 in both cases (and may even be greater in fluxional I type cases).