

Synthesis of cationic organotransition-metal complexes
and kinetic studies of their reactions with nucleophiles

by Leslie James Russell

A thesis presented to the Faculty of Science
of the University of London in candidature for the
degree of Doctor of Philosophy

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DEDICATION

To Christine and my parents

ACKNOWLEDGEMENTS

The author is indebted to his supervisor, Dr. P. Powell, for his help and guidance both during and after his postgraduate studies.

The work described in this thesis was supported by a research studentship from the Science Research Council.

The author would also like to thank Johnson, Matthey and Co. Ltd. for a generous loan of rhodium and iridium salts and also PCMU (Harwell) and King's College, (London) nmr services for supplying many of the spectra.

Finally, the author would also like to thank Mrs E.I. Kearsey for the typing of this thesis.

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The allyl complexes $[\text{Rh}(\eta^3\text{-C}_3\text{H}_4\text{R})(\eta^5\text{-C}_5\text{R}'_5)\text{L}]^+\text{BF}_4^-$
(R = 1-Me, R' = H, Me : R = 2-Me, R' = H) (L = pyridine, triphenyl-
phosphine, triphenylarsine) have been synthesised from the corresponding
neutral chlorocomplexes $[\text{Rh}(\eta^3\text{-C}_3\text{H}_4\text{R})(\eta^5\text{-C}_5\text{R}'_5)\text{Cl}]$ by reaction with
silver tetrafluoroborate, as a halide abstractor, in acetone, followed
by reaction with a stoichiometric quantity of ligand L. This reaction
is believed to proceed through a "solvento" intermediate, (L = acetone).
The proton and carbon-13 nmr spectra of the salts are reported and
discussed.

The preparations of several acyclic diene chlorocomplexes of
rhodium and iridium $[\text{M}(\eta^4\text{-diene})_2\text{Cl}]$ from the reaction of excess
diene with the cyclooctene complexes $[\text{M}(\eta^2\text{-C}_8\text{H}_{14})_2\text{Cl}]$: M = Rh, Ir
are also reported. Further treatment of the ketone and aldehyde
compounds with cyclopentadienyl thallium afforded neutral species of
the type $[\text{M}(\eta^4\text{-diene})(\eta^5\text{-cyclopentadienyl})]$ which are also discussed
in the light of their proton and carbon-13 nmr spectra. The
protonation of these compounds with strong acids is described together
with the formation of the cationic complex $\eta^5\text{-syn-1-methylpentadienyl}$
 $\eta^5\text{-cyclopentadienylrhodium tetrafluoroborate}$ from the protonation of
an alcohol intermediate. The spectra and attempted preparations of
similar salts are compared with the related tricarbonyliron compounds.

In part two, preliminary kinetic data are presented from the
reactions of the cycloheptadienyl tricarbonyliron salt $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)$
 $(\text{CO})_3]^+\text{BF}_4^-$ and the tropylium tricarbonylmolybdenum salt
 $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ with sodium iodide in acetone using stopped-
flow spectrophotometry. Possible mechanisms for the formation of
intermediate species and the final substituted products are discussed.

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PART ONE

ORGANORHODIUM CHEMISTRY

CHAPTER ONE

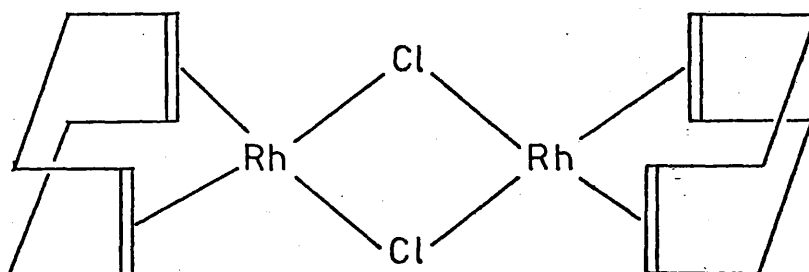
CATIONIC η^3 -ALLYL COMPLEXES OF RHODIUM

CHAPTER ONE

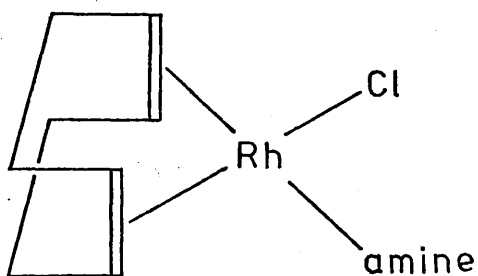
CATIONIC η^3 -ALLYL COMPLEXES OF RHODIUM

1.1 INTRODUCTION

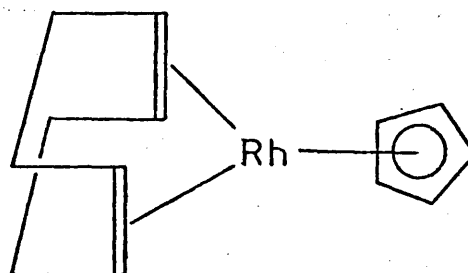
Organorhodium complexes were first reported in 1956 when Chatt¹ and Venanzi synthesised di- μ -chlorobis $\eta(1-2) \eta(5-6)$ cyclooctadiene dirhodium by refluxing an ethanolic solution of rhodium (III) chloride* with cycloocta 1,5 diene. The orange-yellow solid which crystallised on cooling had a dimeric chloro-bridged structure with the metal in square planar configuration (1.1).



(1.1)



(1.2)



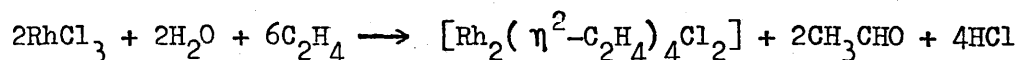
(1.3)

* rhodium (III) chloride means $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ ($x=3$) unless otherwise indicated.

Treatment of this dimer with amine resulted in splitting of the halide bridge and formation of a mononuclear complex

$[\text{Rh } \eta(1-2) \eta(5-6) \text{ COD}^* \text{Cl amine}]$ (1.2). This bridge can also be split by reaction with sodium cyclopentadienide, the resultant complex is then $\eta(1-2) \eta(5-6) \text{ COD } \eta^5\text{-cyclopentadienyl rhodium}$ (1.3). Similar dimeric complexes to (1.1) were also obtained from reactions with dicyclopentadiene and cyclooctatetraene.² These syntheses were extended by Wilkinson et al.³ who found that an ethanolic solution of rhodium (III) chloride was particularly reactive towards ligands containing a chelating diolefin group, giving species of the general formula $[\text{Rh}_2 \text{ L}_2 \text{ Cl}_2]$ where L is the chelating diolefin.

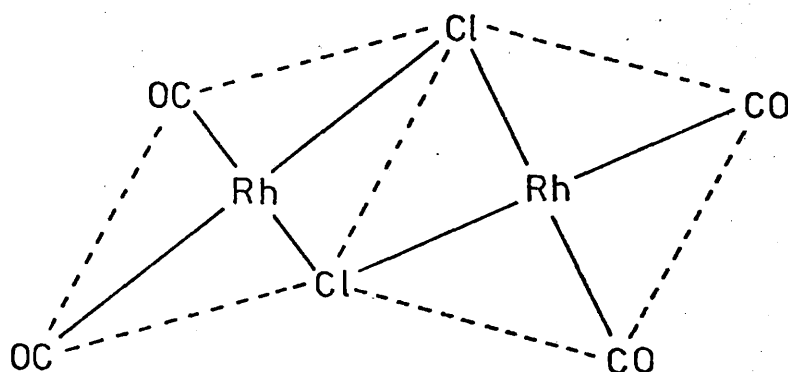
The coordination of a monoolefin to rhodium was first described by Cramer in 1962.⁴ Ethylene was passed through a stirred solution of rhodium (III) chloride in aqueous methanol for several hours at room temperature and an orange-brown solid slowly started to precipitate out which was formulated as the chlorobis $\eta^2\text{-ethylene rhodium dimer}$. In this reaction the rhodium (III) chloride is reduced to rhodium (I) while an equivalent proportion of ethanol is oxidised to acetaldehyde: viz.



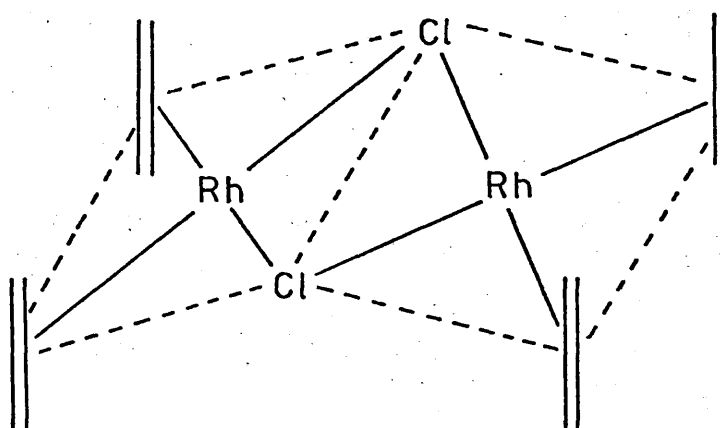
This dimer was proposed to have a similar structure to the analogous carbonyl compound (1.4) which has two essentially square planar $[\text{Rh}(\text{CO})_2\text{Cl}]$ units intersecting at an angle of 124° .⁵ X-ray studies on the ethylene complex (1.5) later confirmed this structure with the two square planar rhodium atoms each bonded to two chlorine atoms and

* COD = cyclooctadiene

the double bond centres of the ethylene molecules, although in this case the angle between the planes was found to be 116° .⁶



(1.4)



(1.5)

This ease of preparation of olefin-rhodium compounds from commercially available rhodium (III) chloride together with the

lability of the coordinated ethylene and carbonyl ligands in the dimeric structures has stimulated interest in the organic chemistry of rhodium. Displacement of the coordinated ethylene has proved possible by several types of ligand. 1,5 COD rapidly displaced ethylene giving complex (1.1) and triphenylphosphine, pyridine, hydrogen cyanide and acrylonitrile all resulted in the evolution of ethylene from the dimer.⁴ The reaction of conjugated dienes with di- μ -chloro η^2 -tetraethylene dirhodium⁷ will be discussed in Chapter 2. Sodium cyclopentadienide also underwent reaction with the dimer resulting in the formation of bis η^2 -ethylene

η^5 -cyclopentadienylrhodium⁸; although this complex may be better synthesised by reaction of the dimeric ethylene complex with cyclopentadienyl thallium and filtering off the thallium residues.* Displacement of the ethylene from this compound is more difficult, exchange not usually occurring until the reaction temperature is above 115°;⁹ although this method of preparation has recently been used to synthesise several bis η^2 -olefin η^5 -cyclopentadienylrhodium species.¹⁰

Reactions of di- μ -chlorotetracarbonyldirhodium have also been widely studied. Acetylacetone and other β -diketones, in the presence of base, cause bridge splitting to occur resulting in monomeric species of the general formula $[\text{Rh}(\beta\text{-diketone})(\text{CO})_2]$.¹¹ These carbonyl groups may be completely displaced by chelating di-olefins or partially replaced by phosphines; while conjugated dienes displayed no reactivity at all. Powell and Shaw¹² have extensively

* see experimental section in Chapter 2.

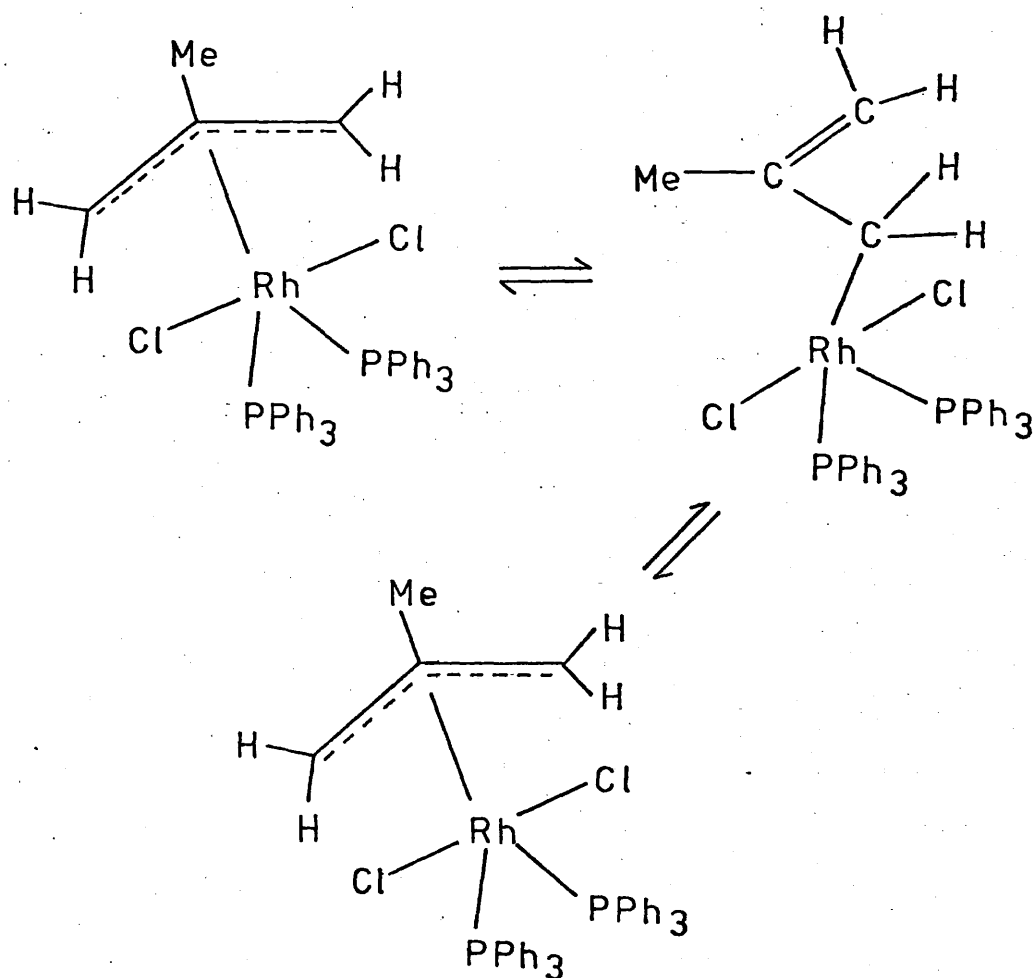
studied the reactions of (1.4) with allyl halides giving rise to the formation of the complexes $[\text{Rh}_2\text{X}_2(\eta^3\text{-all})_4]$ where X is the halogen and (all) is the allylic grouping. The mechanism for this reaction is believed to be the oxidative hydrolysis of the carbonyl complex in aqueous methanol in the presence of an allylic halide. Addition of potassium hydroxide as base gave higher yields of products and a shorter reaction time. Carbon dioxide and olefin (formed from all-H) were found to be evolved and this together with deuteration studies and the observation that allyl halides alone did not react with the carbonyl complex (1.4) led to the proposed reaction scheme (Scheme 1.1).

N.m.r. spectroscopic studies on $[\text{Rh}_2\text{Cl}_2(\eta^3\text{-all})_4]$ (1.6) showed the η^3 -allylic ligand to be asymmetrically bonded to the metal and this was later confirmed by x-ray analysis.¹³ Coupling of the methyl protons to the rhodium-103 nucleus (100% abundance : Spin I = $\frac{1}{2}$) was observed in the η^3 -2-methylallyl complex and a general broadness in the remainder of the η^3 -allylic resonances was attributed to variations in the rhodium coupling to the protons. The spectrum of the η^3 -1-methylallyl complex with its broad overlapping resonances was interpreted in terms of several isomeric forms existing in solution. Reaction of $[\text{Rh}_2\text{Cl}_2(\eta^3\text{-all})_4]$ with allylmagnesium chloride gave η^3 -trisallylrhodium¹⁴ which has three symmetrically bonded allyl groups at room temperature although one differs from the other two. Rapid rotation of one of the allyl groups resulting in magnetic equivalence of the other two or alternatively a more complex mechanism involving the η^3 -allyl groups passing through an η^1 -allyl intermediate were proposed to account for the nmr spectrum. Nixon and co-workers¹⁵

have studied reactions of η^3 -trisallylrhodium with trifluorophosphine forming $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)_3]$ although a more widely applicable precursor to materials of this type is $[\text{Rh}(\text{H}(\text{PF}_3)_4)]$ with replacement of the phosphines.¹⁶

The thallium compounds, acetylacetonate and cyclopentadienide, abstracted halogens from the complexes $[\text{Rh}_2\text{Cl}_2(\eta^3\text{-all})_4]$ forming mononuclear species; the η^5 -cyclopentadienyl derivatives $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-all})(\eta^1\text{-all})]$ which contain one allyl group where all three carbons are bonded to the metal and another where only one carbon is bonded.¹² Further treatment of this complex with dilute hydrochloric acid gave the neutral chlorocomplex $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-all})\text{Cl}]$. A cationic complex could then be isolated by reaction with pyridine and sodium tetraphenylborate in methanol. Phosphines were also found to split the chlorobridge in (1.6) resulting in neutral complexes of general formula $[\text{Rh}(\text{Cl}(\eta^3\text{-all})_2\text{L})]$ where L = phosphine. A cationic species was also prepared from this complex by precipitation from solution with sodium tetraphenylborate, although the insolubility of the resultant product precluded nmr studies. This problem, however, was overcome by Green and Parker¹⁷ who isolated the cationic complexes $[\text{Rh}(\eta^3\text{-all})_2\text{L}_2]^+$ as the tetrafluoroborate salts. Their general method of synthesis was to use the silver tetrafluoroborate salt (soluble in polar organic solvents) to remove the halogen as insoluble silver halide, followed by addition of the ligand L to the remaining filtrate and precipitation with diethyl ether. Nmr spectroscopic studies indicated two equivalent, though asymmetrically bonded, η^3 -allylic groups and the dynamic behaviour of this group in solution was investigated using

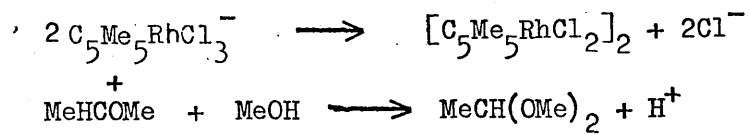
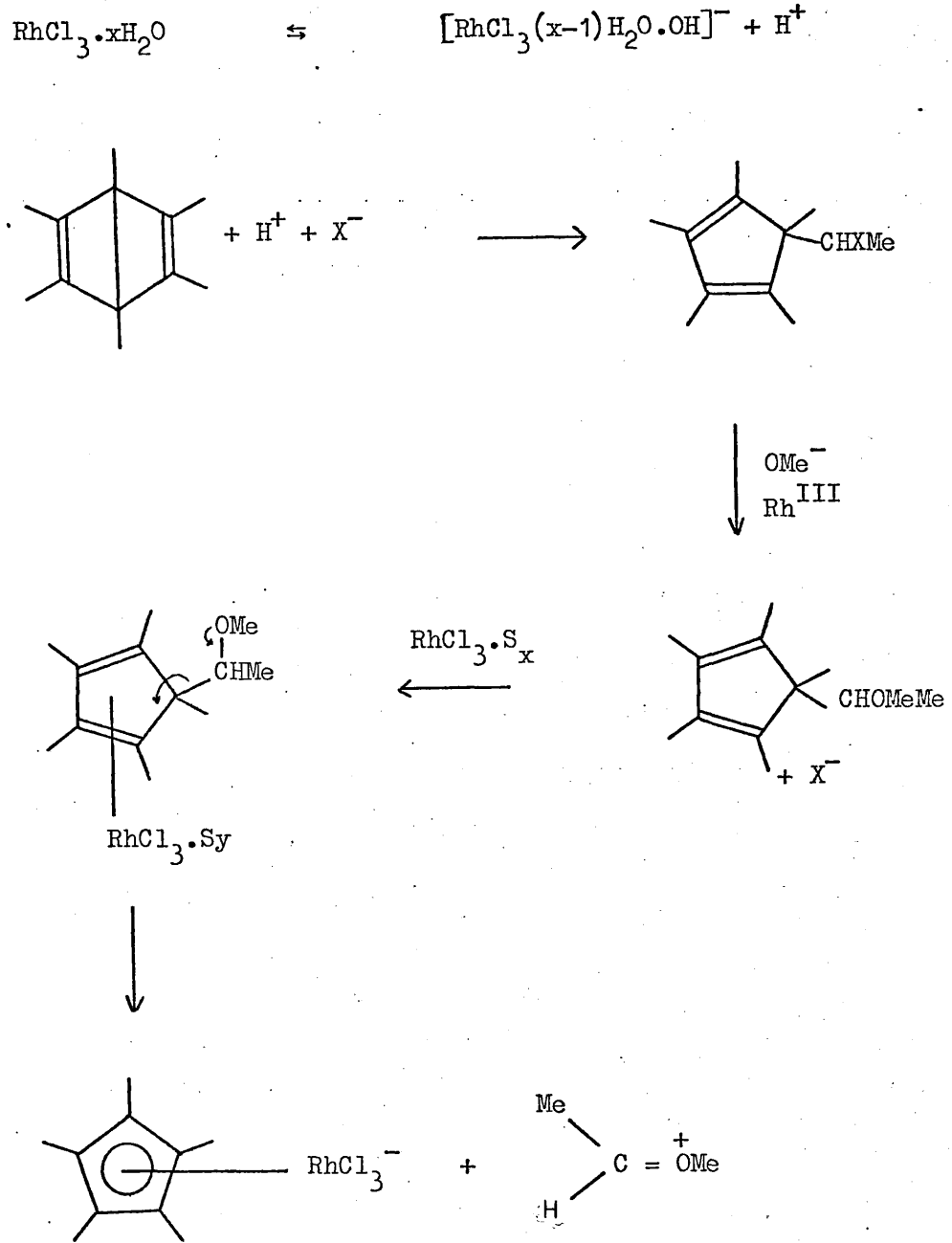
variable temperature techniques. A complicated exchange process was postulated where the protons at each end of the η^3 -allyl group alter their environment together with a "syn" to "anti" change. This involves initial dissociation of the ligand L followed by rupture of a rhodium-carbon bond through rotation of the resultant five-coordinate species and is similar to the mechanism proposed by Vrieze and Vogler¹⁸ to account for the magnetic equivalence of the four allyl protons in the complexes $[\text{Rh L}_2\text{Cl}_2(\eta^3\text{-C}_4\text{H}_7)]$ which involves interconversion of the "syn" and "anti" protons through a " σ "-allyl intermediate. (Scheme 1.2).



(Scheme 1.2)

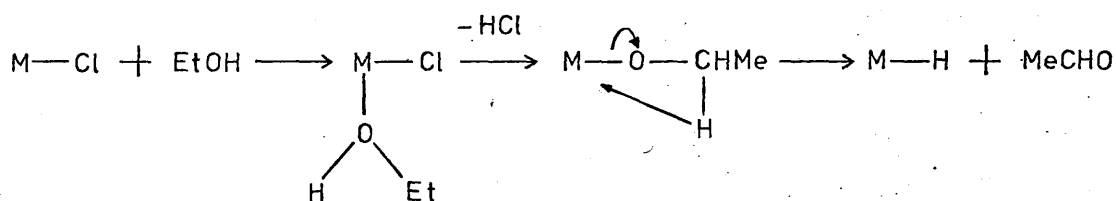
Reaction of butadiene with rhodium (III) chloride in methanol gives the unusual chloro and butadiene bridged complex di- μ -chlorobischloro (η^3 -1-methylallyl) μ - η^2 -butadiene dirhodium¹⁹ which has an extremely complicated nmr spectrum due to the possibility of several isomeric forms existing in solution. Cyclopentadienyl thallium abstracts chlorine from this species forming the chlorocomplex $[\text{Rh}(\eta^3\text{-C}_4\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ with evolution of butadiene. Gubin et al.²⁰ have also synthesised neutral chlorocomplexes of this type in a one stage synthesis involving the simultaneous treatment of rhodium (III) chloride with allylmercury halide and cyclopentadienyl thallium in aqueous methanol at room temperature although the exact mechanism is uncertain. The same group have also reported the formation of some analogous iridium compounds.²¹

Maitlis and co-workers²² have extensively studied the reaction of hexamethyldewarbenzene with rhodium (III) chloride in which ring contraction occurs resulting in formation of the η^5 -pentamethylcyclopentadienyl ring. After refluxing overnight in methanol the dimeric species di- μ -chlorobischlorobis η^5 -pentamethylcyclopentadienylrhodium remains. Analysis of volatile products led to the following proposed mechanism (Scheme 1.3) with the reaction catalysed by acid arising from the hydrated rhodium (III) chloride through ionisation of a coordinated water molecule. The resultant pentamethylcyclopentadienyl dimer is a useful precursor in the synthesis of rhodium-olefin complexes. Reaction with chelating dienes or olefins in the presence of base gives the compounds bis (η^2 -olefin) or (η^4 -di-olefin) (η^5 -pentamethylcyclopentadienyl) rhodium while under the same conditions with conjugated dienes or

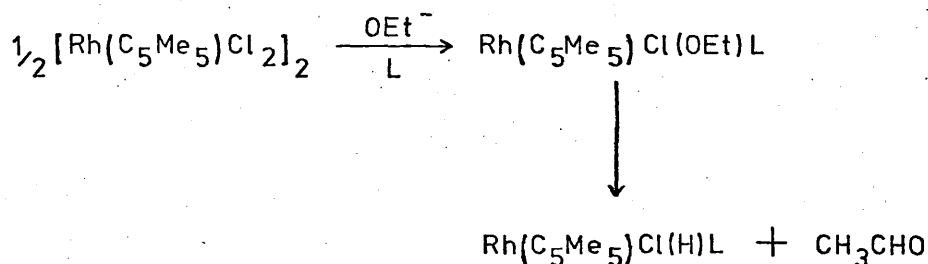


(Scheme 1.3)

trienes, metal-enyl complexes are formed.²³ With butadiene the product is the neutral species $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(1\text{-Me-}\eta^3\text{-C}_3\text{H}_4)\text{Cl}]$ while cycloheptatriene gives the cationic complex $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_7\text{H}_9)]^+\text{Cl}^-$. These reactions have been shown to proceed via an hydrido intermediate with the hydridic hydrogen originating from the α -position of the alcohol (Schemes 1.4 and 1.5).



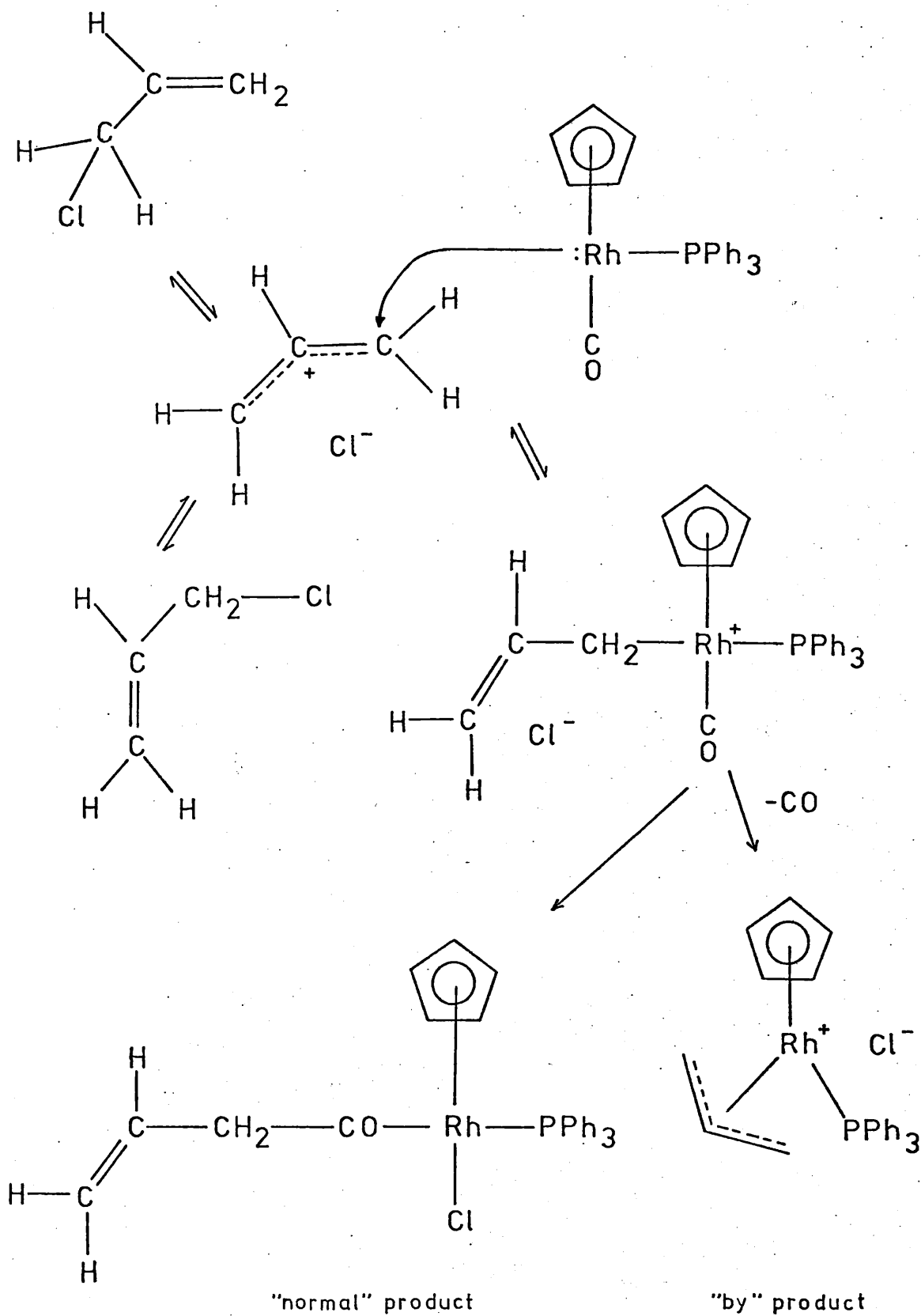
(Scheme 1.4)



(Scheme 1.5)

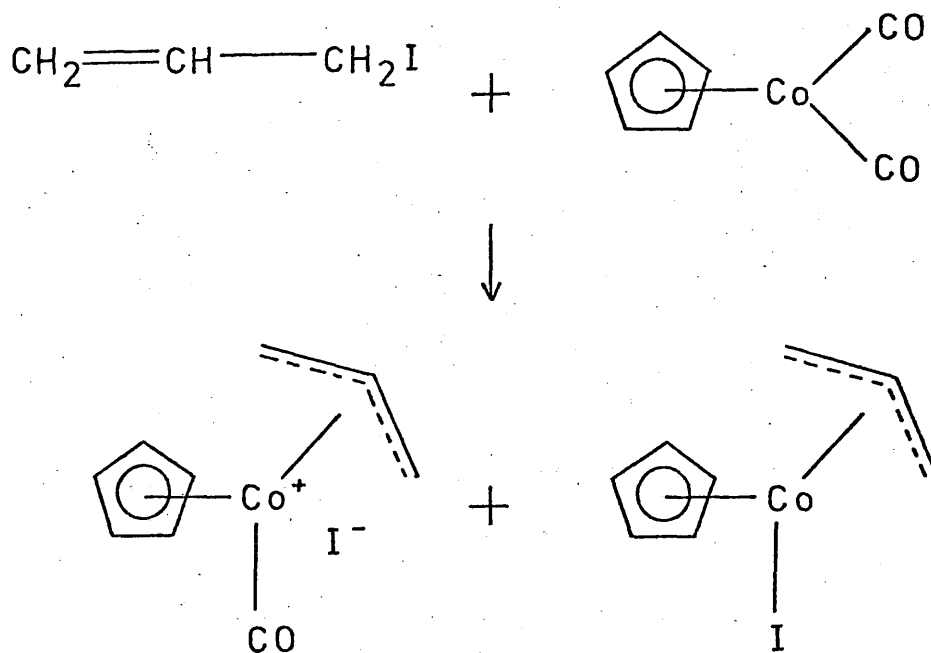
Confirmation for the proposed scheme has come with the isolation of hydridic intermediates²⁴ and more recent studies have prepared several η^3 -allylic neutral chlorocomplexes. Some of these eliminate hydrogen chloride to form η^4 -diene species²⁵ which are analogous to the unsubstituted η^5 -cyclopentadienyl η^4 -diene rhodium compounds.⁷

Neutral chlorocomplexes of the type $[\text{Rh}(\eta^5\text{-C}_5\text{R}_5)(\eta^3\text{-C}_3\text{H}_4\text{R})\text{Cl}]$ where R = H or Me have received considerable attention in the allyl chemistry of rhodium although the cationic species obtained from these have received relatively little mention. The salt $\eta^3\text{-allyl } \eta^5\text{-cyclopentadienyl pyridine rhodium tetraphenylborate}$ has already been mentioned¹² and the preparation involved the addition of a methanol solution of sodium tetraphenylborate to a hot solution of the chlorocomplex and pyridine in aqueous methanol when the product precipitated as yellow prisms in approximately 46% yield. However, a nmr spectrum was not reported, possibly because of a solubility problem. Cationic complexes of this type have also been isolated as by-products from the reaction of triphenylphosphine(carbonyl) $\eta^5\text{-cyclopentadienylrhodium}$ with allyl bromides and chlorides.²⁶ High yields of the "normal" products $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{Br}(\text{PPh}_3)(\text{COC}_3\text{H}_5)]$ and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)(\text{COC}_3\text{H}_5)]$ were obtained together with small yields (~2% for Br and 5% for Cl) of the cationic species. These latter products crystallised as bright yellow needles from the reaction mixture and were found to have no carbonyl stretching bands in the infra-red. They were formulated as cationic complexes from nmr and elemental analysis data and were considered to be produced by elimination of carbon monoxide from an ionic intermediate (Scheme 1.6). In a reference to unpublished results, the authors indicated that these cationic compounds may be better synthesised from the reaction of allyl halides with $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)\text{PPh}_3]$.



(Scheme 1.6)

Some analogous cobalt compounds have also been prepared; Fischer²⁷ has synthesised the η^5 -cyclopentadienyl η^3 -allyl cobalt carbonyl cationic complex as the hexafluorophosphate salt in 36% yield by reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ with allyl halides at 60° followed by precipitation of the salt from aqueous solution with ammonium hexafluorophosphate. Heck²⁸ improved upon this preparation by reacting the same reagents in purified tetrahydrofuran for several days and filtering off the resultant precipitate. With allyl iodide the covalent iodocomplex is also formed but in much lower yield ($\sim 10\%$) (Scheme 1.7). King²⁹ has also prepared an analogous



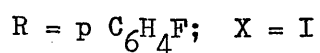
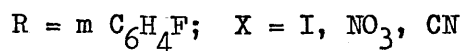
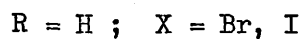
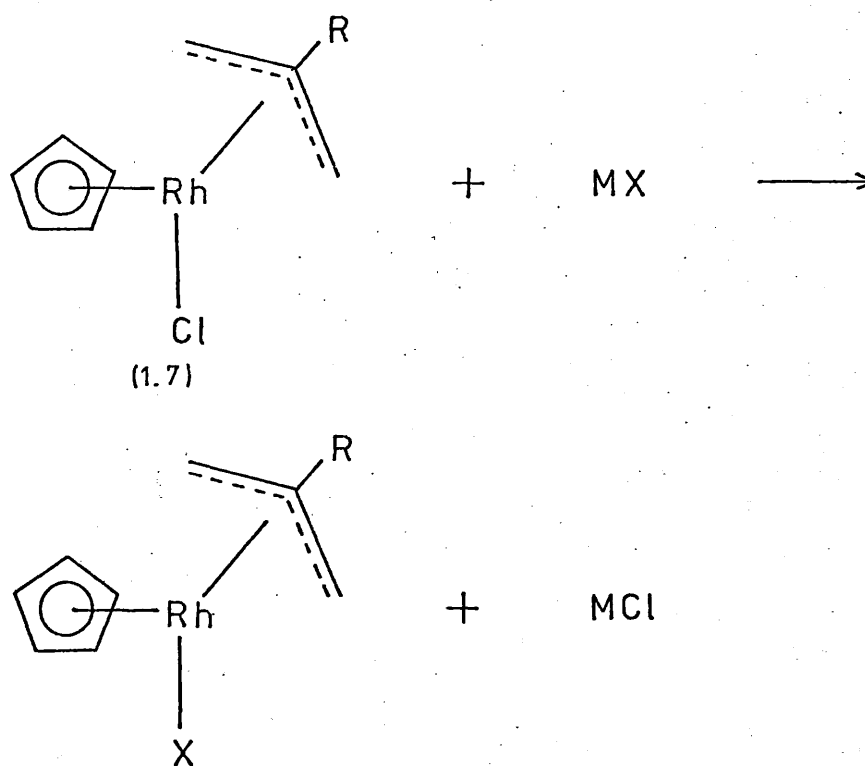
(Scheme 1.7)

pentamethylcyclopentadienylcobalt cationic complex utilising Heck's method but in this case the yield is lower.

This work reports improved preparations of the rhodium salts
 $[\text{Rh}(\eta^5\text{-C}_5\text{R}'_5)(\eta^3\text{-C}_3\text{H}_4\text{R})\text{L}]^+$ (R = 1-Me; R' = H, Me: and
R = 2-Me; R' = H) giving high yields together with a spectroscopic
characterisation using ^1H and ^{13}C nmr spectroscopy. Attempted
reactions of the complexes with sodium borohydride and methyl lithium
are described.

1.2 RESULTS AND DISCUSSION(a) Preparation and properties

Gubin et al.²⁰ have shown that when neutral chlorocomplexes of type (1.7) are treated with appropriate alkali-metal or silver salts in acetone or methanol, the chlorine ligand can be readily exchanged for other anionic groups (Scheme 1.8).

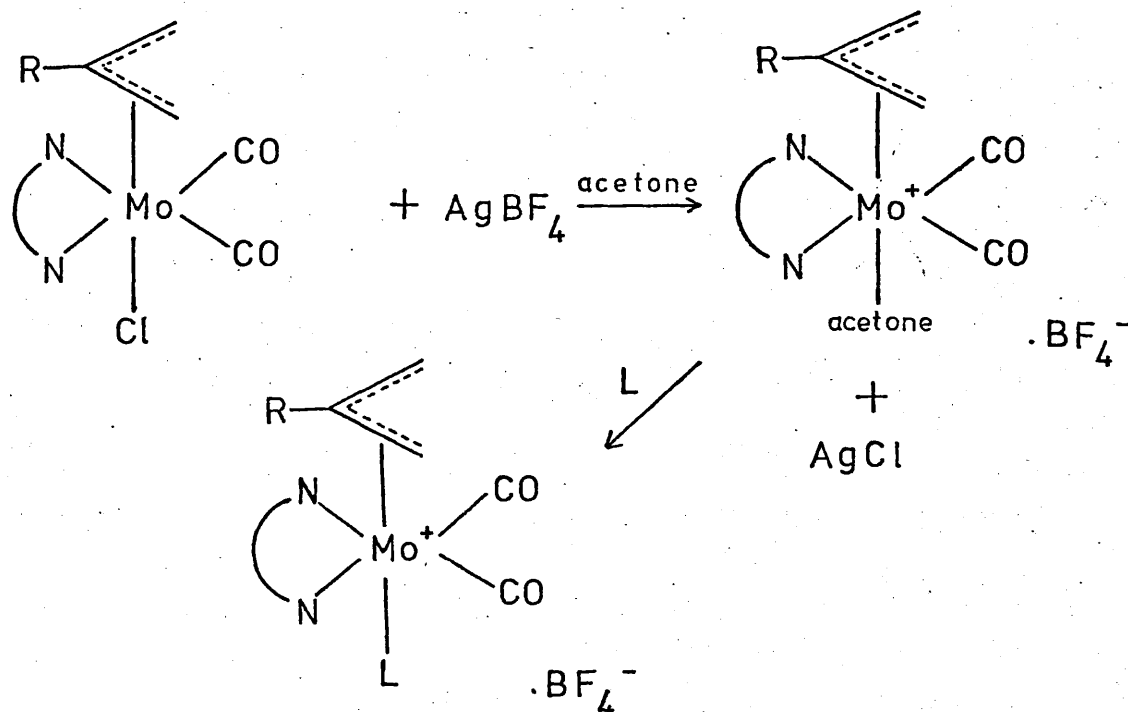


(Scheme 1.8)

A solution of the appropriate reagent was stirred with the chloro-complex at room temperature and the products were isolated after a suitable work-up involving dilution with water and extraction with

benzene. These are stable, crystalline materials characterised by their infra-red and fluorine-19 nmr spectra although these data are not reported and yields for the exchange reactions are not quoted.

The neutral chlorocomplexes also react with silver tetrafluoroborate in acetone giving an immediate precipitate of silver chloride which after filtration leaves a clear orange-red solution. This probably contains the acetone complex $[\text{Rh}(\eta^3\text{-C}_3\text{H}_4\text{R})(\eta^5\text{-C}_5\text{H}_5)\text{L}]^+\text{BF}_4^-$ where L is acetone although attempts to isolate this intermediate proved unsuccessful, a red oil remaining which could not be made to crystallise. However, an acetone intermediate has been isolated in the preparation of some η^3 -allyl 2,2'-bipyridyldicarbonylmolybdenum complexes by a similar route (Scheme 1.9).³⁰ Green and Parker, in their work with rhodium allyl complexes also postulated similar intermediates of the type $[\text{Rh}(\eta^3\text{-all})_2(\text{THF})_2]^+\text{BF}_4^-$ where tetrahydrofuran (THF) was the solvent used.¹⁷



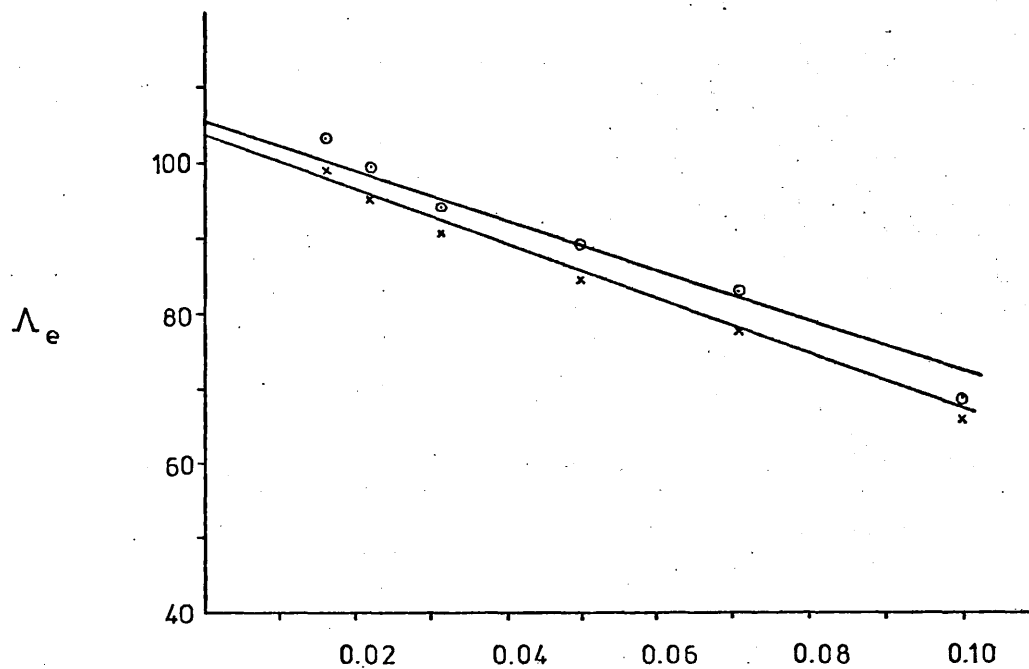
(Scheme 1.9)

When the solution containing the acetone complex is further treated with an equimolar solution of the appropriate ligand L (L = triphenylphosphine, triphenylarsine or pyridine) the coordinated acetone is displaced by the more strongly coordinating ligand and the cationic species can then be isolated in high yields by concentration under reduced pressure and precipitation with diethyl ether. The salts are yellow, crystalline solids characterised by their elemental analyses (Table 1.1), proton and carbon-13 nmr spectroscopy. With acetonitrile as ligand a yellow precipitate was formed which quickly turned darker on standing and it was not possible to isolate a pure product, even after reprecipitation. The salts are stable to air and moisture both as solids and in solution and are soluble in polar organic solvents.

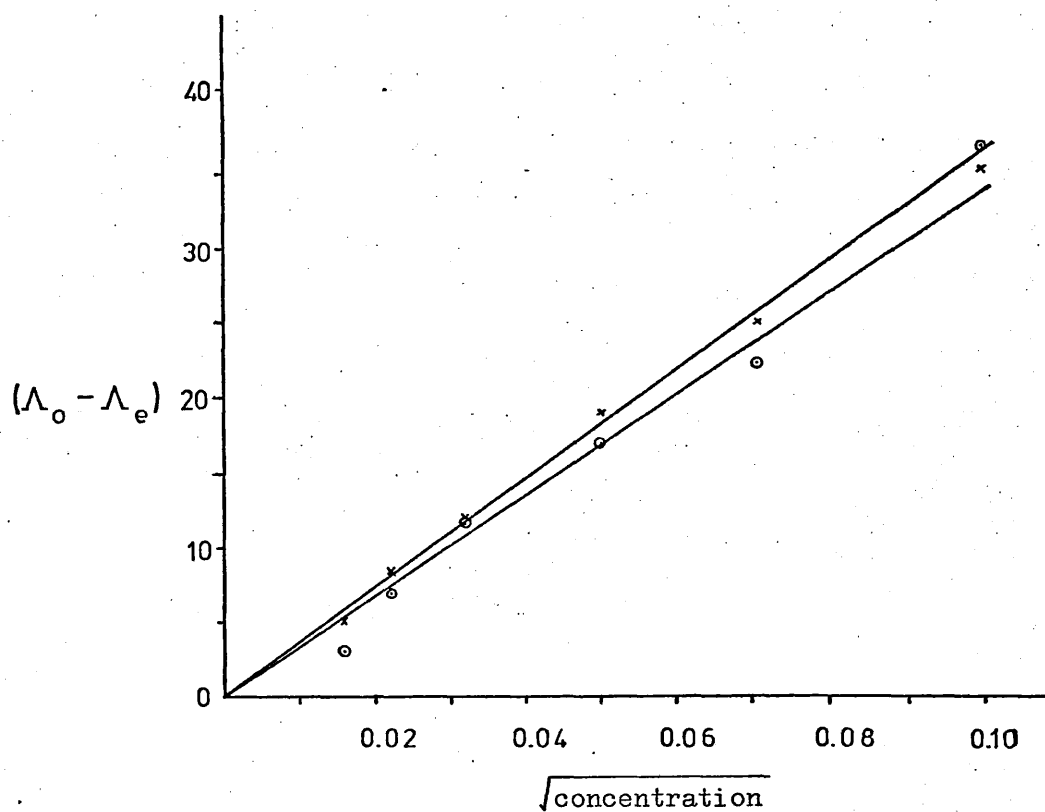
Electrical conductivities of several complexes were measured in methanol (Table 1.1) to confirm the assignment as 1:1 electrolytes, predicted from formulations and elemental analyses. Conductivity measurements were carried out for potassium chloride (known to be a 1:1 electrolyte in methanol)³¹ and complex (X) over a range of concentrations. Plots of equivalent conductivity against the square root of the concentration (P.21) were extrapolated to infinite dilution according to the method of Feltham and Hayter for non-aqueous solvents.³¹ From the plot of the conductivity at infinite dilution minus the conductivity at a known concentration, the slopes were found to be ~320 and ~350 for potassium chloride and the rhodium complex respectively. Literature values for 1:1 electrolyte in methanol are of the order 260-290 and 500-560 for 2:1 electrolytes. Although this agreement is not exceptional, it does indicate the

Complex	No.	Melting point	Analyses		Conductivity Λ^a
			Fd (Calc) (%)	Carbon Hydrogen	
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5\text{N})]^+\text{BF}_4^-$	II	152-4° dec	49.64 (49.70)	5.86 (5.93)	97
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{Me}_5)(\text{PPh}_3)]^+\text{BF}_4^-$	III	146-8° dec	59.63 (59.84)	6.02 (5.81)	
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{Me}_5)(\text{AsPh}_3)]^+\text{BF}_4^-$	IV	160-2° dec	55.98 (56.01)	5.54 (5.43)	90
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_5\text{N})]^+\text{BF}_4^-$	V	144-6° dec	43.47 (43.23)	4.30 (4.40)	
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{H}_5)(\text{PPh}_3)]^+\text{BF}_4^-$	VI	140-2° dec	58.12 (56.68)	4.71 (4.76)	
$[\text{Rh}(\text{1-methylallyl})(\text{C}_5\text{H}_5)(\text{AsPh}_3)]^+\text{BF}_4^-$	VII	168-70° dec	52.10 (52.63)	4.40 (4.42)	
$[\text{Rh}(\text{2-methylallyl})(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_5\text{N})]^+\text{BF}_4^-$	VIII	148-50° dec	43.17 (43.23)	4.48 (4.40)	99
$[\text{Rh}(\text{2-methylallyl})(\text{C}_5\text{H}_5)(\text{PPh}_3)]^+\text{BF}_4^-$	IX	152-4° dec	54.33 (56.68)	4.70 (4.76)	90
$[\text{Rh}(\text{2-methylallyl})(\text{C}_5\text{H}_5)(\text{AsPh}_3)]^+\text{BF}_4^-$	X	150-2° dec	52.32 (52.63)	4.19 (4.42)	91

TABLE 1.1 Analytical data for the rhodium complexes $[\text{Rh}(\text{C}_5\text{R}_5)(\text{C}_3\text{H}_4\text{R})\text{L}]^+\text{BF}_4^-$
(a) Equivalent conductivity (ohm^{-1}) in methanol (10^{-3}M complex). Calc. for KCl at 10^{-3}M , 97 ohm^{-1} .



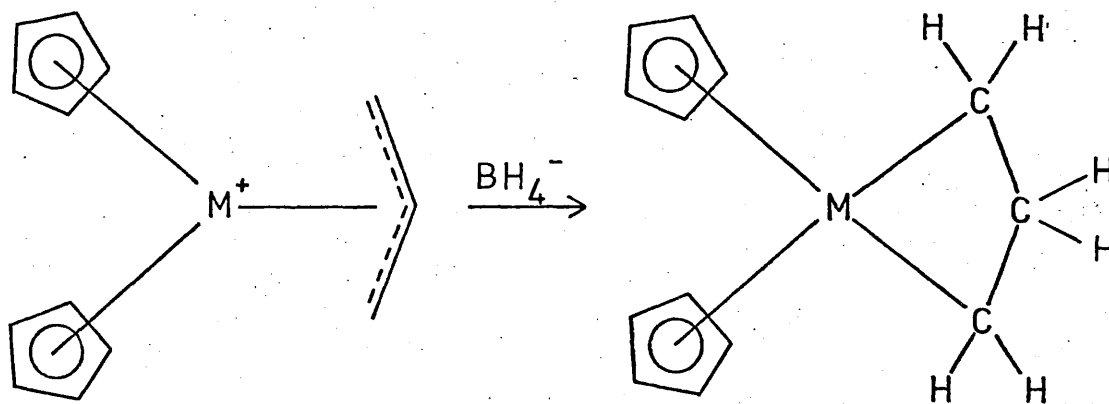
Plot of equivalent conductivity Λ_e v. $(\text{concentration})^{\frac{1}{2}}$ for KCl (○) and complex (×) x.



Plot of equivalent conductivity at infinite dilution minus equivalent conductivity $(\Lambda_0 - \Lambda_e)$ v. $(\text{concentration})^{\frac{1}{2}}$ for KCl (○) and complex (×).

correct formulation as 1:1 electrolytes. The range of concentrations that can be studied is limited by ion-association at high concentrations and inaccuracies in the measurement of low conductivities at low concentrations and this possibly accounts for the scatter in the plots. For several other compounds the conductivities were measured at $10^{-3}M$ concentration and the values were found to lie in the range 90-99 ohm^{-1} . Average values for the equivalent conductivity at $10^{-3}M$ in methanol at $25^{\circ}C$ are of the order 80-115 ohm^{-1} for 1:1 electrolytes and 160-220 ohm^{-1} for 2:1 electrolytes.³² This confirms the assignment of the salts as 1:1 electrolytes.

Attempted reduction of the η^3 -allylic cationic complexes to metal-olefin species with borohydride resulted in the deposition of metallic rhodium. Recently, Green and co-workers³³ have reported the formation of metallacyclobutane derivatives from the reaction of borohydride with the η^3 -allyl bis(η^5 -cyclopentadienyl) molybdenum and tungsten salts (Scheme 1.10). and similar types of complex may be formed



$M = Mo, W$

(Scheme 1.10)

with the rhodium salt which then decompose resulting in deposition of the metal. Preliminary experiments were also carried out with methyl lithium : a red solution was formed initially but this work has so far proved inconclusive.

(b) Characterisation using proton nmr spectroscopy

Nuclear magnetic resonance techniques have been extensively used to elucidate the structures of organic ligands in organometallic compounds. There have been several proton nmr studies of η^3 -allylic complexes of rhodium and some of the results have been discussed in section (1.1). Data for the neutral chlorocomplexes (Ia-Ic) are well documented but there are little available data for the cationic species; Powell and Shaw¹² did not report the spectrum of their isolated tetraphenylborate salt and Hart-Davis and Graham²⁶ reported data for $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)\text{PPh}_3]^+\text{Cl}^-$ only. This showed a sharp resonance at τ 4.32 ppm in deuterated dichloromethane typical of the η^5 -cyclopentadienyl ligand and broad resonances at τ 5.7 (d), 7.0(s) and 8.3(t) ppm which were assigned to the allylic protons. Small splittings by rhodium-103 (spin $\frac{1}{2}$ - 100% abundant) and phosphorus-31 (spin $\frac{1}{2}$ - 100% abundant) were observed on the cyclopentadienyl resonance. A downfield shift (0.4 - 0.6 ppm) of this peak relative to their neutral compounds $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{XPPh}_3(\text{COC}_3\text{H}_5)]$ X = Cl, Br, I was attributed to the presence of the positive charge. The spectrum of this salt, together with the neutral chlorocomplexes (Ia-c) and an analogous cobalt compound²⁹ are summarised in (Table 1.2) with assignments according to (1.7).

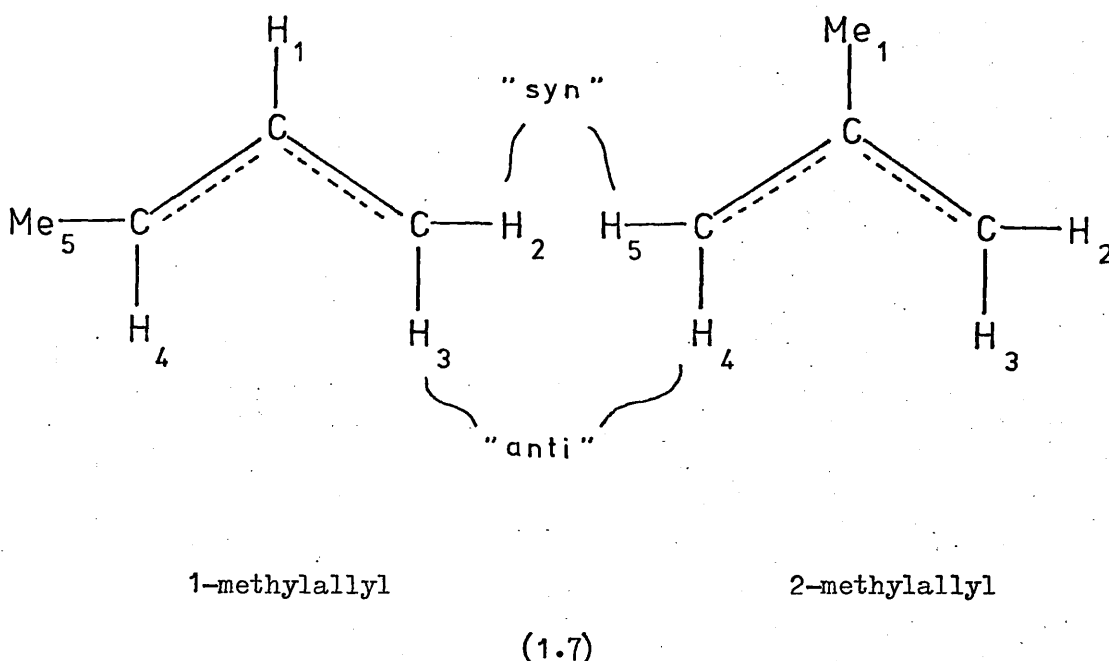
Spectroscopic data for the rhodium salts (II-X) are reported in (Table 1.3) and the spectra were recorded at 100 MHz in deuterated dichloromethane using a Varian Associates HA100 spectrometer. Chemical shifts are quoted in parts per million downfield from TMS*,

* TMS = tetramethylsilane

No.	Complex	H ₁	H ₂	H ₃	H ₄	H ₅ ,Me	Cp	C ₅ Me ₅
Ia	[Rh(1-methylallyl)(C ₅ Me ₅)Cl]	6.04(m) 11, 6.6 Rh 2.2	6.72(d) 6.6	7.12(d) 11	6.42(ddd) 6.2, 11	8.36(d) 6.2		8.27(s)
Ib	[Rh(1-methylallyl)(C ₅ H ₅)Cl]	5.09(m)	5.57(d) 6.5	7.39(d) 11.5	6.22(m) 9	8.17(d)	4.62	
Ic	[Rh(2-methylallyl)(C ₅ H ₅)Cl]	5.37(d) Rh 0.5	7.15(d) Rh 0.2				4.63	
-	[Rh(allyl)(C ₅ H ₅)PPh ₃] ⁺ Cl ⁻	5.70(d)	7.0(s)	8.3(t)			4.32	
-	[Co(allyl)(C ₅ Me ₅)CO] ⁺ PF ₆ ⁻	5.41(tt) 6, 12	6.49(d) 6	7.44(t) 12				8.02(s)

TABLE 1.2 Proton nmr shifts for Ia-c and related complexes. Chemical shifts in ppm from TMS =10 ppm. Coupling constants (where given) in Hz. (a) 100 MHz CDCl₃ ref. 23 (b) 60 MHz CDCl₃ refs. 12, 19 (c) 100 MHz CD₂Cl₂ ref. 26 (d) 100 MHz (CD₃)₂CO ref. 29.

internal reference ($\tau = 10$ ppm) and the numbering of each proton is again based on (1.7); coupling constants are measured in hertz. The spectra are typical of η^3 -allyl compounds with the "anti" protons resonating to high field of the "syn" protons which in turn resonate upfield from the proton on the central carbon atom. The 2-methylallyl



complexes exhibit typical A_2M_2X spectra with equivalence of the "syn" protons H_2 and H_5 and also equivalence of the "anti" protons H_3 and H_4 . No indication of an A_4X spectrum was observed which would result from equivalence of all these protons. These spectra are typical of a symmetrically bonded η^3 -2-methylallyl ligand and this was confirmed from the carbon-13 nmr spectra which showed equivalence of the terminal carbon resonances.

Complex	Proton nmr shifts relative to TMS ($\tau = 10$)							Coupling constants (Hz)				
	H ₁	H ₂	H ₃	H ₄	Me	C ₅ Me ₅	C ₅ H ₅	Others	1,2	1,3	1,4	4-Me
II	5.87(m)	6.42(d)	7.83(d)	7.27(m)	8.27(d)	8.43(s)	Pyridine	1.52(d) 2.53(t)	7	11	11	7
III	6.03(m)	7.01(d)	8.12(d)	7.48(m)	8.42(d)	8.48(s)	PPh ₃	2.5(br)	7	12	11	6
IV	6.04(m)	7.04(d)	8.12(d)	7.45(m)	8.43(d)	8.45(s)	AsPh ₃	2.6(br)	7	11	11	7
V	4.65(m)	5.14(d)	7.95(d)	6.80(m)	7.83(d)		4.35(s) Pyridine	1.08(d) 2.34(t)	7	11	11	7
VI	4.78(m)	5.94(d)	8.47(d)	7.36(m)	8.16(d)		4.63(s) PPh ₃	2.5(br)	7	11	11	7
VII	4.78(m)	5.95(d)	8.36(d)	7.20(m)	8.15(d)		4.53(s) AsPh ₃	2.5(br)	6.5	11	10.5	6.5
VIII	5.20(s)	7.92(s)			8.07(s)		4.62(s) Pyridine	1.42(d) 2.67(t)				
IX	5.94(s)	8.47(s)			7.93(s)		4.80(s) PPh ₃	2.5(br)				
X	5.83(s)	8.17(s)			7.83(s)		4.57(s) AsPh ₃	2.5(br)				

TABLE 1.3 Proton nmr shifts and coupling constants of cationic η^3 -allylic complexes. For numbering see Table 1.1. All data in CD₂Cl₂ at 100 MHz. Shifts in ppm from TMS ($\tau = 10$).

Substitution of pyridine by triphenylphosphine or triphenylarsine resulted in a shift to higher field of all the allylic resonances which can be attributed to an increase in electron density experienced by this ligand as a result of steric compression and ring orientation effects from the incoming bulky phosphine groupings. Chemical shifts of the triphenylphosphine and triphenylarsine complexes were similar with only minor variations. With the 1-methylallyl salts, replacement of the η^5 -cyclopentadienyl unit by the η^5 -pentamethylcyclopentadienyl ligand resulted in a considerable upfield shift (> 1 ppm) of the resonance of the "syn" proton H_2 and the proton on the central carbon atom H_1 and a similar, although smaller, effect is experienced by the allylic methyl group and the "anti" proton H_4 (~ 0.3 ppm). However, the other "anti" proton H_3 experiences these effects in a different manner and has a small, but observable, shift to lower field (~ 0.2 ppm). This could arise from distortion of the η^3 -allyl group with a movement from planarity which would send H_3 away from, and H_2 closer to the remainder of the molecule. Similar effects are also found with the neutral chlorocomplexes (I a,b) and in the carbon-13 nmr spectra of these molecules.

Little change is observed in the spectra of the chlorocomplexes when they are compared with their respective salts other than the expected shifts to higher field resulting from coordination of the bulky phosphines. The resonance of the allylic methyl group in (VII) was partially obscured by the pentamethylcyclopentadienyl resonance. No evidence was found for a downfield shift for any of the salt resonances indicative of the positive charge localised on any particular ligand and it must be concluded that this charge resides largely on the

metal. The observed chemical shifts for the similar cobalt cationic complex prepared by King et al.²⁹ are not dissimilar from those of the pentamethylcyclopentadienyl species described here.

Replacement of the incoming ligand L or the change from a neutral to cationic species seems to have little effect upon the magnitude of the vicinal proton coupling constants and these values are typical for an η^3 -bonded allyl group with the "trans" values (10-12 Hz) e.g. H_1-H_3 slightly larger than the "cis" values (6 - 8 Hz), e.g. H_1-H_2 . Other groups^{7,12,26} have observed small rhodium couplings (~0.9 Hz) to the cyclopentadienyl group and also to some of the allyl resonances. Absence of this coupling, in the salts (II-X) is considered to be due to poor spectrometer resolution, a slight broadening being observed. Indeed, these couplings have been observed in the complexes described in Chapter 2 and further studies with improved resolution have shown a small rhodium coupling (~1 Hz) to the cyclopentadienyl protons in the salts.

(c) Carbon-13 nmr studies

With the advent of commercial Fourier transform instruments, natural abundance carbon-13 nmr spectroscopy has become a routine technique in the study and characterisation of organotransition-metal complexes. However, interpretation of the chemical shifts has proved difficult because the shielding is governed by several parameters. Indeed, Evans and Norton³⁴ have concluded, in agreement with Lauterbur and King,³⁵ that it is still not possible to account for the shifts within the current theories of shielding frameworks. Carbon-13 nmr chemical shifts are considered to be dominated by the sum of three terms³⁶: the diamagnetic contribution σ_d ; the paramagnetic contribution σ_p and the contribution from neighbouring nuclei. It is thought that the paramagnetic shielding term is a major contributor to the upfield shift of organic ligands coordinated to a transition-metal centre³⁷ although the other contributions must be taken into account because of the vicinity of the electron-rich metal atom.

Thus the chemical shifts of the coordinated organic groups seem to have only limited application in describing metal to ligand bonding. However, the magnitude of the M-¹³C (M = metal) coupling constant can provide information although the oxidation state of the metal and its stereochemistry must be accounted for.³⁶ The coupling constant is dependent upon the Fermi contact term which is transmitted through the "s" contribution to the bond and hence reflects the degree of "s" character.

Chemical shifts and coupling constants for the η^3 -allyl complexes (I-X) are reported in Table 1.4. The spectra were recorded in deuterated nitromethane at a concentration of approximately 0.25 mmol in 0.5 cm³ of solvent and the deuterated solvent was employed to enable the spectrometer

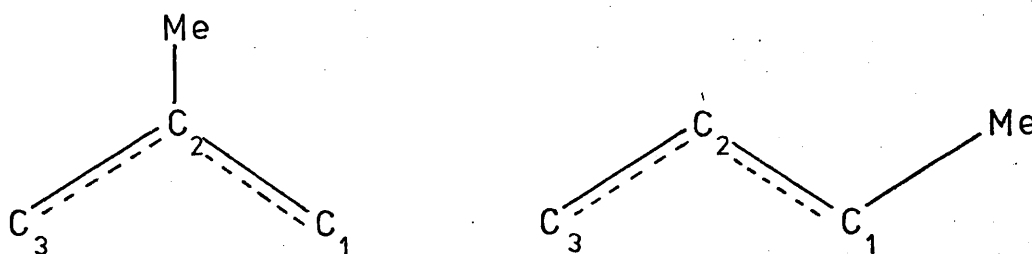
to be locked to the deuterium resonant frequency. These solutions also contained a small amount of TMS as an internal reference and all chemical shifts were recorded in parts per million downfield relative to TMS. Originally, carbon-13 nmr shifts were referred to standards like carbon disulphide or benzene but are now usually quoted relative to TMS, as are protons. The carbon-13 nmr resonant frequencies for each complex were determined by broad-band decoupling; this procedure destroys the $^{13}\text{C}-^1\text{H}$ spin-spin couplings giving rise to a single absorption frequency for each carbon atom, except where it is split by coupling to the rhodium nucleus, hence simplifying the spectrum. Splitting of the resonances due to $^{13}\text{C}-^{13}\text{C}$ spin-spin couplings are not observed in the natural abundance spectra due to the low abundance of the carbon-13 isotope. Proton decoupling also gives rise to an enhancement of the signal intensities by application of the Nuclear Overhauser Effect³⁸ enabling data acquisition in a shorter time, although this does have the disadvantage in that the intensities of the signals are no longer proportional to the number of carbon atoms resonating at a particular frequency. The proton coupled spectrum of (VII) was also obtained to enable measurement of the $^{13}\text{C}-^1\text{H}$ coupling constants for the coordinated ligands. The rhodium-103 nucleus (spin $I = \frac{1}{2}$) occurs in 100% natural abundance and this results in a splitting of all the resonances of the carbon atoms directly bonded to it i.e. η^3 -allyl and η^5 -cyclopentadienyl carbons in this work.

The observed chemical shifts for the η^3 -allyl carbons are typical of those found upon complexation to a transition-metal with the central carbon atom resonating to low field of the terminal carbons^{39,40} (for assignment see 1.8). These shifts can be interpreted as an average of

^{13}C nmr shifts relative to TMS, internal reference 0 ppm									
Complex	C_1	C_2	C_3	Methyl	Cp C atoms	Methyls on Cp ring	Ligand		
Ia	73.1(d) J 9	96.6(d) J 6	58.5(d) J 10	18.0	98.9(d) J 6	9.5			
II	77.3(d) J 9	98.6(d) J 4	60.5(d) J 12	17.8	100.6(d) J 6	9.2	156.8 $\text{C}_{2,6}$:140.6 C_4		
III	71.3(d) J 9	92.4(d) J 6	52.9(d) J 12	17.5	103.9(d) J 4	9.6	128.3 $\text{C}_{3,5}$		
IV	70.7(d) J 9	92.5(d) J 6	51.5(d) J 10	17.6	102.9(d) J 4	9.8	136.1(d) J 10: 132.5(s) C_4		
Ib	81.8(d) J 9	88.3(d) J 6	51.4(d) J 10	22.0	88.3(d) J 6		131.8(s) C_1 :130.1(d) J 10		
VI	76.5(d) J 9	84.6(d) J 4	48.1(d) J 10	22.5	93.9(d) J 4		135.2 $\text{C}_{2,6}$:132.3 C_4		
VII	75.2(d) J 10	84.6(d) J 6	46.8(d) J 10	22.3	91.9(d) J 4		131.9 C_1 :130.8 $\text{C}_{3,5}$		
Io	59.1(d) J 10	107.9(d) J 6	59.1(d) J 10	25.2	88.6(d) J 6		135.8(d) $\text{C}_{2,6}$ J 10		
VIII	60.1(d) J 10	111.8(d) J 6	60.1(d) J 10	25.5	90.1(d) J 4		132.9(s) C_4 : 130.3(d) $\text{C}_{3,5}$		
IX	51.8(d) J 10	108.2(d) J 6	51.8(d) J 10	26.6	94.4(d) J 4		134.7 $\text{C}_{2,6}$: 133.1 C_1		
X	48.7(d) J 10	105.7(d) J 6	48.7(d) J 10	24.0	90.5(d) J 6		132.5 C_4 : 130.8 $\text{C}_{3,5}$		
							158.6 $\text{C}_{2,6}$: 140.6 C_4		
							127.6 $\text{C}_{3,5}$		
							135.8(d) J 10 133.4 C_1		
							130.2(d) J 10 133.0 C_4		
							132.8 $\text{C}_{2,6}$ 130.6 C_1		
							129.5 C_4 128.6 $\text{C}_{3,5}$		

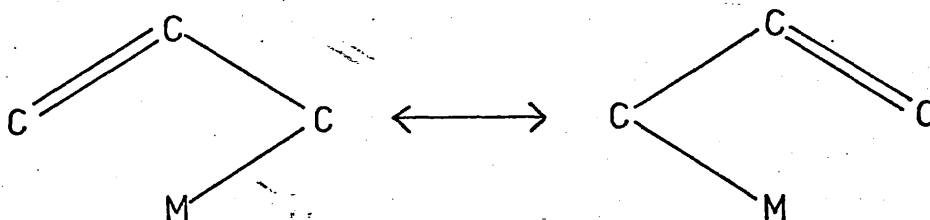
TABLE 1.4 ^{13}C nmr shifts of complexes I - X. For numbering see table 1.1. All data in CD_3NO_2 at 22.63 MHz. Coupling constants J ($^{103}\text{Rh} - ^{13}\text{C}$) in Hz.

the two canonical forms (1.9) with the shifts of the terminal carbons considered to be an average of the value for a carbon-metal " σ " bond and



(1.8)

the free olefin.⁴¹ However, it must be stressed that this is only a qualitative representation and does not include all the contributing factors. The presence of the methyl group on C_1 deshields this carbon



(1.9)

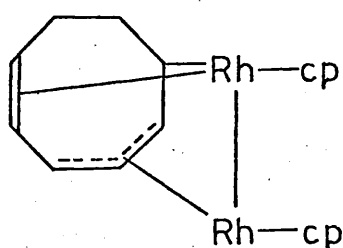
relative to the other terminal carbon atom in the 1-methylallyl compounds and similarly in the 2-methylallyl species the central carbon atom is deshielded relative to C_2 in the 1-methylallyl case. This effect is analogous to the " α "-effect observed in successive methyl substitution in a series of organic aliphatic and olefinic species.^{36,42}

Previous work has indicated that carbon chemical shifts in organotransition-metal complexes are rather insensitive to the formal charge on the complex^{43,44} and conversion of the neutral chloro-complexes (Ia-c) into the cationic species has little effect on either the η^3 -allyl or η^5 -cyclopentadienyl resonances. Substitution of pyridine by triphenylphosphine or triphenylarsine results in an upfield shift of the η^3 -allyl carbons although the methyl group, not directly bonded to the metal remains unaffected. This probably reflects greater contributions from the diamagnetic term σ_d which is dependent upon the electron density at the nucleus under consideration and also changes in neighbouring group and orientation effects when the multi-ring systems are introduced.

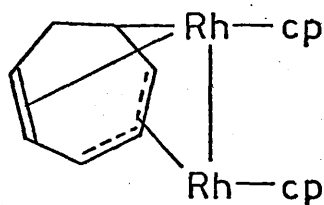
Substitution of the cyclopentadienyl ring by the pentamethyl-cyclopentadienyl ring system results in an expected downfield shift of the ring carbons due to the presence of the methyl groups but the effect on the allyl group is unexpected. Carbons C_2 and C_3 are shifted to lower field while the resonances of C_1 and the methyl group experience upfield shifts. Similar unexpected results were also obtained from the proton spectra when different protons on the same carbon atom were shifted in different directions. This could be due to steric compression effects resulting from the addition of the five methyl groups which may cause deviations from planarity in the allyl systems or could reflect possible changes in the contributions from neighbouring nuclei. No change is found in the $^{103}\text{Rh}-^{13}\text{C}$ coupling constants which would be expected to reflect a change in rehybridisation of these carbon atoms. It is concluded that there appears to be no simple explanation to account for this phenomenon.

In the 2-methylallyl salts the two terminal carbon atoms resonate at the same frequency indicative of a symmetrically bonded allyl group and this is in agreement with the proton nmr data. Here also the replacement of pyridine by the bulky phosphine ligands with their steric and ring current effects results in upfield shifts of the allyl resonances.

^{103}Rh - ^{13}C coupling constants for the cyclopentadienyl group were found to be small, but observable, (4-6 Hz) in agreement with those reported by other workers.^{45,46} Coupling constants for the η^3 -allyl group were found to lie in the range 9-12 Hz for the terminal carbons and 4-6Hz for the central carbon. These also are in good agreement with the results of Lewis et al. for the species shown in (1.10). Values here are 7-10 Hz and 6-7 Hz for the terminal and central carbons respectively. Coupling constants for the olefin-rhodium complexes $[\text{Rh } \eta(1-2) \eta(5-6)\text{COD} (\eta^5\text{-C}_5\text{H}_5)]$ and $[\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2(\eta^5\text{-C}_5\text{H}_5)]$ are 14 and 10 Hz respectively and these are considered to be π -bonded



(a)

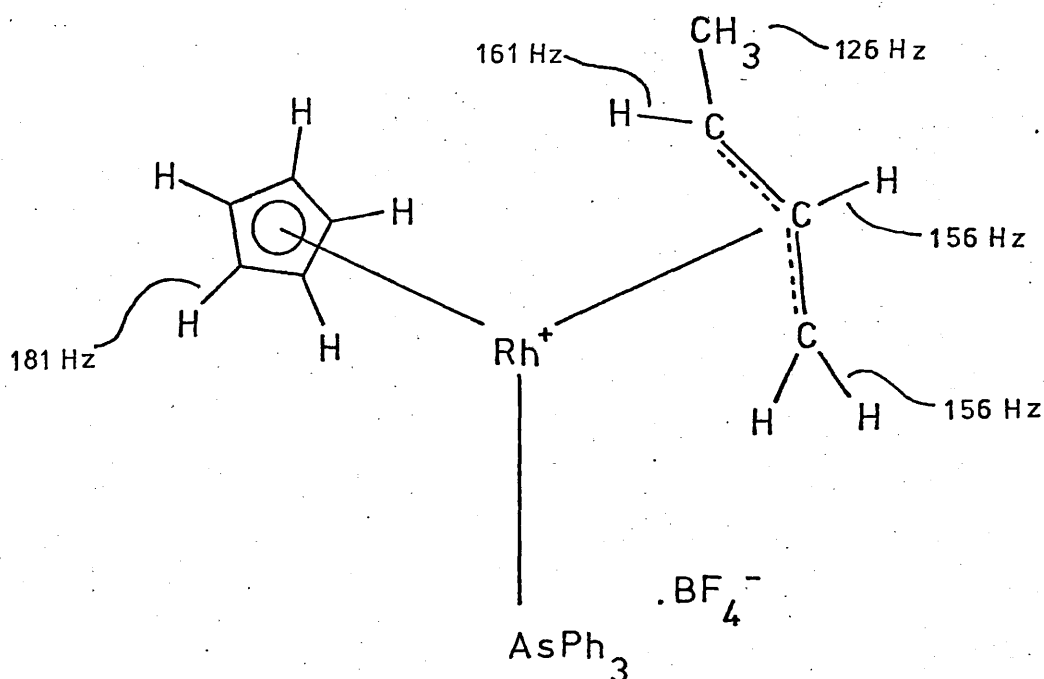


(b)

(1.10)

carbons.⁴⁷ Carbons which are " σ "-bonded to rhodium tend to be higher 47
 - viz. 19 Hz (for 1.10 a and b) and 26 Hz for $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-allyl})(\eta^3\text{-allyl})]$
 Thus, in general, the smaller the ^{103}Rh - ^{13}C coupling constant the greater the
 π -character in the bond: further discussion of rhodium-olefin compounds is
 continued in Chapter 2.

Resonances observed for the pyridine ligand were assigned following the work of Bancroft et al.⁴⁸ and those of triphenylphosphine and triphenylarsine after Gansow and Kimura.⁴⁹ Magnitudes of the ^{13}C - ^1H coupling constants for (VII) (see 1.11) were determined from the proton coupled spectrum. The values for the allyl group vary from 156-161 Hz and this is in accord with sp^2 rather than sp^3 hybridisation of the carbon atoms and the value of 126 Hz for the methyl group is typical of sp^3 hybridisation. A value of 181 Hz was found for the cyclopentadienyl ligand and is also similar to literature values, indicating hybridisation somewhere between sp^2 and sp .^{39,40}



For comparison the analogous ^{13}C - ^1H coupling constants in ethane, ethylene and acetylene are 125, 156 and 248 Hz respectively.³⁶

1.3 EXPERIMENTAL

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. The neutral pentamethylcyclopentadienyl chlorocomplex was prepared by the method of Maitlis et al.²³ and the unsubstituted cyclopentadienyl compounds were synthesised according to the methods of Powell and Shaw.^{12,19}

General method of preparation of the cationic complexes(II-X)

The neutral chlorocomplex (1 mmol) was dissolved in acetone (20 cm³) and a solution of silver tetrafluoroborate (1 mmol) in acetone (5-10 cm³) added with stirring. After ten minutes the precipitated silver chloride was filtered off leaving a clear orange-red solution and a solution of the ligand (1 mmol) in acetone (10 cm³) added to the filtrate. The resultant yellow-orange solution was stirred for thirty minutes and then concentrated by evaporation under reduced pressure. The salt was precipitated by dropwise addition of the concentrate to stirred dry diethyl ether (~50 cm³). Purification was achieved by dissolving the product in a small quantity of acetone, filtering if necessary and reprecipitating with ether. Yields were of the order 70-75%.

Instrumentation

Proton nmr spectra were recorded at 100 MHz in deuterated methylene chloride solution using a Varian HA100 spectrometer with TMS as internal reference. Carbon-13 nmr were obtained at PCMU (Harwell) in deuterated nitromethane at 22.63 MHz using a Bruker HX-90E spectrometer operating

in the Fourier transform mode. TMS was again used as an internal reference. Electrical conductivities were measured at 25°C using a Pye Unicam E7566/4 conductivity bridge at 10^{-3} M concentration in methanol (BDH Analar).

Other reactions

(i) Attempted isolation of the acetone intermediate

A solution of silver tetrafluoroborate (1 mmol) in acetone (5-10 cm³) was added to a stirred solution of the chlorocomplex (1 mmol) in acetone (20 cm³). After stirring for 10 minutes the precipitated silver chloride was filtered off and the resultant filtrate evaporated in vacuo to small volume. Dropwise addition to stirred dry diethyl ether resulted in the formation of a red oil which failed to crystallise after being left under pentane at low temperatures for several days. Attempts to remove all the acetone solvent also left a reddish-black oily residue which would not crystallise. Nmr data for this oil could not be obtained due to decomposition in solution.

(ii) The acetonitrile complex

The general procedure for the preparation of the cationic complexes was followed. On precipitation with ether a yellow solid was formed which quickly turned darker in colour and could not be purified by reprecipitation. Attempts to prepare this salt using acetonitrile as solvent also proved unsuccessful.

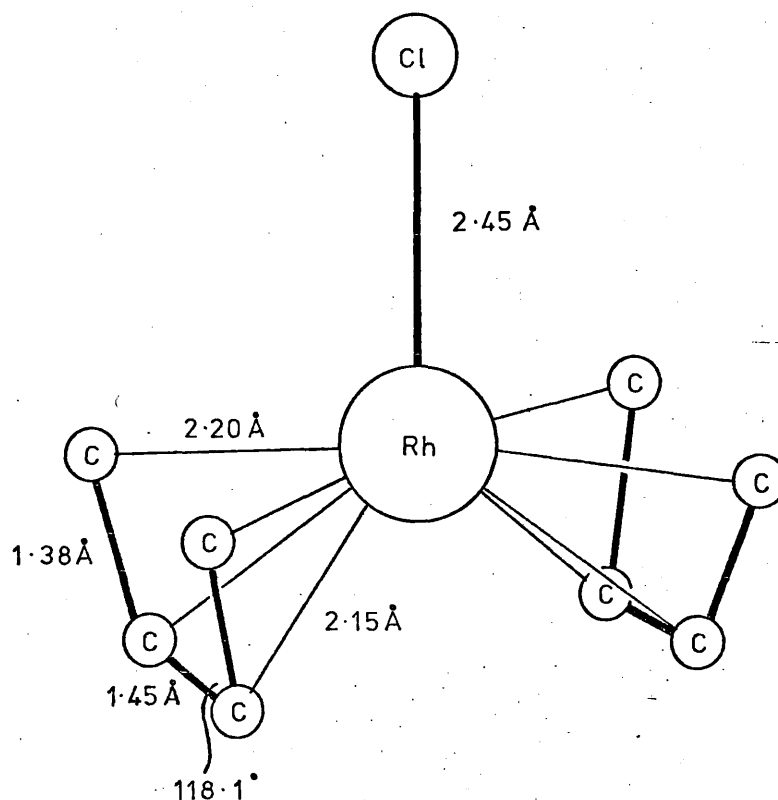
CHAPTER TWO η^4 -DIENE COMPLEXES OF RHODIUM AND IRIIDIUM

CHAPTER 2

 η^4 -DIENE CHEMISTRY OF RHODIUM AND IRIDIUM2.1 INTRODUCTION

There has been considerable interest in the coordination of di-olefins to rhodium and iridium since Chatt and Venanzi synthesised di- μ -chlorobis $\eta(1-2) \eta(5-6)$ cyclooctadiene dirhodium in 1956.¹ Wilkinson and co-workers extended these studies and found that rhodium (III) chloride in ethanol was particularly reactive towards chelating di-olefins.³ Robinson and Shaw later found that 1,5 cyclooctadiene reacted with chloroiridous acid in boiling ethanol to give a complex of formula $[\text{Ir H Cl}_2 (\eta(1-2) \eta(5-6) \text{COD})_x]$ (x probably equals 2) in high yield.⁵⁰ This reacted further with sodium cyclopentadienide to yield $[\text{Ir } \eta(1-2) \eta(5-6) \text{COD} (\eta^5\text{-C}_5\text{H}_5)]$, analogous to the rhodium complex prepared by Chatt. Reactions with conjugated dienes were not reported although $[\text{Rh} (\eta^4\text{-cyclopentadiene}) (\eta^5\text{-C}_5\text{H}_5)]$ had been earlier synthesised by reduction of bis ($\eta^5\text{-cyclopentadienyl}$) rhodium chloride with borohydride.⁵¹ By analogy with the chelating di-olefinic complexes the cyclopentadiene ligand was assumed to provide four bonding electrons to the metal.

Porri et al. found that rhodium (III) chloride reacted with butadiene in ethanol at -5°C to give a mononuclear species chlorobis η^4 -butadiene rhodium (2.1).⁵² X-ray analysis of this complex revealed a square pyramidal structure with two equally bonded butadiene groups, the centres of the four C-C double bonds constituting the basal plane and the chlorine atom in the apical position.⁵² An alternative method of preparation was found by displacement of the coordinated cyclooctene from the species $[\text{Rh} (\eta^2\text{-C}_8\text{H}_{14})_2 \text{Cl}]_x$.

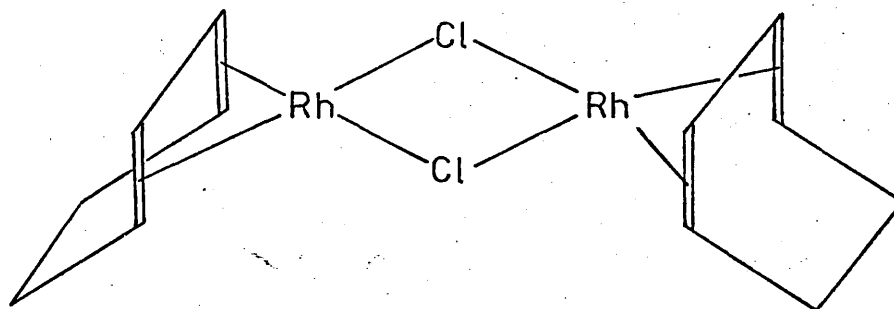


(2.1)

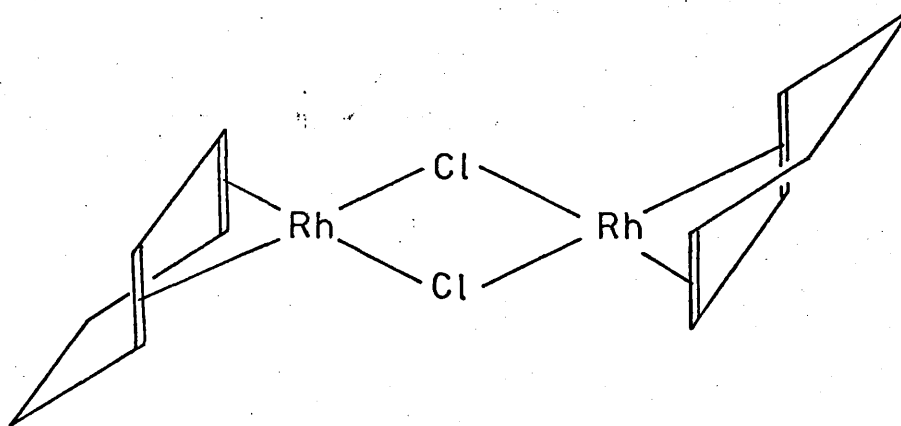
This complex is believed to be dimeric and have a structure analogous to the tetraethylene complex described by Cramer,⁶ although it was found to be too insoluble for molecular weight determinations.⁵³

These measurements have, however, shown the more soluble, analogous iridium complex to be dimeric. The rhodium compound has proved to be a useful precursor to several complexes containing conjugated dienes, including those with functional groups, a particular example being $[\text{Rh}(\eta^4\text{-methylhexa 2,4 dienoate})_2 \text{Cl}]$.⁵⁴ Isoprene and 2,3 dimethylbutadiene displaced only one of the coordinated cyclooctene molecules per rhodium atom giving mixed compounds of the

type $[\text{Rh}(\eta^2\text{-C}_8\text{H}_{14})(\eta^4\text{-diene})\text{Cl}]$. Complexes containing two molecules of these dienes per metal atom could be synthesised by displacement of butadiene from $[\text{Rh}(\eta^4\text{-butadiene})_2\text{Cl}]$ in the boiling diolefin. All the novel complexes described were assumed to have structures analogous to (2.1) although later work has shown that some are dimeric with bridging chlorine atoms.⁷ Winkhaus and Singer then observed a reaction between ethanolic rhodium (III) chloride and cyclohexa 1,3 diene resulting in the formation of the dimeric species $[\text{Rh}(\eta^4\text{-C}_6\text{H}_8)\text{Cl}]_2$.⁵⁵ This was thought to exist in both a "cis" and "trans" form (2.2) the difference lying in the coordination of the cyclic di-olefin. They also confirmed the reactivity of rhodium (III)



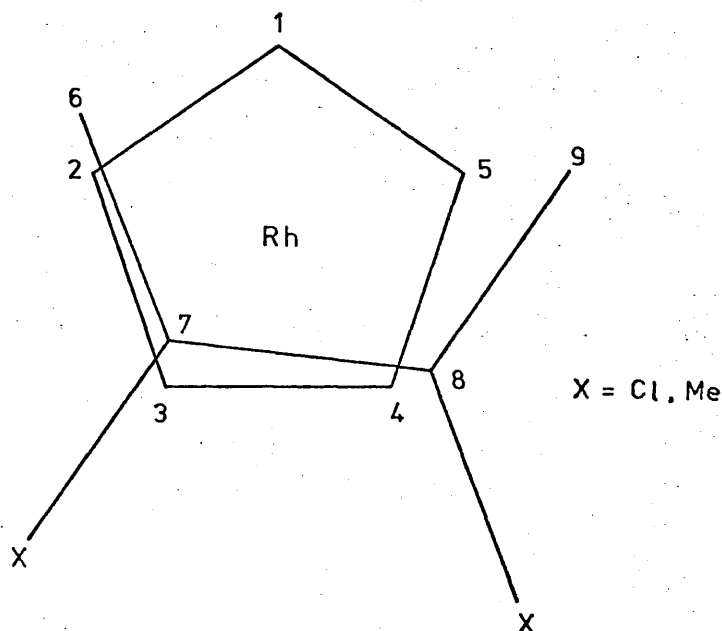
"cis"

"trans"
(2.2)

chloride in ethanol towards chelating di-olefins, but attempted coordination of acyclic conjugated dienes proved unsuccessful, often resulting in the deposition of metallic rhodium. Coordination of mono-olefins was achieved with cycloheptene, cyclooctene and norbornene giving species of the type $[\text{Rh}(\eta^2\text{-olefin})_2\text{Cl}]_2$.⁵⁶ The same authors also synthesised $[\text{Ir} \eta(1-2) \eta(5-6)\text{CODClH}]_x$ through refluxing sodium hexachloroiridate with 1,5 COD in aqueous methanol; this could be converted into the $[\text{Ir} \eta(1-2)\eta(5-6)\text{COD Cl}]_2$ complex by warming with sodium bicarbonate in ethanol. Complexes of iridium with the conjugated dienes, cyclohexa 1,3 diene and 2,3 dimethylbutadiene were also prepared by a method analogous to that for $[\text{Ir} \eta(1-2) \eta(5-6)\text{COD Cl}]_2$. The monoolefins cycloheptene and cyclooctene reacted with chloroiridous acid in aqueous ethanol to give the species $[\text{Ir} (\eta^2\text{-olefin})_3\text{CO Cl}]$ and the cyclooctene complex was shown to lose the olefin reversibly to form the dimer $[\text{Ir} (\eta^2\text{-C}_8\text{H}_{14})_2\text{CO Cl}]_2$.

Another method for coordinating conjugated di-olefins to rhodium involves the displacement of ethylene from Cramer's compound $[\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2\text{Cl}]_2$.⁷ A series of acyclic di-olefinic complexes was synthesised by refluxing an excess of the appropriate diene with the bisethylene dimer and the products usually precipitated out after filtration and concentration. These were either dimeric $[\text{Rh}(\eta^4\text{-diene})\text{Cl}]_2$ or monomeric $[\text{Rh}(\eta^4\text{-diene})_2\text{Cl}]$ species although with 4-methylpenta 1,3 diene a compound of stoichiometry $[\text{Rh}(\eta^4\text{-diene})_2\text{Cl}]_2$ was isolated. The reason why one type of complex is formed and not another is not understood and could not be explained from the nature of the substituents. The dimers were assumed to have the same structure as Cramer's complex with a bidentate diene replacing

the two ethylene molecules. Similarly, the monomeric compounds were assumed to have a structure analogous to bis η^4 -butadiene chlororhodium. The 4-methyl penta 1,3 diene complex was considered from proton nmr spectroscopy and I.R. data to contain monodentate diene, the I.R. data showing a strong band at $\sim 1650 \text{ cm}^{-1}$ characteristic for uncoordinated olefinic ligands. This structure was later confirmed by x-ray analysis.⁵⁷ Reaction of these chlorocomplexes with cyclopentadienyl thallium or thallos acetylacetonate gave rise to mononuclear species containing only one molecule of coordinated diene per rhodium atom with the exception of the 4-methylpenta 1,3 diene complex which again had two monodentate dienes in the species $[\text{Rh}(\text{acac})^*(\eta^2\text{-4-methyl penta 1,3 diene})_2]$. X-ray structures were determined for two of the cyclopentadienyl compounds; those with 2,3 dimethylbutadiene and 2,3 dichlorobutadiene.⁵⁸ Results for both complexes were similar: the molecules have an approximate mirror plane running through carbon C_1 and the mid-points of the $\text{C}_3\text{-C}_4$ and $\text{C}_7\text{-C}_8$ bonds (2.3). Both the cyclopentadienyl and butadiene skeletons



* acac = acetylacetonate (2.3)

are planar with the C_1 end of the ring tilted slightly towards the diene. The carbons of the diene were found to lie slightly closer to the metal nucleus than in bis(η^4 -butadiene)chlororhodium due to the different effects from the cyclopentadienyl fragment. Although in the chloro-substituted cyclopentadienyl compound the C_1-C_2 and C_1-C_5 bond lengths were slightly longer than the remainder of the ring, there was no indication of an η^3 -allylic system from the proton nmr spectrum, equivalence of the cyclopentadienyl ring resonances being observed at -60°C .

Chelation of the dienes in preference to monodentate coordination may be related to the improved $d\pi - p\pi^*$ bonding arising from greater electron delocalisation possible in a conjugated system. The proposed reaction scheme for displacement of the coordinated ethylene illustrates this preference for chelation. (Scheme 2.1). The first stage is thought to be nucleophilic attack of the unsubstituted end of the uncoordinated di-olefin on the coordinatively unsaturated metal atom in the $[\text{Rh}(\eta^2-\text{C}_2\text{H}_4)_2(\text{acac})]$ species resulting in a 5-coordinate intermediate. After dissociation of one of the ethylene molecules, there are two possible routes for continuation:

(i) attack by further uncoordinated olefin.

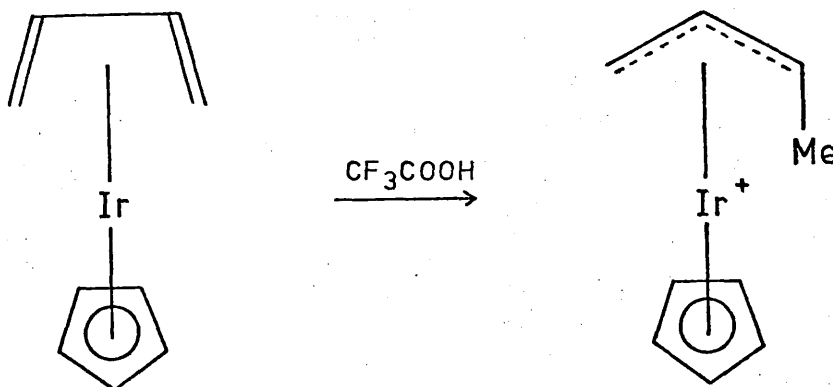
(ii) rotation about the olefin-rhodium axis resulting in

chelation of the monodentate diene to give the bidentate form.

The chosen method is dependent upon the relative coordination capabilities of an uncoordinated diene molecule and the unsubstituted end of the coordinated di-olefin.

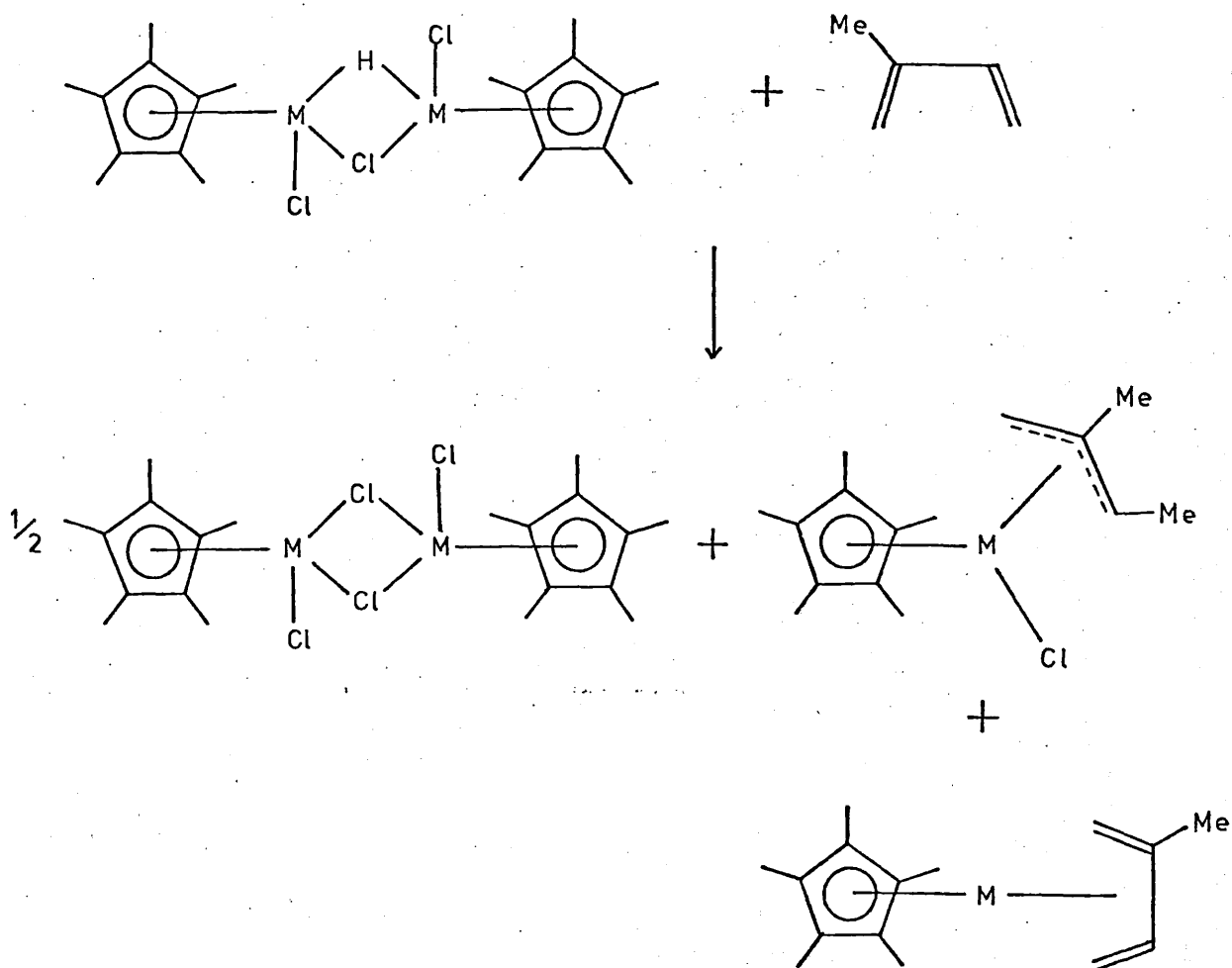
Usually the stability given by chelation of the 1,3 conjugated diene is greater and this leads to the normal product. However, with 4-methylpenta 1,3 diene the preference for attack by a new molecule of diene is optimised and thus two molecules of diene per rhodium atom are coordinated. When the acetylacetonate ligand is replaced by the η^5 -cyclopentadienyl ring this possible balance is upset and the greater stability to be gained by chelation heavily outweighs attack by more diene. A similar reaction scheme for coordination of di-olefins was postulated with the chloro and cyclopentadienyl compounds although the initial stage was thought to be SN1 (dissociative) as these are coordinatively saturated eighteen electron complexes.

The analogous iridium species have received comparatively little attention and only recently has η^4 -butadiene η^5 -cyclopentadienyl iridium been synthesised.⁵⁹ This undergoes protonation in trifluoroacetic acid to give an "anti"-1-methylallyl cationic complex (2.4). The proposed mechanism involved initial protonation at the metal followed by rapid transfer of the proton to the terminal carbons of the butadiene ligand.



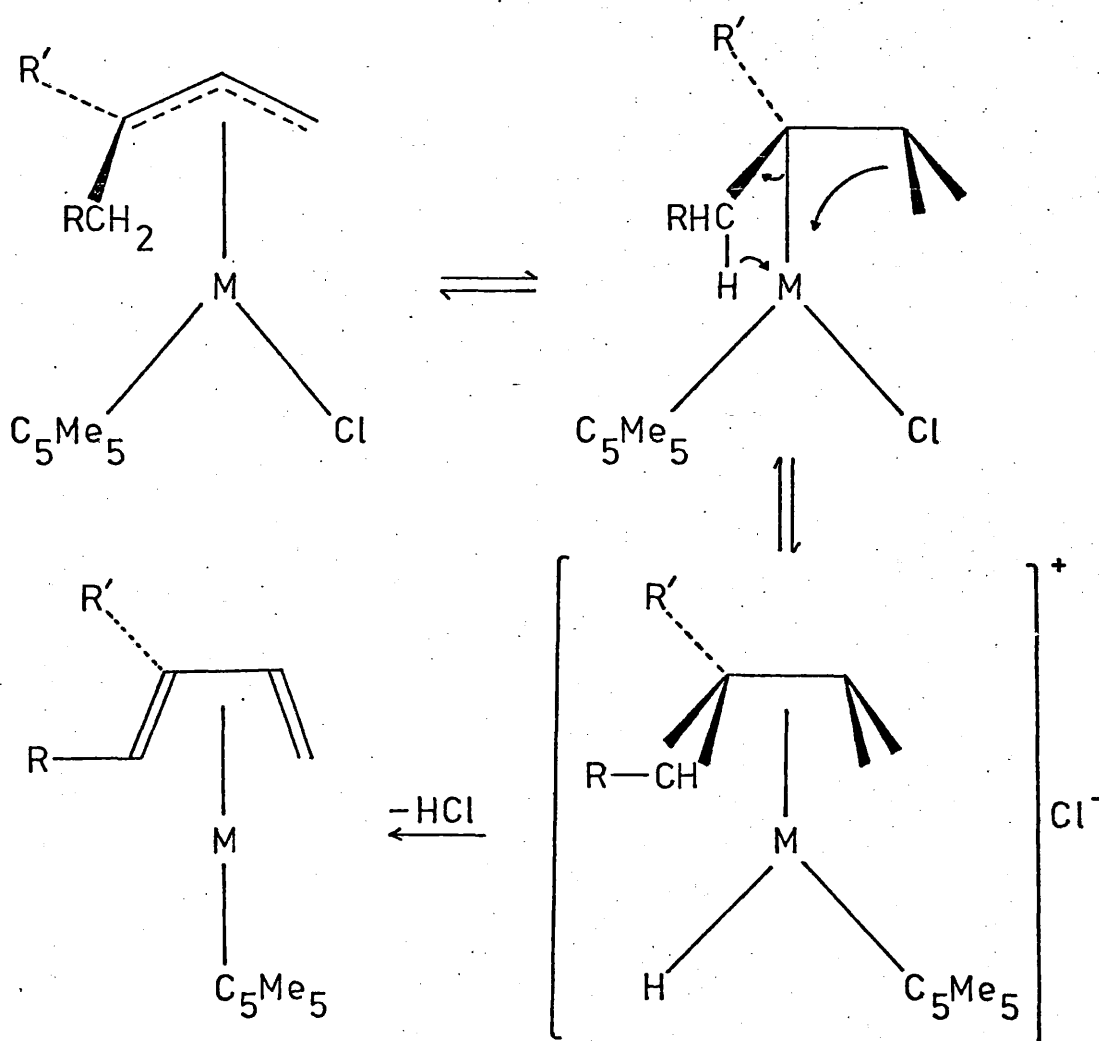
(2.4)

Maitlis and co-workers in their extensive studies on di- μ -chlorobis(chloro η^5 -pentamethylcyclopentadienyl)rhodium and iridium complexes have isolated hydrido intermediates which react with di-olefins in the presence of base.²⁵ A typical example is given with isoprene (Scheme 2.2). Both the η^3 -allylic and η^4 -diene species were formed although other di-olefins gave only one product or the other. Furthermore, some of the η^3 -allylic complexes underwent elimination of hydrogen chloride to form the diene compounds. Extensive examination revealed that the criterion for elimination of hydrogen chloride was the presence of both "syn" and "anti"-1-methylallylic groupings although under extreme conditions



(Scheme 2.2)

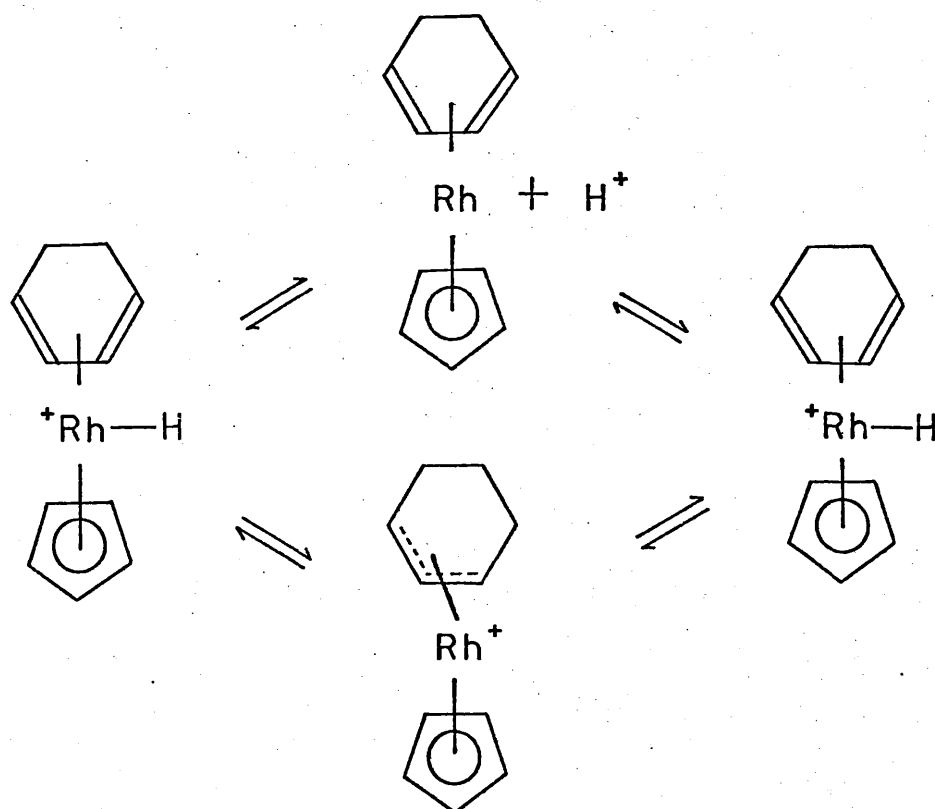
the presence of methyl groups in the 1 and 2 positions on the allyl group would suffice. Compounds which contained methyl groups only in the terminal "syn" position would not under any circumstances undergo hydrogen chloride elimination. These results were rationalised by the following mechanism (Scheme 2.3). It was proposed that with the "anti" methyl (or alkyl) group the allylic ligand was already in the "cis" configuration required for the formation of the diene; the transition state then involved a "σ"



(Scheme 2.3)

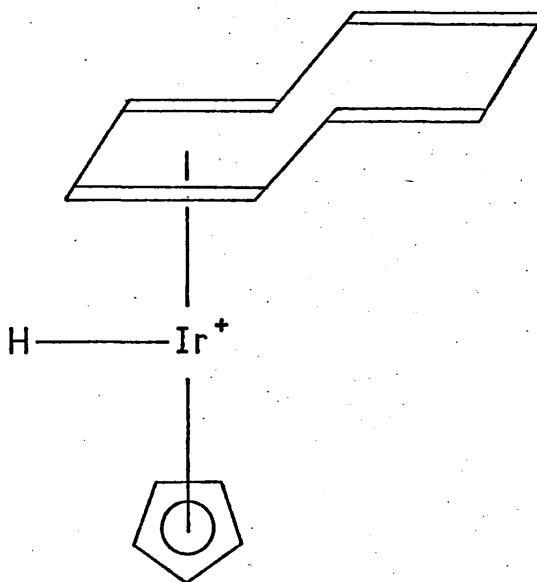
bonded allyl structure followed by formation of a metal-hydrogen bond together with the cleavage of the metal-carbon " σ " bond and the formation of a new " π " bond. This process would be assisted by the ionisation of the chlorine and attack by the other double bond giving a diene metal hydride cationic species. Hydrogen chloride could then be easily eliminated with resultant formation of the neutral diene compound.

Lewis and co-workers during their extensive protonation studies of olefinic rhodium and iridium compounds⁶⁰⁻⁶² have also found evidence for metal hydride complexes. η^4 -cyclohexa 1,3 diene η^5 -cyclopentadienylrhodium undergoes protonation in trifluoroacetic acid resulting in a cationic allyl complex (Scheme 2.4).



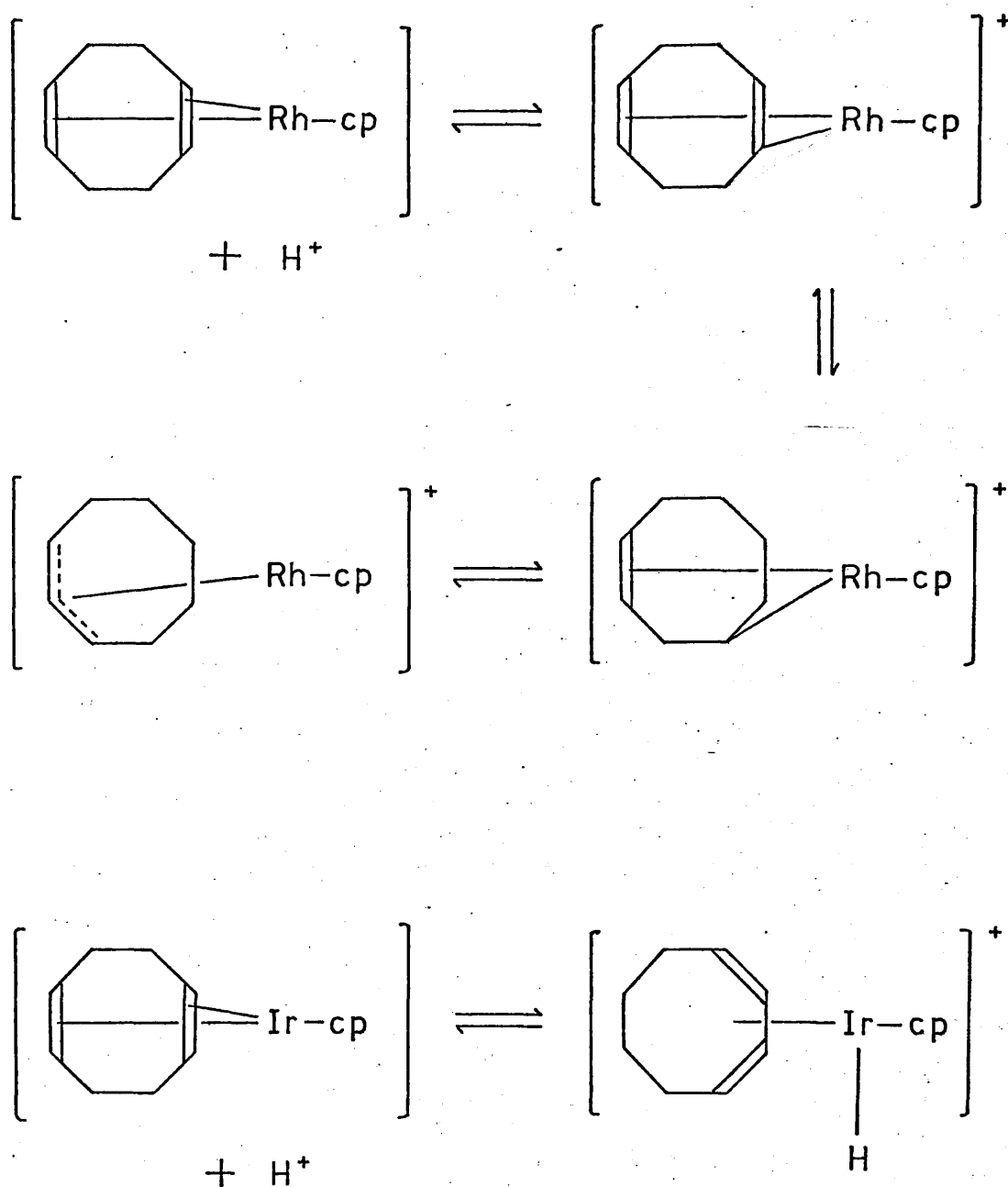
(Scheme 2.4)

Initial attack was thought to occur upon the metal to form a cationic metal hydride species followed by the reversible transfer of the proton to the cyclohexadiene to give the allyl complex. Confirmation for this mechanism came from the analogous iridium species when proton nmr studies revealed the presence of an upfield resonance at τ 25.3 ppm characteristic of a transition-metal hydride bond. A similar hydridic complex has also been found upon protonation of $\eta(1-2) \eta(3-4)$ cyclooctatetraene η^5 -cyclopentadienyl-iridium with trifluoroacetic acid. The high field resonance at τ 19.2 ppm was again indicative of a metal protonated species (2.5).



(2.5)

More recent studies have involved the protonation of $\eta(1-2) \eta(5-6)$ COD η^5 -cyclopentadienyl compounds of rhodium and iridium. With rhodium three reversible cationic species are formed with no evidence from nmr measurements for direct metal protonation although with iridium another cationic hydride was formed together with isomerisation from 1,5 to 1,3 co-ordination (Scheme 2.5).⁶²

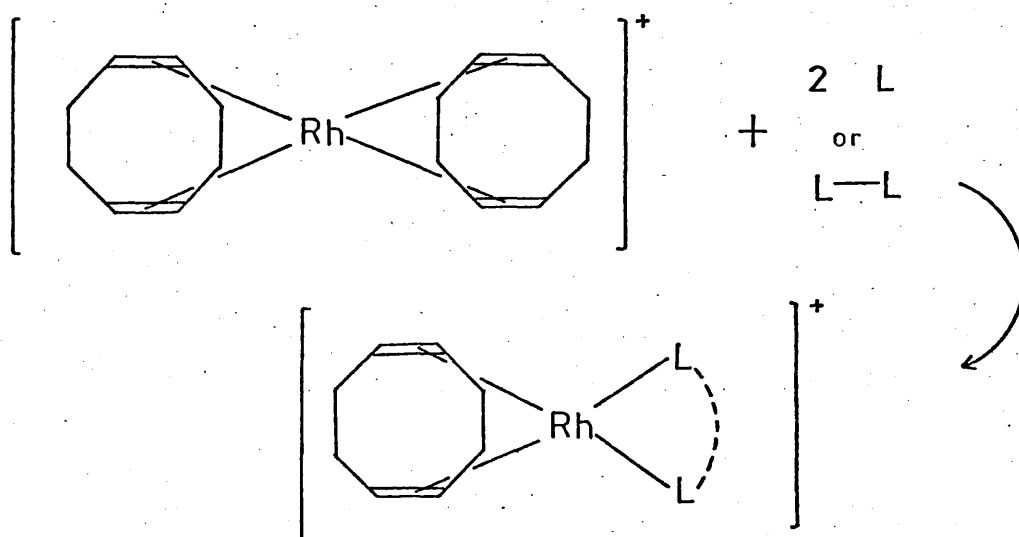


(Scheme 2.5)

The reason for this isomerisation was attributed to the difference in bonding of the metal to a conjugated and non-conjugated diene with the former able to compensate the iridium atom for its loss of

electron density on forming the cationic species by a wider variety of energies and symmetries.⁶³ The same group have also studied reactions of neutral cyclic diene complexes and demonstrated that these are more susceptible to electrophilic rather than nucleophilic attack; this is related to the poor electron accepting properties of the η^5 -cyclopentadienyl ligand compared with carbonyl groups which have largely accepting properties.^{64,65}

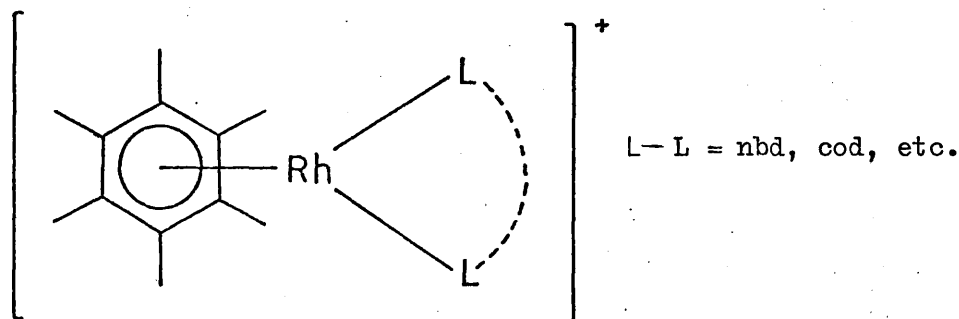
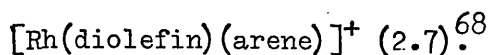
Other groups have also studied the formation of cationic olefinic rhodium and iridium complexes. Green and Kuc⁶⁶ have synthesised the cationic chelating di-olefin systems $[M(\text{diene})_2]^+ \text{BF}_4^-$ (diene = COD, NBD)^{*} by treatment of a solution of $[M(\text{diene})(\text{acac})]$ in dichloromethane with an equimolar quantity of triphenylmethyl tetrafluoroborate in the presence of excess coordinating chelating di-olefin. These compounds can then be reacted with a variety of ligands (for example - phosphines) to give other cationic species by the displacement of one of the chelating di-olefins (2.6).⁶⁷



(2.6)

* NBD = norbornadiene

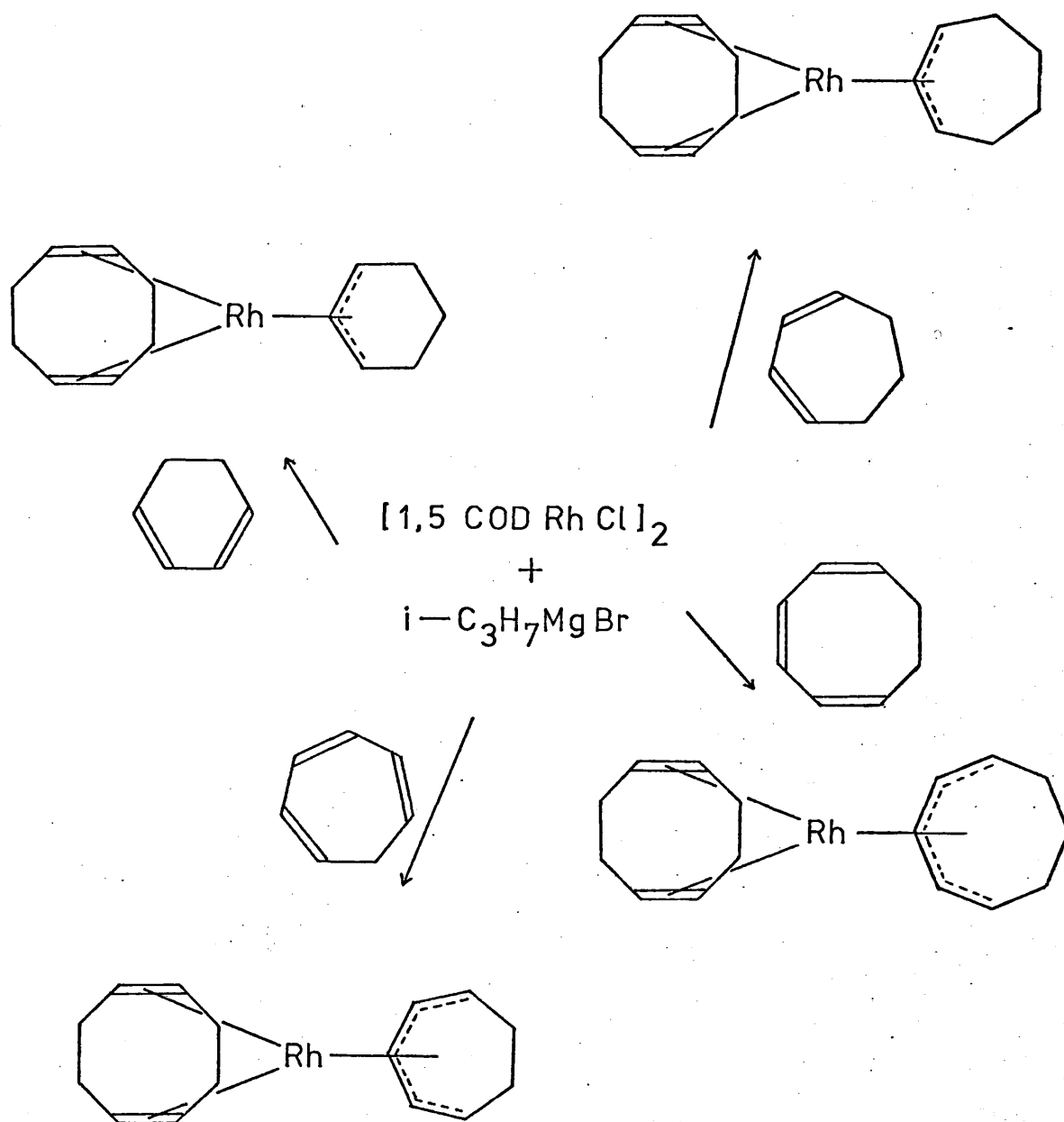
More recent studies have shown that arenes and olefins will also displace the chelating diene with the formation of cationic species



(2.7)

Müller et al.⁶⁹ have prepared several neutral η^4 -cycloolefin complexes by their "isopropyl Grignard method". Reaction of the dimeric compounds $[\text{Rh L Cl}]_2$ (L = cycloocta 1,5 diene, cyclohepta 1,3 diene or norbornadiene) and of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ with isopropyl magnesium bromide in the presence of cyclic olefins of differing ring size resulted in the formation of neutral allyl and pentadienyl products which are sixteen and eighteen electron complexes respectively. (Scheme 2.6). In the sixteen electron complexes, all the carbon atoms which are " π "-bonded to the rhodium show splitting of their carbon-13 nmr resonances due to coupling of the metal and the spectrum is constant over a temperature range of 70° indicating no ligand movement. In contrast to this the carbon-13 nmr spectrum of the eighteen electron compound

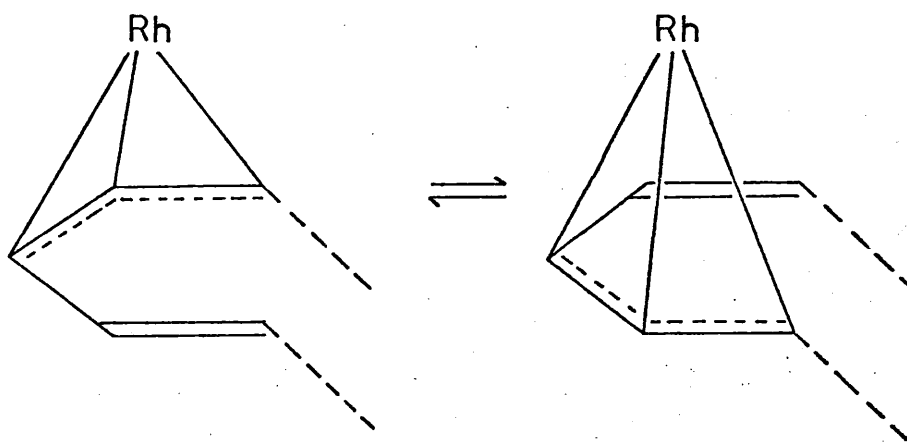
$[\text{Rh } \eta(1-2) \eta(5-6)\text{COD (cyclooctadienyl)}]$ is temperature dependent and both rings move independently from one another. The 1,5 COD ligand rotates about the metal-ligand axis at higher temperatures giving an



(Scheme 2.6)

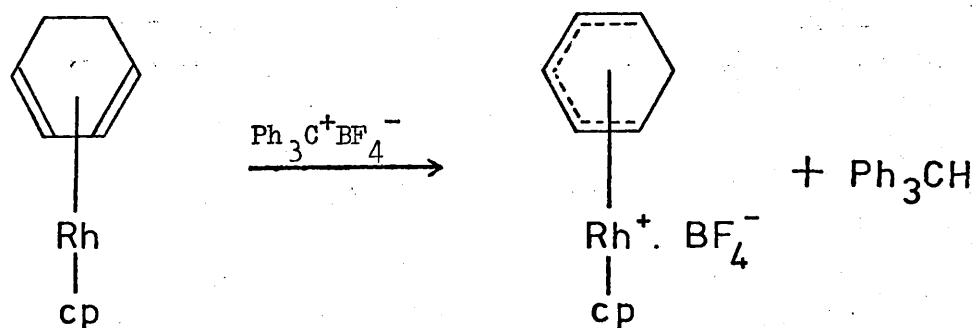
equivalence of all the olefinic resonances and all the methylene resonances in this ligand while at lower temperatures this fluxional behaviour can be "frozen". Only the resonance of the central carbon atom of the cyclooctadienyl ligand shows coupling to the metal although the other resonances of the dienyl unit start to broaden at low temperatures. Observations of the spectrum down to 220 K were interpreted as the movement of this ligand between the limits (2.8) and at even lower temperatures the molecule is probably

"frozen" into one of these sixteen electron conformations. Other of the eighteen electron complexes may or may not exhibit fluxional behaviour in one or both rings but reasons for this have not been established.



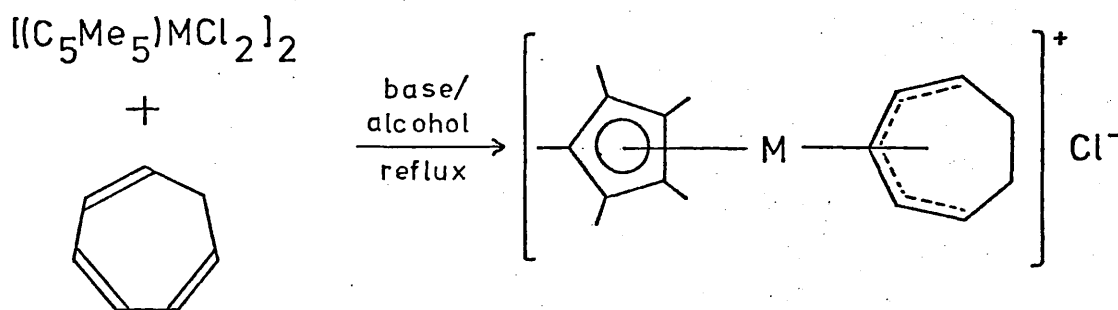
(2.8)

Many examples of the coordination of cyclic η^5 -dienyl systems are known, the most widely used example is the η^5 -cyclopentadienyl ring. Cyclic η^5 -dienyl complexes of rhodium and iridium have been prepared by hydride abstraction from conjugated diene compounds using triphenylmethyl tetrafluoroborate⁶⁰ (Scheme 2.7).



(Scheme 2.7)

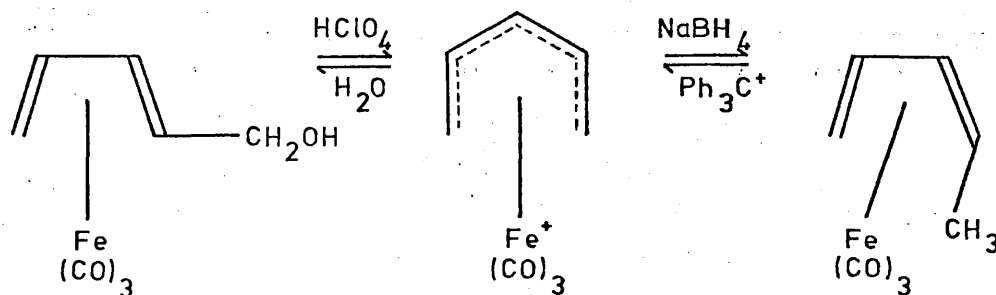
Similar η^5 -dienyl complexes have also been synthesised by Maitlis and co-workers from the reaction of $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ with cycloheptatriene in the presence of base (Scheme 2.8); this reaction is similar to those for the previously described η^3 -allyl species.



(Scheme 2.8)

These salts can be readily converted into their hexafluorophosphates in high yields.

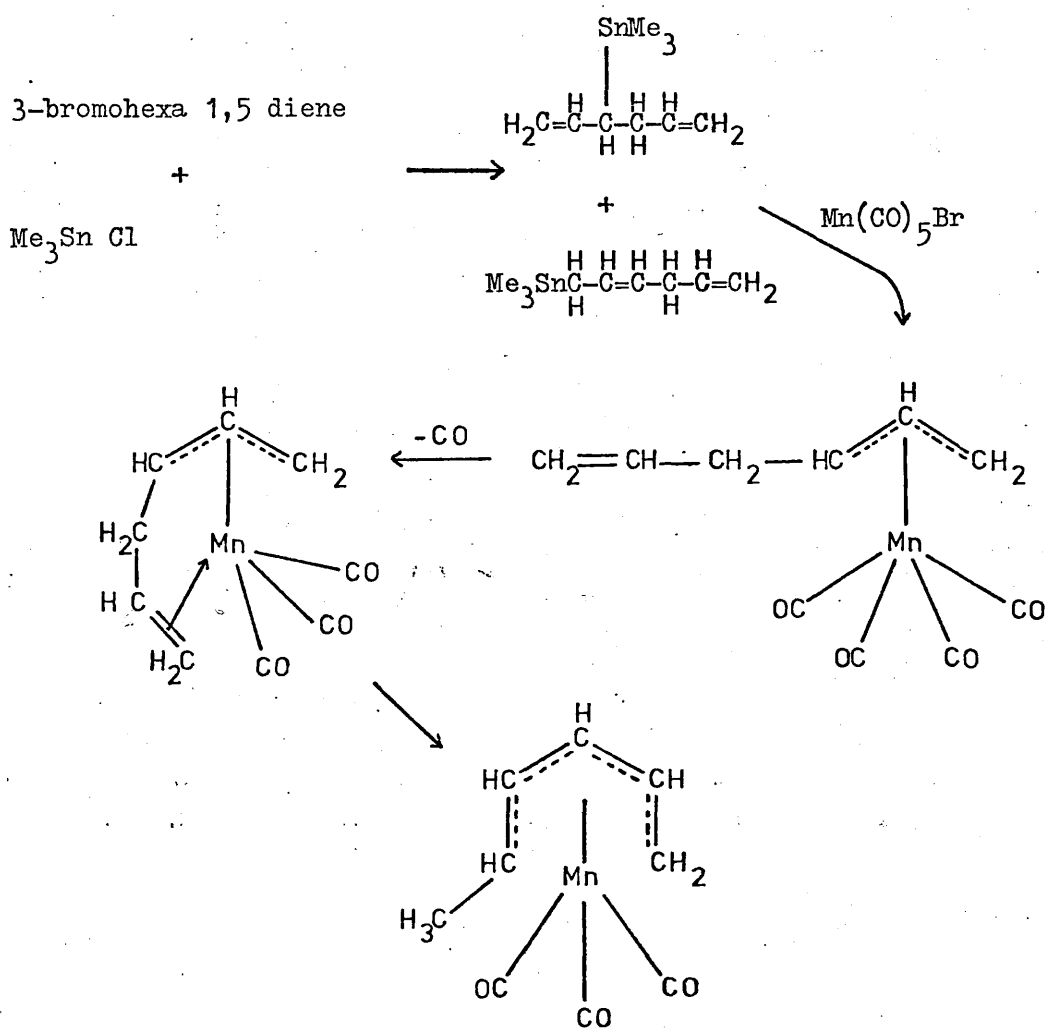
However, coordination of the acyclic η^5 -pentadienyl ligand to a transition-metal is rare and the most widely known examples are found with the tricarbonyliron system. Cationic η^5 -pentadienyl compounds can be prepared by the protonation of conjugated dien-ols with strong acids or by hydride abstraction from a coordinated conjugated diene^{70,71} (Scheme 2.9). These salts have since been the



(Scheme 2.9)

subject of extensive studies including spectroscopic characterisations and also nucleophilic attack. Evidence has been presented for the formation of a "trans" cationic intermediate at low temperatures,⁷² and kinetic results have also been interpreted in terms of a "trans" intermediate.⁷³

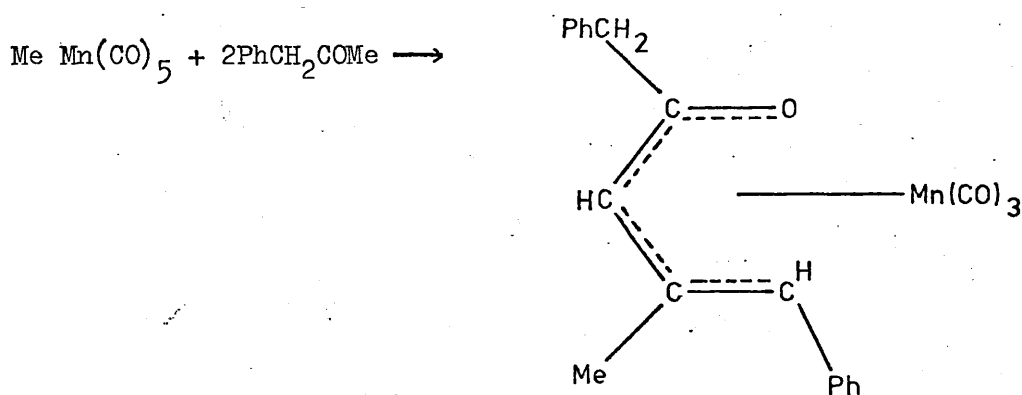
Abel and Moorhouse⁷⁴ have synthesised a neutral η^5 -pentadienyl manganese complex which is formed by the decarbonylation of an allyl tetracarbonyl (Scheme 2.10). Reaction of the Grignard reagent of 3-bromohexa 1,5 diene with chlorotrimethyltin resulted in a mixture



(Scheme 2.10)

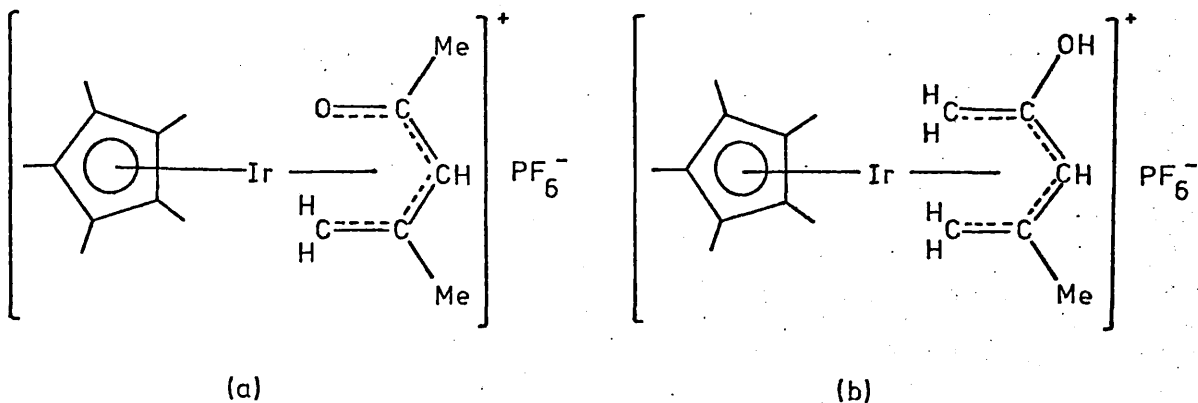
of products but upon further treatment with bromopentacarbonylmanganese the allyl products obtained were identical. A decarbonylated pentadienyl product was also isolated and it was found that the allyl tetracarbonyl species could be converted into the pentadienyl tricarbonyl. These results were rationalised by the uncoordinated olefinic group displacing carbon monoxide followed by an immediate rearrangement via a 1-3 proton shift to form the methyl-pentadienyl complex.

Bennett and Bruce⁷⁵ have obtained a low yield, 9%, of an oxapentadienyl complex from the condensation of two molecules of 1-phenylpropan-2-one with methylpentacarbonylmanganese (Scheme 2.11)



(Scheme 2.11)

and recently Maitlis et al. have reported the preparation of cationic oxapentadienyl and an η^5 -pentadienyl complexes (2.9 a and b).⁷⁶



(2.9)

This chapter reports the facile syntheses of novel species of the type $[M(\eta^4\text{-diene})_2\text{Cl}]$: $M = \text{Rh, Ir}$ by the displacement of coordinated cyclooctene from $[M(\eta^2\text{-cyclooctene})_2\text{Cl}]_2$ using acyclic conjugated dien-ols and dien-ones. The dien-ones react with cyclopentadienyl thallium to form eighteen electron complexes of formula $[M(\eta^4\text{-dienone})(\eta^5\text{-cyclopentadienyl})]$ and these have been studied using proton and carbon-13 nmr spectroscopy. Attempted reductions and protonation studies are discussed. A reaction to form the "syn"-1-methyl $\eta^5\text{-pentadienyl } \eta^5\text{-cyclopentadienylrhodium tetrafluoroborate salt}$, the only known example of the coordination of this ligand to rhodium, is reported and also discussed in the light of its proton and carbon-13 nmr spectroscopic features.

2.2 RESULTS AND DISCUSSION

(a) The complexes $[M(\eta^4\text{-diene})_2\text{Cl}]$: M = Rh, Ir and $[\text{Rh}(\eta^4\text{-diene})\text{Cl}]_2$

(i) Preparation and properties

Porri et al. first prepared complexes of rhodium with acyclic conjugated di-olefins by the displacement of cyclooctene from $[\text{Rh}(\eta^2\text{-cyclooctene})_2\text{Cl}]_2$ although detailed preparative procedures have not been reported.⁵⁴ Similar examples with iridium are rare, the only complexes known are with butadiene, isoprene and trans 1,3 pentadiene as ligands, although the same method of cyclooctene displacement was used.⁷⁷ A series of species of the type $[M(\eta^4\text{-diene})_2\text{Cl}]$ M = Rh, Ir have been synthesised employing conjugated dienes containing alcoholic, ketonic and aldehydic functional groups by an adaptation of this "displacement method". The new complexes are stable to air and moisture as solids although those that are soluble have a tendency to decompose in solution. Analytical data are reported in table 2.1 and all the compounds gave satisfactory elemental analyses for the formula $[M(\eta^4\text{-diene})_2\text{Cl}]$ with the exception of the product from the reaction of 3,5 heptadien-2-one with the cyclooctene rhodium complex which analysed for the formula $[\text{Rh}(\eta^4\text{-3,5-heptadien-2-one})\text{Cl}]_2$ (XVI). The reason for this anomaly is not understood; indeed the analogous iridium compound (XX) analysed well for the monomeric structure. Similar observations have been noted by Drew et al.⁷ who could find no correlation between the nature of the diene substituents and the type of complex formed.

The synthetic procedures of Drew and co-workers, viz: displacement of coordinated ethylene from Cramer's complex using an excess of diene proved unsuccessful for the species reported here. After filtration,

Diene	No.	Analysis Found (Calc.) %		Melting point °C	Colour	Yield of product %
		Carbon	Hydrogen			
2,4 hexadien-1-ol	XI	43.28 (43.07)	6.04 (6.02)	158 - 62 dec.	Orange yellow	70
2,4 hexadien-1-al	XII	43.29 (43.60)	4.74 (4.88)	96-98 melt with dec.	Orange yellow	86
3,5 heptadien-2-ol	XIII	45.99 (46.36)	6.13 (6.67)	150-2 dec.	Orange yellow	65
1,5 diphenyl 2,4 pentadien-1-one	XIV	67.33 (67.28)	4.70 (4.65)	155-7 melt with dec.	Bright yellow	90
5 methyl, 6 phenyl 3,5 hexadien-2-one	XV	61.27 (61.13)	5.56 (5.52)	118-20 melt with dec.	Bright yellow	85
Other: [(3,5 heptadien-2-one) RhCl] ₂	XVI	34.32 (33.83)	4.49 (4.06)	164-7 dec.	Brick red	90

TABLE 2.1 : Analytical data for complexes of the [Rh (η^4 -diene)₂Cl]

Diene	No.	Analysis Found (Calc.) %		Melting point °C	Colour	Yield of product %
		Carbon	Hydrogen			
2,4 hexadien-1-ol	XVII	34.08 (34.00)	4.92 (4.76)	100-2 melt with dec.	Pale yellow	72
2,4 hexadien-1-al	XVIII	34.25 (34.32)	3.63 (3.84)	104-6 dec.	Greenish yellow	90
3,5 heptadien-2-ol	XIX	36.71 (37.20)	4.54 (5.35)	170-4 dec.	White	72
3,5 heptadien-2-one	XX	37.47 (37.53)	4.32 (4.50)	132-5 dec.	Off white	70
1,5 diphenyl 2,4 pentadien-1-one	XXI	58.61 (58.59)	4.09 (4.02)	180-3 dec.	Greenish yellow	88
5 methyl,6 phenyl 3,5 hexadien-2-one	XXII	52.32 (52.03)	4.89 (4.70)	185	Greenish yellow	85

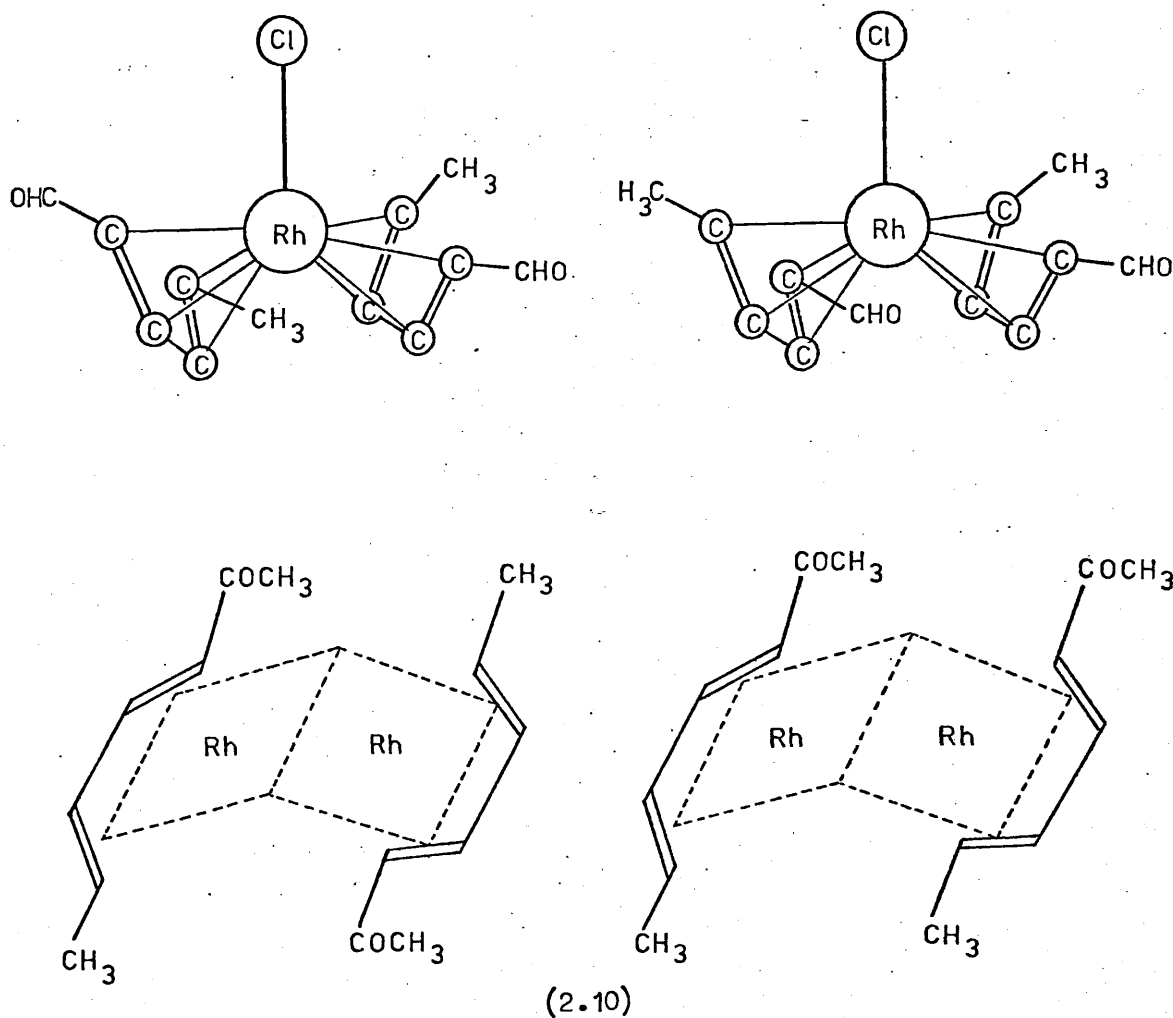
TABLE 2.1 (continued) Analytical data for complexes of the type $[\text{Ir}(\eta^4\text{-diene})_2\text{Cl}]$

essential to remove solid brown impurities, and concentration, the product failed to precipitate out and complete removal of solvent resulted in reddish oils probably containing the required product together with an excess of di-olefin. When an excess of diene was not used little reaction was visible even after prolonged reaction times. Attempts to isolate a pure product from these procedures by reaction of the oily material with cyclopentadienyl thallium also proved unsuccessful, little separation occurring upon chromatography and extensive decomposition upon sublimation. That the required η^5 -cyclopentadienylrhodium complex was present was evident from the proton nmr spectrum with the appearance of a resonance at τ 4.9 ppm in deuterated chloroform, characteristic of the η^5 -cyclopentadienyl ligand although other resonances were swamped by an excess of diene.

The complexes (XI-XXII) were successfully prepared in high yields, generally greater than 70%, by the displacement of labile cyclooctene from the dimeric rhodium and iridium compounds $[M(\eta^2\text{-cyclooctene})_2\text{Cl}]_2$. Reactions were usually carried out in sodium dried hexane and the products precipitated out after stirring with an excess of the appropriate diene for one hour. With dienes that were insoluble in hexane, a similar procedure in dry diethyl ether proved successful. These displacement reactions from the cyclooctene complexes, easily obtainable as precursors, are probably the most convenient known methods for the preparation of η^4 -diene rhodium and iridium complexes in high yields under very mild conditions. Removal of excess diene is straightforward, either by evaporation in vacuo or by the use of a suitable solvent. Examples of this can be found in the experimental section with cycloocta 1,3,5,7 tetraene and cyclohexa 1,3 diene.

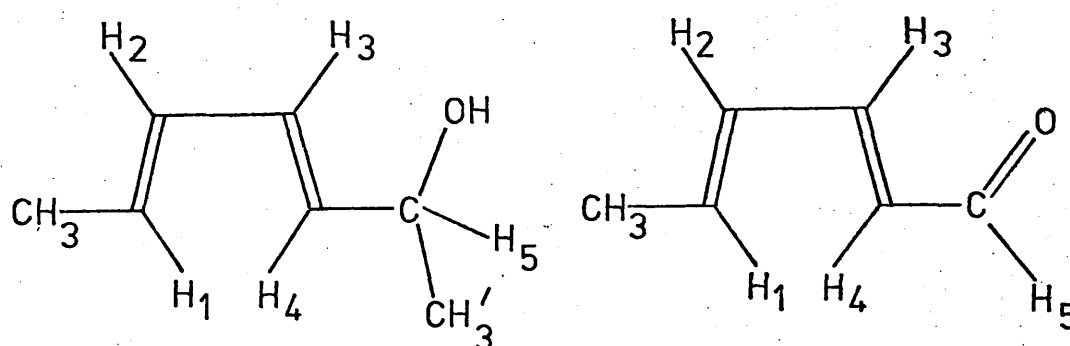
The mechanism for this displacement is probably similar to that proposed by Drew et al. for the displacement of ethylene from Cramer's complex.

The compounds of molecular formula $[M(\eta^4\text{-diene})_2\text{Cl}]$ probably have structures similar to that of $[\text{Rh}(\eta^4\text{-butadiene})_2\text{Cl}]^{54}$ and the dimeric species may be similar to the tetraethylene complex with the chelating diene acting as a bidentate ligand replacing two ethylene molecules.⁶ However, with these dienes there is the possibility of geometrical isomerism, some forms of which are shown in fig. 2.10. In addition there is also optical isomerism with XIII and XIX which would give rise to diastereoisomeric forms.



(ii) Spectroscopic properties of the species $[M(\eta^4\text{-diene})_2Cl]$

Proton nmr data, reported in table 2.2, for the complexes were difficult to obtain; some of the compounds were barely soluble in available solvents while some that were tended to decompose. Spectra that could be obtained were often complicated with broadened resonances, perhaps indicative of the existence of isomeric forms or possible decomposition in solution. Van der Ent and Onderlinden^{de} 77 have found isomers for $[\text{Ir}(\eta^4\text{-isoprene})_2Cl]$ and attributed the major resonances to the trans isomer on steric considerations i.e. the methyl groups are trans to each other. It was not possible here to assign the resonances to any particular isomers, particularly when the resonances are complicated by additional coupling to rhodium, only to protons resonating at particular frequencies. Assignments (according to fig. 2.11) were made by comparison with the analogous η^5 -cyclopentadienylrhodium and iridium and tricarbonyliron compounds, although the inability to



(2.11)

accurately determine the chemical shifts and coupling constants prohibits further discussion of these spectra.

Complex	CH ₃	H ₁	H ₂	H ₃	H ₄	H ₅	Other
XIII	8.5	6.6	4.6	5.1	7.5	5.9	CH ₃ ' 9.7 OH 8.5
XIX	very broad resonances						
XII	9.1	8.5	4.7	4.2	8.2	0.4	
XVIII	9.1	8.5	5.1	4.0	8.2	0.8	

TABLE 2.2 Proton nmr chemical shifts for $[M(\eta^4\text{-diene})_2\text{Cl}]$ complexes in CDCl_3 at 60 MHz, relative to TMS 10 ppm. Resonances are complex multiplets or broad.

Complex	Absorptions (Far I.R. cm^{-1})	Carbonyl region cm^{-1}
XII	228(s) : 260(s) : 288(w)	1680 (s, br)
XIV	250(m) : 268(s)	1650 (s, br)
XV	276(s)	1680 (s, br)
XVI	238(s) : 258(m) : 295(s)	1620 (s, br)
XVII	253(m) : 270(m) : 297(s)	-
XVIII	218(vw) : 240(m) : 260(m) : 265(m) 296(s)	1685 (s, br)
XIX	219(w) : 255(w) : 285(s) : 295(w)	-
XXI	249(m) : 285(s)	1655 (s, br)
XXII		1685 (s, br)
$(\text{C}_5\text{Me}_5)_2\text{Rh}_2\text{Cl}_4$	200(m) : 212(m) : 225(w) : 240(s) 245(s) : 278(s)	-

TABLE 2.3 Infra-red data for complexes $[M(\eta^4\text{-diene})_2\text{Cl}]$. Far I.R. data covers 200-300 cm^{-1} . The letters s, m, w, br in brackets after the absorptions indicate strong, medium, weak and broad respectively.

Far infra-red data are reported in table 2.3 together with absorptions for the carbonyl region in the ketonic and aldehyde ligands. All the complexes studied exhibited absorptions in the 200-300 cm^{-1} region. Van der Ent and Onderlinden⁷⁷ have assigned bands in the 278-296 cm^{-1} range to Ir-Cl stretching vibrations by comparison with corresponding bromo complexes when bands in this region were not observed. By analogy with this work, absorptions in the frequency range 280-300 cm^{-1} are also attributed to the Ir-Cl stretching vibrations. Drew et al. have assigned all bands in the region 200-300 cm^{-1} to Rh-Cl stretching vibrations in their complexes by analogy with other rhodium (I) species, although it was not possible to correlate the number of observed peaks with either monomeric or dimeric structures which have terminal and bridging chlorines respectively.⁷ Similar difficulties in the interpretation of data were found with these complexes and this difficulty can be highlighted by the complexity of the spectrum of $[\text{Rh}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_4]$ which has several absorptions in the region studied. This compound has both terminal and bridging chlorines and these cannot be correlated with the observed absorptions. Shoulders were often found on the low frequency side of some of the peaks and are attributed to the occurrence of the chlorine-37 isotope. The existence of isomeric forms will also give rise to extra absorptions. Bands in the range 1600-1700 cm^{-1} for the ketone and aldehyde ligands are due to the carbonyl stretching vibrations and these bands are somewhat broadened. These absorptions are typical for conjugated dien-ones⁷⁸ and little change is observed on complexing to the metal atom. It is interesting that the carbonyl absorption in the dinuclear rhodium complex (XVI) has been shifted to lower frequency relative to the mononuclear cyclopentadienyl compound (1620 — 1665 cm^{-1}) indicative of a weakening of this bond.

(b) The complexes $[M(\eta^4\text{-diene})(\eta^5\text{-cyclopentadienyl})]$ $M = \text{Rh, Ir}$

(i) Preparation and properties

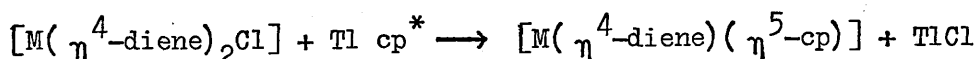
The η^5 -cyclopentadienyl ligand has been widely used in conjunction with the cobalt, rhodium and iridium triad to form eighteen electron species with bis η^2 -olefins and η^4 -di-olefins isoelectronic with similar tricarbonyliron systems. Several η^4 -diene

η^5 -cyclopentadienylrhodium compounds have been prepared by Drew et al.⁷ and Maitlis and co-workers²⁵ have also synthesised some corresponding

η^5 -pentamethylcyclopentadienyl rhodium and iridium complexes.

However, η^4 -butadiene η^5 -cyclopentadienyliridium recently reported by Oro is the only known example of the unsubstituted cyclopentadienyl unit coordinated to an acyclic η^4 -diene iridium residue.⁵⁹

Neutral chlorocomplexes of the type $[M(\eta^4\text{-diene})_2\text{Cl}]$ $M = \text{Rh, Ir}$ readily react with cyclopentadienyl thallium in a suitable solvent to form the species $[M(\eta^4\text{-diene})(\eta^5\text{-cyclopentadienyl})]$ (Scheme 2.12).



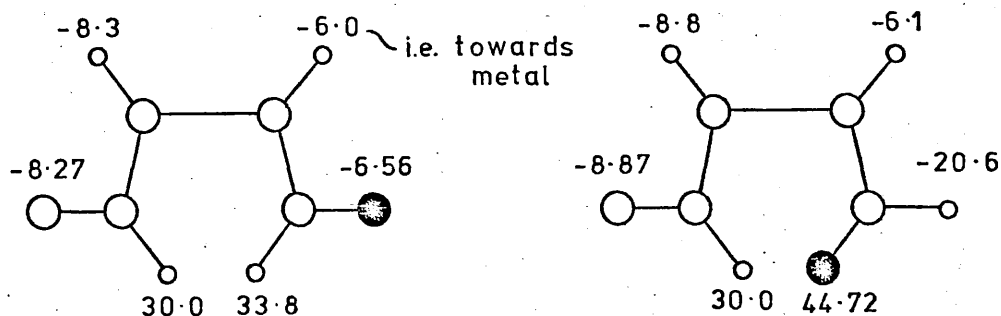
diene = dien-one or -al

(Scheme 2.12)

After filtration of the insoluble thallium residues and evaporation of solvent from the filtrate, the complexes may be obtained in an analytically pure state either by sublimation or chromatography dependent upon the diene used. Yields are generally of the order 70%

* cp = cyclopentadienyl

although with some iridium species they are much lower. All these complexes gave satisfactory elemental analyses and are reported in table 2.4. The rhodium compounds are orange to red solids which slowly decompose in air to give a brownish residue and are readily soluble in most organic solvents forming solutions which are also stable to air for some time. The analogous iridium species are pale yellow solids with properties similar to those of the rhodium complexes. Drew et al. have reported x-ray structures for the 2,3-dimethyl and 2,3 dichlorobutadiene rhodium compounds and have found the diene ligands to be essentially planar.⁵⁸ Similar structures are proposed for the complexes (XXII - XXX) although there may be deviations from planarity due to the substituent effects of the diene ligands in some cases. Immerzi has shown from x-ray diffraction studies on substituted diene tricarbonyliron systems that the C-H bonds can deviate by as much as 30° from the diene plane with "syn" substituents and 45° with "anti" substituents with all substituents except those in the "anti" positions lying below the diene plane (2.12).⁷⁹



(2-m-nitrophenyl)amino trans, trans 3,5 heptadiene tricarbonyliron

(2.12)

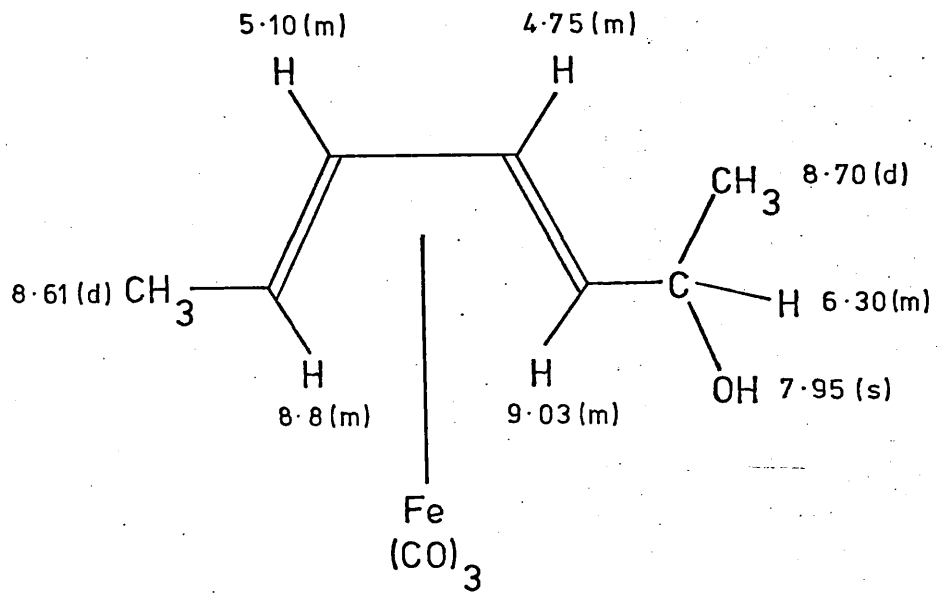
Diene	Metal	No.	Analysis (Found (Calc.) %)		Melting point °C	Colour
			Carbon	Hydrogen		
2,4 hexadien-1-al	Rh	XXIII	50.08 (50.02)	5.03 (4.96)	66-8	Orange
3,5 heptadien-2-one	Rh	XXIV	51.93 (51.82)	5.59 (5.44)	85-6	Orange
1,5 diphenyl 2,4 pentadien-1-one	Rh	XXV	65.65 (65.68)	4.59 (4.76)	154-6	Orange red
5 methyl, 6 phenyl 3,5 hexadien-2-one	Rh	XXVI	61.80 (61.03)	5.49 (5.41)	129-31	Orange red
2,4 hexadien-1-al	Ir	XXVII	38.10 (37.38)	3.91 (3.71)	72-4	Yellow
3,5 heptadien-2-one	Ir	XXVIII	40.30 (39.22)	4.42 (4.11)	98-9	Yellow
1,5 diphenyl 2,4 pentadien-1-one	Ir	XXIX	53.81 (53.75)	4.02 (3.90)	167-70	Yellow
5 methyl, 6 phenyl 3,5 hexadien-2-one	Ir	XXX	48.92 (48.75)	4.35 (4.32)	135-7	Yellow

TABLE 2.4 Analytical data for complexes of the type $[M(\eta^4\text{-diene})(\eta^5\text{-cyclopentadienyl})] : M = \text{Rh, Ir}$.
Yields are given in the experimental section.

Attempts to coordinate the cyclopentadienyl unit to the dien-ol complexes proved unsuccessful. On occasions brown oils were produced which decomposed on attempted purification using sublimation or chromatography. With (XI), although no pure complex could be isolated after treatment with cyclopentadienyl thallium, further reaction with fluoroboric acid in acetic anhydride at 0° gave the cationic complex η^5 -syn-1-methylpentadienyl η^5 -cyclopentadienylrhodium tetrafluoroborate (XXXI). The formation of this salt can be regarded as evidence for the η^4 -dien-ol η^5 -cyclopentadienylrhodium intermediate. Reaction of these dien-ols with bis(η^2 -ethylene) η^5 -cyclopentadienyl rhodium also proved unsuccessful, possibly due to decomposition at the temperatures required to displace ethylene from this complex.¹⁰ It was thought, on steric grounds, that cyclooctene might be more readily displaced from the corresponding $[\text{Rh}(\eta^2\text{-cyclooctene})_2(\eta^5\text{-cyclopentadienyl})]$ species, but attempts to prepare this compound failed, metallic rhodium being deposited. This deposition could be the result of steric effects from the cyclooctene ligands in trying to coordinate the three ring systems about the metal nucleus.

The reactivity of coordinated ligands to the tricarbonyliron residue has been extensively studied and the reduction of coordinated ketones and aldehydes to alcohols is well established.⁸⁰ However, reduction of (XXIV) proved inconclusive. The first attempt yielded an orange oil which was found from proton nmr data to be contaminated with the original ketone complex; evident from the methyl resonance at τ 7.86 ppm, similar to that observed in acetone. Repeated reduction of this product again resulted in the formation of an orange oil together with some decomposition to metallic rhodium. This product did

not exhibit the resonance at τ 7.86 ppm but did show two cyclopentadienyl resonances, one more intense than the other, at τ 4.62 ppm (more intense) and 4.70 ppm, each split by a small coupling to rhodium (~ 1 Hz). The methyl groups appeared as complicated overlapping doublets centred on τ 8.60 and 8.75 ppm, and the coupling was measured to be of the order 6 Hz. Other resonances were exceptionally complicated due to both proton coupling and also coupling to the rhodium-103 nucleus, as well as the possibility of enantiomeric forms. The remaining resonances at τ 4.8, 5.2, 6.4, 8.2 and 9.1 ppm are assigned to the remaining protons of the alcohol. A sharp resonance at τ 5.2 ppm is attributed to the introduction of impurity during the reduction. Clinton and Lillya⁸⁰ have shown the reduction of η^4 -3,5 heptadien-2-one tricarbonyliron with borohydride to be highly stereospecific with the formation of 95% ψ -endo product due to a strong conformational preference for the "s-trans" configuration. The proton nmr data for this product can be seen in (2.13). Although the spectrum for the rhodium reaction product agrees reasonably well with the isoelectronic tricarbonyliron compound, the presence of impurity and extensive decomposition on attempted purification makes it not possible to confirm conclusively the formation of the alcohol species from reduction of the coordinated ketone. Similar inconclusive results were also obtained with the aldehyde complex (XXIII) together with more extensive decomposition to metallic rhodium.



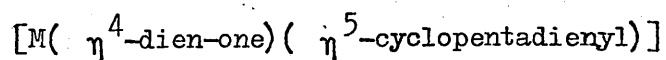
(2.13)

(i) Infra-red studies

Infra-red spectra for the carbonyl region were measured in nujol and the data are reported in table 2.5. In general the carbonyl stretching frequency in the cyclopentadienyl compounds lies to slightly lower frequency than in the chloro-complexes reflecting greater back donation from the cyclopentadienyl ring, slightly weakening the carbon-oxygen bond. An exception is found with the 3,5-heptadien-2-one species and this anomaly has been previously discussed. King et al.⁸¹ have reported the carbonyl stretching frequencies for the organic ligands in the 3,5 heptadien-2-one and 2,4 hexadien-1-al tricarbonyliron compounds to be 1686 and 1690 cm^{-1} respectively in carbon disulphide solution. Slightly higher values in these iron complexes probably reflects the greater electron accepting properties of the tricarbonyliron unit. It was also concluded that the organic carbonyl grouping was not bonded to the metal and similar conclusions can also be drawn here.

Compounds	Carbonyl stretching frequency (cm ⁻¹)
XXIII	1680 (s, br)
XXIV	1665 (s, br)
XXV	1640 (s)
XXVI	1675 (s, br)
XXVII	1685 (s, br)
XXVIII	1675 (s, br)
XXIX	1655 (s, br)
XXX	1680 (s, br)

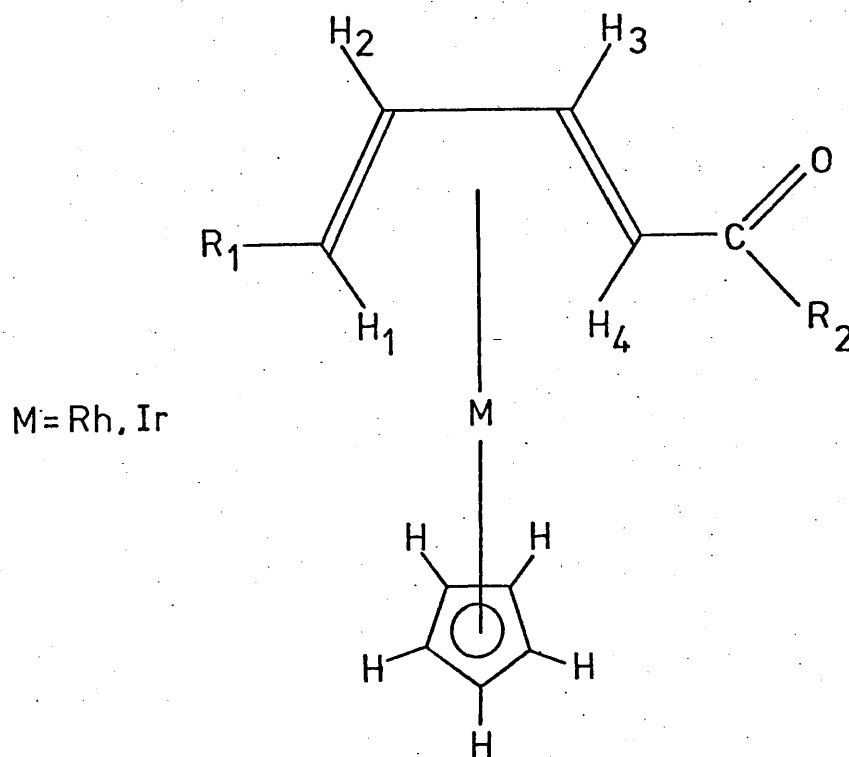
TABLE 2.5 Infra-red data for the complexes



M = Rh, Ir in nujol.

(iii) Investigation using proton nmr spectroscopy1. Characterisation

Proton nmr spectra recorded in deuterated chloroform are reported in table 2.6 and assigned according to 2.14. Chemical shifts are quoted in parts per million (ppm) downfield from TMS (internal reference $\tau = 10$ ppm) and coupling constants are measured in hertz. Letters in parentheses after the shifts s, d, dd, dt, m refer to the multiplicity of the resonance: singlet, doublet, doublet of doublets, doublet of triplets and unresolved multiplet respectively. Peak integrals are not shown but are consistent with the assignments. Assignments were made on the basis of published data on coordinated dienes in related systems, notably the results of Drew et al. together with observations from the tricarbonyliron system.^{7,80}



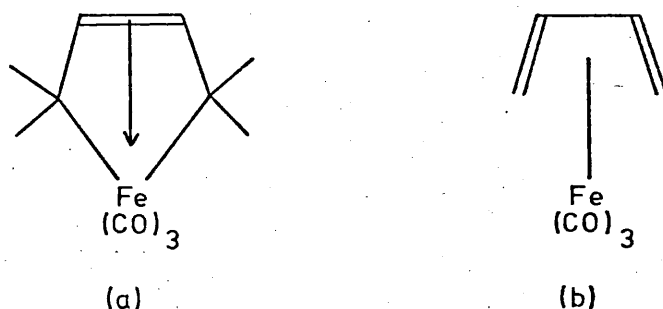
(2.14)

Substituents		Proton chemical shifts relative to TMS ($\tau = 10$ ppm)											
R ₁	R ₂	M	1	2	3	4	R ₂	Cp.	R _{1,1}	1,2	2,3	3,4	4,R ₂
CH ₃	H	Rh	8.52(d) Rh 2.5	5.05(m) Rh 1.0	4.74(m) Rh 1.0	8.38(dt) Rh 2.5	1.02(d)	4.82(d) Rh 1.0	6	8	5	7	7
CH ₃	CH ₃	Rh	8.56(d) Rh 2.5	5.10(m) Rh 1.0	4.55(m) Rh 1.0	8.37(dd) Rh 2.5	7.85(s)	4.92(d) Rh 1.0	6	8	5	6.5	-
Ph	Ph	Rh	1.90— 2.90	4.40(m) Rh 1.0	3.96(m) Rh 1.0	7.43(dd) Rh 2.5	1.90— 2.90	5.17(d) Rh 1.0	-	8.5	5	7.5	-
Ph	CH ₃	Rh	2.75(m) Rh 2.5	7.92(d) Me	4.43(dd) Rh 1.0	8.24(dd) Rh 2.5	7.78(s)	5.01(d) Rh 1.0	-	-	-	7.5	-
CH ₃	H	Ir	8.48(d)	8.64(m)	5.07(dd)	8.53(t)	1.15(d)	4.92(s)	6	8.5	6	7.5	7
CH ₃	CH ₃	Ir	8.53(d)	8.93(m)	5.16(m)	8.35(d)	7.90(s)	4.80(s)	6	7.5	5	6	-
Ph	Ph	Ir	2.05— 3.04	7.42(d)	4.43(m)	7.71(d)	2.05— 3.04	5.20(s)	-	7	5	7	-
Ph	CH ₃	Ir	2.86(s)	8.12(s) Me	7.94(d)	8.21(d)	7.83(s)	4.99(s)	-	-	-	7.5	-

TABLE 2.6 Proton nmr shifts and coupling constants for $[M(\eta^4\text{diene})(\eta^5\text{-cyclopentadienyl})]$ ($M = \text{Rh, Ir}$) complexes. Coupling constants in Hz. 1,2 means $J(\text{H1-H2})$. Couplings to rhodium shown below shifts. All spectra recorded at 220 MHz in CDCl_3 except XXIX and XXX (90 MHz). Assignments according to Fig. (2.14).

Double resonance experiments were also performed to confirm certain assignments.

The coordination of open chain conjugated di-olefins to transition-metals results in an upfield shift of the diene resonances, particularly those attached to the terminal carbon atoms. The spectrum of η^4 -butadiene tricarbonyliron exhibits three resonances, all of equal intensity at τ 4.15 ppm (H_2 and H_3): 8.32 ppm ("syn" protons) and 9.78 ppm ("anti" protons).⁵¹ The authors suggested important contributions from a metallacyclopentene structure (2.15a) rather than the sp^2 hybridised structure (2.15b) although the infra-red stretching frequencies of the C-H bonds were more consistent with (2.15b).



(2.15)

In view of the unknown effects the tricarbonyliron grouping might have on the local magnetic field in the diene residue, the sp^2 hybridised structure suggested from the infra-red data was considered to be a better representation. The bonding of coordinated conjugated dienes to transition-metals has since been the subject of considerable investigation.

A similar pattern of shifts to those described above is experienced by the η^4 -buta 1,3 diene η^5 -cyclopentadienyl complexes of rhodium and

iridium^{7,59} and other analogous compounds with the "anti" protons resonating to high field of the "syn" components. This same pattern is observed for the novel complexes (XXIII-XXX) when substituent effects are considered. Thus protons H₁ and H₄ are found to resonate considerably upfield from H₂ and H₃ which resonate in the olefinic region. There is little difference in the chemical shifts of the analogous rhodium and iridium compounds although in general the resonances in the spectra of the former lie to lower field than those in the latter. A similar trend is found with the η^4 -butadiene η^5 -cyclopentadienyl rhodium and iridium compounds and can be accounted for by the greater electron density found at the iridium atom. The assignments of H₁ and H₄ in the iridium species (XXVII) and (XXVIII) are reversed relative to the analogous rhodium complexes (XXIII) and (XXIV). Assignments in the 3,5 heptadien-2-one compounds were confirmed by double resonance experiments, irradiating at selected proton frequencies and observing changes in the spectra. With the 2,4 hexadien-1-al species assignments were based on chemical shift data and multiplicities of the resonances. Reversal of these assignments could possibly indicate slight distortion of the diene bringing H₁ closer to the metal than H₄, although the changes are rather small and not observed in the carbon-13 nmr spectra. Altering the nature of the substituents R₁ and R₂ also has effects on the spectrum. There is little difference in the chemical shifts of (XXIII) and (XXIV) with the exception of the low field resonance at 1.02 ppm due to the aldehyde grouping and a similar effect is observed in the analogous iridium compounds. When R₁ and R₂ are phenyl groups there are low field shifts of all the diene resonances H₁, H₂, H₃ and H₄ due to a decrease in electron density on the diene from these substituents and the loss of the methyl inductive effects. Changes in the spectra of

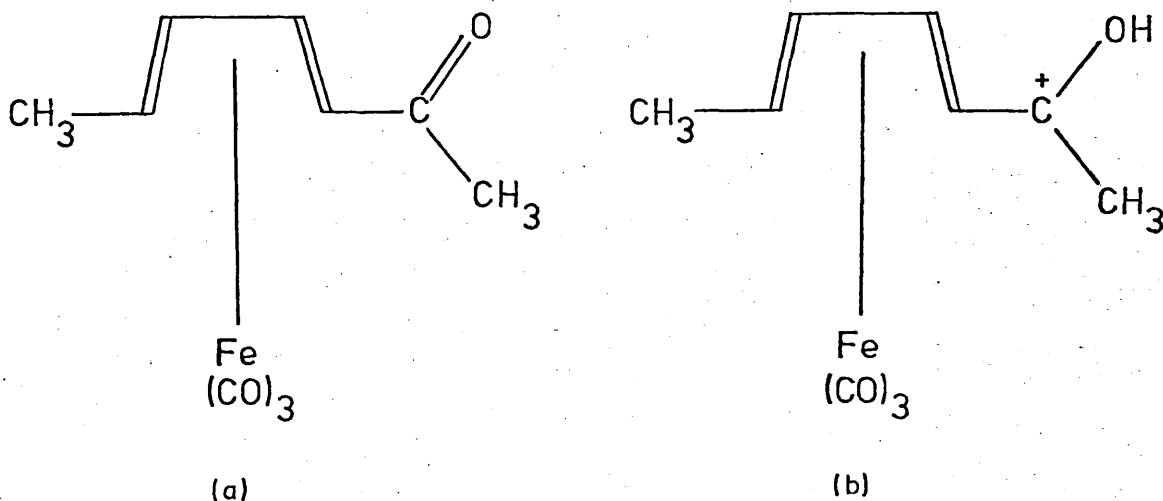
compounds (XXVI) and (XXX) are more complicated because of the introduction of the methyl group in place of H₂ but the shifts of the remaining protons are to slightly lower field relative to the 3,5 heptadien-2-one complexes. Chemical shifts for the 3,5 heptadien-2-one species (XXIV) and (XXVIII) are comparable with those of η^4 -3,5 heptadien-2-one tricarbonyliron reported by Clinton and Lillya with only minor variations in the shifts.⁸⁰

The spectra of the rhodium complexes were complicated by additional coupling to the metal centre of all protons on carbons directly bonded to rhodium and the magnitudes of these $^2J(^{103}\text{Rh}-^1\text{H})$ coupling constants are similar to those obtained by Drew and co-workers,⁷ viz ~1 Hz on H₂, H₃ and the cyclopentadienyl carbons and 2.5 Hz on H₁ and H₄.

Confirmation that the substituents R₁ and R₂ are in the "syn-syn" or "trans-trans" conformation was found from both chemical shift and vicinal proton coupling constant data. There are no upfield resonances as would be expected from "anti" substitution and the vicinal coupling constants are not significantly altered upon changing the substituents. The "cis" couplings e.g. 2,3 tend to be of the order 5-6 Hz while the "trans" couplings are slightly larger 7-9 Hz. It is noted that the "trans" couplings 1,2 are slightly larger than the 3,4 couplings, possibly indicating that H₃ and H₄ are no longer co-planar and similar effects have been observed in the tricarbonyliron system with x-ray diffraction studies confirming deviations from planarity due to the effects of steric hindrance from the substituents.⁷⁹

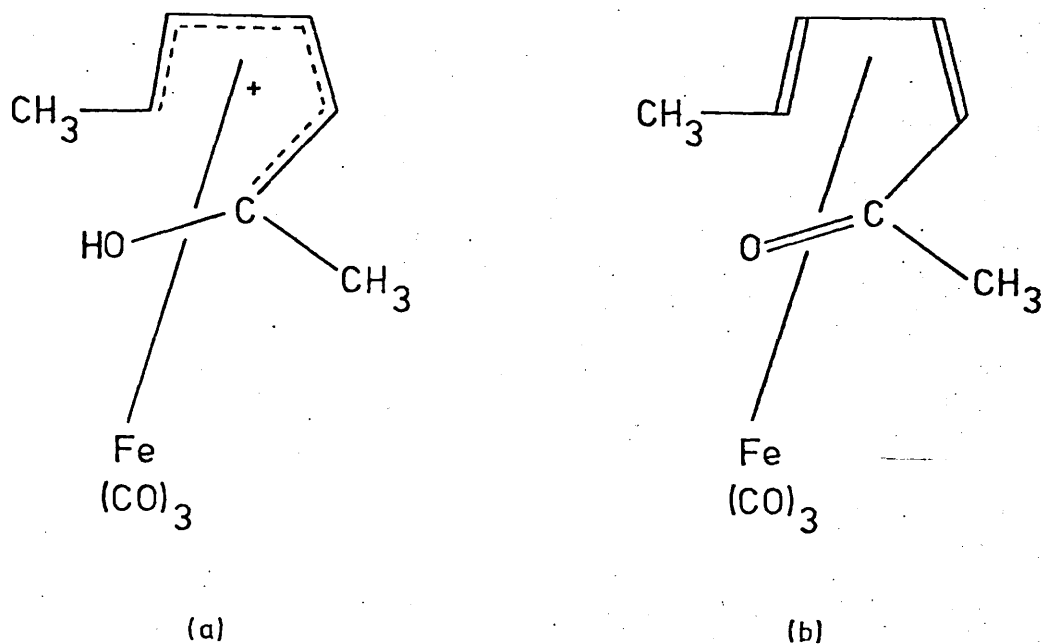
2. Protonation studies

Protonation of cyclic η^4 -diene η^5 -cyclopentadienyl-rhodium and iridium complexes using strong acids has been extensively studied by Lewis and co-workers.^{60-62, 64, 65} Oro has interpreted the protonation of η^4 -buta 1,3 diene η^5 -cyclopentadienyliridium with trifluoroacetic acid in terms of initial protonation on the metal followed by a rapid transfer of this proton to the terminal protons of the diene to give a cationic "anti"-1-methylallyl species.⁵⁹ In an attempt to observe "trans" η^5 -pentadienyl tricarbonyliron cationic systems, Clinton and Lillya have protonated η^4 -3,5 heptadien-2-one tricarbonyliron (2.16a).⁸⁰ Dissolution in concentrated sulphuric acid at -10° gave a deep red solution which exhibited broad resonances attributed to the "trans" structure (2.16b) and upfield scans to



(2.16)

τ 18.5 ppm did not reveal protonation on the metal nucleus. If this solution was warmed or allowed to stand for 15-20 minutes then the spectrum had changed to the "cis" oxygen protonated cationic species (2.17a) and after suitable work-up procedures, a new complex, the "cis" ketone complex was obtained (2.17b).



(2.17)

Protonation studies were attempted on the corresponding η^5 -cyclopentadienyl rhodium and iridium compounds. At -10° in concentrated sulphuric acid the rhodium species gave a clear deep-orange-red solution while the iridium complex gave an orange-yellow solution together with slight charring. Even on warming up to 40° , little change was visible in the spectrum except for a sharpening of the resonances due to the concentrated acid becoming less viscous. With these samples there was also no evidence for protonation on the metal from scans up to $\tau 40$ ppm. Chemical shift data are shown in table 2.7 and the spectra can be seen in (2.18). The spectrometer (Varian HA100) was locked on to the concentrated sulphuric acid resonance ($\tau \sim -2$ ppm) and chemical shifts compared with those obtained using a fixed lock instrument (Varian EM 360), aligned with chloroform/TMS both before and after the spectrum had been recorded, to check for signal drift. The rhodium complex was also dissolved in freshly distilled fluoro-

Metal	Acid	Proton chemical shifts in ppm relative to TMS ($\tau = 10$ ppm)										
Rh	H ₂ SO ₄	3.40(d)	3.80(d)	6.15(t)	6.65(m)	6.95(s)	7.1(s)	7.4(m)	7.85(m)	8.2(d)	8.8(t)	
		Cp J ~ 1Hz										
Ir	H ₂ SO ₄	Shifts very similar to rhodium, but broadened by decomposition.										
Rh	HSO ₃ F	3.40(d)	3.80(d)	4.18(s)	6.25(t)	6.7(m)	7.1(s)	7.2(s)	7.4(m)	8.0(m)	8.3(d)	8.9(t)
		Cp J ~ 1Hz										
Rh	CF ₃ COOH	4.66(m)	4.8(d)	5.2(m)	7.0(m)	7.4(m)	8.1(s)	8.3(s)	8.4(s)			
		Cp J ~ 1Hz										

TABLE 2.7 Proton nmr chemical shifts of [metal(η^4 -diene)(η^5 -cp)] complexes: diene = 3,5 heptadien-2-one

M = Rh, Ir upon protonation with strong acids.

sulphonic acid and trifluoroacetic acid. Only in the latter case were significant changes in the spectrum observed. As can be seen from the table and figure the spectra were exceedingly complex although the rhodium couplings could not be resolved. It is only possible to safely assign the cyclopentadienyl resonances from their sharpness and the slight observable coupling to the metal. These resonances at τ 3.40 and 3.80 ppm with the sulphuric and fluorosulphonic acids are significantly shifted to lower field relative to the non-protonated complexes, indicative of some delocalisation of the positive charge onto this group. The presence of two cyclopentadienyl resonances upon protonation, one more intense than the other, also indicates that more than one product is formed, although it did not prove possible to completely analyse the spectra. There does, however, seem to be a curious absence of resonances in the olefinic region which would be expected by analogy with the tricarbonyliron complex where a largely delocalised system exists. Some resonances seem to have moved to higher field while others to lower field and with the cyclopentadienyl ligands seemingly taking the bulk of the positive charge, it is surprising that protonation at the metal centre could not be found. Charring with the iridium complex indicated that decomposition had occurred with possible liberation of the diene but these results are inconclusive. Further studies are obviously necessary and possibly proton-decoupled carbon-13 nmr spectroscopy experiments with less resonances and a larger range of chemical shifts could prove more informative.

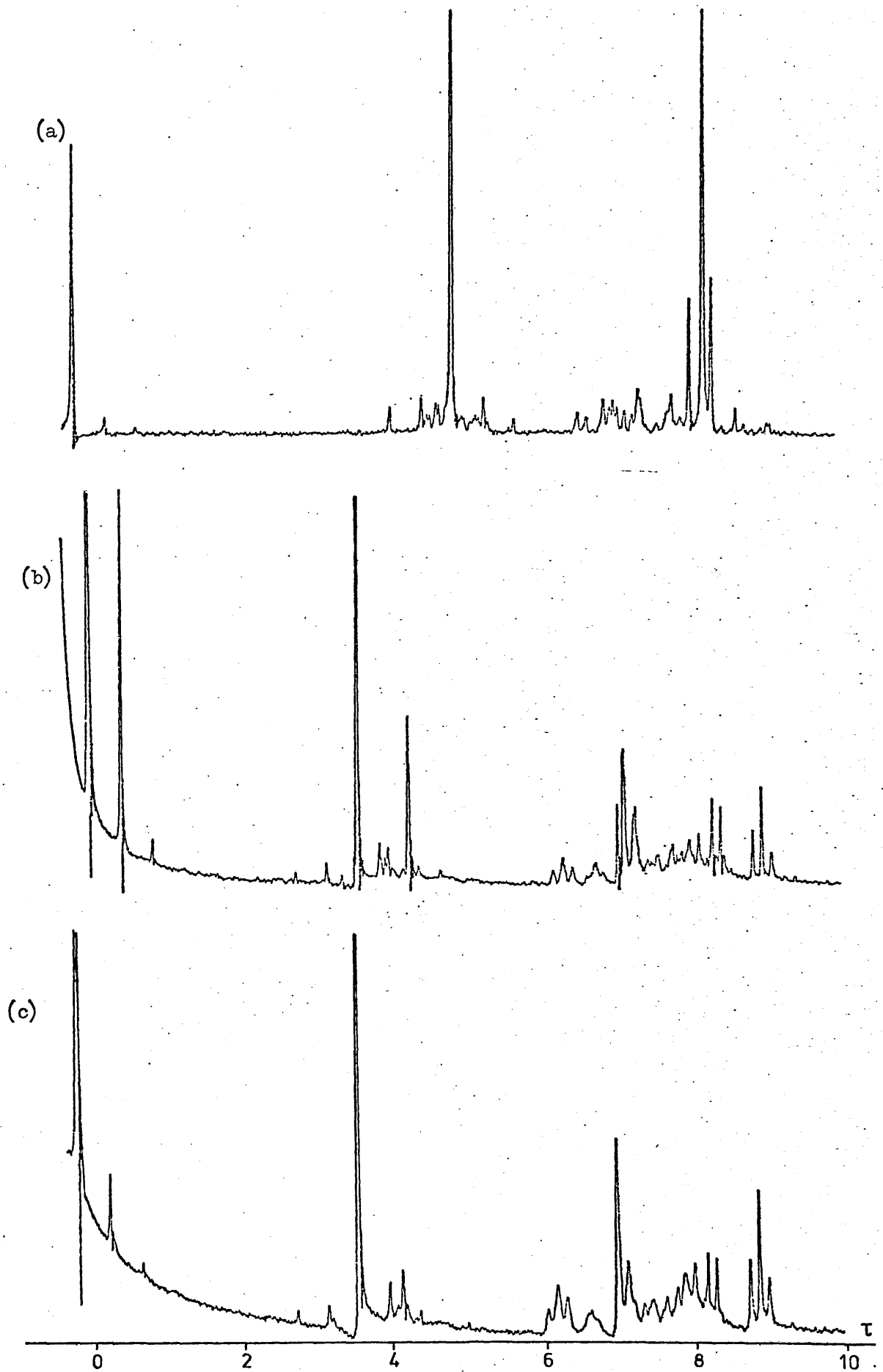
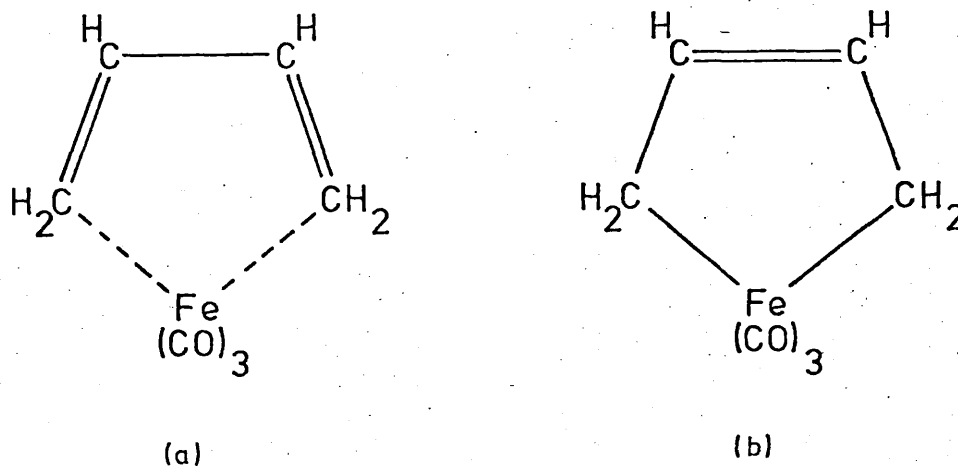


Fig. (2.18) Protonation studies of rhodium (η^4 -3,5 heptadien-2-one)
 (η^5 -cyclopentadienyl) in (a) CF_3COOH (b) HSO_3F (c) H_2SO_4 .

(iv) Spectroscopic investigation using carbon-13 nmr

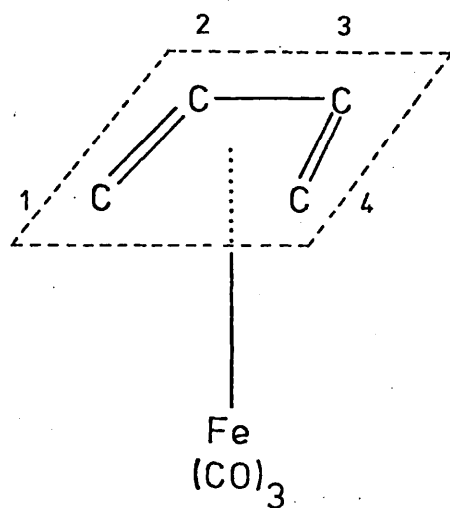
Despite the considerable difficulties in the interpretation of the chemical shifts of organic ligands coordinated to transition-metals, carbon-13 nmr spectroscopy has become increasingly used as an experimental technique in the study of these complexes. Recently, organic groups coordinated to the tricarbonyliron residue have been extensively studied to elucidate the bonding modes in these coordinated systems.

Reihlen and co-workers first prepared η^4 -buta 1,3 diene tricarbonyliron in 1930 by reacting iron pentacarbonyl with butadiene in a pressure tube.⁸² They proposed structure (2.19a) in which the iron was " σ "-bonded to the terminal carbon atoms of the diene forming a five-membered ring although an alternative structure with " σ " bonded iron and the formation of a new double bond was not excluded (2.19b). Hallam and Pauson in 1958,⁸³ by

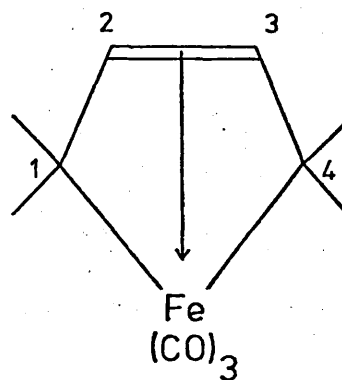


(2.19)

comparison with η^4 -cyclohexa 1,3 diene tricarbonyliron concluded that η^4 -buta 1,3 diene tricarbonyliron existed in the "cis" configuration (2.20a) and x-ray analysis later confirmed that indeed all the diene carbon atoms adopt a "cis" conformation with all those carbon atoms co-planar and equidistant from the metal nucleus which lies below the plane.⁸⁴ Wilkinson et al. considered another alternative from nmr



(a)



(b)

(2.20)

experiments, similar to (2.19a) but with the exception that the free double bond was also coordinated to the metal (2.20b).⁵¹ A structure such as (2.20a) implies that the electrons are largely delocalised as in uncoordinated butadiene while the metallacyclopentene structure (2.20b) is indicative of considerable localisation of the bonding electrons between the terminal carbons and the metal and also between the central carbon atoms and the metal centre. With carbon-13 nmr spectroscopy now a routine technique in the laboratory the η^4 -buta 1,3 diene tricarbonyliron system has been subjected to considerable study.

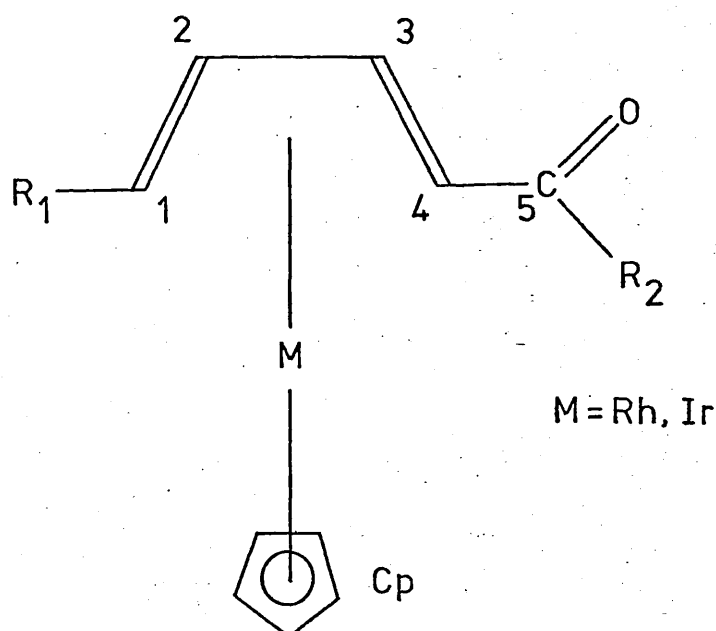
Retcofsky et al.⁸⁵ studied the spectra of η^4 -buta 1,3 diene tricarbonyliron and also η^4 -methyloctadecadienoate tricarbonyliron and concluded that the major contributor to the bonding was a structure such as (2.20a) with all the butadiene carbons essentially sp^2 hybridised. Steric effects from the terminal groups then resulted in a twisting of the C_1-C_2 and C_3-C_4 bonds but the sp^2 hybridisation at both terminal carbons

was considered to be largely unaffected. Preston and Davies⁸⁶ also favoured a similar representation from the magnitude of the vicinal ^{13}C - ^1H coupling constants which were similar to those observed in uncoordinated butadiene. However, the authors of both papers failed to comment upon the observation of a single sharp resonance in the carbonyl region, inconsistent with either of the considered structures. Similar results were also obtained by Kruczynski and Takats⁸⁷ who stated that this single sharp resonance was clearly inconsistent with the static geometries (2.20 a and b) and was the result of an intramolecular rearrangement via carbonyl scrambling. Separate carbonyl resonances were resolved at low temperatures and different rearrangement rates observed for conjugated and non-conjugated diene systems with the increased activation barrier for carbonyl scrambling in the formally five-coordinate conjugated diene compounds attributed to a significant contribution from the six-coordinate " $\sigma - \pi$ " structure (2.20b). The bonding between a diene and the metal residue is assumed to consist of two interdependent factors; donation from the highest occupied molecular orbital of the ligand into vacant metal "d" orbitals and back donation of electron density from the metal into the lowest unoccupied molecular orbital of the diene. For conjugated 1,3 di-olefins the form of these orbitals is such that their participation in bonding to the metal weakens the bonds $\text{C}_1\text{-C}_2$ and $\text{C}_3\text{-C}_4$, originally carbon-carbon double bonds, but strengthens the $\text{C}_2\text{-C}_3$ bond, originally a single bond. This seemingly favours the metallacyclopentene structure over the sp^2 hybridised system, although other data has tended to favour the latter configuration. It would seem that both structures make significant contributions to the bonding consistent with x-ray data. Pearson⁸⁸ has also concluded that contributions from (2.20b) are significant from a study of " β "-methyl

effects, found in the carbon-13 nmr spectra of conjugated 1,3 dienes both when and not coordinated to the tricarbonyliron unit. He proposed a modified type of bonding between the iron atom and the butadiene ligand in which the two occupied " π " orbitals of butadiene are localised, thus allowing for retention of sp^2 character of all the diene carbon atoms while giving the appearance of bonding from the " $\sigma - \pi$ " structure. This model appears to meet the requirements of all observations on the tricarbonyliron system, allowing for slight deviations from planarity by the diene ligand by partial rotation about the C_1-C_2 and C_3-C_4 bond axes, consistent with x-ray observations. Thus, this allows for the retention of the sp^2 hybridised vicinal $^{13}C-^1H$ coupling constants while forming the " σ " framework. Similar conclusions have also been drawn by von Philipsborn^{89,90} from a high resolution study of the proton coupled carbon-13 nmr spectrum of η^4 -buta 1,3 diene tricarbonyliron and ruthenium. On the basis of vicinal $^{13}C-^1H$ and $^1H-^1H$ coupling constants as well as long range $^{13}C-^{13}C$ couplings a non-planar C-H skeleton was proposed in which the carbon-carbon bond lengths are nearly equal and the terminal carbon atoms exhibit some rehybridisation towards sp^3 .

By comparison with the tricarbonyliron system, the η^5 -cyclopentadienyl rhodium and iridium units have relatively poor accepting properties and will guarantee considerable back donation to the conjugated diene fragment allowing for greater electron density to accumulate in the diene than with the tricarbonyliron system and its better acceptor properties. The η^5 -cyclopentadienylrhodium and iridium units would thus be expected to stabilise a contribution from the six-coordinate " $\sigma - \pi$ " structure relative to the tricarbonyliron residue.

The carbon-13 proton decoupled nmr spectra for the novel complexes (XXIII-XXVIII) are reported in table 2.5. All the spectra were recorded at 22.63 MHz in deuterated chloroform with TMS as internal reference and all shifts are quoted in parts per million downfield from TMS. Coupling constants are measured in hertz and assignments are shown in (2.21). The difficulties in the interpretation of chemical



(2.21)

shifts in coordinated complexes have already been emphasised and these shifts have little application in describing the bonding in these systems although the metal-carbon coupling constant may have some validity in assessing bonding modes provided that the oxidation states and stereochemistries of the compounds are taken into account. The $M-^{13}C$ spin-spin coupling interactions are largely dependent upon the

¹³C nmr chemical shifts relative to TMS, internal reference 0 ppm

Substituents		No.	C ₁	C ₂	C ₃	C ₄	C ₅	Cp.	Other
R ₁	R ₂	R ₃							
CH ₃	H	Rh	XXIII 53.9(d) J 15	82.1(d) J 7	77.7(d) J 9	56.0(d) J 15	196.5	84.3(d) J 7	R ₁ 21.8
CH ₃	CH ₃	Rh	XXIV 51.0(d) J 15	80.7(d) J 8	75.8(d) J 9	54.4(d) J 16	205.4	84.4(d) J 7	R ₁ 21.8 R ₂ 28.6
Ph	Ph	Rh	XXV 47.1(d) J 16	79.0(d) J 7	76.6(d) J 8	57.4(d) J 13	198.1	85.4(d) J 5	R ₁ } 125.4 132.0 R ₂ } 126.0 136.5 } 127.7 139.1 } 128.4
Ph	CH ₃	Rh	XXVI 50.6(d) J 16	93.4(d) J 7	77.6(d) J 8	60.2(d) J 13	205.8	85.5(d) J 5	R ₁ 125.4 129.4 126.7 134.3
CH ₃	H	Ir	XXVII 41.0	72.3	66.8	46.6	198.4	77.3	R ₁ 22.8
CH ₃	CH ₃	Ir	XXVIII 40.0	70.7	65.7	43.6	206.8	77.6	R ₁ 22.9 R ₂ 28.7

TABLE 2.8 ¹³C nmr shifts of [M(η⁴-diene(η⁵-cyclopentadienyl)] complexes M = Rh, Ir. All resonances are singlets except where stated. All data in CDCl₃ at 22.63 MHz. Coupling constants J(¹⁰³Rh-¹³C) in Hz. For assignments see Fig. (2.21).

Compound	Chemical shifts			^{13}C - ^1H couplings		
	$\text{C}_{1,4}$	$\text{C}_{2,3}$	$\text{C}_{1,4}$	$\text{C}_{1,4}$	$\text{C}_{2,3}$	$\text{C}_{2,3}$
* Butadiene	116.6	137.2	158	158	158	158
* η^4 -butadiene tricarbonyliron	41.1	85.8	158	158	158	169
** η^4 -butadiene tricarbonylruthenium	32.7	86.3	158	158	158	168
η^4 -butadiene η^5 -cyclopentadienylrhodium	32.5(d)	76.8(d)	158	158	158	167
	J 17	J 8				

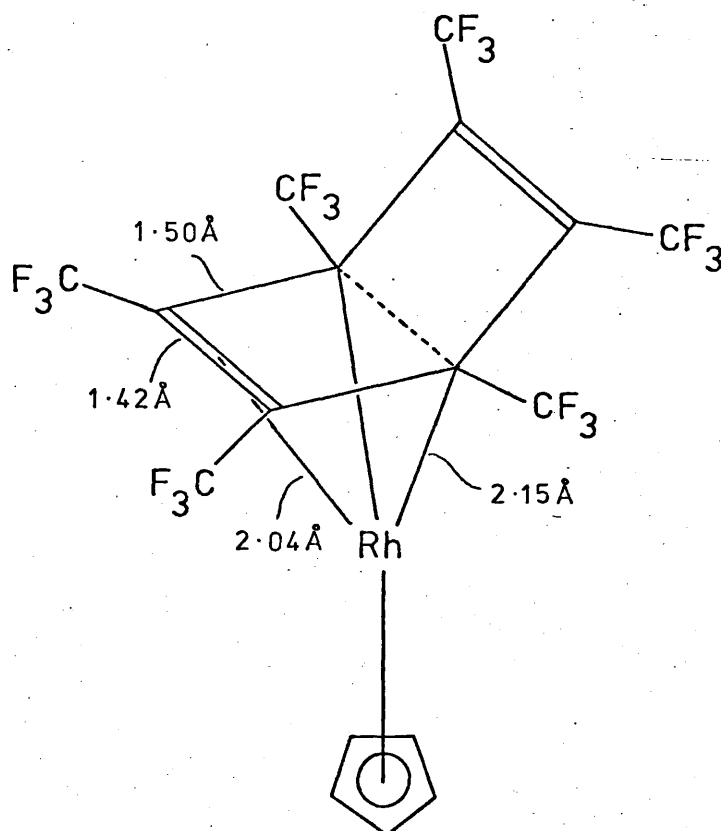
TABLE 2.9 ^{13}C nmr data for butadiene complexes. Chemical shifts are in ppm downfield from TMS, coupling constants are in Hz. All data come from proton coupled spectra at 22.63 MHz in CDCl_3 with the exception of ^{13}C - ^{103}Rh coupling constants (obtained from proton decoupled spectrum).

* see ref. 88 for data.

** data taken from ref. 90.

Fermi contact term transmitted through the "s" contribution to the bond and hence the degree of "s" character should be reflected in the magnitude of the M- ^{13}C coupling constant.^{36,40} Examples of these can be seen in table 2.9 which shows a comparison between chemical shifts and coupling constants for some coordinated η^4 -butadiene complexes and butadiene itself. Assignments are again based on (2.21). The second-row transition-metal complexes exhibit chemical shifts to higher field than for the tricarbonyliron complex: this is expected from increased contributions from the diamagnetic shielding contributor and the upfield chemical shifts of the di-olefin resonances on complexation to the metal are clearly observed. Little variation in the magnitude of the vicinal ^{13}C - ^1H coupling constants for the complexed diene is seen and these values all lie in the range expected for sp^2 hybridised carbons³⁶; reasons for this have already been discussed. However, the additional information gained from coupling to the metal nucleus reveals that the values for the ^{103}Rh - ^{13}C coupling constants to the terminal carbon atoms $\text{C}_{1,4}$ at 17 Hz are substantially larger than for $\text{C}_{2,3}$ at 8 Hz. This value of 8 Hz is typical for a carbon atom " π "-bonded to rhodium while the value of 17 Hz approaches the borderline for both " σ " and " π "-bonded carbons. Lewis and co-workers⁴⁵ have reported a value of 19 Hz for a " σ "-bonded carbon atom, although larger values have been reported, while values of 14-16 Hz have been attributed to " π "-bonded carbons. These data can be interpreted by significant contributions from a six-coordinate metallacyclopentene structure similar to that represented by 2.20b. Churchill and Mason have shown, from x-ray analysis,⁹¹ that the structure of hexakis(trifluoromethyl)benzene

η^5 -cyclopentadienylrhodium has a free double bond, although, of course, this complex must be viewed as an extreme example because of the strong electron withdrawing effects of the fluorine substituents (2.22).



(2.22)

Carbon-13 nmr spectroscopic studies on this complex would be informative to enable comparison between the ^{103}Rh - ^{13}C coupling constants with those of the diene complexes reported here. Similar values for the rhodium-carbon coupling constants are also observed in the compounds (XXIII-XXVI) and for η^4 -cyclohexa 1,3 diene η^5 -cyclopentadienyl rhodium which must

also adopt the "cis" configuration. The slightly smaller values found at the terminal carbon atoms in some cases can be attributed to substituent effects at the 1 and 4 positions. Coupling to the rhodium-103 nucleus (100% abundant, $I = \frac{1}{2}$) was observed on all carbons directly bonded to the metal whereas coupling to either of the iridium isotopes ^{191}Ir and ^{193}Ir with their spins of $5/2$ was never observed in any spectra.

Chemical shifts for the diene carbons bonded to iridium were found to lie about 10 ppm upfield relative to the rhodium species and this is attributed to an increased contribution from the diamagnetic shielding constant. Little change was observed in the substituents on the diene indicating that these are not significantly involved in bonding to the metal. Carbons C_2 and C_3 resonate to lower field of C_1 and C_4 , similar to the pattern of the chemical shifts of the protons on these respective carbons, possibly indicating the greater olefinic character of the $\text{C}_2\text{-C}_3$ bond, although caution must be taken with these interpretations. The aldehyde and ketone carbonyl resonances are found to lie at much lower field than the remaining resonances due to a residual positive charge resulting from the canonical contributors $\text{C}=\text{O}$ and $\overset{+}{\text{C}}-\overset{-}{\text{O}}$. These are typical of organic carbonyl groupings readily observable in the rapid pulsing technique employed in the acquisition of this data. Metal carbonyl resonances are generally not observed under these conditions due to their longer relaxation times, unless small quantities of a relaxation agent are added.

Assignments in $\eta^4\text{-3,5 heptadien-2-one } \eta^5\text{-cyclopentadienyliridium}$ (XXVIII) were confirmed using double resonance techniques with irradiations at selected frequencies in the proton nmr spectrum. Irradiation of the

proton at τ 4.68 ppm gave rise to a single sharp absorption in the carbon-13 nmr spectrum at 65.7 ppm while other carbons remained as low intensity multiplets without the Overhauser enhancement. This indicates that the proton at τ 4.68 ppm (H_3) is coupled to the carbon atom resonating at 65.7 ppm (C_3). Similarly irradiation at τ 8.35 ppm resulted in a sharp singlet at 43.6 ppm in the carbon spectrum, indicating that C_4 is coupled to H_4 : this can be seen in (2.23). Attempts at double resonance in the analogous rhodium complex proved inconclusive; the loss of Overhauser enhancement together with the residual coupling to the rhodium nucleus makes acquisition of the data difficult in this experiment and the data from the other rhodium and iridium species are assigned by analogy with the fully resolved iridium complex. The pattern of assignments is similar to those observed by Anderson and co-workers⁹² with $\eta^{4-3,5}$ -hexadien-2-ol tricarbonyliron although Kreiter et al.⁹³ differ in their assignments of C_2 and C_3 in $\eta^{4-3,5}$ heptadien-2-one tricarbonyliron. Changes in the nature of the substituents R_1 and R_2 have little effect on the chemical shifts of carbons C_2 and C_3 , the variation being of the order 3 ppm. The " α " effect of the methyl³⁶ group in (XXVI) of course deshields C_2 ; this being of the order 14 ppm with respect to the unsubstituted compounds. When R_1 is methyl, there is a substantial downfield shift (~ 20 ppm) of the C_1 resonance with respect to η^4 -buta 1,3-diene η^5 -cyclopentadienyl-rhodium, again due to the " α " effect and there is also a downfield shift when R_1 is phenyl although this is not so great. These effects are typical of those observed in the carbon-13 nmr spectra of uncoordinated ligands.

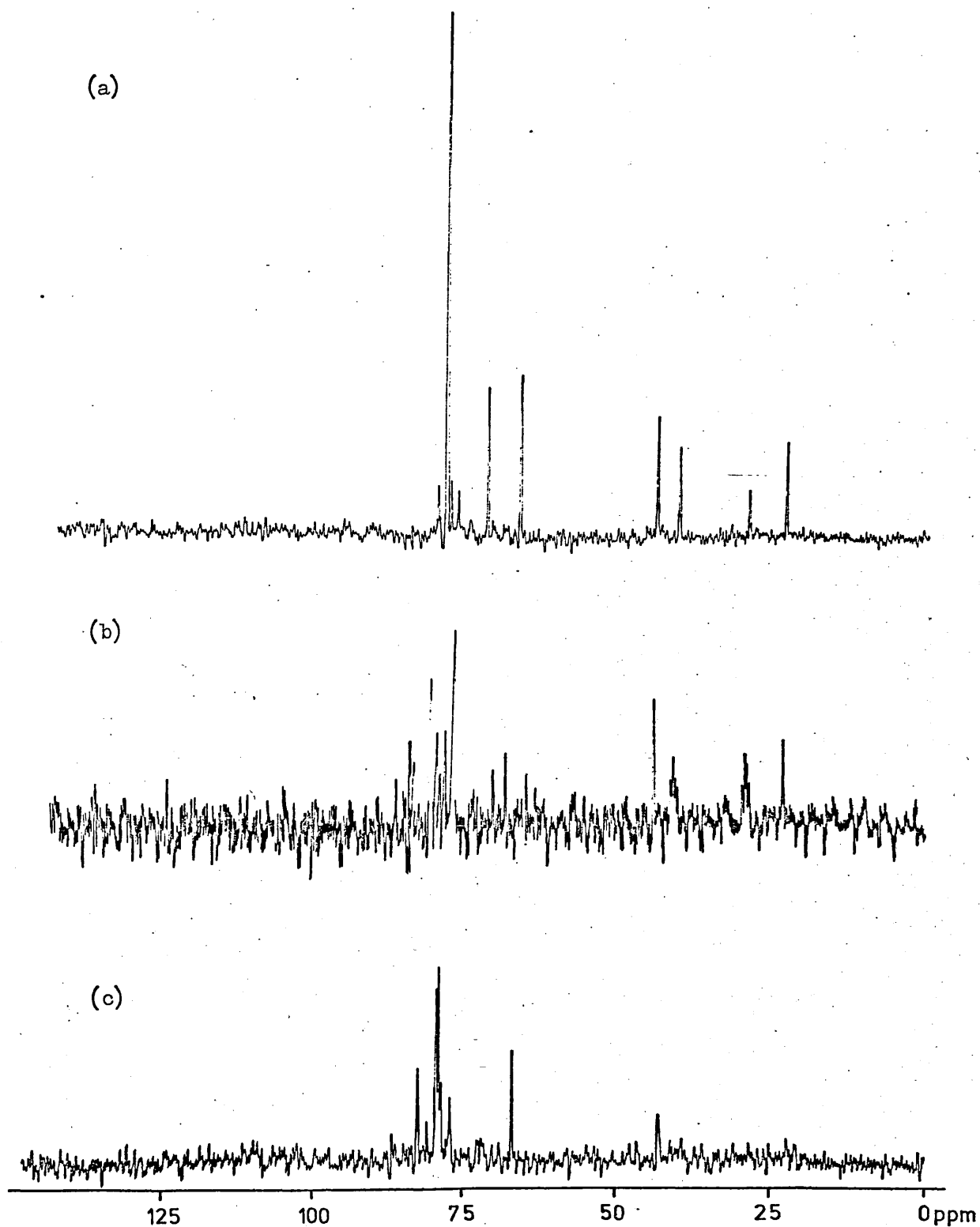


Fig. 2.23 ^{13}C nmr spectrum of $[\eta^4\text{-3,5 heptadien-2-one } \eta^5\text{-cyclopentadienyl-iridium}]$

(a) proton decoupled spectrum.

(b) proton coupled spectrum with irradiation at τ 8.35 ppm on the ^1H spectrum

(c) proton coupled spectrum with irradiation at τ 4.68 ppm on the ^1H spectrum

Proton coupled spectra were also obtained for some complexes to enable measurement of the vicinal $^{13}\text{C}-^1\text{H}$ coupling constants (Table 2.10) and were compared with data obtained from some related η^4 -diene complexes of rhodium (Table 2.11). Difficulty was again found with the rhodium complexes because of the loss of Overhauser enhancement and residual rhodium coupling which means that satisfactory spectra often may not be obtained, even after overnight accumulation. However, values obtained gave good agreement with similar tricarbonyliron compounds. The magnitudes for the couplings to C_1 and C_4 are smaller than for the C_2 and C_3 carbons possibly resulting from an increase in double bond character between C_2 and C_3 although both sets of values lie in a range typical for sp^2 hybridisation.³⁶ Similar observations by other workers have already been discussed and the same parameters are probably dominant here. Values for the methyl and cyclopentadienyl groups are also typical of those found by other groups⁴⁰ and also for the η^3 -allyl complexes described in Chapter 1. It is interesting that there are only minor changes in the spectra of both the cyclic and open chain compounds probably indicating that substituent effects do not greatly affect the major contributors to the chemical shifts and coupling constants.

The data for these complexes seem to indicate that the " $\sigma-\pi$ " structure is indeed a significant contributor to the bonding with increased back donation into the antibonding orbitals of the organic ligand similar to that observed in analogous tricarbonyliron systems, although the actual bonding and the degree to which the antibonding orbitals are involved will vary in the different species.

Complex	Vicinal ^{13}C - ^1H coupling constants (Hz)					
	$\text{C}_1\text{-H}$	$\text{C}_2\text{-H}$	$\text{C}_3\text{-H}$	$\text{C}_4\text{-H}$	Cp	Other
XXIII	156	168	168	155	177	C_5 167; Me 127
XXV	158	171	168	158	178	
XXVIII	158	173	171	158	179	Me 128

TABLE 2.10 ^{13}C nmr coupling constants of $[\text{M}(\eta^4\text{-diene})(\eta^5\text{-cp})]$ complexes.
All data refer to CDCl_3 solutions at 22.63 MHz.

Complex	^{13}C nmr chemical shifts				
	C_1	C_2	C_3	C_4	Cp
η^4 -buta 1,3 diene	32.5(d)	76.8(d)	76.8(d)	32.5(d)	82.6(d)
η^5 -cyclopentadienylrhodium	J 17	J 8	J 8	J 17	J 5
	158	167	167	158	176
η^4 -cyclohexa 1,3 diene	55.2(d)	75.8(d)	26.7(s)	$\text{C}_{5,6}$	82.5(d)
η^5 -cyclopentadienylrhodium	J 16	J 7			J 4
	158	163	126		177
η^5 -cyclohexadienyl	* 26.6(s)	Resonances at			50.5(d) J 8
η^5 -cyclopentadienylrhodium tetrafluoroborate				94.3(d) J 5	J 5

TABLE 2.11 ^{13}C nmr chemical shifts in ppm downfield from TMS, internal-reference (0 ppm). All data in CDCl_3 at 22.63 MHz except * in CD_3NO_2 . Couplings to rhodium quoted in Hz (J 8) below chemical shifts. Vicinal ^{13}C - ^1H couplings (Hz) quoted below these. For assignments see text.

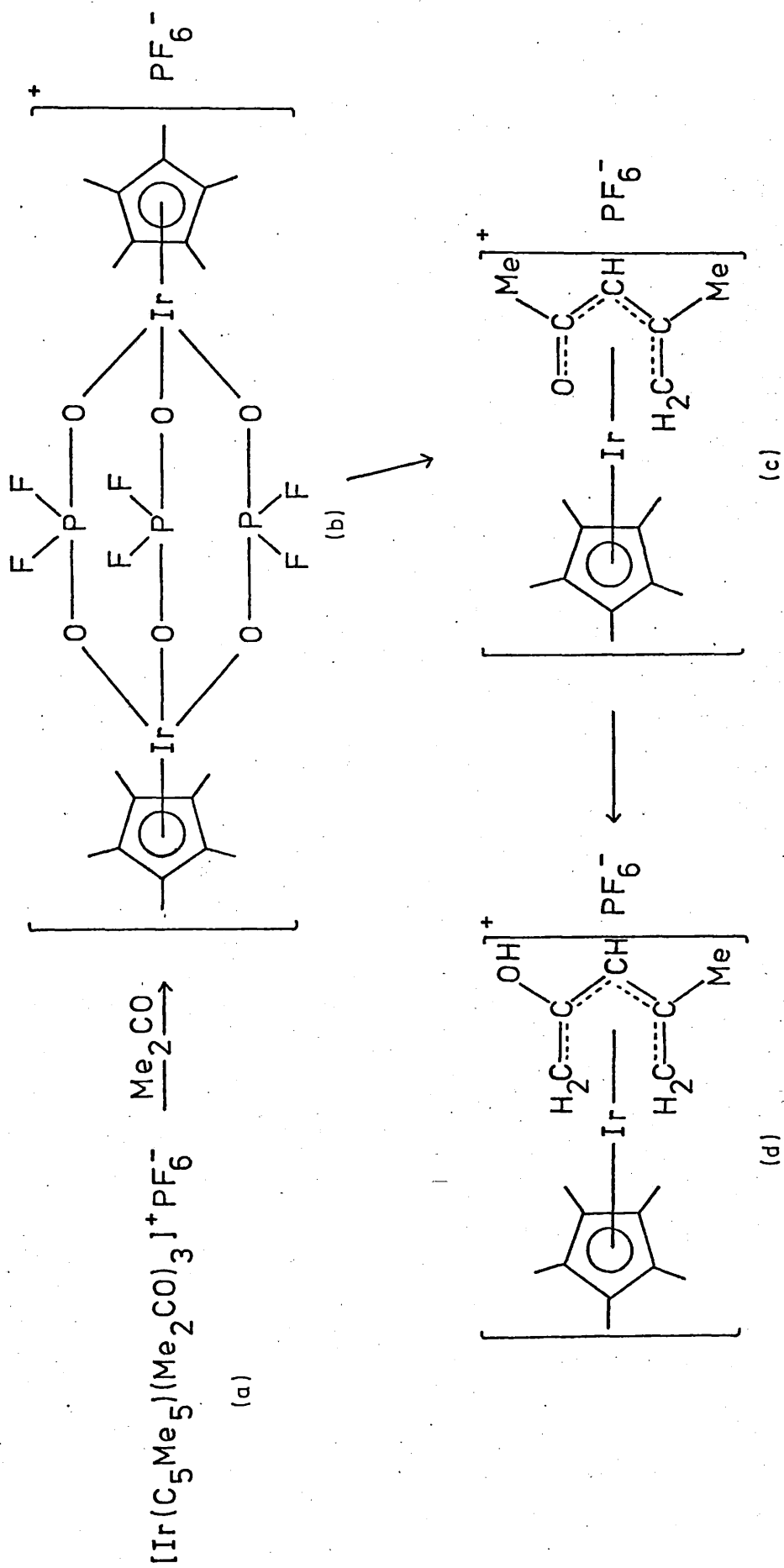
(c) η^5 -syn-1-methylpentadienyl η^5 -cyclopentadienylrhodium
tetrafluoroborate

(i) Preparation and properties

Coordination of the acyclic η^5 -pentadienyl ligand to a transition-metal other than iron is rare and although the tricarbonyliron salts have been subjected to intensive preparative, spectroscopic and kinetic studies, similar research with other metal systems has received little attention. Abel and Moorhouse⁷⁴ have prepared η^5 -syn-1-methylpentadienyl-tricarbonylmanganese and Maitlis et al. have recently reported the syntheses of the η^5 -1-oxa 1,3 pentadienyl and η^5 -2-hydroxy-4-methylpentadienyl η^5 -cyclopentadienyliridium cationic species,⁷⁶ (Scheme 2.13).

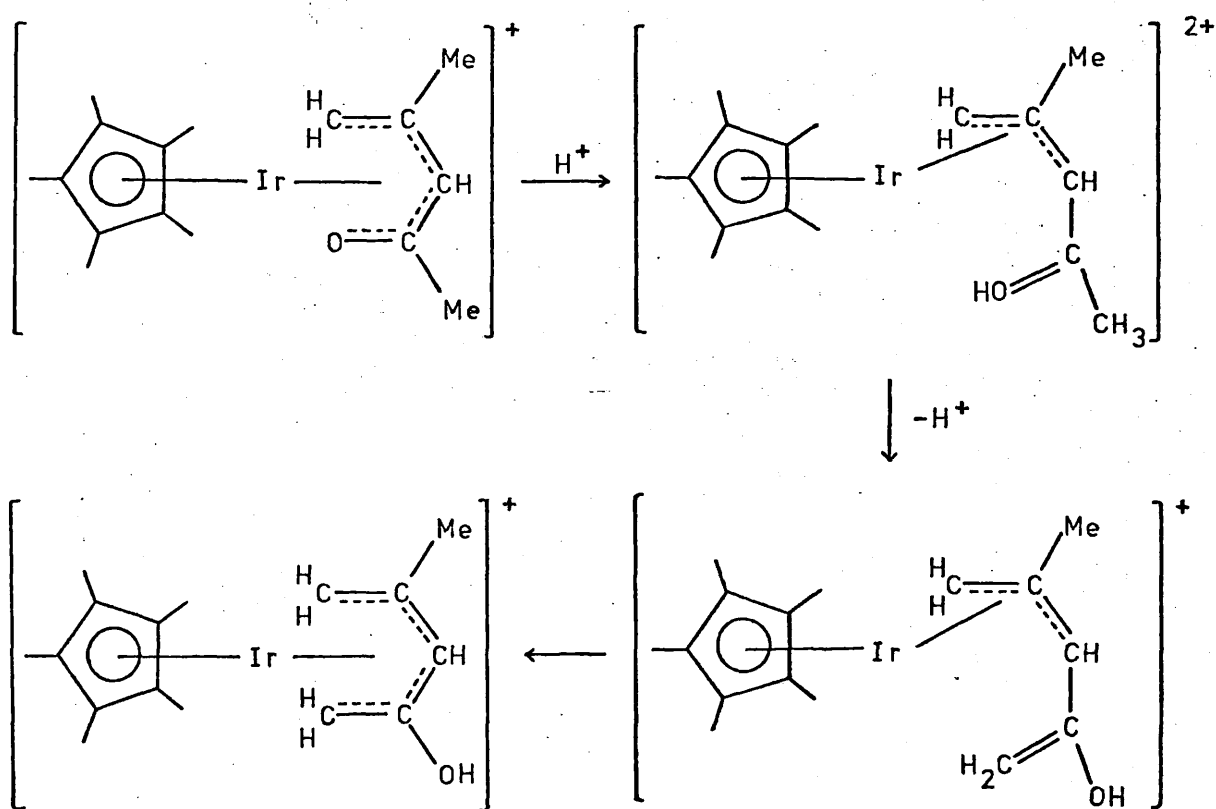
When the acetone species (a) was allowed to stand in acetone at 35° a series of rearrangements occurred which could be observed by following the change in the chemical shift of the pentamethylcyclopentadienyl group using proton nmr spectroscopy and after twenty-one days at 35° or three days at 50° only the salt (d) remained. The pentadienyl ligand in (d) is the deprotonated "enol" form of mesityl oxide $\text{CH}_3\text{C}(\text{CH}_3) = \text{CHCOCH}_3$ and could also be synthesised by reaction of the acetone complex (a) with mesityl oxide. Initially the intermediate product (c) was formed which could then be slowly converted into (d) in the presence of difluorophosphoric acid (HPO_2F_2) or trifluoroacetic acid. A mechanism for these rearrangements was considered to involve three separate reactions:

- (i) the selective solvolysis of the PF_6^- anion to coordinated PO_2F_2^-
- (ii) the deprotonation of mesityl oxide to give the oxapentadienyl ligand and
- (iii) the isomerisation of the oxapentadienyl ligand to the hydroxypentadienyl species.



(Scheme 2.13)

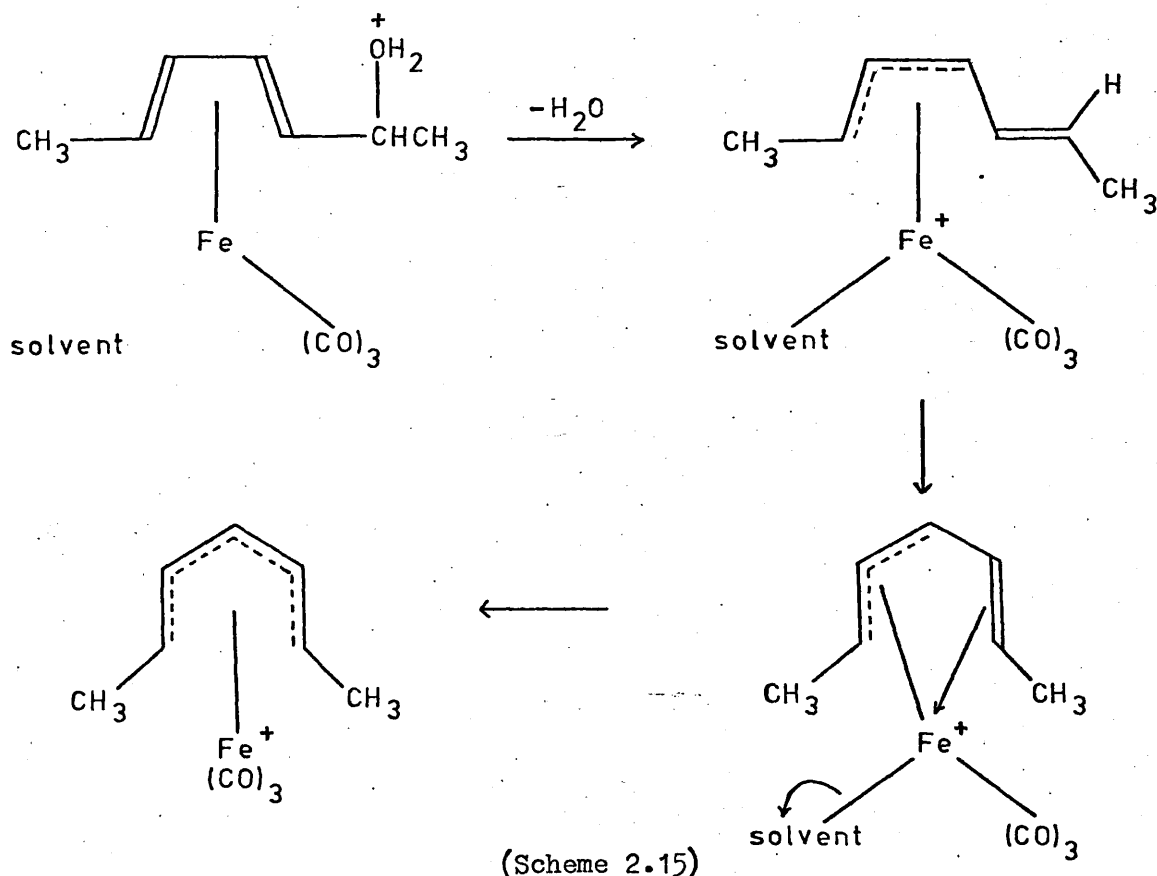
Initial formation of the difluorophosphate species was presumed to result from the effects of the metal and mesityl oxide, this being produced "in situ" from the catalysed aldol condensation of acetone. Deprotonation then follows giving an η^3 -allylic intermediate which then rearranges to give the favoured η^5 form of bonding of iridium(III). Salt (c) is thought to isomerise to (d) by formation of the thermodynamically favoured all carbon bonded system over the carbon and oxygen bonded species. A further mechanism was postulated involving decomplexation and deprotonation of the carbonyl group, elimination of H^+ from the adjacent methyl resulting in the "enol" form followed by rotation about the carbon-carbon bond and finally recomplexation (Scheme 2.14).



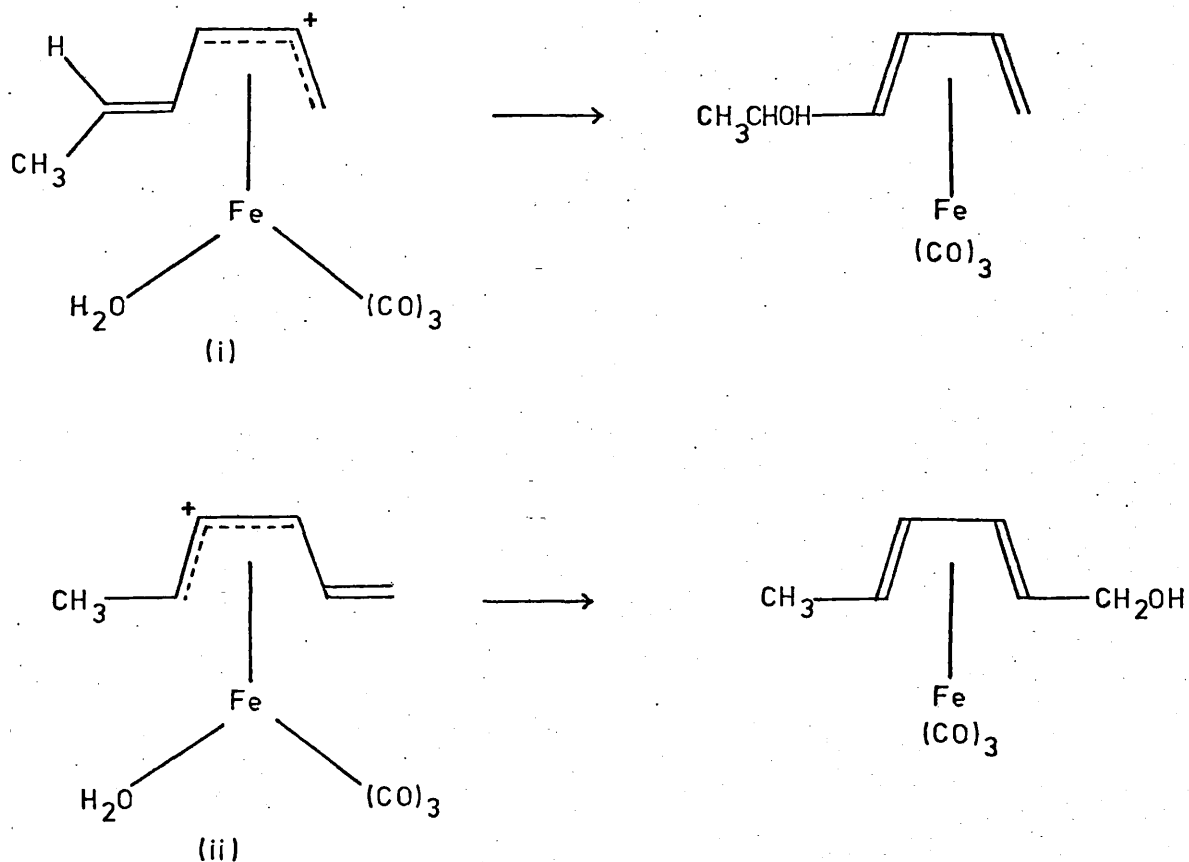
(Scheme 2.14)

However, this synthesis is not of general application. Salts of the η^5 -pentadienyl tricarbonyliron system have usually been prepared from the corresponding diene complex with an hydroxy group adjacent to the diene unit by protonation with strong acids.^{71,72} The "syn-syn"

η^5 -1,5 dimethylpentadienyl tricarbonyliron salt has been prepared by reaction of the coordinated 3,5 heptadien-2-ol complex with fluoroboric acid in acetic anhydride and the reaction is thought to proceed via initial protonation of the alcohol followed by loss of water and rearrangement to yield the "cis" cation. Reaction of this salt with water leads to the trans alcohol complex through geometrical inversion and this scheme is similar to that for the formation of the cationic species (2.15). The η^5 -syn-1-methyl pentadienyl tricarbonyliron salt

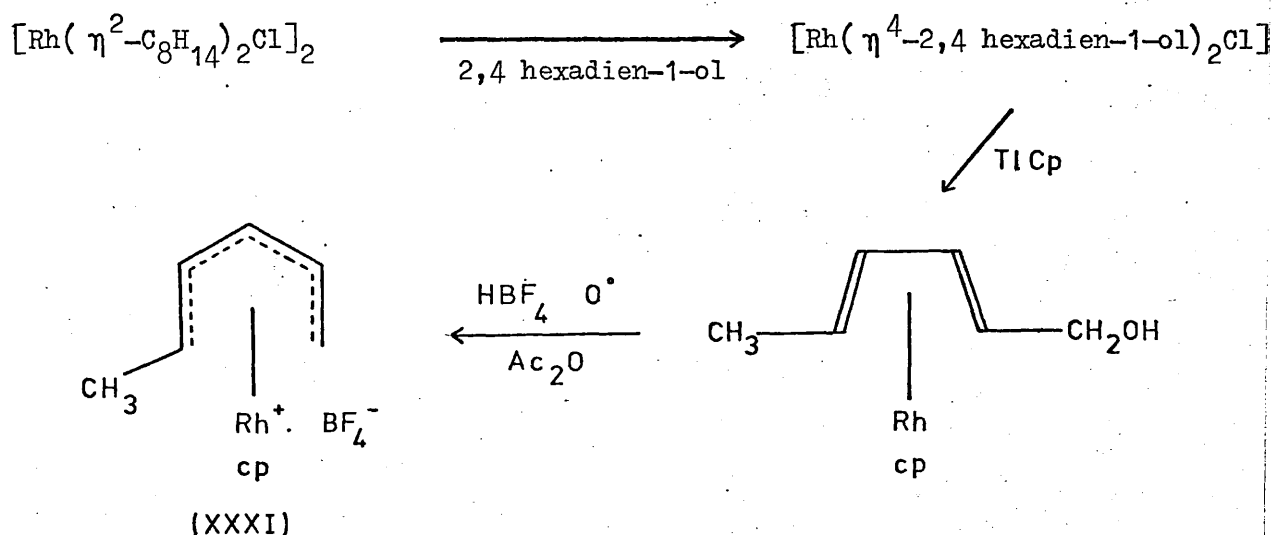


also undergoes geometrical isomerisation with water and two intermediates can be envisaged which would then give two different alcohol complexes (Scheme 2.16). However intermediate (i) is thought to be more stable because it contains the most substituted olefin and the least sterically crowded hydrated π -allyl tricarbonyliron cation and the inductive effect of the methyl group in (ii) is thought to lead to a decrease in bonding via back donation from the iron atom to the allyl system relative to (i). 2,4 Hexadien-1-ol has previously been found to displace the coordinated cyclooctene from $[\text{Rh}(\eta^2\text{-cyclooctene})_2\text{Cl}]_2$ to give the new species (XI). This will undergo reaction with cyclopentadienyl thallium



(Scheme 2.16)

in the absence of light to give a brownish oil which probably contains the alcohol complex (η^4 -2,4 hexadien-1-ol) (η^5 -cyclopentadienyl)rhodium. Although this product could not be isolated, it underwent a further reaction with fluoroboric acid to give the "cis" salt η^5 -syn-1-methyl-pentadienyl η^5 -cyclopentadienylrhodium tetrafluoroborate (XXXI) analogous to the corresponding tricarbonyliron complex (Scheme 2.17). By analogy to the tricarbonyliron system a similar mechanism probably holds to result in the formation of the "cis" salt. The rhodium compound



(Scheme 2.17)

is a pale yellow salt readily soluble in polar organic solvents and stable to air and moisture both as a solid and in solution. In this respect it seems to be much more stable than the similar tricarbonyliron salt. Attempts to prepare similar cationic species by this method proved less successful due to difficulty in coordinating the cyclopentadienyl ligand to the alcohol complexes, although further studies might produce more successful results.

The reaction of 1,5 diphenyl 2,4 pentadien-1-ol with Cramer's tetraethylene complex gave a product which was not isolated but after similar work-up procedures described above an impure brownish-yellow solid was isolated. Nmr spectroscopy showed the presence of the "syn-syn" η^5 -1,5 diphenylpentadienyl cationic complex together with substantial impurity but the product could not be isolated in a pure state even after repeated recrystallisation. When 1,3,5 hexatriene was used as the diene with the rhodium cyclooctene species only oily products could be isolated and after treatment with acid a yellow solid was isolated but nmr studies on this proved inconclusive.

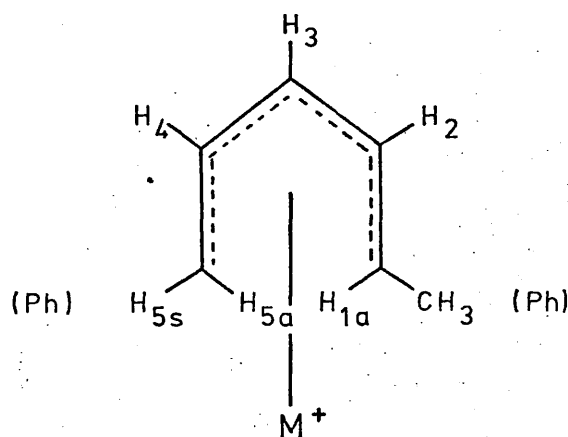
Heck²⁸ has shown that allyl halides react with η^5 -cyclopentadienyl dicarbonylcobalt to give cationic species together with small amounts of a covalent halogeno-complex. A similar experiment was carried out with 1-bromo 2,4-hexadiene and after suitable procedures, an orange-brown product was isolated. After repeated recrystallisation, the nmr spectrum indicated the presence of the η^5 -syn-1-methylpentadienyl η^5 -cyclopentadienylcobalt cationic species together with a strong impurity resonance at τ 4.01 ppm in deuterated nitromethane. This latter resonance is thought to be due to formation of the cobalticinium salt $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+ [\text{PF}_6]^-$ which exhibited a resonance at τ 4.04 ppm in d^6 acetone.⁹⁴

It can be concluded that rhodium and iridium may also have an extensive acyclic diene chemistry in addition to the tricarbonyliron system. There is the advantage in these systems over ruthenium and osmium species that there is less likelihood of the formation of polymeric material.

However, kinetic studies on these cyclopentadienyl systems may prove difficult due to the lack of carbonyl groups for observation in the infra-red and little colour change in the visible spectra, although a possible technique could be to monitor changes in the cyclopentadienyl resonance in the proton nmr spectrum.

(ii) Proton nmr characterisation

The proton nmr spectra of the η^5 -pentadienyltricarbonyliron salts^{71,72,95} are well documented and were of particular use in the assignment of (XXXI). Data for this compound together with the impure cobalt and rhodium salts are shown in comparison with the corresponding tricarbonyliron species in table (2.12) and assignments are according to fig. (2.24). The 220 MHz ^1H nmr spectrum for (XXXI), shown in fig (2.25),



(2.24)

appears quite straightforward under normal operation of the spectrometer but on expansion the spectrum becomes much more complex due to coupling to the rhodium nucleus of all protons with the exception of those of the methyl group. Resonances at τ 3.84, 5.68 and 7.84 ppm are impurities introduced by the deuterated nitromethane solvent. This spectrum was assigned by analogy with the corresponding tricarbonyliron salt together with observation of the resonance multiplicities. The proton resonances of H_2 and H_4 are almost overlapping and this resulted in difficulties with the interpretation of the carbon-13 nmr spectrum as well. Values for the vicinal proton coupling constants were of similar magnitudes to those of the tricarbonyliron system with the "trans" couplings (10-11 Hz) larger than for the "cis" couplings (6-7 Hz).⁹⁵ An exception was found with

(a)

M	CH ₃	1 _a	2	3	4	5 _s	5 _a	Cp
Rh(η ⁵ C ₅ H ₅) ⁽¹⁾	8.18(d)	6.72(m)	4.33(m)	3.39(dt)	4.27(m)	5.82(m)	7.75(m)	4.08(d)
	6	6,11	11,6	6.5	6,11	10,3.5	10,3.5	
* Co(η ⁵ C ₅ H ₅)	8.23(d)	6.1(m)	4.6(m)	3.15(t)	4.3(m)	5.7(m)	7.5(m)	4.12(s)
	6			7			11	
Fe(CO) ₃ ⁽²⁾	8.18(d)	6.65(dd)	4.04(dd)	3.04(t)	3.78(dd)	6.39(dd)	7.72(dd)	
	7	7,12	12,7	7	7,10	10, 3.5	12.5, 3.5	

(b)

* Rh(η ⁵ C ₅ H ₅)	5.52(d)	3.26(dd)	2.85(t)	Other (phenyl)	2.50(m)	4.56(d)
	12	12,6	7			
Fe(CO) ₃	4.90(d)	2.63(dd)	2.11(t)	Other (phenyl)	2.22(m)	
	13	8	7			

TABLE 2.12 Proton nmr data for (a) [(syn-1-methylpentadienyl)M]⁺ BF₄⁻ and (b) [(syn,syn 1,5 diphenylpentadienyl)M]⁺ BF₄⁻ compounds, except Co- as PF₆⁻ salt. All data recorded at 60 MHz except (1) 220 MHz, (2) 100 MHz. Fe(CO)₃ data taken from ref. 96. Chemical shifts in ppm downfield from TMS (τ=10 ppm): coupling constants in Hz. (1) Rhodium coupling omitted, less than 1 Hz - see text. * Impure samples, impurity peaks omitted.

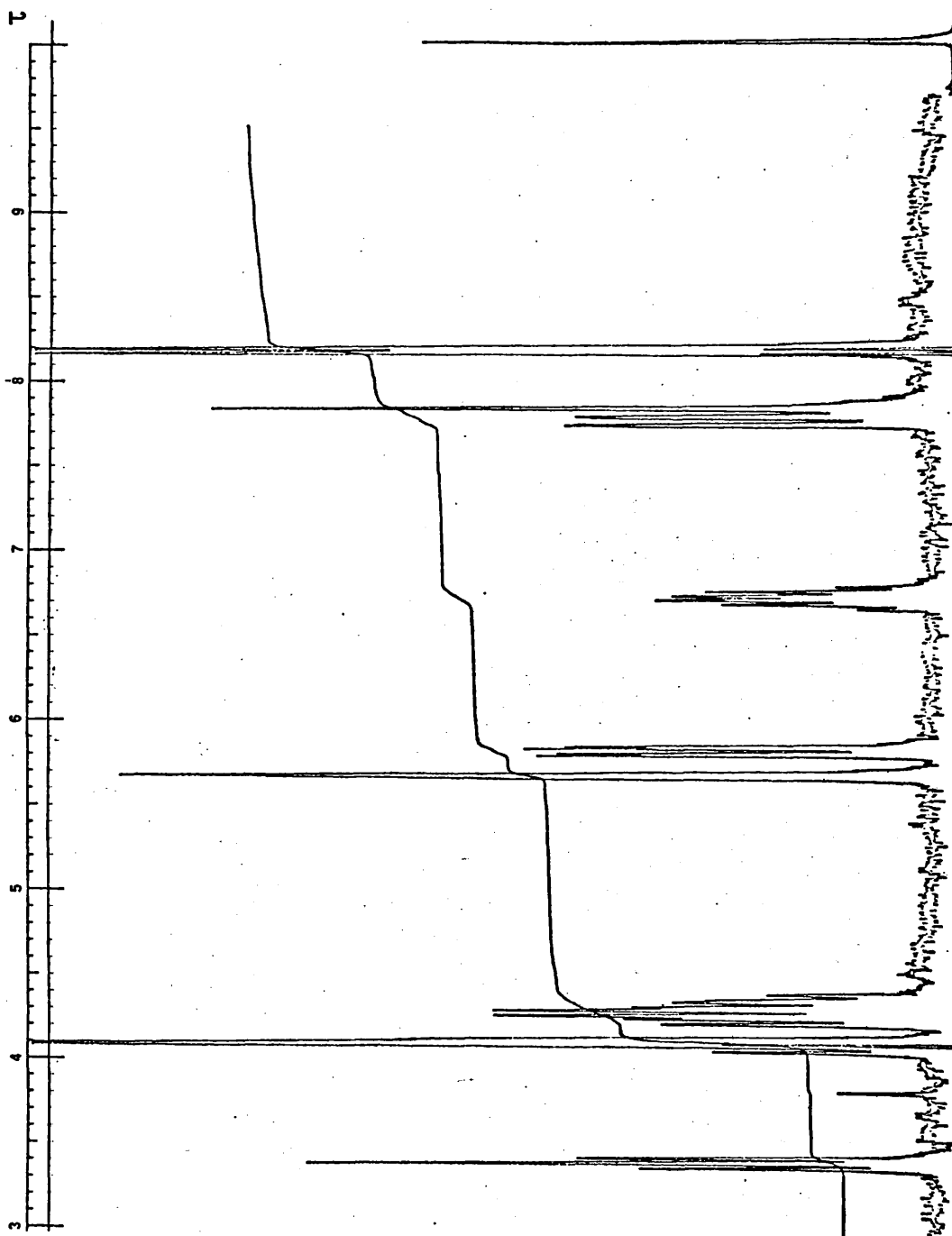


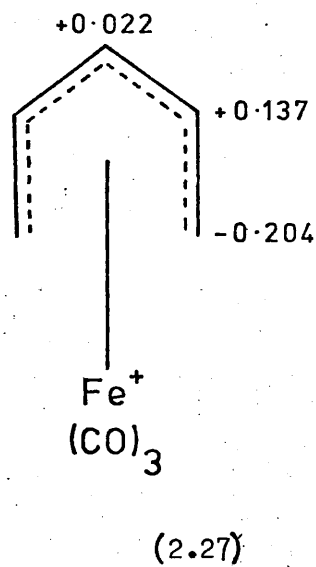
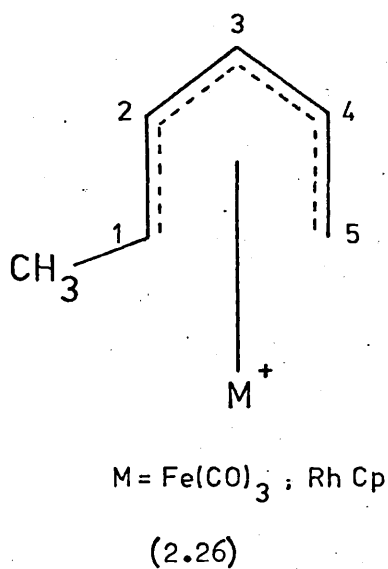
Fig. 2.25 ^1H nmr spectrum of η^5 -syn-1-methyl pentadienyl η^5 -cyclopentadienylrhodium tetrafluoroborate (XXXI) in CD_3NO_2 at 220 MHz.

the coupling $5s-4$ which was slightly larger at 10 Hz. Similar observations have been noted from the tricarbonyliron system when $5s = 5a = H$ (or $1s = 1a = H$) and this is within the range typical for alkyl substituted ethene derivatives.⁹⁶ Geminal couplings of protons $5s$ and $5a$ were also similar to the iron salt. Coupling to the rhodium nucleus was small, but observable on expansion; less than 1 Hz in all cases.

Data for the impure rhodium and cobalt compounds are included and these also are similar to data for the iron complexes: in general the rhodium resonances lie to slightly higher field than for iron, probably due to greater electron density effects from the η^5 -cyclopentadienylrhodium unit. Impurity resonances have been omitted for the sake of clarity and obviously further study is required on these species to confirm the shifts and assignments.

- (iii) A carbon-13 nmr spectroscopic study of the cationic complex η^5 -syn-1-methylpentadienyl η^5 -cyclopentadienyl-rhodium tetrafluoroborate

Several groups have recently studied the carbon-13 nmr spectra of the η^5 -pentadienyl tricarbonyliron salts and when the different solvent effects are considered, agreement is good with the exception of the syn-1-methylpentadienyl⁹⁵ species.^{97,98} In this complex the resonances of carbon atoms 2,3 and 4 are similar and there is discrepancy over the assignment of C₂ and C₄ (2.26), although these shifts have been confirmed by double resonance experiments.



Lillya et al. have related the chemical shifts of the dienyl carbons to the calculated charge densities and concluded that the atomic charge had a major influence upon the chemical shifts:

the greater the calculated charge density, the greater

the observed shielding, thus $C_{1,5} > C_3 > C_{2,4}$. A similar pattern was also observed after substituent effects had been taken into account and while the calculated charge densities (2.27) were quantitatively unreliable, it was considered that this calculated charge distribution pattern should be valid. These results thus predicted that carbons

1,3,5 will be electron rich relative to carbons 2 and 4 and the observed chemical shifts gave good correlation with these predictions. However, nucleophilic attack is known to occur at the terminal carbon atoms in these species, where the carbons would be thought to be electron deficient and these observations seem at variance with the carbon-13 nmr spectroscopic data. Pearson et al.⁹⁹ have reported data for several substituted η^5 -cyclohexadienyltricarbonyliron salts and observed the relationship between irreversible nucleophilic attack at the terminal positions and the observed chemical shifts at these carbon atoms. Borohydride reduction was found to take place at the more positive carbon atom, i.e. the more deshielded carbon, when an uneven distribution of charge was present. However, a more sterically demanding nucleophile may be hindered from attack at this position by a substituent next to it; attack then occurring at the less positive carbon atom. With reversible addition the situation was more complex and thermodynamic considerations were thought to dominate. Shubin et al.¹⁰⁰ have also reported data for η^5 -cyclohexadienyltricarbonyliron salts and cautiously concluded that the tricarbonyliron unit participates in delocalisation of the positive charge.

Carbon-13 nmr spectroscopic data for (XXXI) and some related cyclic dienyl salts are reported in table 2.13 and the spectrum of (XXXI) can be seen in fig. 2.28. The resonances of carbons 2,3 and 4 are close together and could not be identified from selective decoupling techniques. The proton resonances of carbons 2 and 4 are almost overlapping and it was not possible to irradiate one resonance without affecting the other and the graphical method of Birdsall et al.¹⁰¹ was not employed due to loss of Overhauser enhancement and residual rhodium coupling which greatly

Complex	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	Cp	Other
η^5 -syn-1-methylpentadienyl	83.7(d)	95.5(d)	99.4(d)	98.1(d)	58.1(d)			91.6(d)	Me
η^5 -cyclopentadienylrhodium tetrafluoroborate	10	6	4	6	12			6	23.3(s)
η^5 -cycloheptadienyl η^5 -pentamethyl cyclopentadienylrhodium hexafluorophosphate	92.3(d)	98.7(d)	101.1(d)	98.7(d)	92.3(d)	35.5(s)	35.5(s)	6	104.2(d) Me
η^5 -cyclohexadienyl η^5 -cyclopenta-dienylrhodium tetrafluoroborate	12	6	4	6	12			5	9.9(s)
η^5 -cyclohexadienyl η^5 -cyclopenta-dienylrhodium tetrafluoroborate								8	26.6(s)
								5	89.8(d)
									5

TABLE 2.13 Carbon-13 nmr data for cationic rhodium complexes. All data recorded at 22.63 MHz in deuterated nitromethane. Chemical shifts in ppm downfield from TMS internal reference (0 ppm); coupling constants in hertz.

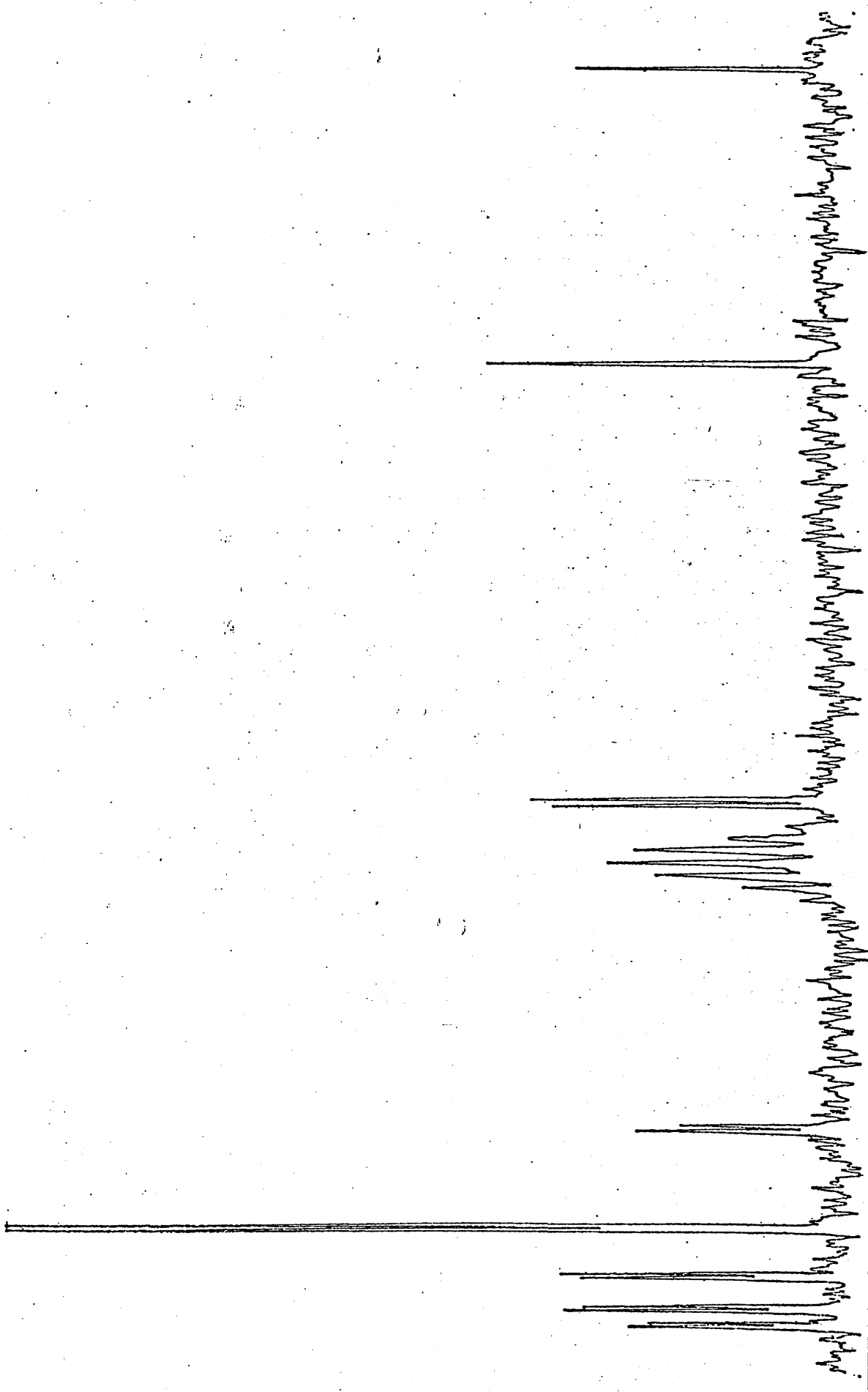
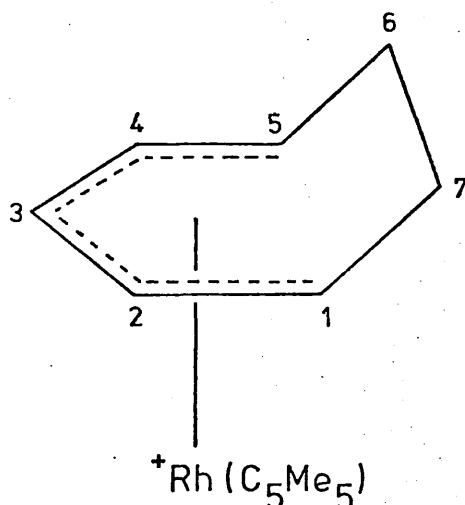


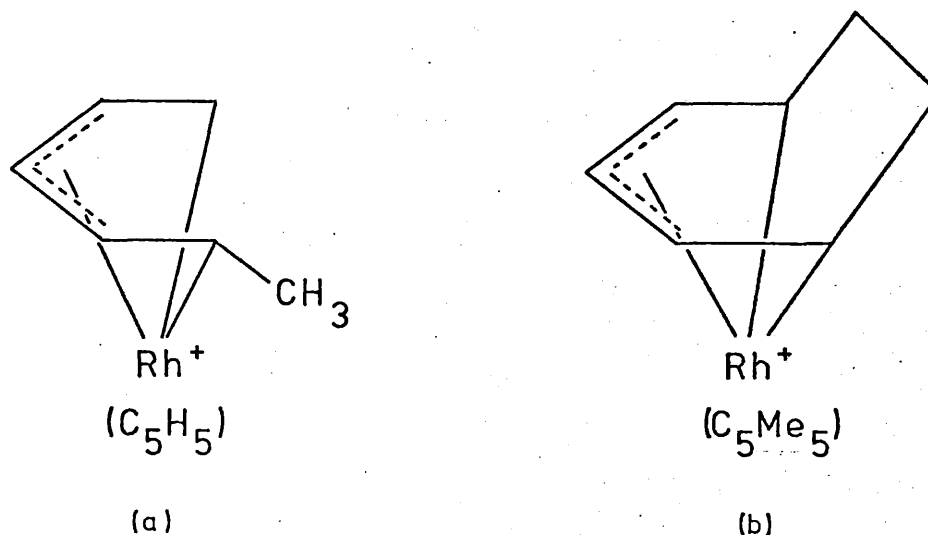
Fig. 2.28 ¹³C nmr proton decoupled spectrum of η^5 -syn-1-methylpentadienyl η^5 -cyclopentadienylrhodium in CDCl₃ at 22.63 MHz.

reduced the intensities of the signals. Assignments for (XXXI) are based on comparison with the shifts and coupling constants for the η^5 -cycloheptadienyl salt (2.29) prepared by the method of Maitlis. The η^5 -cyclohexadienyl complex exhibited only two dienyl resonances



(2.29)

at 50.5 and 94.3 ppm and the cyclopentadienyl resonance at 89.8 ppm; the remaining resonance probably lies under one of these. In (XXXI) carbon C₁ is substantially deshielded (~25 ppm) with respect to the unsubstituted carbon C₅ and this is due to the deshielding effect of the methyl grouping. Rhodium couplings were observable on all carbons directly bonded to the metal and values were typical of "π"-bonded carbons. Couplings to C₁ and C₅ were slightly larger than for C_{2,3} and 4 possibly due to "σ-π" contributors such as 2.30 a and b.



(2.30)

Müller and co-workers have reported chemical shifts for a neutral cyclooctadienyl complex $[\text{Rh } \eta(1-2) \eta(5-6) \text{COD } (\text{C}_8\text{H}_{14})]$ and the fluxional nature of this complex can be "frozen" at lower temperatures,⁶⁹ (2.8). Maitlis et al. have characterised their η^5 -pentadienyliridium salt using carbon-13 nmr spectroscopy although the resonances of carbons 2 and 4 lie to considerably lower field on account of substituent effects. However, the resonances of C_1 and C_5 are to higher field when compared with (XXXI) even accounting for substituent effects and this pattern of greater shielding with iridium than with rhodium is consistent with the trend observed from their corresponding diene chemistry. Similarly the trend towards higher field for the rhodium salt when compared to the analogous tricarbonyliron species is also consistent with their respective diene chemistry.

2.3 EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Di- μ -chlorotetra (η^2 -cyclooctene) dirhodium and iridium were prepared according to the method of van der Ent and Onder^{de}linden.⁵³ Hexane (b.pt. 60-80°) and diethyl ether were dried over sodium. Proton nmr spectra were recorded in deuterated solvents usually at 220 or 90 MHz using Varian HR-220 or Bruker HX-90 spectrometers at PCMU (Harwell) and King's College (London) respectively. Carbon-13 nmr spectra were also recorded in deuterated solvents at 22.63 MHz using the Bruker HX-90 spectrometer at King's College (London) operating in the Fourier Transform mode.

(i) Preparation of the complexes $[\text{Rh}(\eta^4\text{-diene})_2\text{Cl}]$

For details of experimental yields see table 2.1.

(a) Diene = 2,4 hexadien-1-al; 3,5 heptadien-2-one

A solution of the appropriate diene (10 mmol, ~1 g) in dry hexane (30 cm³) was added to a well stirred suspension of the cyclooctene compound (0.5mmol 358.5 mg) also in dry hexane and stirring continued for one hour. At the end of this period the precipitated product was filtered, washed with several small portions of cold dry hexane and dried in vacuo.

(b) Diene = 2,4 hexadien-1-ol

(1) The alcohol (2 g) was added to the cyclooctene complex (0.5 mmol 358.5 mg) and stirred for one hour at 35°C. The yellow-orange solid dissolved to form a bright red solution from which the product was precipitated by addition of dry hexane (75 cm³). This was then filtered and washed as before and dried in vacuo to yield the product.

(2) A solution of the dien-ol (10 mmol ~1 g) in chloroform (5 cm³) was added to the cyclooctene complex and stirred for one hour. Dry hexane (75 cm³) was then added to precipitate the product which was then worked up as before.

Samples prepared by the previous method for 2,4 hexadien-1-al resulted in oily, sticky solids which could be purified by removal of the liquor, dissolving the residue in a minimum quantity of chloroform followed by precipitation using hexane.

(c) Diene = 1,5 diphenylpenta 2,4 diene-1-one; 5 methyl 6 phenylhexa 3,5 diene-2-one

A solution of the appropriate diene (4 mmol) in dry ether (40 cm³) was added to a well stirred suspension of the cyclooctene compound (0.5 mmol) also in dry ether (15 cm³). The solution became orange-red in colour and after a few minutes a yellow precipitate started to form. After stirring for one hour the solution was concentrated by about 10 cm³ to complete precipitation. The product was then filtered, washed several times with small portions of cold ether and dried in vacuo.

(ii) Preparation of the complex [Rh(η⁴-3,5 heptadien-2-one)Cl]₂

The method used was the same as for (a); with the exception that the yellow-orange suspension gradually gave way to a brick-red microcrystalline product.

(iii) Preparation of the compounds [Ir (η⁴-diene)₂Cl]

(a) Diene = 2,4 hexadien-1-al; 3,5 heptadien-2-ol; 3,5 heptadien-2-one

A solution of the diene (5 mmol) in dry hexane (30 cm³) was added to a well stirred suspension of the yellow cyclooctene complex (0.3 mmol, 330 mg) in dry hexane (20 cm³) and stirring continued for one hour.

The yellow suspension gradually changed colour (depending on the product) and the product precipitated out which was then filtered and worked up as before.

(b) Diene = 2,4 hexadien-1-ol

The dien-ol (2 g) was added to the cyclooctene complex (0.3 mmol, 330 mg) and stirred at 35° for one hour. The yellow complex dissolved in the alcohol to give a green coloured solution and the product was precipitated from this by addition of dry hexane (70 cm³). The white product was then filtered, washed and dried as before.

(c) Diene = 1,5 diphenylpenta 2,4 dien-1-one; 5 methyl
6 phenylhexa 3,5 diene-2-one

A similar procedure as for the rhodium species was followed using (0.25 mmol) of the yellow cyclooctene iridium precursor.

(iv) Preparation of the complexes [(η⁴-diene) (η⁵-cyclopentadienyl)
rhodium]

(a) Diene = 2,4 hexadien-1-al; 3,5 heptadien-2-one

An equimolar quantity of cyclopentadienyl thallium was added to a stirred solution of the previously prepared chlorocomplex (0.5 mmol) in dichloromethane (50 cm³) and stirring continued overnight in the absence of light. The resultant insoluble thallium residues were filtered off and the filtrate then refiltered through "Florasil" (100 - 200 mesh). After removal of the solvent in vacuo the residue was pumped for several hours and then transferred to a sublimation apparatus. The sample was then sublimed in vacuo (100 - 120°, 0.1 mm) to give the required product as orange needles. When the temperature had reached 50 - 70° a little diene appeared on the probe and after removal of this, sublimation was continued to give an analytically pure product. Yields were 76 and 73% for 2,4 hexadien-1-al and 3,5 heptadien-2-one respectively.

(b) Diene = 1,5 diphenylpenta 2,4 dien-1-one

To a well stirred suspension of the previously described chlorocomplex (0.5 mmol) in ether (60 cm³) was added an equimolar quantity of cyclopentadienyl thallium and stirring continued overnight in the absence of light. The insoluble thallium residues were filtered off and the orange-red filtrate concentrated in vacuo. This was then chromatographed with ether through a short column (1 x 30 cm) of "Florisil" (100 - 200 mesh). Evaporation of the eluate resulted in an orange-red oil which failed to crystallise on pumping for several hours under high vacuum (10⁻⁴ mm). Crystallisation was achieved by dissolving the oil in a minimum volume of dry ether and precipitation with hexane (60 cm³). Filtration gave an analytically pure orange-red solid. (Yield 85%).

(c) Diene = 5 methyl 6 phenyl hexa 3,5 dien-2-one

An equimolar quantity of cyclopentadienyl thallium was added to a stirred suspension of the chlorocomplex (0.5 mmol) in ether (60 cm³) and stirred overnight in the absence of light. Removal of the insoluble thallium residues by filtration resulted in an orange-yellow solution which was concentrated in vacuo and then purified by chromatography through "Florisil" (100 - 200 mesh: 1 x 30 cm column) using ether as eluant. Evaporation of the solvent gave an oily orange-yellow solid which gave a pure sample after pumping under high vacuum (10⁻⁴ mm) for 24 hours (Yield 71%).

(v) Preparation of the species $[(\eta^4\text{-diene})(\eta^5\text{-cyclopentadienyl})\text{iridium}]$ (a) Diene = 2,4 hexadien-1-al; 3,5 heptadien-2-one

The procedure used was similar as for the corresponding rhodium compounds with the exception that stirring with cyclopentadienylthallium was continued for three days to give yellow solutions. Yields for the respective dienes were 70 and 84%.

(b) Diene = 1,5 diphenylpenta 2,4 dien-1-one

Similar procedures as for the analogous rhodium compound were used with stirring for three days. The yield was 38%.

(c) Diene = 5 methyl 6 phenylhexa 3,5 dien-2-one

Again similar procedures as for rhodium were employed with stirring for three days. Yield 43%.

(vi) Attempted preparations of $[(\eta^4\text{-dien-ol})(\eta^5\text{-cyclopentadienyl})\text{rhodium}]$

Similar reactions as before with the corresponding alcohol complexes proved unsuccessful. After reaction with cyclopentadienyl thallium it did not prove possible to isolate pure species. With 3,5 heptadien-2-ol a brown oil remained after removal of solvent which could not be purified by sublimation or chromatography due to decomposition. With 2,4 hexadien-1-ol an orange-brown oil resulted which would not sublime, although it did react with fluoroboric acid to form the salt (XXXI).

(vii) The formation of $\eta^5\text{-syn-1-methylpentadienyl } \eta^5\text{-cyclopentadienyl-rhodium tetrafluoroborate}$

$(\eta^4\text{-2,4 hexadien-1-ol})_2\text{RhCl}$ (0.5 mmol) was prepared as previously described and dissolved in dichloromethane (50 cm³). An equimolar quantity of cyclopentadienyl thallium was added and stirring continued overnight in the absence of light. The insoluble thallium residues were filtered off and the filtrate refiltered through "Florisil" (100 - 200 mesh), then evaporated in vacuo leaving an orange-brown oil. This was dissolved in a small quantity of acetic anhydride (2 cm³) and cooled to 0°C. A cold solution of fluoroboric acid (42% tech) (1 cm³) in acetic anhydride (2 cm³) was added to the complex solution dropwise with stirring. When the

addition was complete stirring was continued for a further 30 minutes and then the solution was added dropwise to stirred diethyl ether to give a yellow precipitate. Purification was achieved by dissolving in a minimum quantity of nitromethane, filtering and reprecipitation with dry diethyl ether to leave a pale yellow solid. Yield 74% (Analysis C: 38.15%; H, 4.05%. $C_{11}H_{14}RhBF_4$ requires C: 39.33%; H: 4.20%)
M. Pt. 164° dec.

Other preparations

(i) Bis (η^2 -ethylene) η^5 -cyclopentadienylrhodium

The bis(η^2 -ethylene) chlororhodium dimer (1 mmol) and cyclopentadienyl thallium (1 mmol) were stirred in dichloromethane (40 cm³) in the absence of light for several hours. After the insoluble thallium residues were filtered off, the resultant yellow filtrate was evaporated in vacuo. The residue was sublimed, also in vacuo (50-70° 0.1 mm) to give the product as bright yellow crystals. (Yield 82% M. Pt 72° Lit. 72-3⁸).

(ii) Bis (η^2 -cyclooctene) η^5 -cyclopentadienylrhodium

A similar procedure to above was carried out but the solution deposited metallic rhodium, turning black after the addition of cyclopentadienyl thallium.

(iii) η^4 -cyclohexa 1,3 diene η^5 -cyclopentadienylrhodium

Cyclohexa 1,3 diene (2 cm³) was added to the cyclooctene complex (0.5 mmol) and stirred until the orange-yellow colour of the cyclooctene material had been completely replaced by the pale yellow colour of $[Rh (\eta^4\text{-cyclohexa 1,3 diene})Cl]_2$. The excess diene was then evaporated off, in vacuo, and the resultant yellow solid treated with cyclopentadienyl thallium and worked up as in the previously described procedures. (Yield 83%).

(iv) η^5 -cyclohexadienyl η^5 -cyclopentadienylrhodium tetrafluoroborate

This was prepared from the chloro-cyclohexadiene complex using literature methods.⁶⁰

(v) η^4 -buta 1,3 diene η^5 -cyclopentadienylrhodium

Bis (η^4 -buta 1,3 diene) chlororhodium was prepared by the method of Porri et al. and then treated with cyclopentadienyl thallium and worked up as before.⁵²

(vi) $\eta(1-2)\eta(3-4)$ cyclo-octa tetraene η^5 -cyclopentadienylrhodium

Cycloocta 1,3,5,7 tetraene (1.5 cm³) was added to the cyclooctene complex (0.5 mmol) and stirred for one hour. Dry hexane (60 cm³) was added and stirring continued for a further fifteen minutes. The bright yellow precipitated product was filtered and dried in vacuo to give a virtually quantitative yield of $[\text{Rh}(\eta^4\text{-C}_8\text{H}_8\text{Cl})_2]^*$. After reaction with cyclopentadienyl thallium, the required product was isolated in 76% yield.

These reactions illustrate the usefulness of the cyclooctene precursor complexes in the preparation of η^4 -diene complexes of rhodium and iridium.

(vii) The reaction of hexa 1,3,5 triene with $[\text{Rh}(\eta^4\text{-C}_8\text{H}_{14})_2\text{Cl}]_2$

Hexa 1,3,5 triene (1 g) was added to the cyclooctene complex (0.5 mmol) and stirred in dry hexane (40 cm³) for one hour. The solvent was then removed in vacuo leaving a reddish oil which was further pumped for two hours. Cyclopentadienyl thallium (1 mmol) was added and stirred in dichloromethane (50 cm³) in the absence of light for several hours. After filtration of the insoluble thallium residues followed by purification through "Florisil" the solvent was removed under vacuum to leave a brown tar. Chromatography on "Florisil" (100 - 200 mesh) yielded two bands an immovable red one and a pale yellow band. Removal of the solvent

* should read $[\text{Rh}\eta(1-2)\eta(3-4)\text{C}_8\text{H}_8\text{Cl}]_2$

(ether) from this pale yellow band resulted in a clear orange oil but the ^1H nmr spectrum proved inconclusive. Further reaction with fluoroboric acid as before gave a buff-coloured solid but nmr studies were again inconclusive.

(viii) η^5 -cycloheptadienyl η^5 -pentamethylcyclopentadienylrhodium hexafluorophosphate

This was synthesised by the method of Maitlis et al.²³

(ix) Attempted reduction of η^4 -3,5 heptadien-2-one η^5 -cyclopentadienyl-rhodium

A cold slurry of sodium borohydride (1.5 g) in water (15 cm³) was added to the dien-one complex (180 mg) dissolved in methanol (Analar 20 cm³) cooled to 0° and stirred for two hours. The resultant mixture was then poured into excess water (75 cm³) to destroy unreacted borohydride and then extracted with diethyl ether until no yellow colour remained in the aqueous layer (4 x 25 cm³). Some decomposition to metallic rhodium was observed. The combined extracts were washed with water (2 x 25 cm³) shaken with dried magnesium sulphate and left overnight. After decantation, removal of the ether in vacuo left an orange oil which was shown by proton nmr spectroscopy to be still contaminated with the parent ketone compound. This procedure was repeated until the nmr spectrum showed that the ketone complex was no longer present.

(x) Attempted protonation of η^4 -3,5 heptadien-2-one η^5 -cyclopentadienyl rhodium and iridium complexes

A small sample of each complex (50 mg) was dissolved in concentrated sulphuric acid (Analar 1.5 cm³) cooled to 0° and then placed in a pre-cooled nmr tube. The rhodium complex dissolved to give an orange-red solution while with iridium, an orange-yellow solution resulted

together with some charring. The nmr spectra were then obtained at -10° (Varian HA 100) locking on to the acid signal ($\tau \sim -2$ ppm) and then warmed to 30° . The only visible change was a slight sharpening of the resonances. Similar procedures were then followed for the rhodium complex with fluorosulphonic and trifluoroacetic acids. Chemical shifts were measured using a fixed-lock instrument (Varian EM 360) aligned with TMS (10 ppm). No change in the chemical shift of this resonance with time was detected in the duration of the experiment.

(xi) The reaction of bis(η^2 -ethylene) η^5 -cyclopentadienylrhodium with 1-bromo 2,4 hexadiene

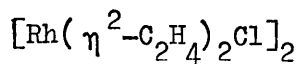
A solution of sorbyl bromide (3 g) in n-octane (20 cm^3) was added to a solution of the rhodium complex (1 mmol) also in n-octane (30 cm^3). On warming to 50° a brown precipitate was produced and no other change was observed even after heating for one hour at 125° . The precipitate was shaken with water, filtered and dripped into a concentrated solution of ammonium hexafluorophosphate (0.5 g) in water (2 cm^3). A reddish brown precipitate was produced but the nmr indicated the absence of the cyclopentadienyl resonance.

(xii) The reaction of (η^5 -cyclopentadienyl)dicarbonylcobalt with 1-bromo 2,4 hexadiene

1-Bromo 2,4 hexadiene (2.5 cm^3) in purified tetrahydrofuran (10 cm^3) was added to the cobalt compound (1 cm^3), stirred for fifteen minutes and allowed to stand at room temperature for two days. A blackish tarry solid remained after the THF had been decanted. This product was dissolved in a small quantity of nitromethane, filtered and poured into stirred dry diethyl ether (50 cm^3) to give a green flocculent precipitate. After filtration this was dissolved in water to give a yellow-brown

solution to which a concentrated solution of ammonium hexafluorophosphate (0.5 g) in water (2 cm³) was added. An orange-yellow precipitate was produced which was reprecipitated from nitromethane/ether. The nmr spectrum indicated a mixture of products.

(xiii) The reaction of 1,5 diphenylpenta 2,4 dien-1-ol with



An excess of the dien-ol (1 g) was added to the rhodium complex (0.5 mol, 194 mg) in diethyl ether (30 cm³) and heated under reflux with stirring for 30 minutes. The resultant red solution was filtered, cyclopentadienyl thallium (1 mmol) added and stirred overnight in the absence of light. After filtration through "Florisil" to remove all the thallium residues, the filtrate was evaporated in vacuo to leave a red oil. This was treated with fluoroboric acid, as previously described, and a dirty yellow precipitate was the result. (Yield 65%). However, even after repeated recrystallisations from nitromethane/ether and dichloromethane/ether, it was not possible to obtain a pure sample.

(xiv) The reaction of 6 phenyl 3,5 hexadien-2-one with $[\text{Rh}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}]_2$

A similar procedure to that described for (xiii) was employed but chromatography or sublimation would not remove excess dien-one. Nmr studies did, however, show the presence of a cyclopentadienyl group bonded to rhodium. This procedure was abandoned in favour of the "cyclooctene method".

PART I

REFERENCES

1. J. Chatt and L.M. Venanzi, Nature (1956) 177 852.
2. J. Chatt and L.M. Venanzi, J. Chem. Soc. (1957) 4735.
3. E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc. (1959) 3178.
4. R. Cramer, Inorg. Chem. (1962) 1 722.
5. L.F. Dahl, C. Martell and D.L. Wampler, J. Amer. Chem. Soc. (1961) 83 1761.
6. K. Klanderma, Diss. Abst. (1965) 25 6253.
7. S.M. Nelson, M. Sloan and M.G.B. Drew, J. Chem. Soc. (Dalton) (1973) 2195.
8. R. Cramer, J. Amer. Chem. Soc. (1964) 86 217.
9. R. Cramer and L.P. Seiwell, J. Organomet. Chem. (1975) 92 245.
10. L.P. Seiwell, Inorg. Chem. (1976) 15 2560.
11. F. Bonati and G. Wilkinson, J. Chem. Soc. (1964) 3156.
12. J. Powell and B.L. Shaw, J. Chem. Soc. (A) (1968) 583.
13. M. McPartlin and R. Mason, Chem. Comm. (1967) 16.
14. J. Powell and B.L. Shaw, Chem. Comm. (1966) 323.
15. D.A. Clement, J.F. Nixon and B. Wilkins, J. Organomet. Chem. (1972) 37 C43.
16. J.F. Nixon, B. Wilkins and D.A. Clement, J. Chem. Soc. (Dalton) (1974) 1993.
17. M. Green and G.J. Parker, J. Chem. Soc. (Dalton) (1974) 333.

18. K. Vrieze and H.C. Vogler, *J. Organomet. Chem.* (1967) 9 537.
19. J. Powell and B.L. Shaw, *J. Chem. Soc. (A)* (1968) 597.
20. A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, *Izv. Akad. Nauk. SSSR (Ser. Khim)* (1975) 5 1196.
21. A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, *Izv. Akad. Nauk. SSSR (Ser. Khim)* (1974) 4 2651.
22. J.W. Kang, K. Moseley and P.M. Maitlis, *J. Amer. Chem. Soc.* (1969) 91 5970.
23. K. Moseley, J.W. Kang and P.M. Maitlis, *J. Chem. Soc. (A)* (1970) 2875.
24. C. White, A.J. Oliver and P.M. Maitlis, *J. Chem. Soc. (Dalton)* (1973) 1901.
25. H.B. Lee and P.M. Maitlis, *J. Chem. Soc. (Dalton)* (1975) 2136.
26. A.J. Hart-Davis and W.A.G. Graham, *Inorg. Chem.* (1971) 10 1653.
27. E.O. Fischer and R.D. Fischer, *Z. Naturforsch* (1961) 16b 475.
28. R.F. Heck, *J. Org. Chem.* (1963) 28 604.
29. R.B. King, A. Efraty and W.M. Douglas, *J. Organomet. Chem.* (1973) 56 345.
30. P. Powell, *J. Organomet. Chem.* (1977) 129 175.
31. R.D. Feltham and R.G. Hayter, *J. Chem. Soc.* (1964) 4587.
32. W.J. Geary, *Coord. Chem. Rev.* (1971) 7 81.
33. M.Ephritikhine, B.R. Francis, M.L.H. Green, R.E. Mackenzie and M.J. Smith, *J. Chem. Soc. (Dalton)* (1977) 1131.

34. J. Evans and J.R. Norton, *Inorg. Chem.* (1974) 13 3042.
35. P.C. Lauterbur and R.B. King, *J. Amer. Chem. Soc.* (1965) 87 3266.
36. J.B. Stothers, *Carbon 13 nmr*, Academic Press (London) 1972.
37. D.G. Cooper, R.P. Hughes and J. Powell, *J. Amer. Chem. Soc.* (1972) 94 9244.
38. G.C. Levy and G.L. Nelson, *Carbon 13 nmr for Organic Chemists*. Wiley (London) 1972.
39. M.H. Chisholm and S. Godelski, in S.J. Lippard (Ed) *Progress. in Inorg. Chem. Vol. 20 Interscience* (New York) 1976 p.299.
40. B.E. Mann, in F.G.A. Stone and R. West (Eds). *Advances in organometallic chemistry*, Academic Press (New York) 1974 12 p.135.
41. B.E. Mann, R. Pietrapaolo and B.L. Shaw, *Chem. Comm.* (1971) 790.
42. D.E. Dorman, M. Jautelat and J.D. Roberts, *J. Org. Chem.* (1971) 13 470.
43. J.B. Brill and A.J. Kotlar, *Inorg. Chem.* (1974) 13 470.
44. H.C. Clark and J.E.H. Ward, *Canad. J. Chem.* (1974) 52 570.
45. J. Evans, B.F.G. Johnson, J. Lewis and R. Watt, *J. Chem. Soc. (Dalton)* (1974) 2368.
46. D.E. Axelson, C.E. Holloway and A.J. Oliver, *Inorg. Nucl. Chem. Lett.* (1973) 9 885.
47. G.M. Bodner, B.N. Storhoff, D. Doddrell and L.J. Todd, *Chem. Comm.* (1970) 1530.

48. G.M. Bancroft, K.D. Butler, L.E. Manzer, A. Shaver and J.E.H. Ward, *Canad. J. Chem.* (1974) 52 782.
49. O.A. Gansow and B.Y. Kimura, *Chem. Comm.* (1970) 1621.
50. S.D. Robinson and B.L. Shaw, *Tetrahedron Lett.* (1964) 1301.
51. M.L.H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1959) 3753.
52. L. Porri, A. Lionetti, G. Allegra and A. Immerzi, *Chem. Comm.* (1965) 336.
53. A. van der Ent and A.L. Onder^{de}linden, *Inorg. Synth.* (1973) 14 93.
54. L. Porri and A. Lionetti, *J. Organomet. Chem.* (1966) 6 422.
55. G. Winkhaus and H. Singer, *Chem. Ber.* (1966) 99 3602.
56. G. Winkhaus and H. Singer, *Chem. Ber.* (1966) 99 3610.
57. M.G.B. Drew, S.M. Nelson and M. Sloan, *J. Chem. Soc. (Dalton)* (1973) 1484.
58. M.G.B. Drew, S.M. Nelson and M. Sloan, *J. Organomet. Chem.* (1972) 39 C9.
59. L. Oro, *Inorg. Chim. Acta* (1977) 21 L6.
60. B.F.G. Johnson, J. Lewis and D.J. Yarrow, *J. Chem. Soc. (Dalton)* (1972) 2084.
61. J. Evans, B.F.G. Johnson, J. Lewis and D.J. Yarrow, *J. Chem. Soc. (Dalton)* (1974) 2375.
62. J. Evans, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. (Dalton)* (1977) 510.
63. M.L.H. Green, *Organometallic compounds, Vol. 2: The transition elements*, 3rd Edition, Chapman and Hall (1968) p.67.

64. B.F. Johnson, J. Lewis and D.J. Yarrow, J. Chem. Soc. (Dalton) (1974) 1054.
65. J. Evans, B.F.G. Johnson, J. Lewis and R. Watt, J. Chem. Soc. (Dalton) (1974) 2368.
66. M. Green, T.A. Kuc and S.H. Taylor, J. Chem. Soc. (A) (1971) 2334.
67. M. Green and T.A. Kuc, J. Chem. Soc. (Dalton) (1972) 832.
68. P.T. Draggett, M. Green and S.F.W. Lowrie, J. Organomet. Chem. (1977) 135 C60.
69. J. Müller, H.O. Stühler and W. Goll, Chem. Ber. (1975) 108 1074.
70. J.E. Mahler and R. Pettit, J. Amer. Chem. Soc. (1963) 85 3955.
71. J.E. Mahler, D.H. Gibson and R. Pettit, J. Amer. Chem. Soc. (1963) 85 3959.
72. T.S. Sorenson and C.R. Jablonski, J. Organomet. Chem. (1970) 25 C62.
73. T.G. Bonner, K.A. Holder and P. Powell, J. Organomet. Chem. (1974) 77 C37.
74. E.W. Abel and S. Moorhouse, JCS (Dalton) (1973) 1706.
75. R.L. Bennett and M.I. Bruce, Aust. J. Chem. (1975) 28 1141.
76. C. White, S.J. Thompson and P.M. Maitlis, J. Organomet. Chem. (1977) 134 319.
77. A.L. Onder^{de}linden and A. van der Ent, Inorg. Chim. Acta (1972) 6 420.
78. L.J. Bellamy, "The infra-red spectra of complex molecules" p.149
2nd Edition (1958) Methuen (London).
79. A. Immerzi, J. Organomet. Chem. (1974) 76 65.
80. W.A. Clinton and C.P. Lillya, J. Amer. Chem. Soc. (1970) 92 3065.

81. R.B. King, T.A. Manuel and F.G.A. Stone, *J. Inorg. and Nuclear Chem.* (1961) 16 233.
82. H. Reihlen, A. Gruhl, G. Hessling and O. Pfrengle, *Liebig Ann. Chem.* (1930) 482 161.
83. P.F. Hallam and P.L. Pauson, *J. Chem. Soc.* (1958) 642.
84. O.S. Mills and G. Robinson, *Proc. Chem. Soc.* (1960) 421.
85. H.L. Retcofsky, E.W. Frankel, H.S. Gutowsky, *J. Amer. Chem. Soc.* (1966) 88 2710.
86. H.G. Preston and J.C. Davis, *J. Amer. Chem. Soc.* (1966) 88 1585.
87. L. Kruczynski and J. Takats, *Inorg. Chem.* (1976) 15 3140.
88. A.J. Pearson, *Aust. J. Chem.* (1976) 29 1679.
89. K. Bachmann and W. von Philipsborn, *Org. Magn. Resonance* (1976) 8 648.
90. S. Ruh and W. von Philipsborn, *J. Organomet. Chem.* (1977) 127 C59.
91. M.R. Churchill and R. Mason, *Proc. Chem. Soc.* (1964) 226.
92. M. Anderson, A.D.H. Clague, P.L. Blaauer and P.A. Couperous, *J. Organomet. Chem.* (1973) 56 307.
93. C.G. Kreiter, S. Stüfer and L. Wackerle, *J. Organomet. Chem.* (1974) 66 C49.
94. N.F. Murr, *J. Organomet. Chem.* (1976) 112 189.
95. K.A. Holder, Ph. D. Thesis, London (1976).
96. N.F. Chamberlain, "The practice of nmr spectroscopy" (Plenum Press) London (1974).

97. G.A. Olah, S.H. Yu and G. Laing, *J. Org. Chem.* (1976) 41 2383.
98. P.A. Dobosh, D.G. Gresham, C.P. Lillya and E.S. Magyer, *Inorg. Chem.* (1976) 15 2311.
99. A.J. Birch, P.W. Westerman and A.J. Pearson, *Aust. J. Chem.* (1976) 29 1671.
100. A.I. Rezvukhin, V.N. Pittukh-Peletskii, R. Berezina and V.G. Shubin, *Izv. Akad. Nauk. SSR (Ser Khim)* (1975) 3 705.
101. B. Birdsall, N.J.M. Birdsall and J. Feeney, *Chem. Comm.* (1972) 316.

PART TWO

KINETIC STUDIES OF THE REACTIONS OF CATIONIC ORGANOTRANSITION

METAL COMPLEXES WITH NUCLEOPHILES

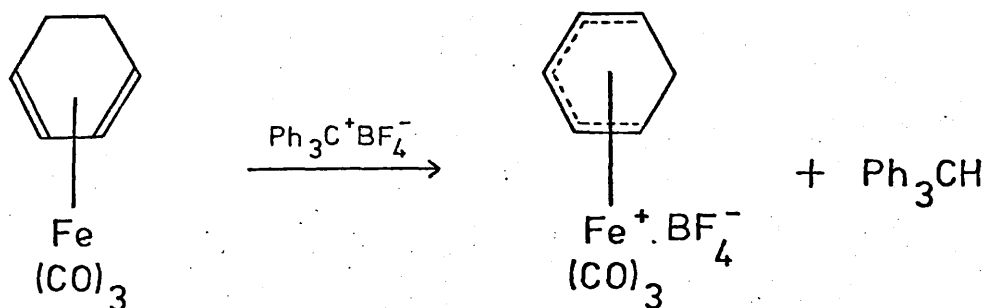
KINETIC STUDIES OF THE REACTIONS OF CATIONIC ORGANOTRANSITION-METAL
COMPLEXES WITH NUCLEOPHILES

3.1 INTRODUCTION

(a) Preparation of cationic η^5 -dienyltricarbonyliron complexes
and related species

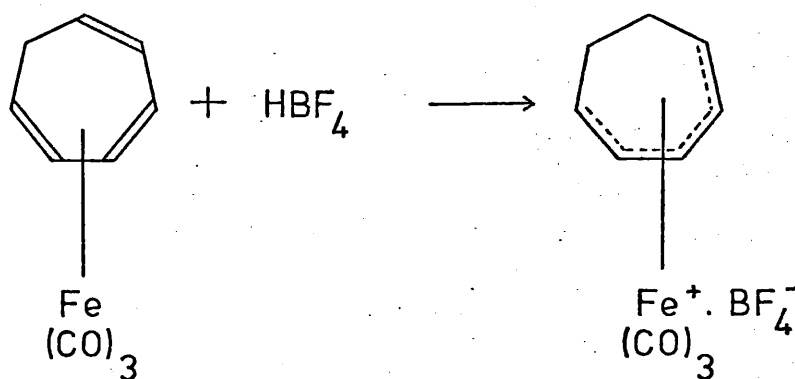
Although Reihlen et al.¹ first reported the preparation of η^4 -buta 1,3 diene tricarbonyliron in 1930, further investigation of similar complexes was not carried out until 1958 when Hallam and Pauson² succeeded in preparing η^4 -cyclohexa 1,3 diene tricarbonyliron. Since this reinvestigation a large number of compounds containing both open chain and cyclic olefinic ligands coordinated to the tricarbonyliron unit have been synthesised.

Dauben and Honnen³ also in 1958, were able to abstract a proton from η^6 -cycloheptatriene tricarbonylmolybdenum, using triphenylmethyl tetrafluoroborate, to form the cationic coordinated tropylium salt $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$. Fischer⁴ extended this reaction to η^4 -cyclohexa 1,3 diene tricarbonyliron and synthesised the cyclohexadienyl salt (3.1) which has all five carbon atoms of the dienyl ring system bonded to the metal centre.



(3.1)

The η^5 -cycloheptadienylium salt was simultaneously prepared by two groups of workers. Dauben and Bertelli⁵ reacted freshly distilled cycloheptatriene with iron pentacarbonyl under nitrogen at 135° for several hours and found the major product to be η^4 -cycloheptatriene tricarbonyliron, which on treatment with fluoroboric acid in propionic anhydride gave the η^5 -cycloheptadienylium cationic species as the tetrafluoroborate salt (3.2). Reaction of cycloheptadiene with iron

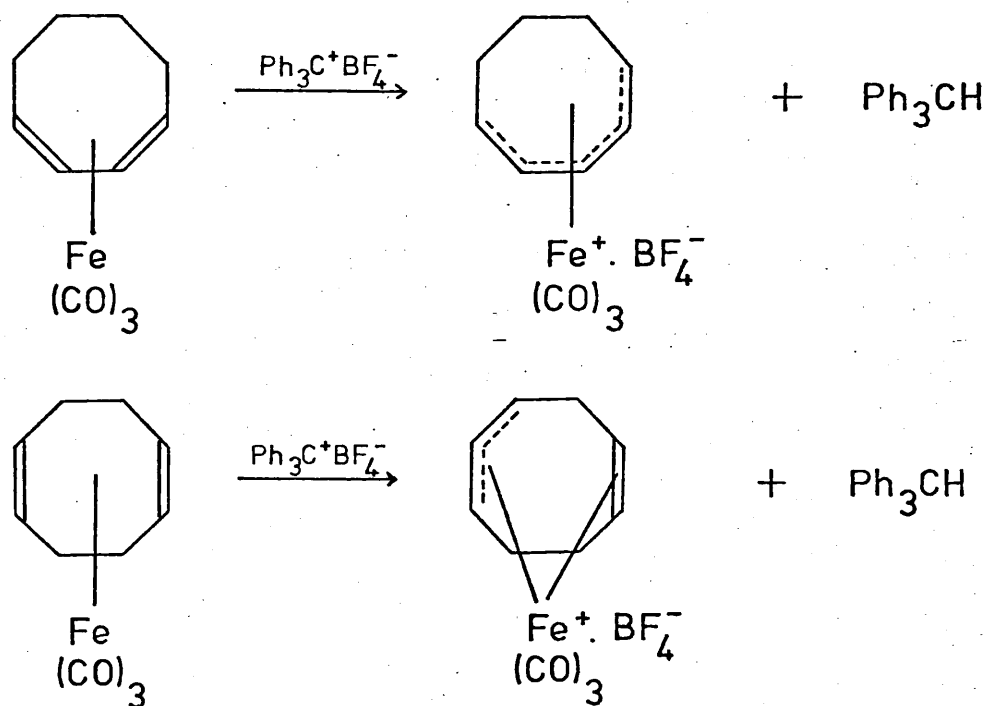


(3.2)

pentacarbonyl at 160° under nitrogen gave η^4 -cyclohepta 1,3 diene tricarbonyliron and the cycloheptadienylium salt was synthesised from this by proton abstraction using $\text{Ph}_3\text{C}^+\cdot\text{BF}_4^-$ as before. These workers also found that the salt underwent a reaction with potassium iodide in acetone at room temperature to give a neutral η^5 -cycloheptadienyl complex, the dicarbonyliodide, by carbonyl displacement. Independently, Wilkinson and co-workers⁶ also investigated the reaction of cycloheptatriene with iron pentacarbonyl and by analogy with the η^6 -cycloheptatriene tricarbonylmolybdenum species, the product was considered to be η^6 -cycloheptatriene dicarbonyliron, although elemental analysis,

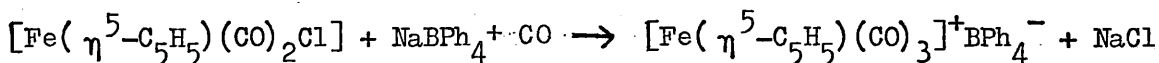
I.R. and nmr spectroscopy later showed the product to in fact be the tricarbonyliron compound prepared by Dauben. Similar reactions were also studied with cycloheptadiene. Dry hydrogen chloride and hydrogen bromide were found to be absorbed by η^4 -cycloheptatriene tricarbonyliron in inert solvents resulting in a yellow precipitate, soluble in water although with decomposition and evolution of carbon monoxide. Stabilisation of the product, the η^5 -cycloheptadienyl salt, could be achieved, however, by precipitation from water with a large anion.

Treatment of η^4 -cycloocta 1,3 diene tricarbonyliron with triphenylmethyl tetrafluoroborate resulted in a similar cyclooctadienyl salt while the non-conjugated diene complex $\eta(1-2) \eta(5-6)$ cyclooctadiene tricarbonyliron also underwent the proton abstraction reaction but this time to give an η^2 -olefin η^3 -allyl salt (3.3).⁷



(3.3)

The reaction of iron pentacarbonyl with cyclopentadiene or di-cyclopentadiene produced the binuclear carbonyl $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ ^{8,9} although the mononuclear cyclopentadiene complex $[\text{Fe}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})_3]$ has been suggested to be an intermediate.¹⁰ This dimer can be oxidised by air in hydrochloric acid/methanol solution to give an almost quantitative yield of the dicarbonylchloride $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ and η^5 -cyclopentadienyl tricarbonyliron salts were initially synthesised from this dicarbonylhalide. The reaction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ with sodium tetraphenylborate in acetone solution under a pressurised atmosphere of carbon monoxide resulted in a virtually quantitative yield of the tricarbonyliron cation as the tetraphenylborate salt¹⁰ (3.4). An alternative preparation involves reaction of the binuclear carbonyl

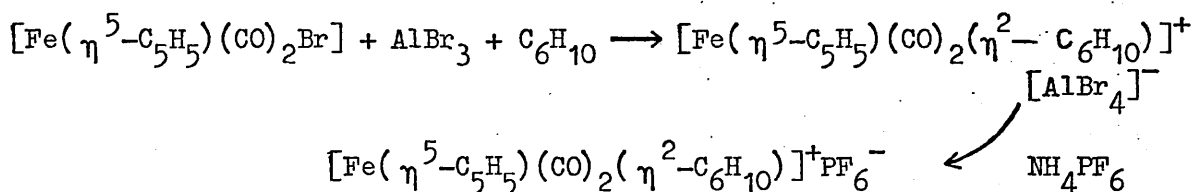


(3.4)

compound and sodium amalgam with ethyl chloroformate in freshly distilled tetrahydrofuran under nitrogen for several hours. Removal of the solvent and extraction of the residue with benzene were followed by treatment with hydrogen chloride gas; the resultant yellow precipitate was then dissolved in water and re-precipitated as the hexafluorophosphate salt by addition of an excess of aqueous ammonium hexafluorophosphate solution.¹¹

Although cationic compounds of the type $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]^+$ where L = olefin have been known for several years, it is only recently that they have been extensively studied. Fischer and Fichtel first prepared complexes of this type in the early 1960's from the η^5 -cyclopentadienyl

iron dicarbonylhalides by reaction with the olefin and a Lewis acid halogen acceptor, usually aluminium tribromide.^{12,13} Further reaction with ammonium hexafluorophosphate enabled precipitation as the hexafluorophosphate salt (3.5). In this way, species with ethylene,



(3.5)

propene, "cis" but-2-ene, octadeca-1-ene, cyclooctene and cyclohexene were prepared together with some di-olefinic complexes which contained a free olefinic grouping.

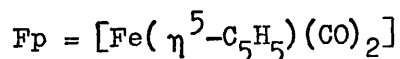
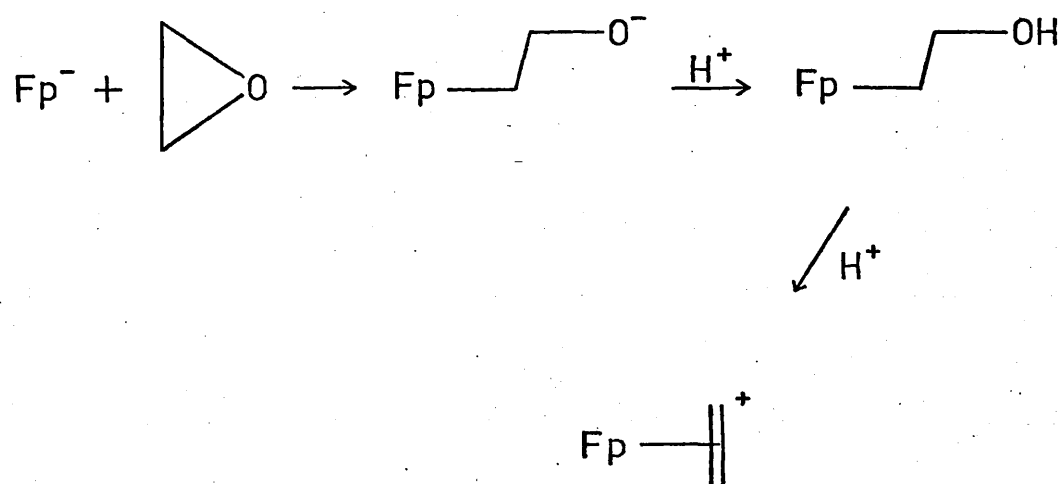
Green and Nagy also synthesised similar open chain compounds by protonation of " σ "-allyl complexes with strong acids^{14,15} or by hydride abstraction from related alkyl species using triphenylmethyl tetrafluoroborate.¹⁶ For example the reaction of allyl chloride with $\text{Na}^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ resulted in high yields of a volatile, yellow oil $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^1\text{-CH}_2\text{CH=CH}_2)]$, the " σ "-allyl complex, which dissolved in dilute hydrochloric acid to give the propene salt, identical to that prepared by Fischer. The alkyl complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{R}]$ R = ethyl or n-propyl were prepared by reacting the appropriate alkyl halide with $\text{Na}^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ and further treatment with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ afforded similar cationic species.

These methods of preparation were augmented by Rosenblum and co-workers who have extensively studied reactions of the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ unit. A general route to the salts $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-olefin})]^+\text{BF}_4^-$

has been described by Giering and Rosenblum who found that a variety of olefins would displace the coordinated isobutene from $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-isobutene})]^+\text{BF}_4^-$ under mild conditions.¹⁷ A solution of the isobutene complex in dichloromethane was heated with an excess of the olefin at 65° until the evolution of isobutene had ceased, usually about ten minutes, and the product was then isolated by precipitation with ether. The isobutene complex itself may be readily prepared by protonation of the η^1 -methylallyl compound

$[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^1\text{-CH}_2\text{-C}(\text{CH}_3)=\text{CH}_2)]$ with fluoroboric acid.¹⁸

The same group have also reported an alternative general synthesis utilising the reduction of epoxides to olefins. Treatment of a tetrahydrofuran solution of $\text{Na}^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ with an epoxide, at or below room temperature, resulted in rapid conversion to an alkoxide which underwent further reaction with two equivalents of fluoroboric acid to yield the olefin complex which was then isolated by precipitation with ether.¹⁹ (Scheme 3.6).

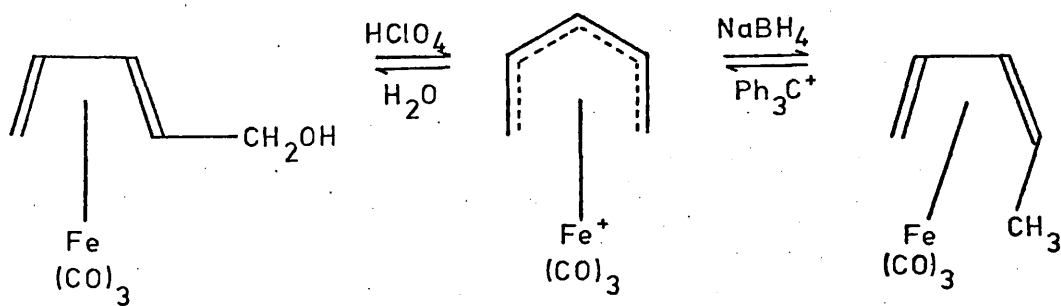


Scheme (3.6)

Boyle and Nicholas have devised a one-stage synthesis of these olefinic salts starting from the readily available dimer $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ through reaction with excess olefin and triphenylmethyl tetrafluoroborate.²⁰ After stirring at room temperature for 48 hours any precipitated tricarbonyl salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^+\text{BF}_4^-$ was removed, the filtrate concentrated under reduced pressure and the olefinic product precipitated with ether. For olefins which underwent reaction with the triphenylmethyl salt, for example norbornadiene, the dimer was pre-oxidised with excess $\text{Ph}_3\text{C}^+\text{BF}_4^-$ for 48 hours, the excess removed with cycloheptatriene and an excess of olefin added. The product was then isolated using a similar "work-up" procedure as before although the yields were lower.

More recently Reger and Colman have isolated the tetrahydrofuran (THF) salt $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2^{\text{THF}}]^+\text{BF}_4^-$ from reaction of the dicarbonyliodide with silver tetrafluoroborate in THF.²¹ This was found to react with olefins in dichloromethane to give the olefinic species by displacement of the coordinated THF. For most olefins the yields were already high but could be increased by reaction of the THF salt and olefin with boron trifluoride to complex the THF as the THF-BF_3 adduct.

Acyclic η^5 -pentadienyl tricarbonyliron salts have also been synthesised; usually by protonation of coordinated conjugated dien-ols where the hydroxy grouping is adjacent to the diene although they have been prepared by hydride abstraction from a "cis" coordinated conjugated diene^{22,23} (3.7).



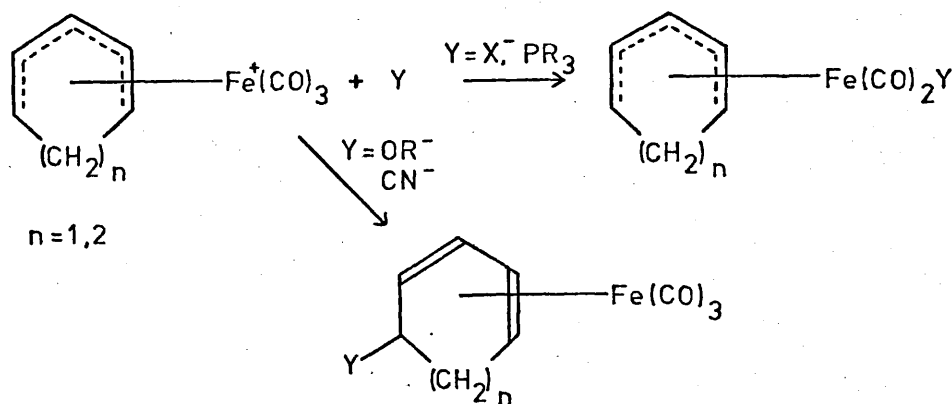
(3.7)

(b) Substitution reactions

Metal complexes of the type $[M(\eta\text{-C}_n\text{H}_m)(\text{CO})_3]$ where M is a transition metal and $n = 4-8$ have been found to undergo substitution reactions with a nucleophilic ligand L by a variety of routes:

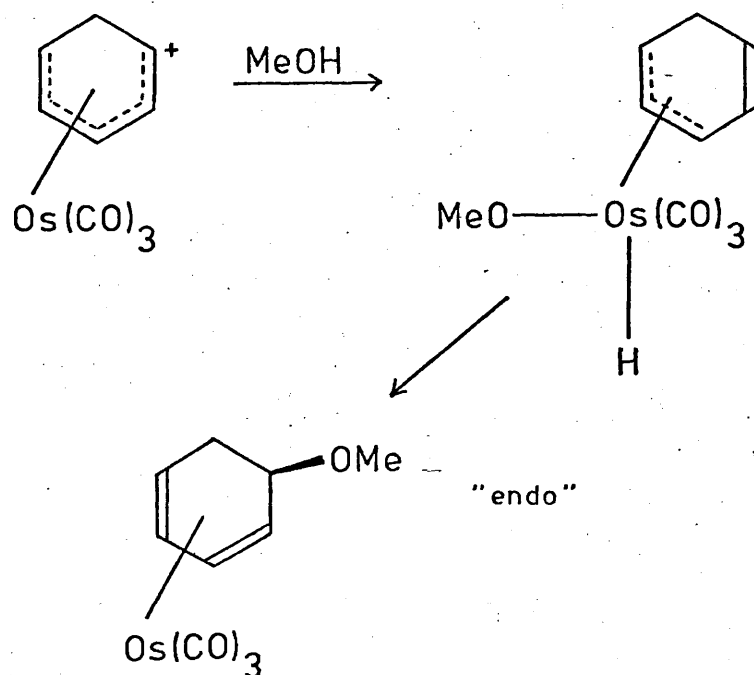
- (i) addition to the coordinated organic ligand C_nH_m
- (ii) ring displacement
- (iii) carbonyl substitution and
- (iv) attack at the carbonyl carbon atom.

Reaction of the η^5 -cyclohexadienyl and η^5 -cycloheptadienyl tricarbonyliron salts with potassium iodide at 30° in acetone for three hours resulted in carbonyl displacement to give the corresponding dicarbonyliodides in 47 and 51% yields respectively²⁴ and phosphines were also found to displace one of the carbonyl ligands.²⁵ Whereas the dicarbonyliodides underwent reaction with potassium cyanide to yield the dicarbonylcyanide derivatives, the tricarbonyliron species gave products in which cyanide had added to the cyclohexadiene and cycloheptadiene rings. These reactions have been summarised in (3.8). Nucleophilic attack on

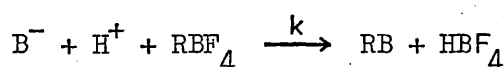
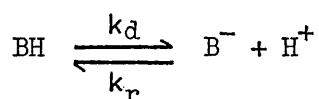


(Scheme 3.8)

η^5 -cyclohexadienyl tricarbonyliron tetrafluoroborate by methoxide ion results in "exo" substituted cyclohexadiene derivatives²⁶ and evidence has been found for a carbomethoxy intermediate arising from initial attack at the carbonyl carbon atom. Indeed, with the osmium analogue the ester-type intermediate $[M(\eta^5-C_6H_7)(CO)_2(CO_2Me)]$ has been isolated which undergoes a stereospecific rearrangement to the "exo" product on warming. Attack by methanol, however, formed the "endo" substituted derivative as the major product.²⁷ Further studies with the osmium analogue also gave the "endo" product which was considered to arise from the oxidative addition of methanol to the metal (3.9).²⁸



Kane-Maguire has studied kinetically the reactions of the β -diketones dimedone and acetylacetone with several η^5 -cyclohexadienyl tricarboxyl species to give substituted cyclohexadiene products^{29,30} and the results were rationalised in terms of a pre-equilibrium dissociation of the β -diketone to yield a reactive carbanion which then reacted directly with the coordinated dienyl unit in a rapid but rate determining step.

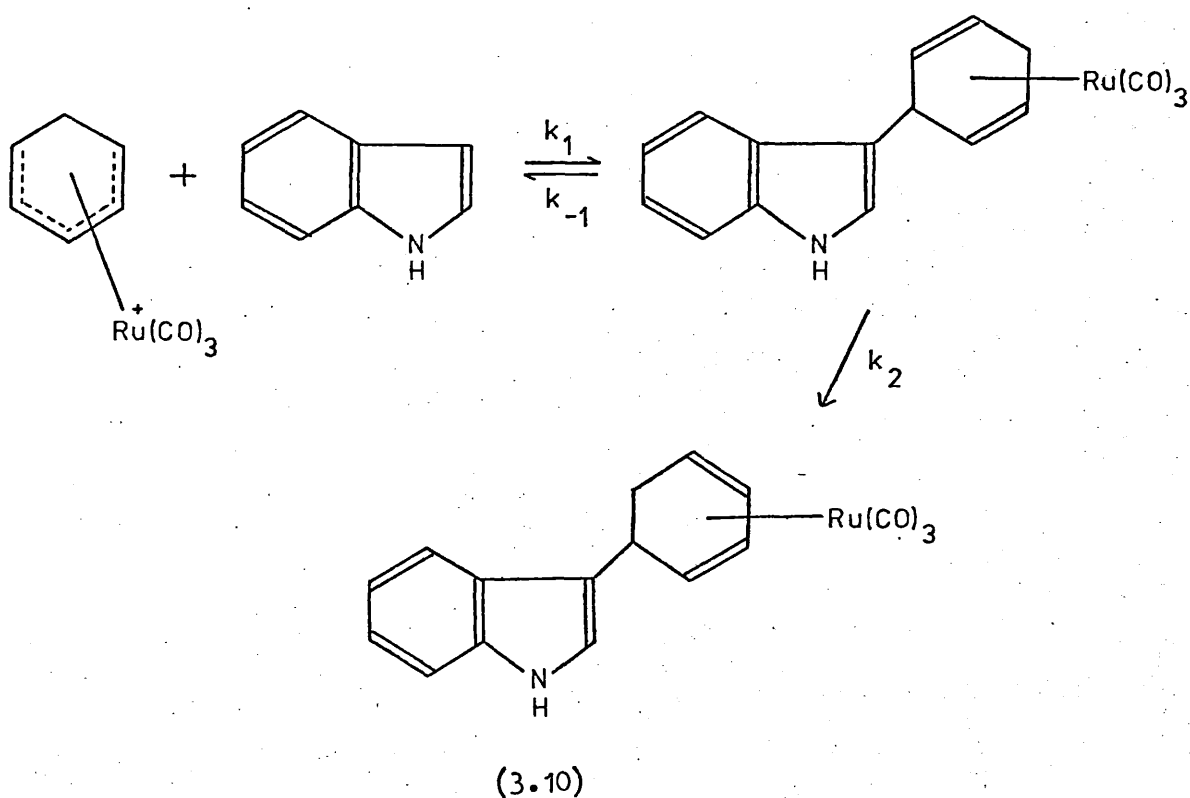


R = η^5 -cyclohexadienyl
tricarboxyliron unit

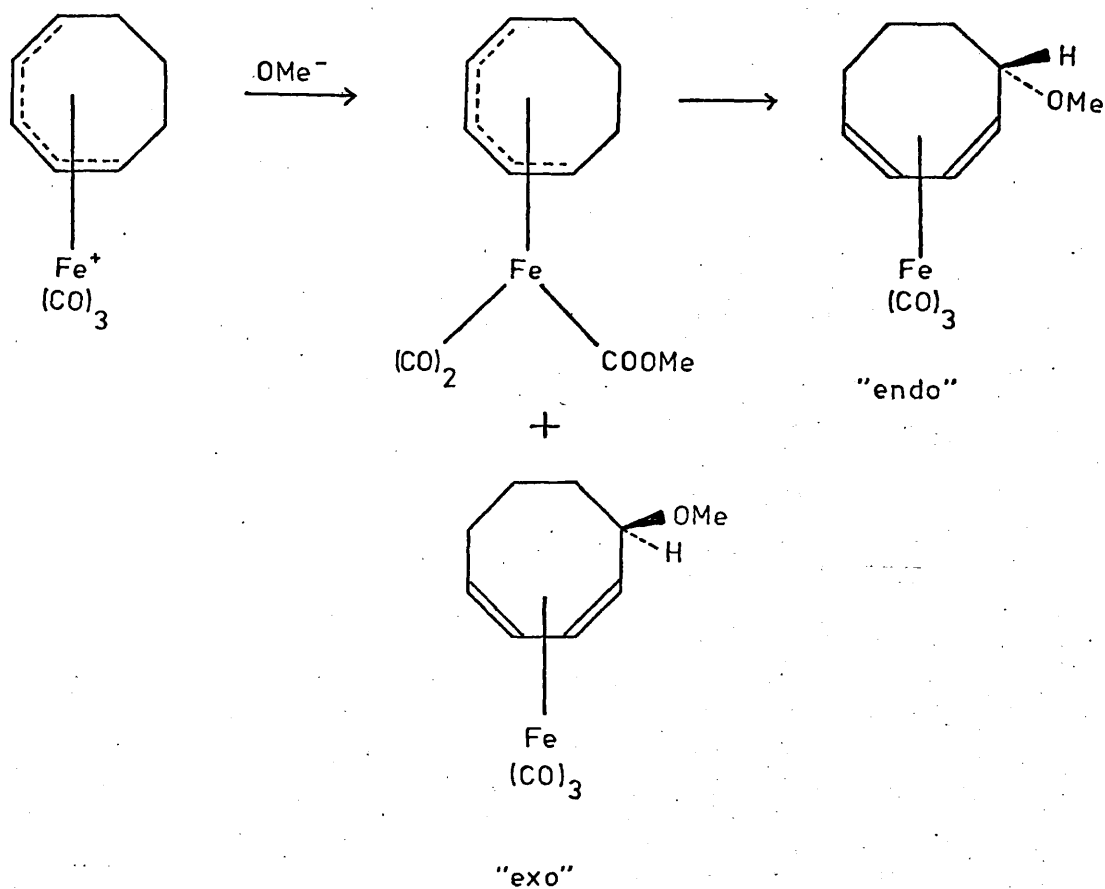
$$\frac{-d[\text{R}]}{dt} = \frac{k_d k}{k_r} \frac{[\text{R}][\text{BH}]}{[\text{H}^+]} = k_{\text{obs}}[\text{R}] \quad \text{where } k_{\text{obs}} = \frac{k_d k[\text{BH}]}{k_r[\text{H}^+]}$$

The same group have also studied the reactions of the η^5 -cyclohexadienyl tricarboxyliron salt with heterocyclic aromatics³¹ and activated arenes³² to yield novel substituted diene compounds. Extensive investigation has shown that, in general, a second order rate law, $\text{Rate} = k[\text{complex}][\text{RH}]$, holds for electrophilic attack on the heterocyclic aromatics by the dienyl cations. The reactions were monitored by the disappearance of the highest frequency carbonyl band in the infra-red spectrum of the salt or by stopped-flow spectrophotometry if the reactions were too fast to monitor by the previous method. In particular, the addition of indoles to $[\text{M}(\eta^5\text{-C}_6\text{H}_7)(\text{CO})_3]^+$ M = Fe, Ru revealed a change in mechanism with the metal. For iron the second order rate law is again obeyed, but with ruthenium, kinetic results gave evidence for an unexpected intermediate (3.10).^{33,34}

In a reference to unpublished work, the authors stated that a similar situation may hold for attack by iodide ion where the formation of the product has been found to be about 100 times faster for ruthenium than for iron.



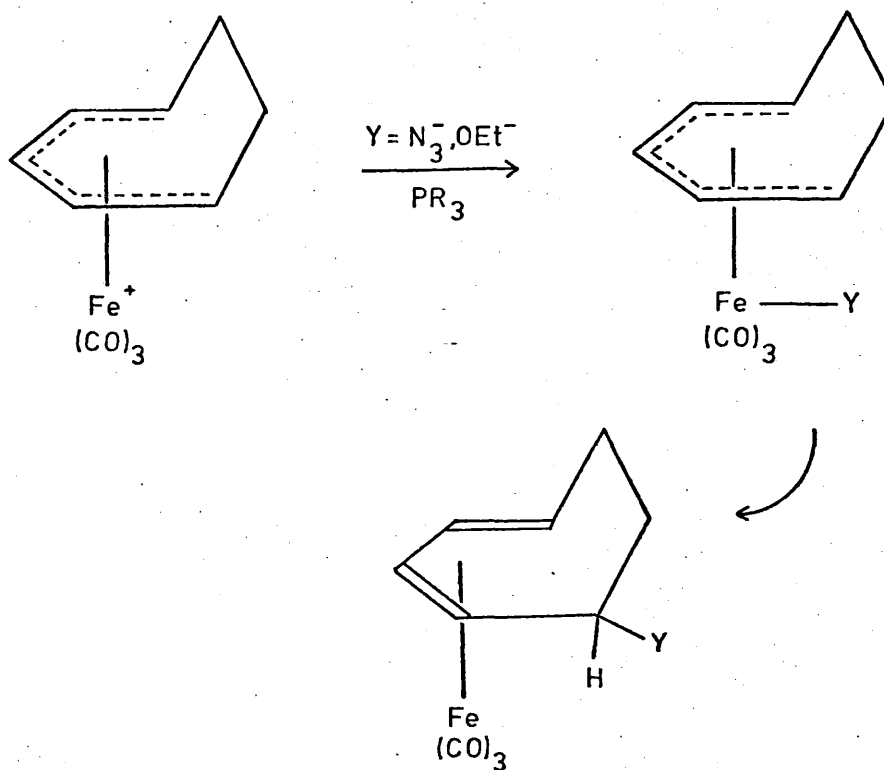
Schiavon et al.³⁵ have found that the reaction of the η^5 -cyclooctadienyl tricarbonyliron cationic species with methoxide ion results in two modes of attack; the first involves initial attack at the carbonyl carbon atom yielding an ester-type species as could be observed from the appearance of a ketone band at 1720 cm^{-1} in the infra-red spectrum: this then underwent a further reaction to give the ring substituted complex. The other mode involved direct attack at the organic ring also resulting in the ring substituted product (3.11). These observations are similar to those found



by Lewis and co-workers for methoxide ion attack on the similar cyclohexadienyl salts although they were able to isolate only the "exo" substituted product.^{27,28} It is noted, however, that both the final substituted cyclooctadiene products exhibited the same infra-red spectrum and hence they may also both be the "exo" derivative. Azide also reacted with the cyclooctadienyl cation salt by two mechanisms although direct attack this time gave a product in which the organic fragment is coordinated to the iron through "σ" and "π"-allyl bonds. Attack at the carbonyl carbon atom was inferred from the evolution of gaseous nitrogen and the presence of an infra-red band at 2173 cm⁻¹ assigned to the isocyanate grouping. In this case, however, the rearrangement product could not be

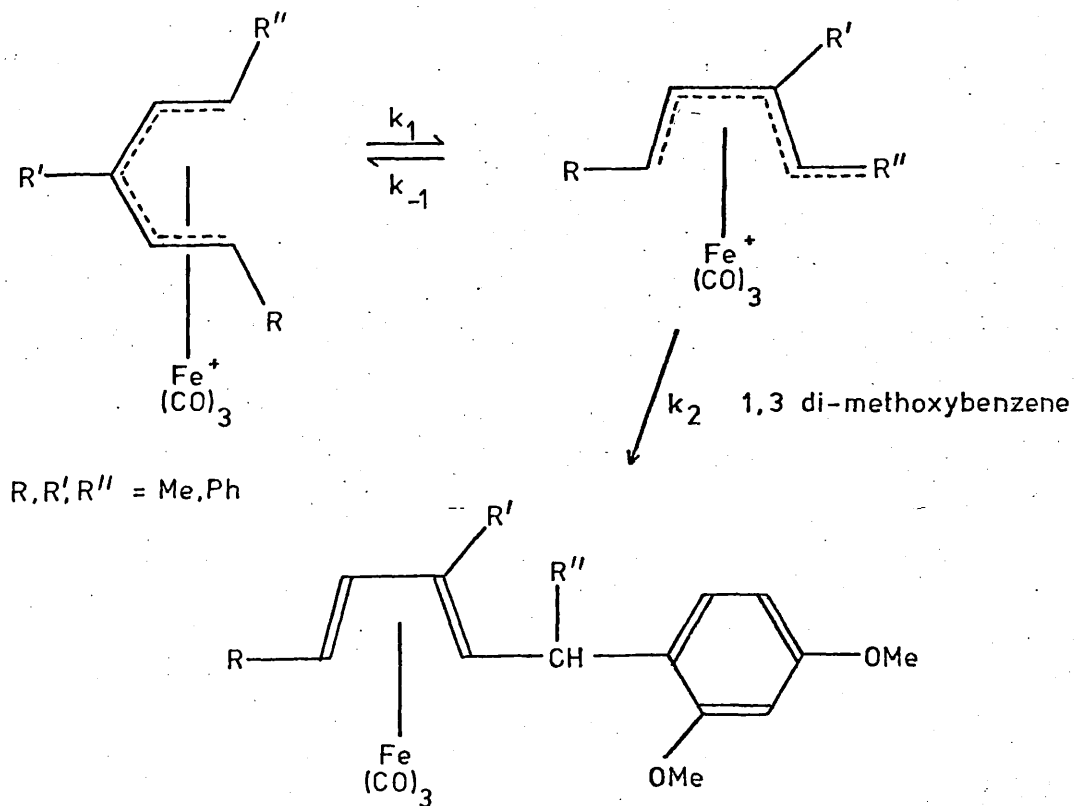
characterised on account of decomposition and evolution of carbon monoxide. This reaction may be compared with that of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^+$ with sodium azide from which Angelici and Busetto³⁶ isolated a similar isocyanate derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCO})]$ but this did not undergo further reaction with the elimination of carbon monoxide. Iodide ion reacted smoothly with the cyclooctadienyl salt, the resultant product being the covalent dicarbonyliodide.

In a recent communication, Brown et al.,³⁷ in contrast to the results of Schiavon, have found that with the analogous cycloheptadienyl salt $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3]^+\text{BF}_4^-$, nucleophilic attack of azide, ethoxide and some phosphines occurs initially at the metal centre and is then followed by ring addition (3.12). The addition of sodium azide to the iron salt in dichloromethane gave an immediate red solution together with



the growth of a shoulder in the infra-red spectrum at 2033 cm^{-1} which then decayed to give another band at 2085 cm^{-1} . The former band was attributed to the asymmetric stretch of an azide group directly bonded to the metal while the latter was assigned to the asymmetric stretch of the azide grouping bonded to the organic diene unit.

Powell and co-workers have examined the reactions of di-methoxybenzenes with the open-chain η^5 -pentadienyl tricarbonyliron salts and interpreted results in terms of an equilibrium involving a "trans" intermediate which then reacts with the nucleophile giving rise to the substituted product (3.13).³⁸ However, the reaction of the acyclic



1,5 diphenylpentadienyl salt tended to an equilibrium position and further investigations with tri-methoxybenzenes have revealed the formation of complex equilibria with several of these salts.³⁹ A comparison of the reaction rates of the open-chain species with the cyclohexadienyl salt has shown the former to be substantially faster; this being attributed to the formation of the "trans" intermediate which cannot be formed from reaction with the cyclic salt.

The reactions of nucleophiles with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]^+$ where L is an olefin have received considerable attention in recent years and have been found to proceed by one or more of three pathways:

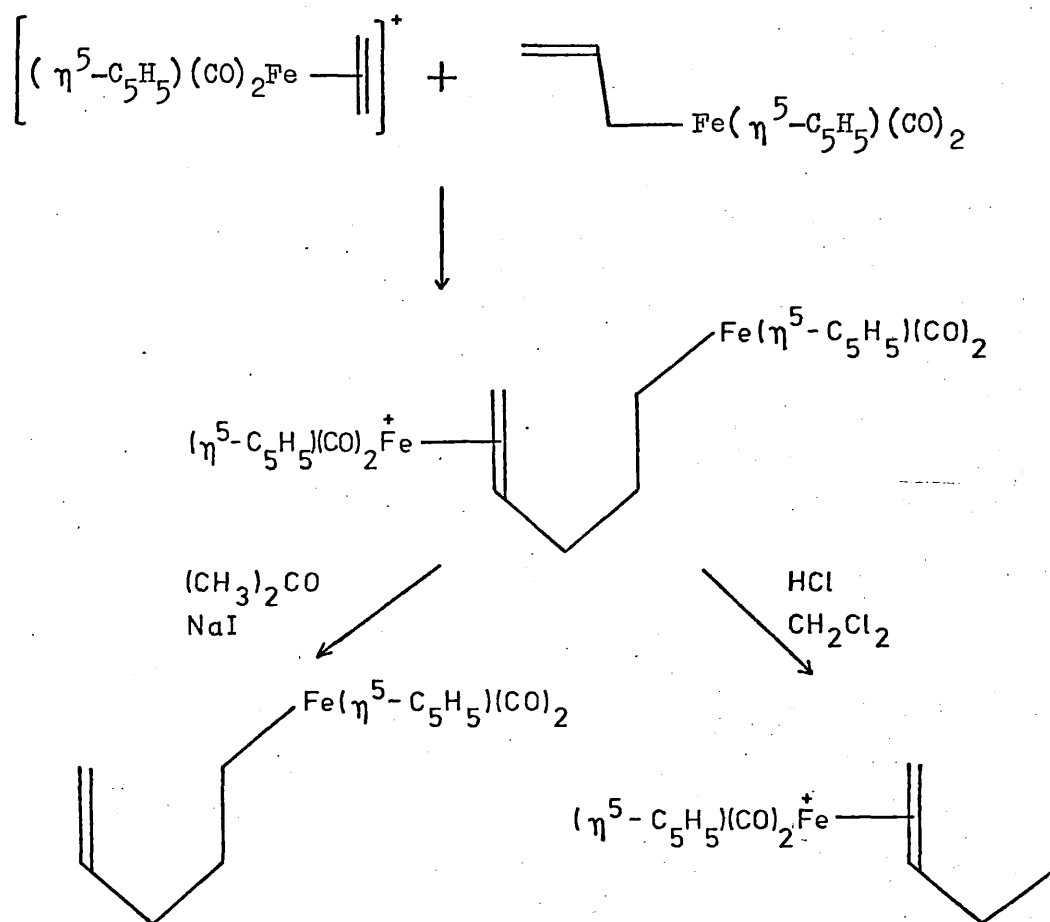
- (i) direct addition to the complexed olefinic bond, often reversible with uncharged nucleophiles
- (ii) displacement of the coordinated olefin and
- (iii) reductive mechanisms giving rise to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$

These latter two reactions often compete with the direct addition to the coordinated olefinic bond and may dominate, especially with reactive anionic nucleophiles.

Busetto et al.⁴⁰ described the reactions of the ethylene salt with several nucleophiles. Methylamine or methoxide ion gave stable "σ"-bonded carbon compounds of the type $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CH}_2\text{CH}_2\text{L})]$ L = OCH_3^- or CH_3NH_2 and on further treatment with hydrogen chloride the original salt was regenerated. Isocyanate and cyanide reacted smoothly by ethylene displacement to yield the dicarbonyl substituted product $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]$, but azide attacked a carbonyl group resulting in the formation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NCO})(\eta^2\text{-C}_2\text{H}_4)]$; a reaction similar to that found for attack on the tricarbonyl salt by sodium azide.

This reaction with azide was unexpected, the olefin being considered to be more electrophilic than the carbonyl group, and was attributed to a more favoured mode of loss of molecular nitrogen and the greater stability of the product relative to the azide adduct $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_2\text{H}_4\text{N}_3)]$. Rosan and Rosenblum⁴¹ later repeated this reaction but were unable to isolate an isocyanate derivative and instead found the product to be $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}_3)]$ by olefin displacement; the isocyanate species only being obtained under extreme conditions and then in low yield.

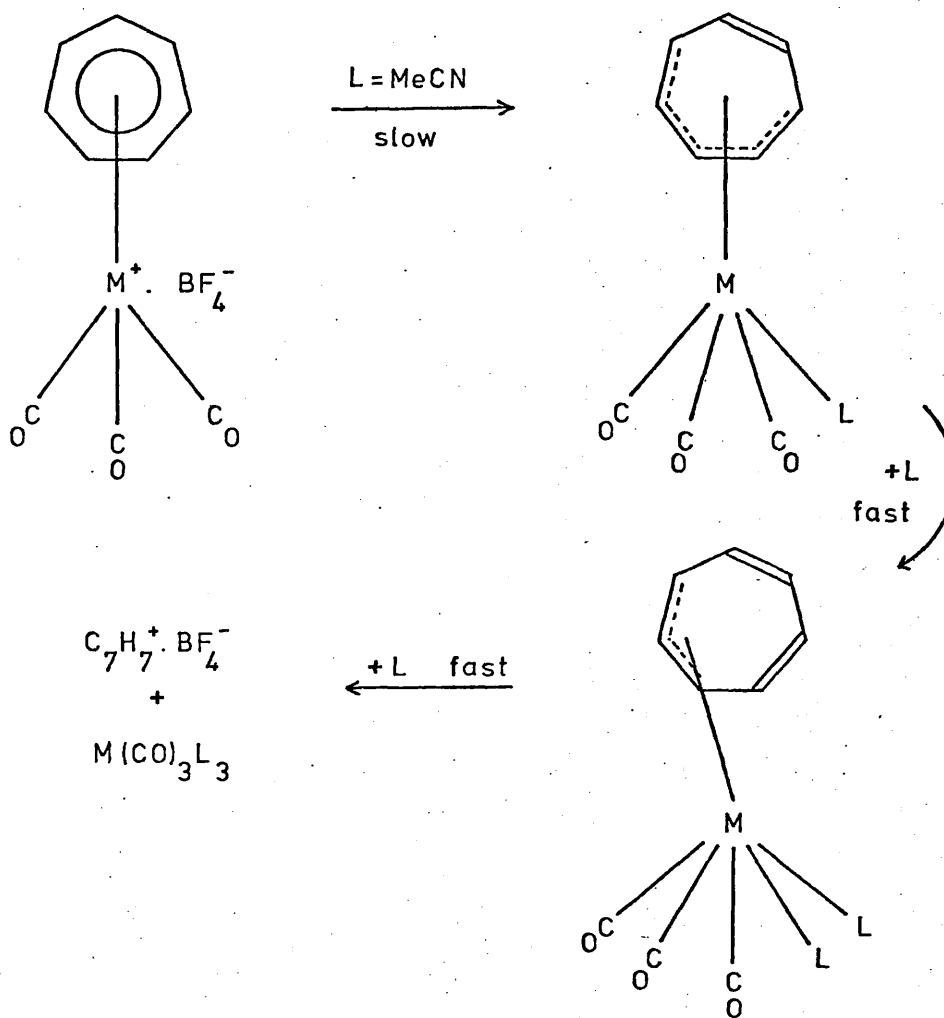
Reactions of these coordinated olefin salts have been extensively studied by Rosenblum and co-workers. Treatment of the salts with an acetone solution of sodium iodide for fifteen minutes at room temperature liberated the coordinated olefin together with formation of the covalent dicarbonyliodide and this has proved to be useful in their later studies for removal of the metal function. The ethylene complex also reacted with several enolate anions at -78° giving rise to neutral " σ "-bonded species and these reactions were also applied to the corresponding cyclopentene and cyclohexene salts.⁴² Nucleophilic attack on the ethylene salt by the allyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^1\text{-C}_3\text{H}_5)]$ in nitromethane at room temperature for four hours afforded a condensation product with two $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ units; the olefinic iron unit was removed by treatment with sodium iodide in acetone and the " σ "-bonded unit was selectively removed by reaction with hydrogen chloride in dichloromethane (Scheme 3.14). The coordinated cyclopentyl species also reacted similarly with the ethylene salt and the reaction of the acyclic allyl species with the butadiene salt resulted, after treatment with iodide, in the formation of a mixture of cyclohexene and vinylcyclopentane



(3.14)

compounds. More recent investigations have involved the addition of a variety of heteroatomic ligands, for example methanol, and usually result in a single adduct which may or may not be thermally stable depending upon the reactants employed.⁴³

Acetonitrile has been found to displace the tropylium ring from $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ according to a second-order rate law resulting in a tris-acetonitrile complex (3.15). For ease of displacement of the tropylium ring the order is $\text{Mo} > \text{W} \gg \text{Cr}$ and the relative rates were suggested to be largely enthalpy controlled, the observed order reflecting a balance between ease of the $[\text{M}-\text{C}_7\text{H}_7]^+$ cleavage

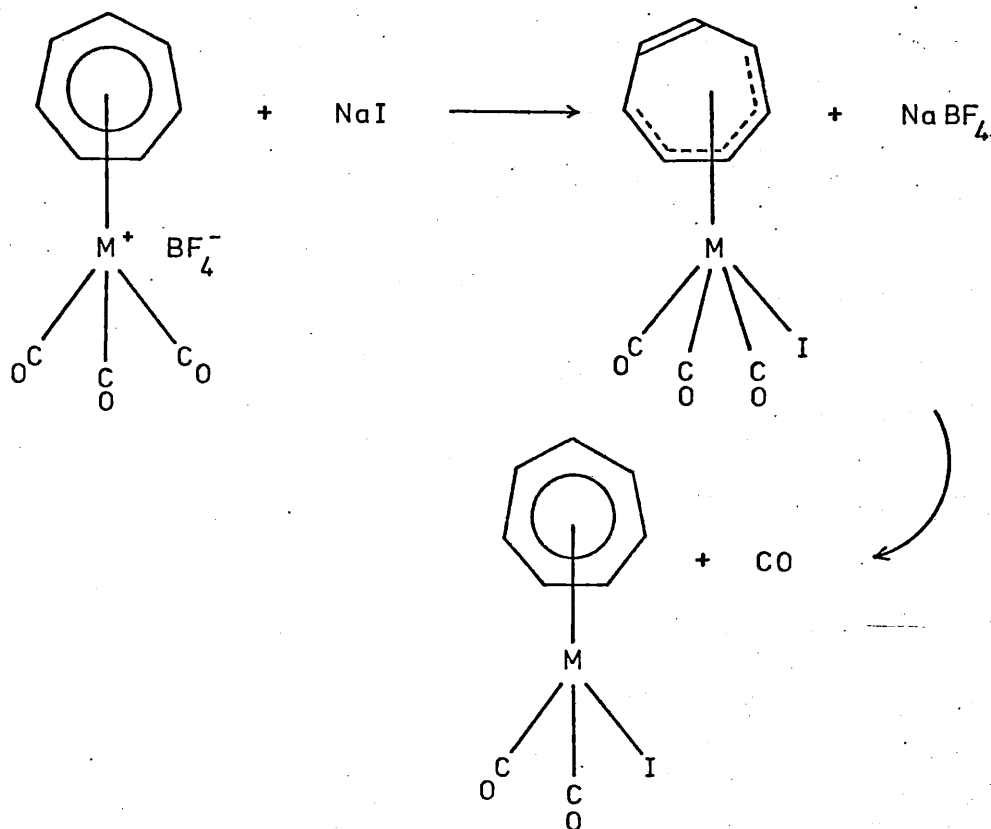


and the energy gained by the M-NCMe bond formation which was expected to decrease in the order $W > Mo > Cr$. These results were interpreted as indicating the strengths of the $[M-C_7H_7]^+$ bonds to be $W > Mo$ and are similar to observations from analogous arene and cycloheptatriene systems.⁴⁴

Phosphine attack on the tropylium salts has been found to proceed by three different routes: displacement of the tropylium ring, carbonyl displacement and phosphonium adduct formation; depending upon the base strength of the nucleophile and the stoichiometric quantities

of phosphine used. Kane-Maguire and co-workers⁴⁵ have shown that phosphonium adduct formation (ring addition) is the initial reaction when the salts are treated with tri-n-butylphosphine although when excess phosphine is employed with the molybdenum and tungsten salts, this adduct formation gives way to ring displacement. Little variation was found in the rate of adduct formation upon changing the metal from chromium to tungsten and this was explained by the similar electrophilicities of the tropylium ring in all the coordinated complexes; direct attack at the metal being expected to lead to large rate differences.⁴⁶ Salzer has summarised phosphine attack on the tropylium salts and, in addition, found that adduct formation occurred at low temperatures but that carbonyl or ring displacement occurred at room temperature.⁴⁷

The reaction of iodide ion with the tropylium complex $[M(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ $M = \text{Mo}, \text{W}$ results in displacement of carbon monoxide to give the covalent dicarbonyliodide as product.⁴⁸ An intermediate stage in this reaction is evident from a noticeable colour change when the initial orange colour of the tropylium salt quickly turns dark brown before giving rise to the dark green product. King and co-workers envisaged the dark intermediate to be an η^5 -pentadienyl intermediate with coordination of both the attacking halide ion and the tricarbonylmetal unit (3.16).⁴⁹ Recent studies involving stopped-flow Fourier Transform nmr spectroscopy together with stopped-flow spectrophotometry have revealed a more complex mechanism considered to involve initial attack at the metal, resulting in the fluxional intermediate proposed by King, followed by transfer of the iodide to the



(3.16)

ring. A molecule of carbon monoxide is then substituted by the solvent, acetone, which itself is further substituted by the iodide to give the dicarbonyliodide as the product.⁵⁰

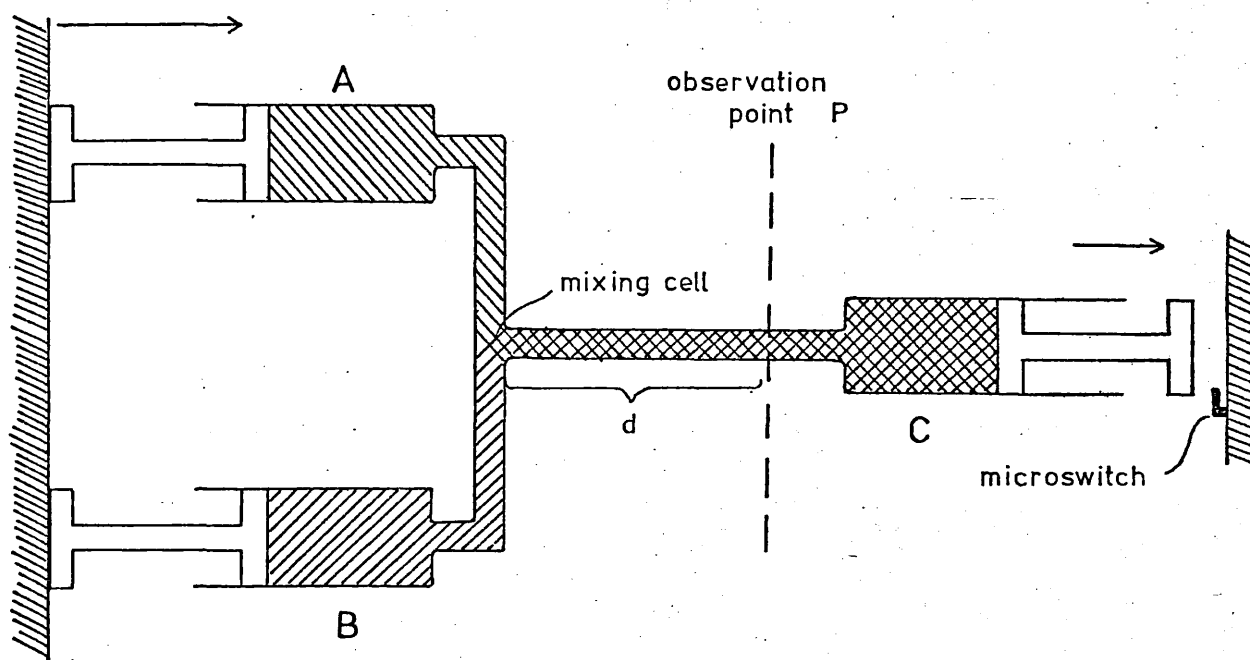
This chapter reports preliminary kinetic investigations of the reactions of halide ion with the salts $[Fe(\eta^5-C_7H_9)(CO)_3]^+BF_4^-$ and $[Mo(\eta^7-C_7H_7)(CO)_3]^+BF_4^-$ in acetone solution using stopped-flow spectrophotometry.

(c) The stopped-flow spectrophotometric technique

Until 1923, there existed no direct, generally applicable technique for the determination of the rates of rapid reactions in the liquid phase with half-lives of less than about ten seconds. Hartridge and Roughton⁵¹ then developed flow systems to enable the reaction of haemoglobin with carbon monoxide to be followed. In their studies, a solution of carboxyhaemoglobin flowed up a vertical tube illuminated by bright light and then into a dark tube. Under the influence of the light the carbon monoxide in combination with the haemoglobin was photochemically displaced by dissolved oxygen and upon entering the dark tube, the initial dark state of equilibrium was progressively attained; the amount of return reaction in the flowing liquid being monitored at various distances along the tube. The principle of the stopped-flow method is that the two solutions which are to react are placed in reservoirs and then driven into a special mixing chamber in which the reaction occurs and the emerging fluid flows past an observation point where the composition of the reacting solution can be determined by available analytical methods. Earlier, because of the lack of instrumentation, it was only possible to measure stopped-flow reactions which took several seconds to reach completion. With the introduction of more sophisticated electronic instrumentation, notably storage oscilloscopes and storage recorders, it is now possible to measure reactions with half-lives of fractions of a second although the basic stopped-flow principles are still applied.

For the stopped-flow technique, the reagents are kept in two hypodermic syringes of equal volume, usually between 2 and 50 cm³ and

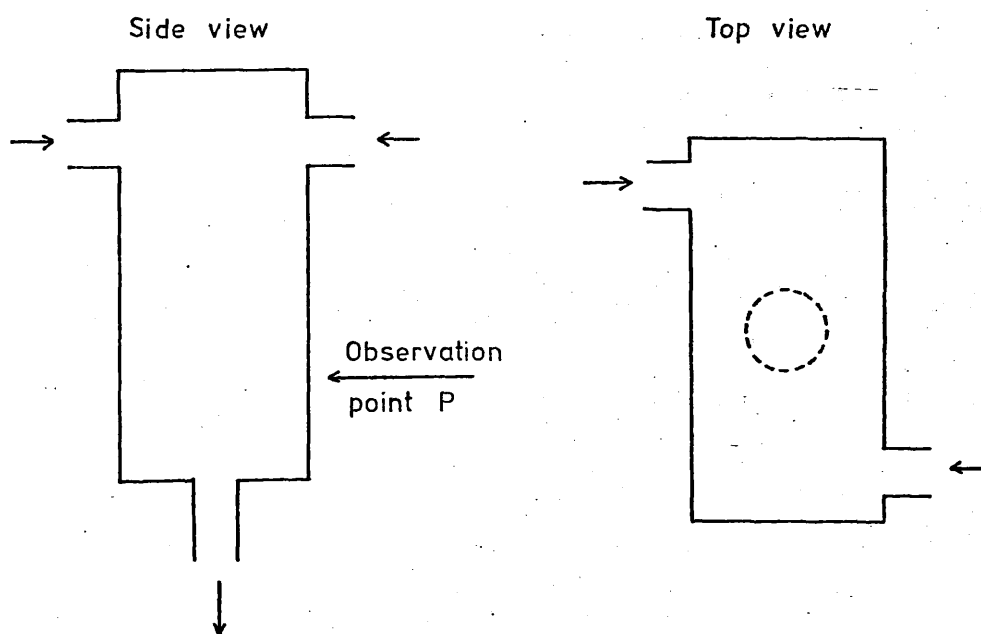
the plungers are simultaneously pushed so as to deliver equal amounts of the two solutions to the mixing cell (3.17).



(3.17)

Constancy in the relative delivery of the two syringes is ensured provided that they are leak-tight and that the plungers are both acted upon by the same rigid platform: the movement of which forces the plungers to deliver their relative solutions to the mixing chamber. In the apparatus used the mixing chamber has two horizontally opposed entrances (3.18) to ensure instantaneous mixing. The reactant liquids are thus made to flow into the mixing chamber and are then suddenly halted by passing this mixed solution into a third syringe arranged

such that its plunger is forced against a stop. At the same time this also pushes against a microswitch which disengages the driving gear (compressed gas, if used) and triggers the recording device. The change in concentration of a small volume of liquid with respect to time is thus followed at the observation point.



Mixing cell

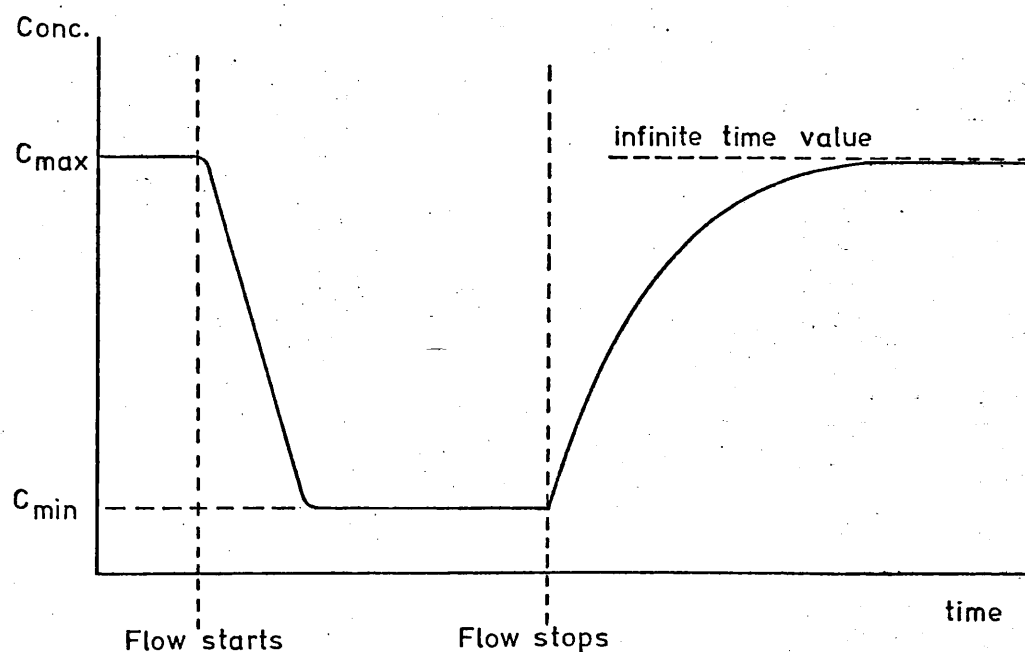
(3.18)

Consider the reaction,



and also consider the sequence of events at the observation point, P, which is at a distance, d , from the mixing point. Before the flow is started, the apparatus will be completely filled with the reactant solutions, A and B, up to the mixing point and with the product, C, after the mixing point. When the reactant solutions are driven

through the mixing point, a steady state condition will be observed at the observation point, P, which will be characterised by the percentage of completed reaction which has already occurred in d/v seconds where d is the distance between the mixing and observation points and v is the flow velocity of the liquid. When the flow is abruptly halted, the steady state solution stops at the point, P, and the reaction proceeds. If the concentration of the product was monitored continuously at P, this would start from a maximum value before the flow is commenced and would reach a minimum value, C_{\min} ; the steady state values which will then be maintained for as long as the flow continues and finally reach the maximum value, C_{\max} , when the flow has been stopped (3.19). By the time the mixed liquid has reached the



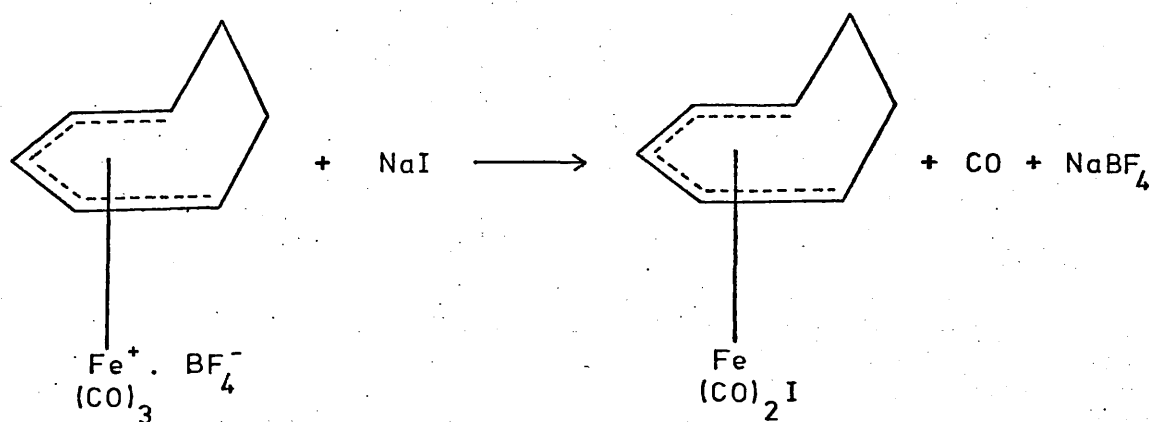
(3.19)

observation point a certain fraction of the reaction will be complete (the exact amount is dependent upon the rate constant) and this is the limiting condition for stopped-flow spectrophotometry i.e. the dead or paralysis time. In order to monitor reactions by this technique, the "dead-time" must be small compared to the half-life of the reaction under consideration. If the flow of liquid had been instantaneously stopped, the half-life of the fastest reaction that could be studied would be d/v seconds, while the slowest is usually determined by the rate of diffusion of the reactant liquids from the delivery or mixing point to the observation point.

Stopped-flow spectrophotometry has the advantage of being a fast and convenient technique to use although it has limitations due to the "dead-time" and also because the reaction can be monitored at one wavelength only which does not give any structural information.

3.2 RESULTS AND DISCUSSION

Salts of the η^5 -cycloheptadienyl tricarbonyliron cation may be readily prepared by protonation of the neutral η^4 -cycloheptatriene complex with strong acids or by hydride abstraction from the η^4 -cyclohepta 1,3 diene species using triphenylmethyl tetrafluoroborate. The tetrafluoroborate salt is a yellow solid, soluble in polar organic solvents and stable to air and moisture both as a solid and in solution for prolonged periods. Treatment with sodium iodide in acetone solution results in an immediate reaction with evolution of carbon monoxide and a considerable colour change from pale yellow to dark brown-black affording the covalent dicarbonyliodide in high yield (3.20). This reaction was followed using a stopped-flow spectrophotometer to

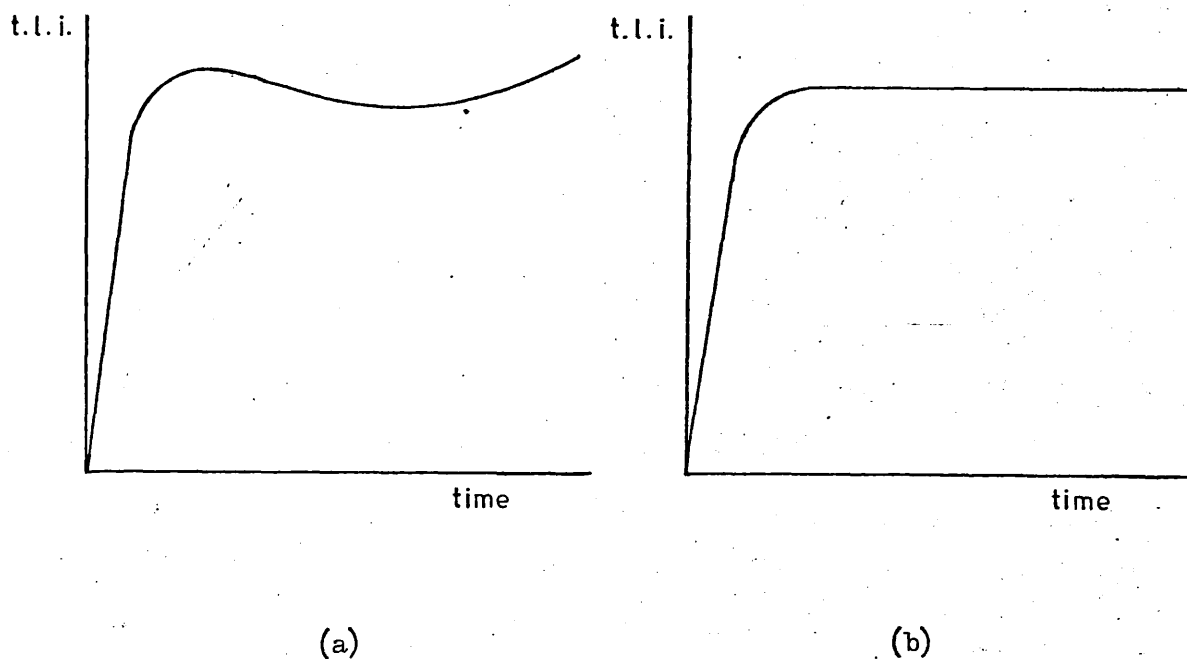


(3.20)

monitor the colour change; the reaction being essentially complete within a few seconds. A similar reaction with lithium bromide (used in place of sodium bromide on account of its greater solubility in acetone)

was also studied. With iodide as reagent only one product was isolated, the dicarbonyliodide, in high yield. However, when bromide was employed, it did not prove possible to isolate a product, although similar kinetic traces to those for the dicarbonyliodide were observed; on this basis, the product was assumed to also be the dicarbonylhalide. With the experimental conditions employed i.e. monitoring the absorbance at 470 nm, only the dicarbonylhalide products were found to have a measurable absorbance and both the tricarbonyliron salt and covalent dicarbonyliodide obeyed the Beer-Lambert relationship. Acetone was chosen as solvent, both reactants and products being soluble at room temperature and also having negligible absorption at the monitoring wavelength.

Preliminary investigations were carried out under an oxygen-free nitrogen atmosphere with both reagents degassed several times by the "freeze-pump-thaw" method and transferred to the reactant reservoirs using nitrogen pressure. However, satisfactory reproducible kinetic traces could not be obtained (3.21a) and it did not prove possible to observe a constant infinite time reading. When the experiment was repeated under an air atmosphere, exponential traces of the type (3.21b) were observed from which satisfactory infinite values of the transmitted light intensity (t.l.i.) could be measured. Kane-Maguire has found evidence, from infra-red studies, for the formation of an acyl iodide intermediate and the traces observed under the degassed conditions may be due to this absorbing intermediate product which then decays to give the dicarbonyliodide. The different traces observed under the air atmosphere indicate that the reaction is modified to some extent under these conditions.



(3.21)

The observed traces were digitised using a transient storage recorder, observed upon a cathode ray oscilloscope and paper chart recorder, and finally stored on punched tape until processed. These traces are the changes in the transmitted light intensity through the solution as a function of time, the light intensity decreasing with an increase in time. A suitable computer program was then employed to transform the values of t.l.i. into optical density according to (3.22) and a typical plot of optical density against time can be seen

Optical density = \log_{10}

$$\frac{I_o}{I_t}$$

t.l.i. of non-absorbing sample at the observation wavelength

t.l.i. of absorbing sample at time t at the observation wavelength

(3.22)

in graph (3.1). A least mean squares analysis was then performed on the values of the log optical density as a function of time to give a value for the pseudo first-order rate constant. The log values were also printed to allow for manual calculation of the rate constant and it is these values which are reported. These latter values are considered to be more accurate than the computer calculated values due to deviations from linearity towards the end of a kinetic run when small changes in absorbance could not be detected by the digitisation procedure of the binary punch system. As a result, towards the completion of a run the program was attempting to fit a straight line to increasingly deviating values giving large errors in the least squares analysis. Satisfactory plots could thus be obtained for at least two half-lives of the reaction (75%) and usually three; graph (3.2) illustrates an example of a manually plotted analysis. This procedure was repeated for several runs at each concentration and an average value for the rate constant found, expressed in units of sec.⁻¹. Typical examples can be found in tables (3.1) and (3.2) for iodide and bromide ion respectively. Average values are calculated together with the standard deviation of the mean and the percentage error in the rate constant at two standard deviations.

To establish the order of reaction with respect to halide, kinetic runs were carried out at several concentrations under pseudo first-order conditions with at least a ten-fold excess of the halide. These results are reported in tables (3.3) and (3.4) for iodide and bromide respectively. With iodide a linear plot of k_{obs} against the halide ion concentration was obtained within the limits of the experiment

TABLE 3.1

Halide conc. $2.5 \times 10^{-2} \text{M}$ $[\text{I}^-]$ Fe complex $0.5 \times 10^{-3} \text{M}$

RUN NO.	k_{obs} (sec^{-1})
1	0.516
2	0.512
3	0.501
4	0.523
5	0.508
6	0.511
Average value	0.512

Standard deviation = 0.0074

Percentage error at two standard deviations of the mean = $\pm 1.2\%$

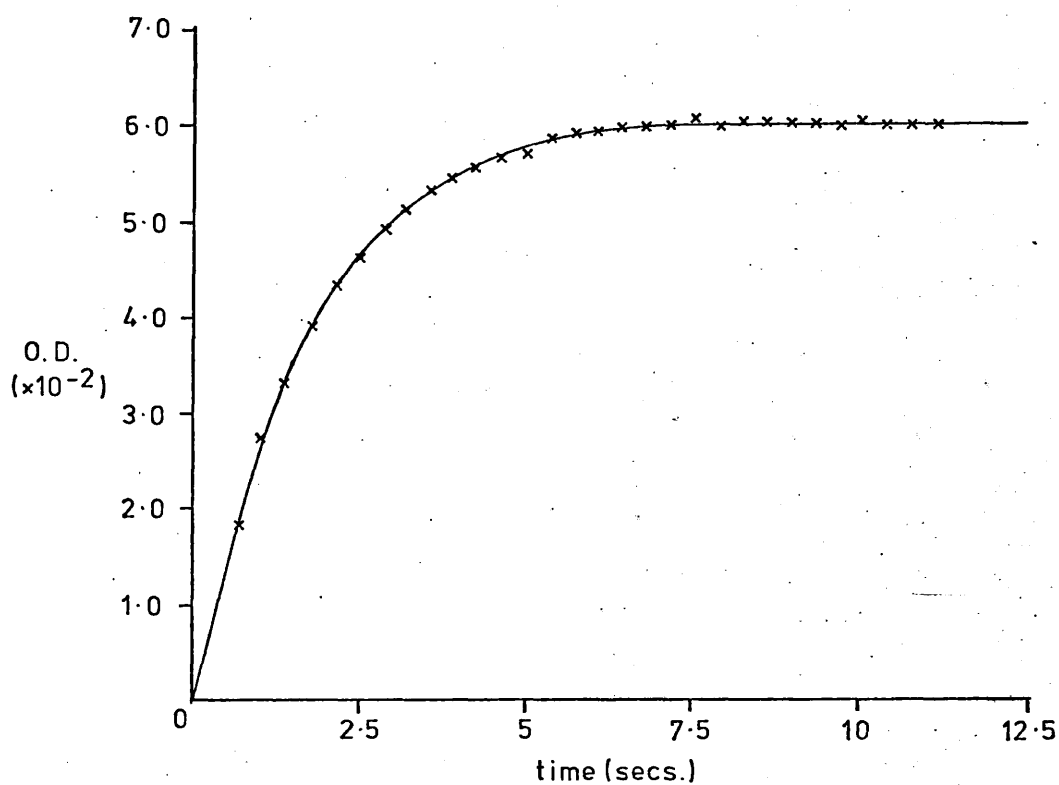
TABLE 3.2

Halide conc. $2.5 \times 10^{-3} \text{M}$ $[\text{Br}^-]$ Fe complex $0.5 \times 10^{-3} \text{M}$

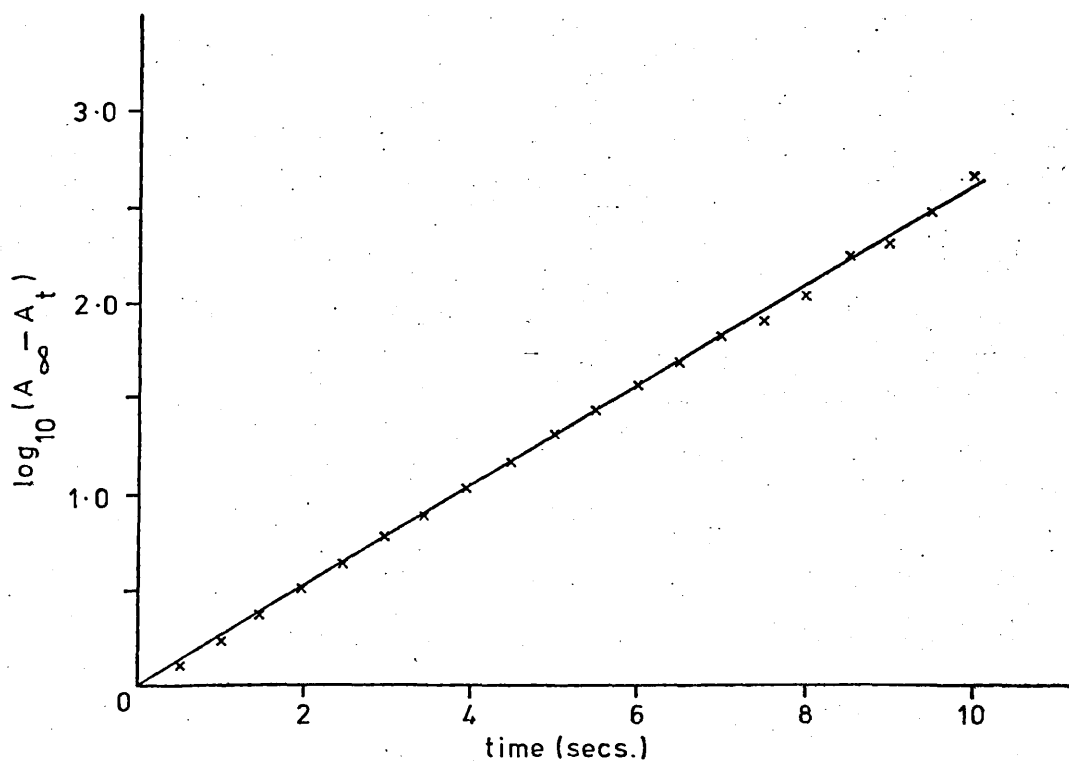
RUN NO.	k_{obs} (sec^{-1})
1	0.256
2	0.265
3	0.262
4	0.269
5	0.264
Average value	0.263

Standard deviation = 0.0048

Percentage error at two standard deviations of the mean = $\pm 1.6\%$



Graph 3.1: Plot of absorbance v. time for the reaction of $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3]^+\text{BF}_4^-$ ($0.5 \times 10^{-3}\text{M}$) with NaI ($2.5 \times 10^{-3}\text{M}$) at 25° .



Graph 3.2: Plot of \log_{10} (infinite absorbance - absorbance at time t) v. time for the reaction of $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3]^+\text{BF}_4^-$ ($0.5 \times 10^{-3}\text{M}$) with LiBr ($2.5 \times 10^{-2}\text{M}$) at 25° .

TABLE 3.3

$$[\text{Fe}] = 0.5 \times 10^{-3} \text{M}$$

No. of times excess $[\text{I}^-]$	Conc. of $[\text{I}^-] \text{M}$	$k_{\text{obs}} (\text{sec}^{-1})$
10	0.5×10^{-2}	0.194
20	1.0×10^{-2}	0.246
30	1.5×10^{-2}	0.337
40	2.0×10^{-2}	0.438
50	2.5×10^{-2}	0.513
60	3.0×10^{-2}	0.593
80	4.0×10^{-2}	0.799
100	5.0×10^{-2}	1.007

TABLE 3.4

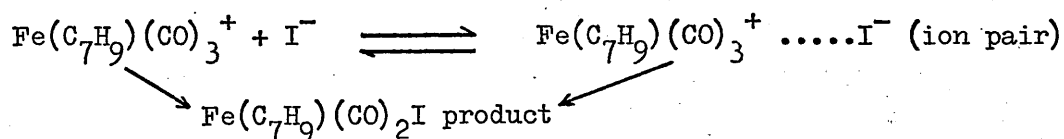
$$[\text{Fe}] = 0.5 \times 10^{-3} \text{M}$$

No. of times excess $[\text{Br}^-]$	Conc. of $[\text{Br}^-] \text{M}$	$k_{\text{obs}} (\text{sec}^{-1})$
10	0.5×10^{-2}	0.119
20	1.0×10^{-2}	0.155
30	1.5×10^{-2}	0.180
40	2.0×10^{-2}	0.219
50	2.5×10^{-2}	0.265
60	3.0×10^{-2}	0.279
70	3.5×10^{-2}	0.281
80	4.0×10^{-2}	0.274
100	5.0×10^{-2}	0.290
120	6.0×10^{-2}	0.296
150	7.5×10^{-2}	0.300

All reactions were studied under pseudo first-order conditions with at least a ten-fold excess of halide ion and gave linear kinetic plots for at least 75% reaction. Each k_{obs} value is the average of at least five separate stopped-flow runs with reproducibility usually better than $\pm 3\%$.

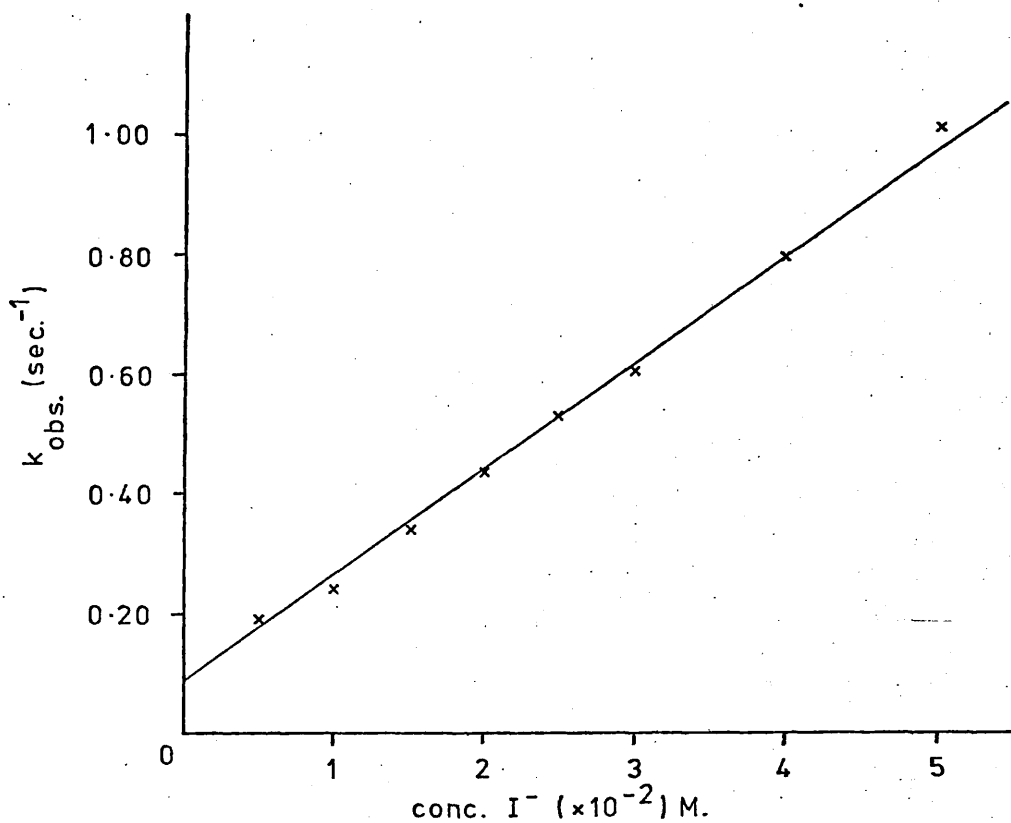
$5 \times 10^{-2} \text{M}[\text{I}^-]$ with an intercept on the k_{obs} axis at 0.08 sec^{-1} (graph 3.3). Bromide ion gave a similar intercept but a limiting rate condition was reached at a concentration approaching $3.00 \times 10^{-2} \text{M}$. $[\text{Br}^-]$ (graph 3.4). This limiting rate condition indicates that the rate of reaction is independent of the concentration of the bromide ion and a similar situation may possibly be envisaged with iodide ion although the limiting rate was not attained within the experimental limits. Addition of sodium perchlorate ($0.5 - 2.0 \times 10^{-3} \text{M}$) to hold the ionic strength constant was found to have negligible effect on the reaction rate with iodide ion within the experimental errors.

Observations such as these could indicate the presence of ion-association known to occur in inorganic systems in non-aqueous solvents⁵² where the reaction rate will be explained in terms of a pre-equilibrium association between the reactant ions to form the ion-pair which then reacts more quickly than the free ion (3.23). The initial step is

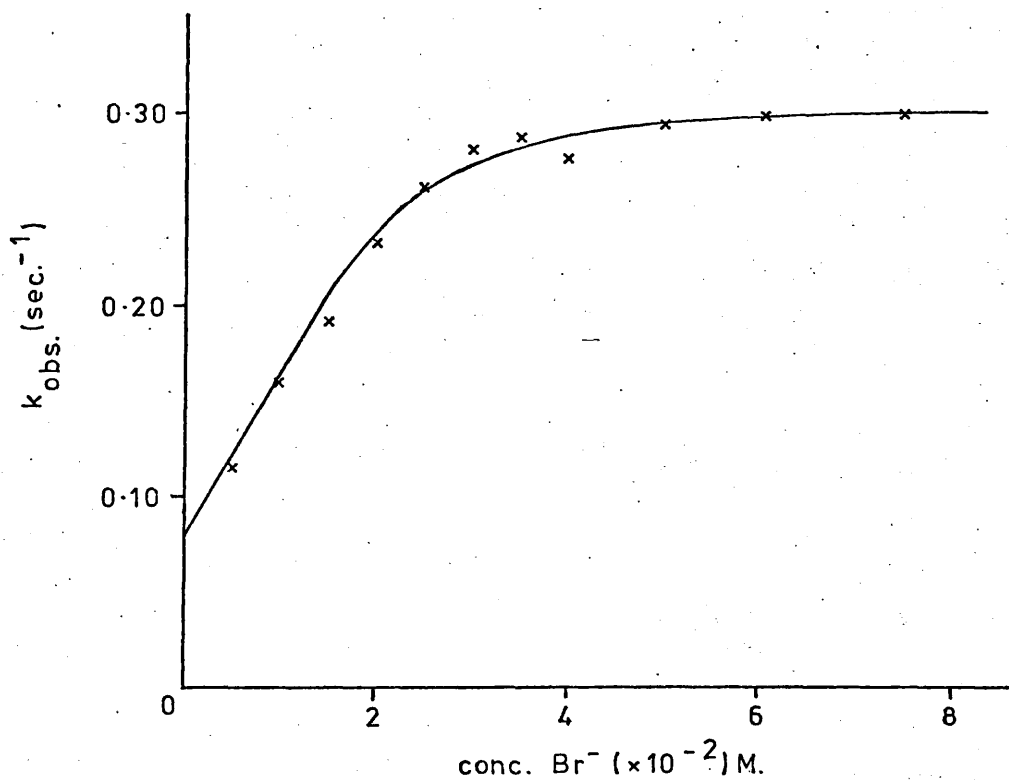


(3.23)

then the attainment of the rapid equilibrium to form the ion-pair followed by a slower step: the reaction of the free ions to form the product and the reaction of the ion-pair to form the product. The intercept will then be the rate of reaction of the free ions and at low concentrations of halide, this will be dominant. As the halide concentration is increased, the concentration of ion-pairs will be increased and these are still reacting more quickly than the free ions. Eventually the



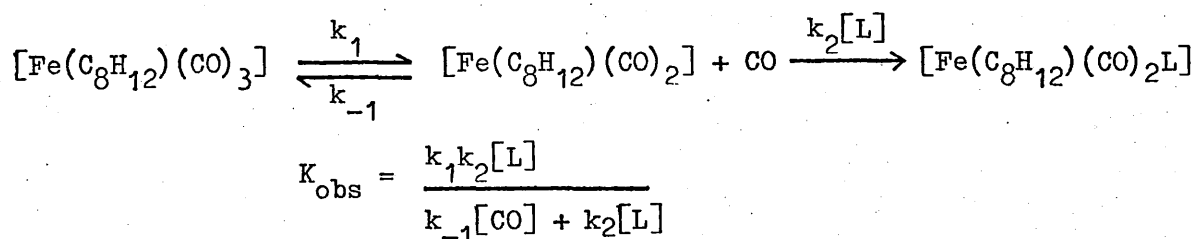
Graph 3.3: Plot of k_{obs} v. iodide ion concentration for the reaction of $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3]^+ \text{BF}_4^-$ with NaI at 25°.



Graph 3.4: Plot of k_{obs} v. bromide ion concentration for the reaction of $[\text{Fe}(\eta^5\text{C}_7\text{H}_9)(\text{CO})_3]^+ \text{BF}_4^-$ with LiBr at 25°.

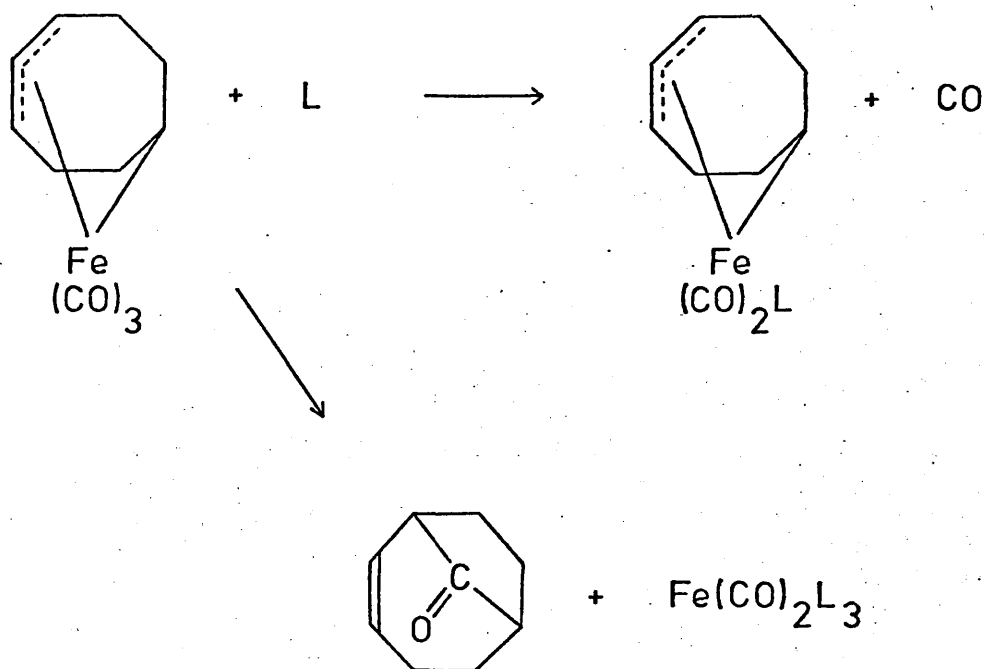
situation will be reached when all the complex ions are in the form of ion-pairs giving rise to a zero order reaction with respect to halide where the rate is independent of the halide ion concentration. The difference in rates between the free ion and the ion-pair can be related to their respective inner solvation shells which in the former will contain only solvent molecules while in the latter the iron complex will be in association with the halide which occupies a position in the inner solvation shell. Any alteration in these environments will then result in a change in the substitution process.

However, the observed kinetic forms may also be indicative of a dissociative mechanism with the initial stage involving the displacement of carbon monoxide followed by reaction with the halide ion. Similar kinetic forms have been found by Lewis and co-workers for substitution of a carbonyl ligand in the neutral complex (η^1 -3, η^6)cyclooctadiene tricarbonyliron with tertiary phosphines.⁵³ Reaction with triphenylphosphine or triphenylphosphite resulted in the formation of a mono-carbonyl substituted product through a carbonyl dissociative mechanism and the following rate law was observed (3.24). With more nucleophilic ligands, for example triethylphosphite, a different rate law was observed : $k_{\text{obs}} = k_1 + k_2[\text{L}]$ due to the formation of two products:



(3.24)

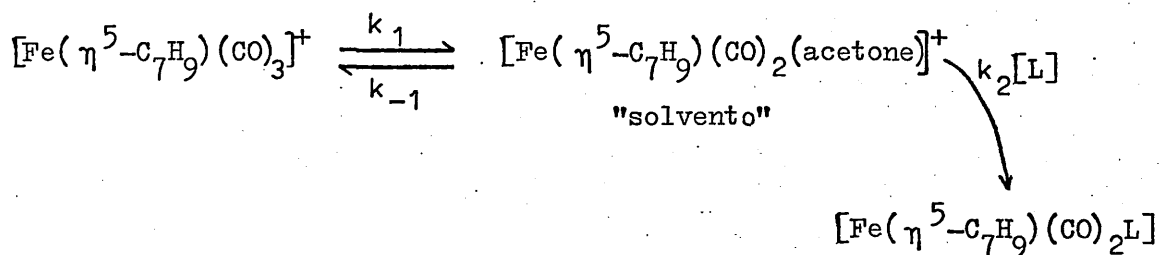
k_1 referring to the dissociative formation of the carbonyl substituted derivative and $[k_2]L$ referring to the formation of a cyclic ketone, produced from the organic ligand, and a dicarbonyliron product (3.25). This kinetic form allows for two concurrent reactions and may account for the observed plot from the reaction with iodide with two different pathways leading to the formation of the same product.



(3.25)

The similar intercepts for the reaction with both iodide and bromide ions may also be indicative of a solvent assisted pathway when the intercept will be the rate of formation of the "solvento" intermediate

(3.26). This intermediate will then undergo a further reaction with



(3.26)

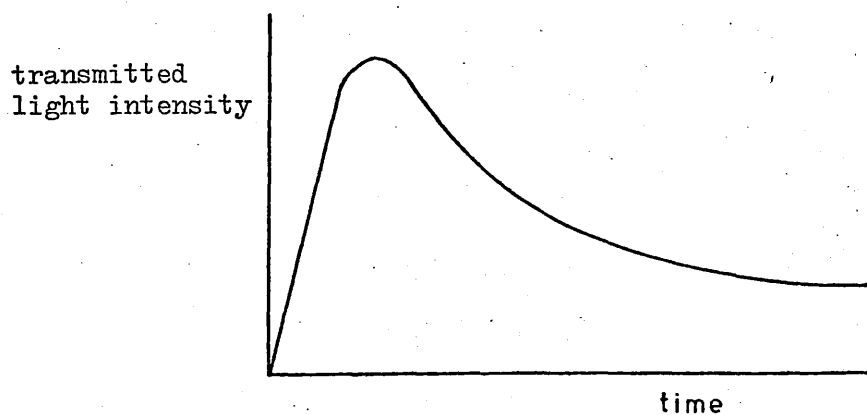
the attacking nucleophile resulting in the product; this mechanism giving rise to a similar kinetic form as before.

From the limited data available it is not possible to establish a mechanism for the carbonyl displacement in the salt $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3]^+\text{BF}_4^-$ by alkali-metal halides; indeed, it is not possible to ascertain whether the similar intercepts observed are indicative of a specific mechanism or merely fortuitous. Further investigations of these reactions were not pursued after communication with Kane-Maguire revealed that he and co-workers had already extensively explored these systems.

Reactions of the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]^+\text{BF}_4^-$ salts L = carbon monoxide, isobutene, cyclohexene and cyclooctene with iodide ion proved similarly inconclusive. Addition of iodide ion to the tricarbonyliron complex resulted in an immediate deep orange-yellow colouration, with an absorption maximum close to 360 nm, which appeared to remain stable for some time. However, even after thirty minutes a satisfactory infinite time value for the absorbance was not obtained and a change in solvent to methanol or nitromethane did not prove any more successful. Similar difficulties were also found with the olefinic species: a surprising

result in view of the extensive investigations by Rosenblum and co-workers¹⁹; Reger and Coleman²¹ have also found from proton nmr spectroscopy that acetone displaces the coordinated cyclohexene when the salt is dissolved in acetone solution. However, similar confusing results have also appeared in the literature with related species: Busetto et al.⁴⁰ reported that the reaction of sodium azide with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]^+$ yielded the isocyanato derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{NCO})]$ although Rosan and Rosenblum⁴¹ were unable to repeat this but isolated an alternative azide product $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{N}_3]$ from a ligand displacement reaction. A similar situation is found with the cationic cycloheptadienylium³⁷ - and cyclooctadienylium - tricarbonyliron³⁵ complexes which undergo different reactions with sodium azide.

Preliminary investigations were also carried out on the reaction of $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ with sodium iodide in acetone solution at 25°. An immediate reaction occurred with the initial orange solution quickly turning dark brown before changing to the final green product, the dicarbonyliodide. Stopped-flow spectrophotometric observations at 470 nm revealed kinetic traces of the double exponential form (3.27);



(3.27)

the reaction being essentially complete within five seconds.

Analysis of this spectrophotometric trace proved complex and a suitable variable parameter computer program was obtained, although extensive analysis of this reaction was not pursued after communication with Kane-Maguire. Available results, however, show the rate of decay of the intermediate species to be independent of the iodide concentration (Table 3.5). Reaction of iodide ion with the analogous tungsten salt has also been studied by both stopped-flow spectrophotometry and stopped-flow Fourier Transform nmr spectroscopy.⁵⁰ The decay of the intermediate species in this case is much slower (>100 secs) than for molybdenum and the spectrophotometric double exponential trace was analysed by separation into two independent curves. These results together with the nmr data have revealed a more complex mechanism than that proposed by King et al.⁴⁹ although the initial attack is still considered to occur at the metal. This gives rise to a fluxional intermediate, evident from a broadening of the tropylium resonance in the proton nmr spectrum, which is followed by iodide addition to the ring. A molecule of carbon monoxide is then considered to be substituted by the solvent, acetone, which itself is then further substituted by the iodide (3.28). Evidence for the transfer of the iodide to the ring was presented from the low temperature proton nmr spectrum; this being similar to that obtained from the product of the reaction of $[W(\eta^7-C_7H_7)(CO)_3]^+$ with tri-n-butylphosphine at room temperature. Kinetic investigations of this latter reaction have been interpreted in terms of direct addition of the tri-n-butylphosphine to the tropylium ring although excess phosphine resulted in initial adduct formation

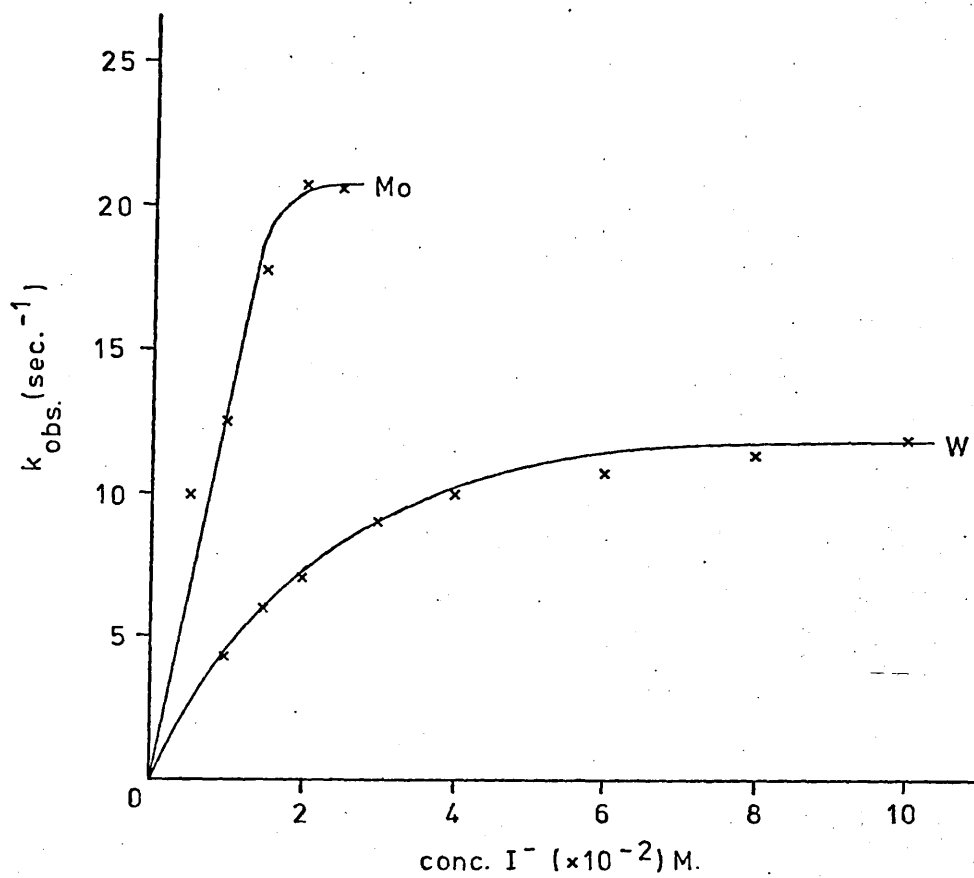
TABLE 3.5

[Mo] concentration = $0.5 \times 10^{-3} \text{M}$

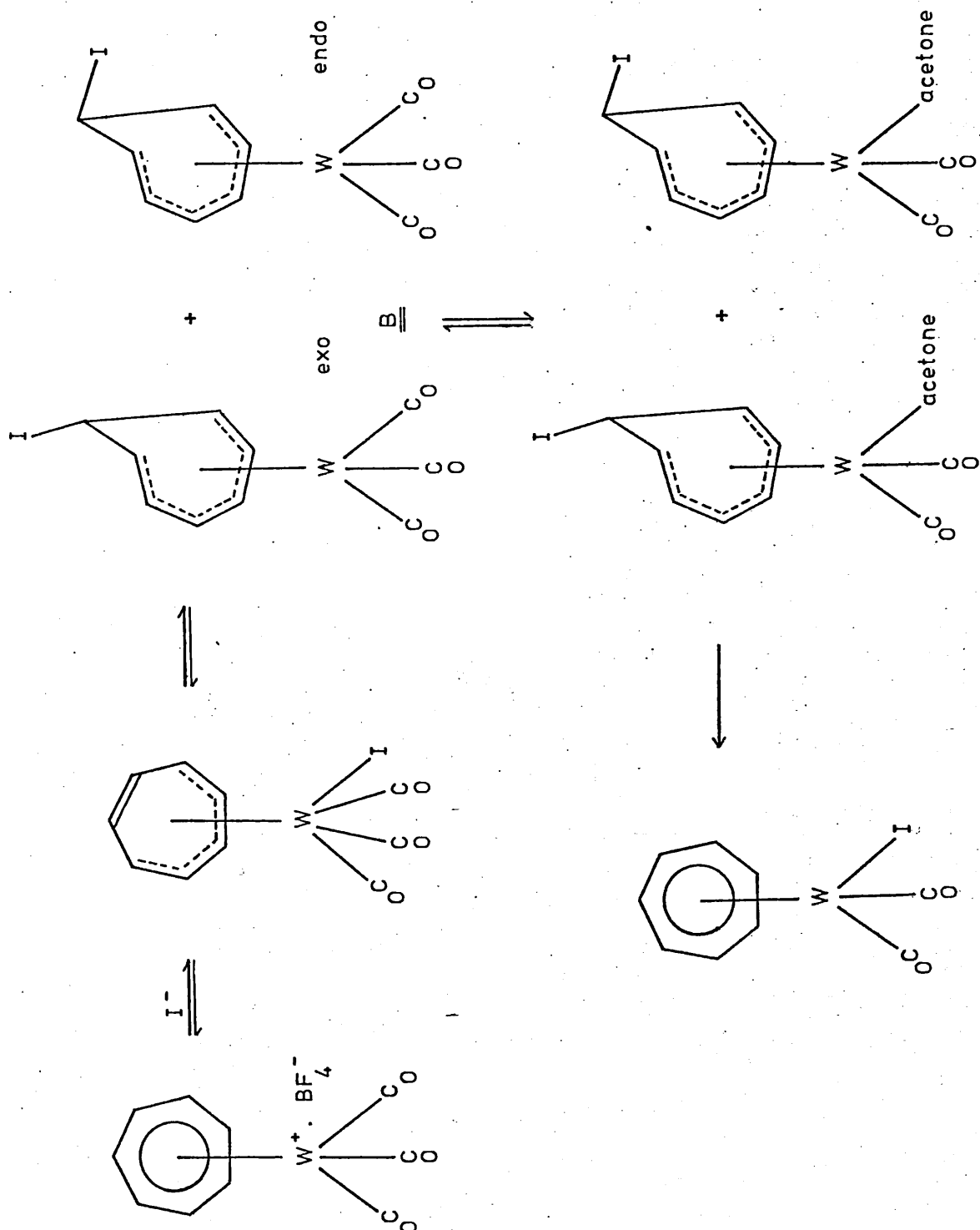
No. of times excess $[\text{I}^-]$	Conc. of $[\text{I}^-] \text{M}$	Rate of formation of brown intermediate $\underline{\text{B}}$ (sec^{-1})	Rate of decay of intermediate $\underline{\text{B}}$
10	0.5×10^{-2}	10.0	1.19
20	1.0×10^{-2}	12.5	1.14
30	1.5×10^{-2}	17.9	1.21
40	2.0×10^{-2}	21.5	1.23
50	2.5×10^{-2}	21.3	1.20

The reactions were studied under pseudo first-order conditions with at least a ten-fold excess of halide ion. Rate constants were measured from the equation $t_{\frac{1}{2}} = \frac{\ln 2}{k}$.

followed by displacement of the tropylium ring.⁴⁶ Preliminary results for the formation of the brown molybdenum intermediate (Table 3.5) give rise to a similar kinetic form as for the tungsten species with both reactions reaching a limiting rate (graph 3.5). The reaction of iodide ion with the tropylium molybdenum salt $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ may be assumed to proceed by a mechanism similar to that proposed for the analogous tungsten species and our preliminary kinetic data support this suggestion.



Graph 3.5: Plot of k_{obs} v. iodide ion concentration for the reaction of $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+ \text{BF}_4^-$; $\text{M} = \text{Mo}, \text{W}$ with NaI at 25° . Data for tungsten reaction supplied by Dr. P. Powell.



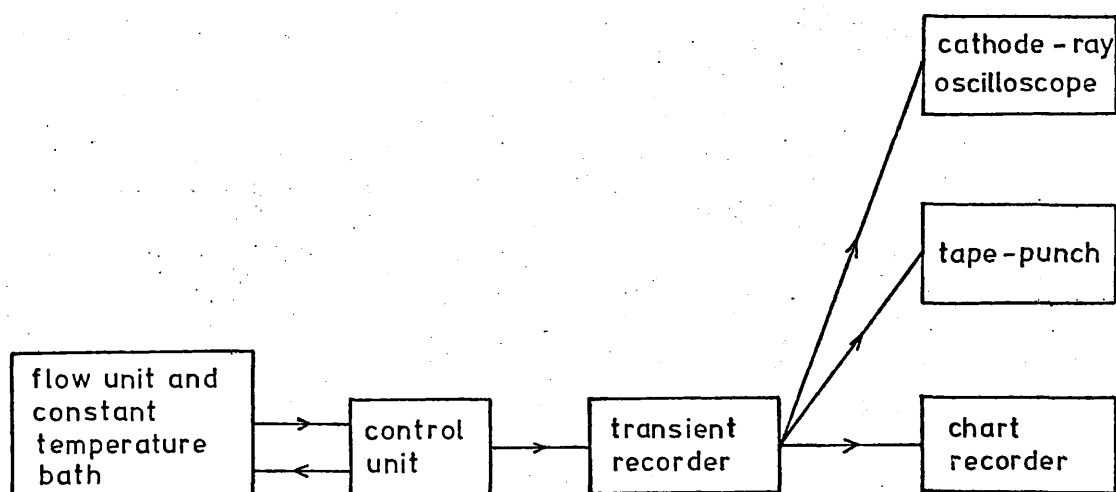
3.3 EXPERIMENTAL SECTION

(i) The reaction of η^5 -cyclohepta 1,3 dienyltricarbonyliron tetrafluoroborate with iodide and bromide ion

(a) Materials

η^5 -cyclohepta 1,3 dienyl tricarbonyliron tetrafluoroborate was prepared according to literature methods.⁵⁴ Sodium iodide and lithium bromide (BDH Analar) and acetone (Koch-Light Analar) were used without further purification.

(b) Apparatus



(3.29)

A Nortech Laboratories, Canterbury SF3A Mk. III stopped-flow spectrophotometer was used in conjunction with Datalab DL 901 transient recorder linked to tape-punch, cathode-ray oscilloscope and chart recorder (3.29). The temperature was maintained at $25 \pm 0.1^\circ\text{C}$ and the required wavelength for observation determined using a Pye-Unicam SP 1800 U.V/Visible spectrophotometer.

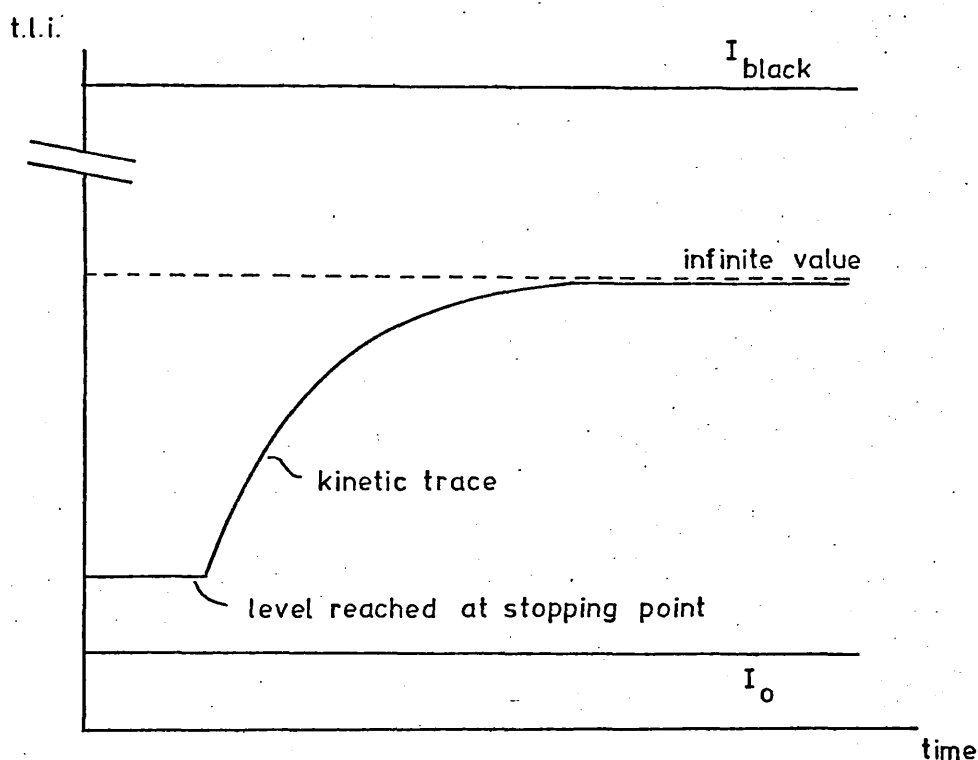
(c) Kinetic procedure

Fresh solutions of each reagent were prepared in acetone prior to each series of kinetic runs at the required concentration and protected from light. These solutions were then transferred to the reservoirs of the flow unit, also protected from light, flushed through the thermostatted coils and allowed to equilibrate at the constant temperature for 10-15 minutes. Care was taken to ensure that the solutions in the flow unit were entirely free from bubbles: a cause of unsatisfactory traces. Monochromatic light, from a tungsten source equipped with filter monochromator, of the required wavelength (470 nm) was shone through the solutions at the observation point. The plungers of the reservoir syringes were then simultaneously pushed and the reactants entered the mixing cell and were then forced into the stopping syringe which pushed against a microswitch and triggered the recording device; the change in transmitted light intensity (t.l.i.) with time being monitored. The trace observed on the oscilloscope was stored in the transient recorder and then plotted with the aid of a chart recorder and stored on punched tape; this procedure was repeated at least five times for each concentration.

Before the kinetic data can be processed it is necessary to convert the t.l.i. values into optical density and this was made possible by the following procedure:

(i) Before the start of each series of runs at a given concentration, an " I_{black} " value was taken which is the value of infinite absorbance.

(ii) A blank solution was run into the cell and the value of the t.l.i. noted. In practice both the reagent solutions were found to have negligible absorbance at the observation wavelength, 470 nm, although the halide solution was always used as the blank (3.30).



(3.30)

These values were then fed into a suitable computer program and trace transformed according to the equation (3.31) and processed using

$$\text{Optical density} = \log_{10} \frac{I_o}{I_t} \quad \text{ie} \quad \frac{I_{\text{black}} - I_o}{I_{\text{black}} - I_t}$$

t.l.i. of non-absorbing sample at observation wavelength

t.l.i. of absorbing sample at time t

(3.31)

a least mean squares analysis to give values of the log optical density and rate constant. From the plot of log optical density against time a pseudo first-order rate constant was found with at least a ten-fold excess of halide ion employed. The rate constant was then found at several concentrations to establish the order of reaction with respect to halide ion.

(d) Preparation of η^5 -cyclohepta 1,3 dienyl dicarbonyliodide iron

This was prepared according to literature methods.⁵⁴

(Yield after 2 washings with hexane - 86%).

(e) Reaction of η^5 -cyclohepta 1,3 dienyl tricarbonyliron tetrafluoroborate with lithium bromide

A similar procedure was carried out as for the iodide reaction. The yellow iron salt changed to orange-red upon addition of the bromide solution and after stirring for four hours the solvent was removed in vacuo and the solid residue washed several times with dichloromethane, filtered under nitrogen and the filtrate evaporated in vacuo to leave a red oil. After pumping for several hours recrystallisation was attempted from acetone/pet. ether (40-60°) and a red oil again obtained. On cooling in a cardice/acetone slush bath (-78°) a reddish-yellow sticky solid was formed which was filtered under nitrogen and washed with cold pentane. On warming to room temperature, however, the red oil was again formed. It was not possible to obtain nmr data due to decomposition resulting in broad unresolved resonances and similar difficulties precluded infra-red analysis.

(ii) Reactions with the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]^+$ species(L = carbon monoxide, isobutene, cyclohexene and cyclooctene)(a) Preparation1. L = carbon monoxide

This was prepared as the tetrafluoroborate salt as a "by-product" from the preparation of the complex L = cyclooctene using the method of Boyle and Nicholas.²⁰

2. L = isobutene

Sodium amalgam was prepared by dissolving small pieces of sodium (~ 2 g) in mercury (20 cm³) in an oxygen-free atmosphere of nitrogen. η^5 -cyclopentadienyl dicarbonyliron dimer (3 g) was added to the amalgam together with dry, purified tetrahydrofuran (50 cm³) and the contents carefully shaken for 30 minutes, until the reaction mixture had changed from purple to dark orange-brown. The contents were then allowed to settle and the resultant solution of $\text{Na}^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ decanted off under nitrogen into a solution of methylallyl chloride (4 cm³) in dry tetrahydrofuran (20 cm³). After stirring for ten minutes the solvent was carefully removed in vacuo to leave a brown oil which was further pumped for thirty minutes to ensure complete removal of the solvent. To a solution of the brown oil in acetic anhydride (20 cm³) cooled in ice was added dropwise an ice cold solution of fluoroboric acid (42% technical) (3 cm³) in acetic anhydride (6 cm³) with vigorous stirring. When the addition was complete, stirring was continued for a further thirty minutes. The resultant solution was then added dropwise to stirred diethyl ether (150 cm³) whereupon orange-yellow crystals were precipitated. These were filtered under nitrogen, washed with several

small portions of diethyl ether and dried under vacuum. However, this product was severely contaminated with sodium salts (acetate or tetrafluoroborate) which were removed by dissolving the isobutene complex in dichloromethane, filtering off the insoluble sodium salts, concentration of the filtrate and re-precipitation with ether. Final purification was achieved by dissolving the product in a small quantity of acetone and re-precipitation with ether (Yield 2.51 g, 48%).

[Nmr data: C_5H_5 , 4.22 (s) int. 5: CH_3 8.01(s) int. 6: H 6.00(s) int. 2. in CD_3NO_2 relative to TMS $\tau = 10$. Int. = relative intensity. Varian EM 360 60 MHz].

3. L = cyclohexene

This was synthesised according to the method of Fischer and Moser.⁵⁵

4. L = cyclooctene

The cyclooctene complex was prepared by the method of Boyle and Nicholas.²⁰

(b) Reactions with iodide ion

The reactions of these species with iodide ion were inconclusive. Addition of sodium iodide to an acetone solution of the tricarbonyl salt gave an immediate deep orange-yellow colouration (λ_{max} 370 nm) which remained on standing in air. However, monitoring this reaction under kinetic conditions with a fifty-fold excess of iodide at 25° in air using a Pye-Unicam SP 1800 U.V./Visible spectrophotometer equipped with thermostat cell gave an increasing absorbance value even after thirty minutes: the eventual product being a brown gelatinous

precipitate. This product is thought not to be the covalent dicarbonyliodide which is black in the crystalline state, giving stable clear black solutions. Similar results were also found with the olefin species and further studies were discontinued.

(iii) The reaction of $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+\text{BF}_4^-$ with sodium iodide

(a) Materials

η^7 -cycloheptatrienyl tricarbonylmolybdenum tetrafluoroborate and η^7 -cycloheptatrienyl dicarbonyliodide molybdenum⁵⁴ were prepared according to literature methods. Sodium iodide (BDH Analar) and acetone (Koch-Light Analar) were used without further purification.

(b) Apparatus and kinetic procedure

The same apparatus and a similar kinetic procedure as described in 3.3(i) were employed with the measurement of absorbance at 470 nm. Fresh solutions of the reagents were degassed using the "freeze-pump-thaw" cycle and transferred to the reactant reservoir using nitrogen pressure. These solutions were also protected from strong light.

REFERENCES

1. H. Reihlen, A. Gruhl, G. Hessling and O. Pfrengle, *Liebigh Annal. Chem.* (1930) 482 161.
2. P.F. Hallam and P.L. Pauson, *J. Chem. Soc.* (1958) 642.
3. H.J. Dauben and L.R. Honnen, *J. Amer. Chem. Soc.* (1958) 80 5570.
4. E.O. Fischer and R.D. Fischer, *Angew. Chem.* (1960) 72 919.
5. H.J. Dauben and D.J. Bertelli, *J. Amer. Chem. Soc.* (1961) 83 497.
6. R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.* (1961) 594.
7. F.A. Cotton, A.J. Deeming, P.L. Josty, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, *J. Amer. Chem. Soc.* (1971) 93 4624.
8. T.S. Piper, F.A. Cotton and G. Wilkinson, *J. Inorganic and Nuclear Chem.* (1955) 1 165.
9. P.F. Hallam and P.L. Pauson, *J. Chem. Soc.* (1956) 3030.
10. A. Davison, M.L.H. Green and G. Wilkinson, *J. Chem. Soc.* (1961) 3172.
11. L. Busetto and R.J. Angelici, *Inorg. Chim. Acta* (1968) 2 391.
12. E.O. Fischer and K. Fichtel, *Chemische Ber.* (1961) 94 1200.
13. E.O. Fischer and K. Fichtel, *Chemische Ber.* (1962) 95 2063.
14. M.L.H. Green and P.L.I. Nagy, *Proceedings Chem. Soc.* (1961) 378.
15. M.L.H. Green and P.L.I. Nagy, *J. Chem. Soc.* (1963) 189.
16. M.L.H. Green and P.L.I. Nagy, *J. Organomet. Chem.* (1963) 1 58.
17. W.P. Giering and M. Rosenblum, *Chem. Comm.* (1971) 441.
18. W.P. Giering and M. Rosenblum, *J. Organomet. Chem.* (1970) 25 C71.
19. W.P. Giering, M. Rosenblum and J. Tancrede, *J. Amer. Chem. Soc.* (1972) 94 7170.

20. P.F. Boyle and K.M. Nicholas, *J. Organomet. Chem.* (1976) 114 307.
21. D.L. Reger and C. Coleman, *J. Organomet. Chem.* (1977) 131 153.
22. J.E. Mahler and R. Pettit, *J. Amer. Chem. Soc.* (1963) 85 3955.
23. J.E. Mahler, D.H. Gibson and R. Pettit, *J. Amer. Chem. Soc.* (1963) 85 3959.
24. M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, *J. Chem. Soc. (A)* (1967) 240.
25. F.M. Chaudhari and P.L. Pauson, *J. Organomet. Chem.* (1966) 5 73.
26. R.H. Cowles, B.F.G. Johnson, P.L. Josty and J. Lewis, *Chem. Comm.* (1969) 392.
27. K.E. Hine, B.F.G. Johnson and J. Lewis, *Chem. Comm.* (1975) 81.
28. E.G. Bryan, A.L. Burrows, B.F.G. Johnson, J. Lewis and G.M. Schiavon, *J. Organomet. Chem.* (1977) 129, C19.
29. L.A.P. Kane-Maguire, *J. Chem. Soc. (A)* (1971) 1602.
30. C.A. Mansfield and L.A.P. Kane-Maguire, *J. Chem. Soc. (Dalton)* (1976) 2187.
31. L.A.P. Kane-Maguire and C.A. Mansfield, *Chem. Comm.* (1973) 540.
32. C.A. Mansfield, K.M. Al-Kathumi and L.A.P. Kane-Maguire, *J. Organomet. Chem.* (1974) 71 C11.
33. G.R. John, C.A. Mansfield and L.A.P. Kane-Maguire, *J. Chem. Soc. (Dalton)* (1977) 574.
34. L.A.P. Kane-Maguire and C.A. Mansfield, *J. Chem. Soc. (Dalton)* (1976) 2192.
35. G. Schiavon, C. Paradisi and C. Boanini, *Inorg. Chim. Acta* (1975) 14, L5.
36. R.J. Angelici and L. Busetto, *J. Amer. Chem. Soc.* (1969) 91 3197.

37. D.A. Brown, S.K. Chawla and W.K. Glass, *Inorg. Chim. Acta* (1976) 19 L31.
38. T.G. Bonner, K.A. Holder and P. Powell, *J. Organomet. Chem.* (1974) 77 C37.
39. T.G. Bonner, K.A. Holder, P. Powell and E. Styles, *J. Organomet. Chem.* (1977) 131 105.
40. L. Busetto, A. Palazzi, R. Ros and U. Belluco, *J. Organomet. Chem.* (1970) 25 207.
41. A. Rosan and M. Rosenblum, *J. Organomet. Chem.* (1974) 80 103.
42. A. Rosan, M. Rosenblum and J. Tancrede, *J. Amer. Chem. Soc.* (1973) 95 3062.
43. P. Lennon, M. Madhavarao, A. Rosan and M. Rosenblum, *J. Organomet. Chem.* (1976) 108 93.
44. K.M. Al-Kathumi and L.A.P. Kane-Maguire, *J. Chem. Soc. (Dalton)* (1973) 1683.
45. D.A. Sweigart, M. Gower and L.A.P. Kane-Maguire, *J. Organomet. Chem.* (1976) 108 C15.
46. G.R. John, L.A.P. Kane-Maguire and D.A. Sweigart, *J. Organomet. Chem.* (1976) 120 C47.
47. A. Salzer, *Inorg. Chim. Acta* (1976) 17 221.
48. R.B. King and M.B. Bisnette, *Inorg. Chem.* (1964) 3 785.
49. R.B. King and A. Fronzaglia, *Inorg. Chem.* (1966) 5 1837.
50. P. Powell, L.J. Russell, E. Styles, A.J. Brown, O.W. Howarth and P. Moore, submitted for publication.
51. H. Hartridge and J.J.W. Roughton, *Proc. Royal Soc.* (1923) A104 376.

52. M.L. Tobe, *Advances in Chemistry Series No. 49* P.7 Amer. Chem. Soc. (1965).
53. B.F.G. Johnson, J. Lewis and M.V. Twigg, *J. Chem. Soc. (Dalton)* (1974) 241.
54. R.B. King, *Organometallic syntheses. Vol. 1 Transition-metal compounds.* Academic Press (1965) p.141-144.
55. E.O. Fischer and E. Moser, *Inorg. Syntheses Vol. XII* (1970) p.35.