

Trimethylenemethane and Oxodimethylenemethane Metal Complexes

A thesis presented for the
Degree of Doctor of Philosophy
in the
Faculty of Science
by

Michael David Jones

University of Leicester

September 1986

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*To My Mum
and
In Memory of My Dad*

SUMMARY

Chapter 1 reviews the literature concerning trimethylenemethane and oxodimethylenemethane metal complexes and their rôle in organic synthesis.

The preparation and characterisation of η^4 -trimethylenemethane metal complexes of iridium, rhodium, osmium and ruthenium are presented in Chapter 2, together with the molecular structure of three of these complexes which establishes the presence of the η^4 -trimethylenemethane ligand. The room temperature ^1H n.m.r. spectra show the expected features for a static structure and no sign of rotation of the trimethylenemethane ligand was observed at higher temperatures.

Preliminary investigation into the reactivity of these trimethylene-methane complexes is detailed in Chapter 3. A series of cationic η^4 -trimethylenemethane complexes are prepared by the reaction of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ with silver hexafluorophosphate in the presence of a donor ligand such as carbon monoxide or ethene. The reactions of these cationic complexes with neutral and anionic nucleophiles are investigated and show that displacement of other donor ligands or attack on co-ordinated carbonyl and ethene ligands occurs, rather than attack at, or displacement of the trimethylenemethane ligand.

Chapter 4 describes the reaction of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene with d^{10} -metal complexes of platinum, palladium and nickel. The isolation of η^3 -2-trimethylsilylmethylallyl palladium and platinum complexes are of interest since they are postulated intermediates implicated in the generation of the catalytic species $[\text{Pd}(\eta^3\text{-trimethylenemethane})(\text{PPh}_3)_2]$. The d^{10} -nickel complex $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ catalyses the cycloaddition of trimethylenemethane to

electron-deficient alkenes and imines, the latter reaction affords a high yield synthesis of 4-methylenepyrrolidines.

The final Chapter describes the reactions of 3-chloro-1-(trimethylsilyl)propan-2-one and 3-chloro-2-(trimethylsiloxy)prop-1-ene with low-valent metal complexes to afford oxodimethylenemethane complexes of platinum, iridium, and osmium. The molecular structure of two of these complexes establishes the presence of an η^3 -oxodimethylenemethane ligand. The silylenol ether, 3-chloro-2-(trimethylsiloxy)prop-1-ene was readily prepared from 3-chloro-1-(trimethylsilyl)propan-2-one, the isomerisation being catalysed by a number of low-valent metal complexes.

STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1983 and September 1986, under the supervision of Dr. R. D. W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

Date: 10th September 1986 Signed: Michael Jones...

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ABBREVIATIONS & SYMBOLS

GENERAL AND PHYSICAL:

Å	Angström unit
br	Broad
°C	Centigrade
cm ⁻¹	Wave number
cm ³	Cubic centimetres
d	Doublet
e.s.r.	Electron spin resonance
eV	Electron volt
ΔG [‡]	Free energy of activation
g	Gramme
Δ	Heat
Hz	Hertz
HOMO	Highest occupied molecular orbital
h	Hour
i.r.	Infrared
kJ mol ⁻¹	Kilojoule per mole
MHz	Megahertz
m.p.	Melting point
m	Medium (i.r.); Multiplet (n.m.r.)
mmHg	Millimetres of mercury
mmol	Millimole
M	Mol dm ⁻³
M ⁺	Molecular ion
n.m.r.	Nuclear magnetic resonance
n.O.e.	Nuclear Overhauser effect
p.p.m.	Parts per million
{ ¹ H}	Proton decoupled
p.s.i.	Pounds per square inch
q	Quartet
s	Singlet (n.m.r.); Strong (i.r.)
t	Tertiary (chemical); Triplet (n.m.r.)
vs	Very strong
w	Weak

ABBREVIATIONS & SYMBOLS (Continued)

CHEMICAL:

Ac	Acetyl
acac	Anion of pentane-2,4-dione
bipy	2,2 -Bipyridyl
dppe	<u>Bis</u> -(diphenylphosphino)ethane
Bu ^t	t-Butyl
COD	Cycloocta-1,5-diene
COT	Cyclooctene
dba	Dibenzylideneacetone
Et	Ethyl
Me	Methyl
Ph	Phenyl
Pr ⁱ	<u>iso</u> -Propyl



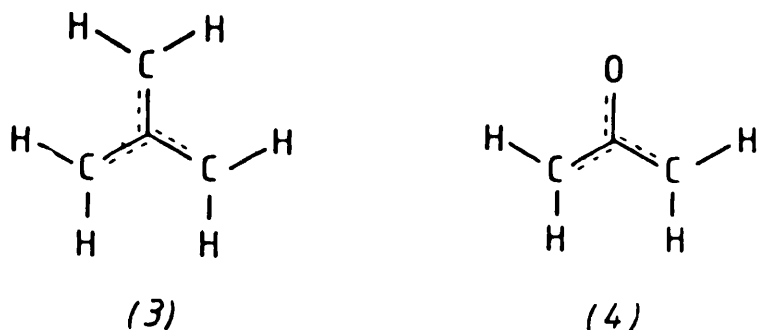
CHAPTER 1

Trimethylenemethane and Oxodimethylenemethane
Metal Complexes

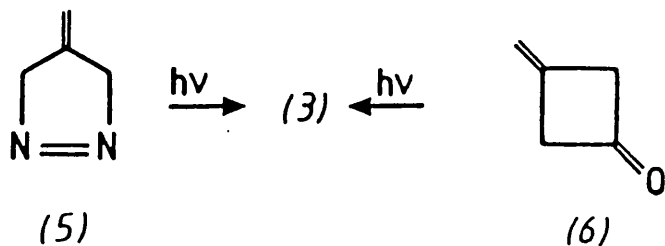
1.1 INTRODUCTION

The ability of transition metal centres to co-ordinate highly reactive organic species has become increasingly important in modern organometallic and organic chemistry. Cyclobutadiene (1) is one such reactive intermediate which forms stable transition metal complexes.¹ The oxidative degradation of the η^4 -cyclobutadiene iron complex (2) allows a convenient method of generating cyclobutadiene in situ and Scheme 1 shows some of the Diels-Alder type reactions of cyclobutadiene with various dienophiles.^{1,2}

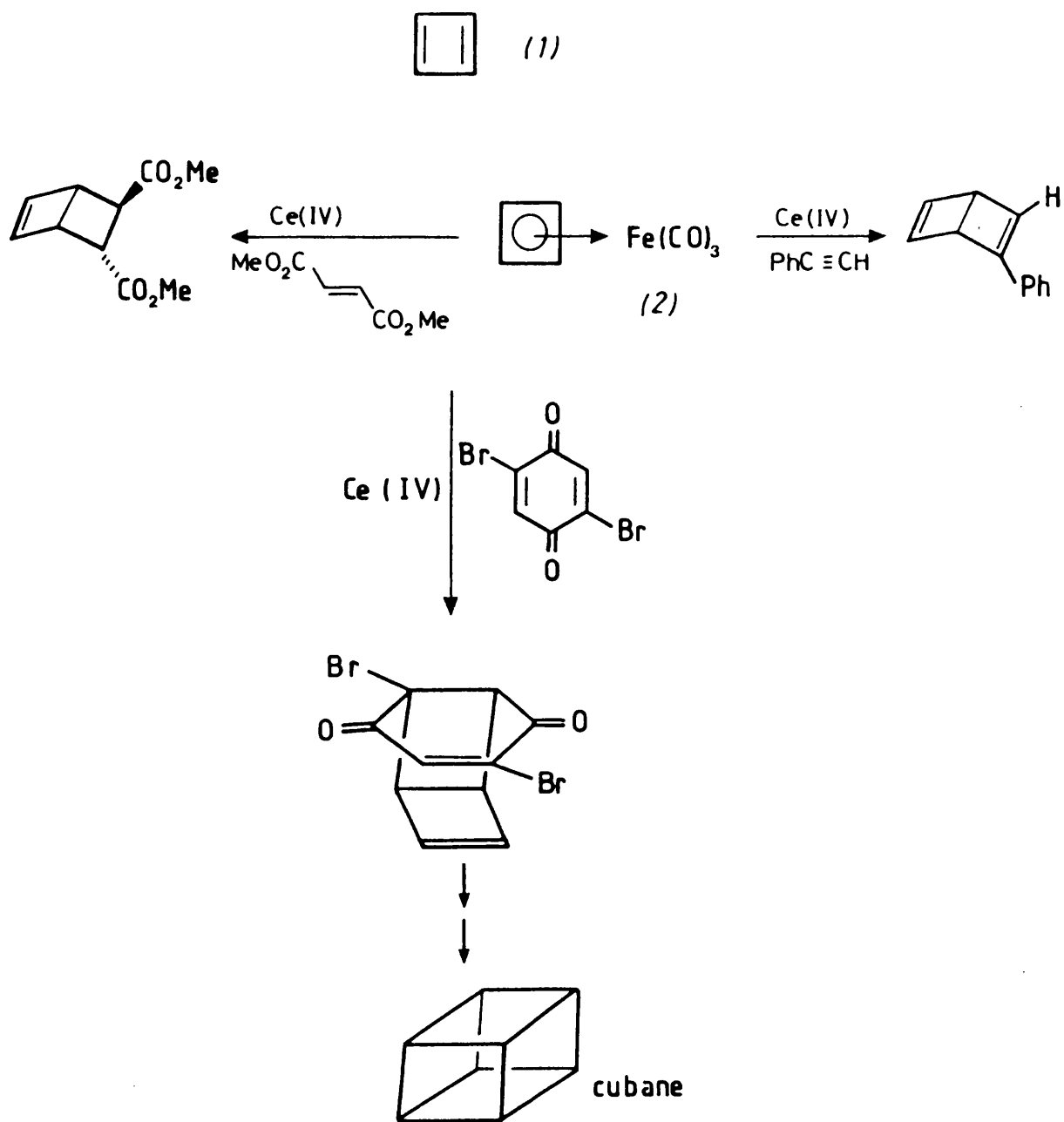
Trimethylenemethane (3) and oxodimethylenemethane (4) are two other very reactive organic species which have been co-ordinated to transition metal centres.



The triplet diradical trimethylenemethane (3) has been observed by e.s.r. spectroscopy from the low temperature matrix photolysis of 4,5-dihydro-4-methylene-3H-pyrazole (5) or 3-methylenecyclobutanone (6).³⁻⁶ Attempts to detect the oxodimethylenemethane (4) diradical by e.s.r. spectroscopy have been unsuccessful,⁵ however the diradicals of both (3)



and (4) are postulated as intermediates in the reaction of potassium vapour with 3-iodo-2-iodomethylprop-1-ene or α, α' -dihaloketones in the



Scheme 1

gas phase.^{7,8} Interestingly the base-induced Favorsky rearrangement of α -haloketones is believed to proceed via an oxodimethylenemethane intermediate.^{9,10}

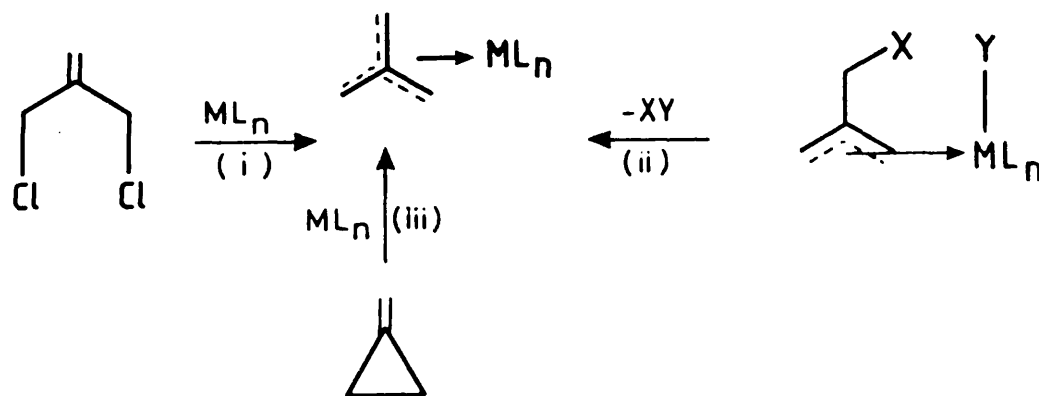
This first chapter reviews the literature on the principal synthetic routes to trimethylenemethane and oxodimethylenemethane metal complexes

and the rôle of both intermediates in modern organic synthesis.

1.2 SYNTHESIS OF TRIMETHYLENEMETHANE METAL COMPLEXES

Trimethylenemethane metal complexes have been synthesised via three main routes; (i) the dehalogenation of α,α' -dihalosubstituted precursors, (ii) the thermal extrusion of XY (XY = HCl, Br₂ and CH₄) from η^3 -methylallyl complexes, and (iii) the ring opening of alkylidenecyclopropanes,

Scheme 2.

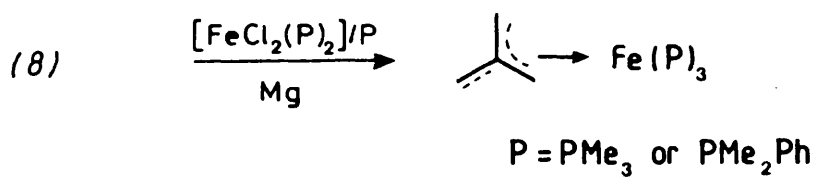
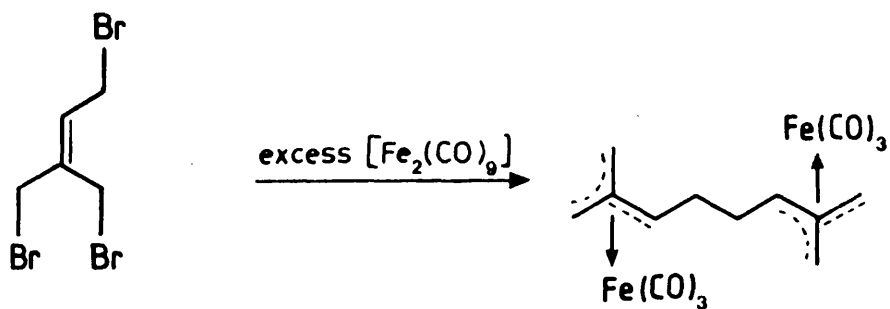
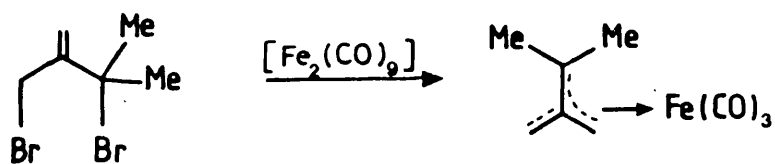
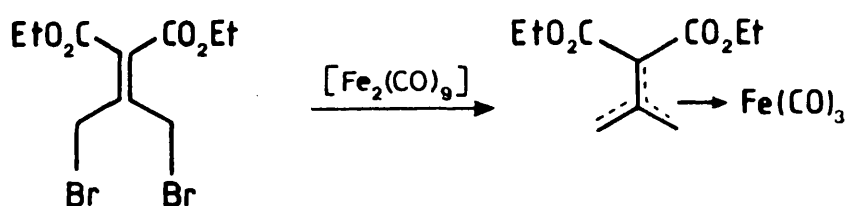
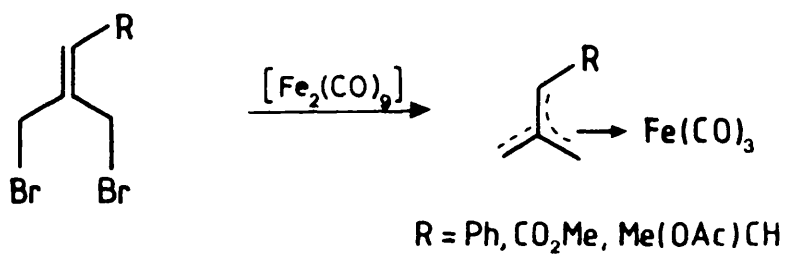
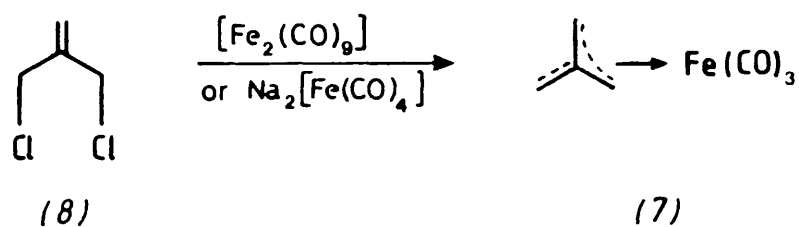


Scheme 2

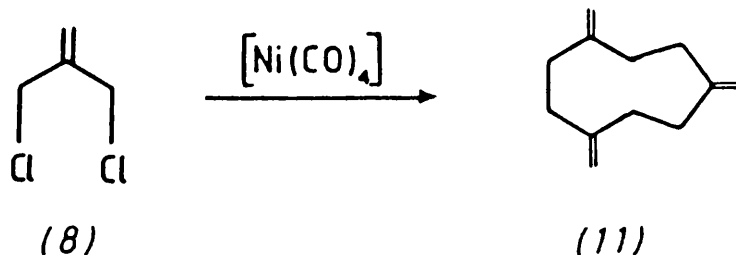
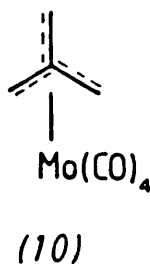
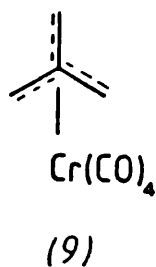
(i) Dehalogenation of α,α' -dihalosubstituted precursors

Tris(carbonyl)- η^4 -trimethylenemethane-iron(0) (7) was the first trimethylenemethane metal complex to be synthesised and was obtained from the reaction of 3-chloro-2-chloromethylprop-1-ene (8) with $[Fe_2(CO)_9]$ or $Na_2[Fe(CO)_4]$.¹¹⁻¹³ A number of substituted trimethylenemethane iron complexes have been prepared by similar methods to those used to prepare (7) and the results are summarised in Scheme 3.^{12,14,15}

Treatment of 3-chloro-2-chloromethylprop-1-ene (8) with $[Cr(CO)_6]$ or $[Mo(CO)_5]^{2-}$ afforded low yields of the trimethylenemethane complexes (9) and (10) respectively.¹³ Interestingly treatment of (8) with the d^{10} -complex $[Ni(CO)_4]$ gave the hydrocarbon (11) and not a stable nickel trimethylenemethane complex.¹⁶



Scheme 3

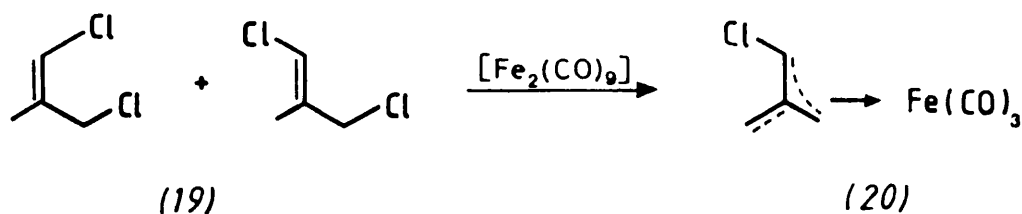
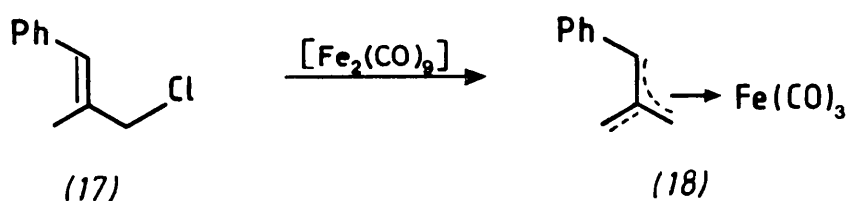
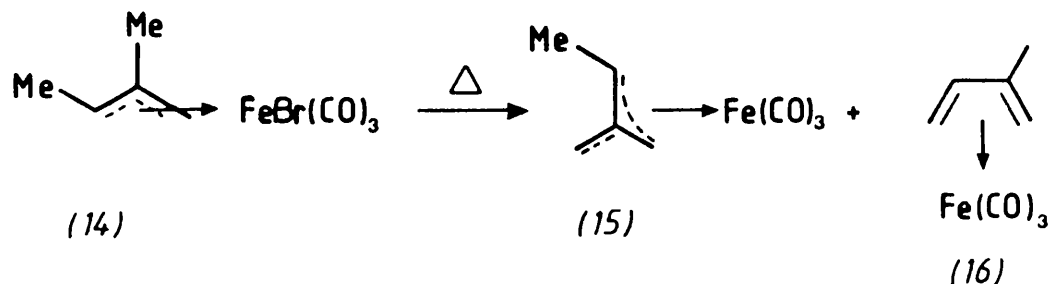
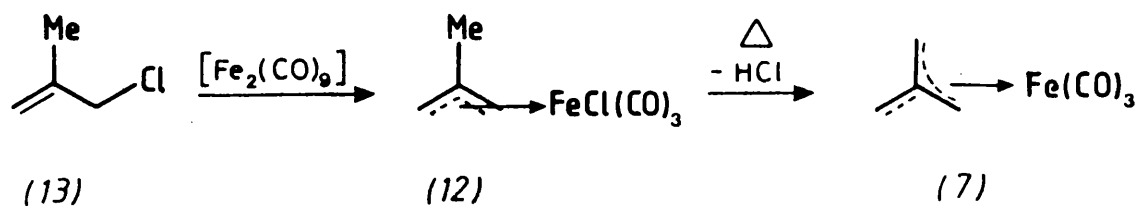


The reaction of the allyl chloride (8) with $[Fe_2(CO)_9]$ is promoted by ultrasound to afford the trimethylenemethane complex (7) in quantitative yield.¹⁷ The use of ultrasonics in promoting reactions may find applications in the synthesis of various substituted trimethylenemethane complexes.

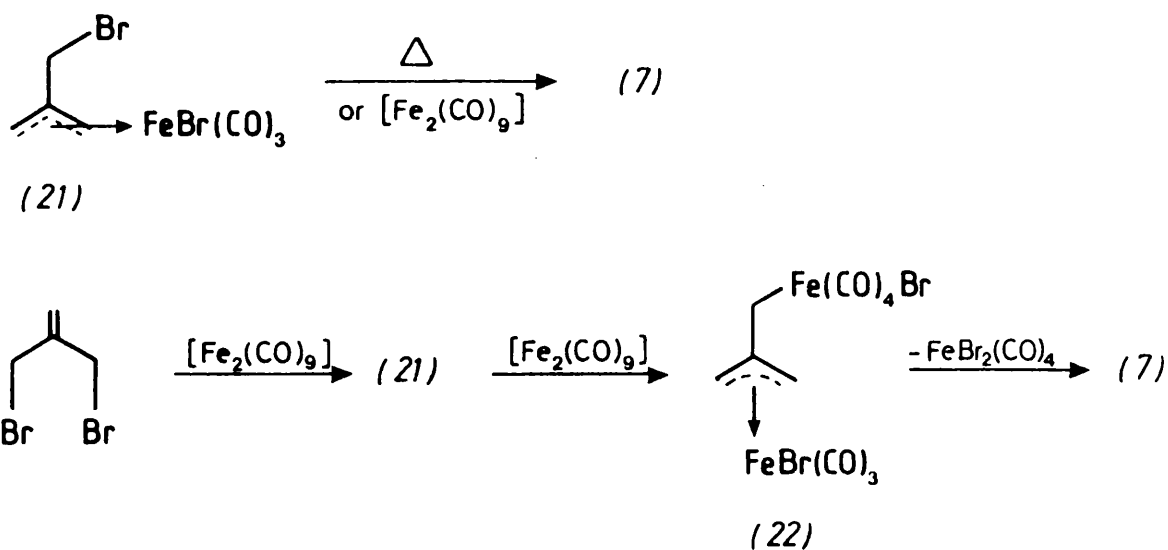
(ii) Thermal extrusion from η^3 -allyl complexes

The thermal extrusion of a simple molecule from an η^3 -allyl complex, to generate an η^4 -trimethylenemethane metal complex, was originally observed by Emerson. The iron allyl complex (12), obtained from the reaction of 3-chloro-2-methylprop-1-ene (13) with $[Fe_2(CO)_9]$, decomposed on heating to afford the iron trimethylenemethane complex (7).^{12,18} Similarly, the decomposition of the allyl complex bromotris(carbonyl)-1,2-dimethylallyliron(II) (14) gave a mixture of the methyltrimethylenemethane complex (15) and tris(carbonyl)isopreneiron(0) (16).¹² In certain cases the intermediate η^3 -methylallyl complex could not be isolated. Thus 2-chloromethyl-1-phenylprop-1-ene (17) reacts with $[Fe_2(CO)_9]$ to give the η^4 -trimethylenemethane complex (18), and similarly a mixture of cis and trans-1,3-dichloro-2-methylprop-1-ene (19) reacted

with $[\text{Fe}_2(\text{CO})_9]$ to give the complex (20).¹²

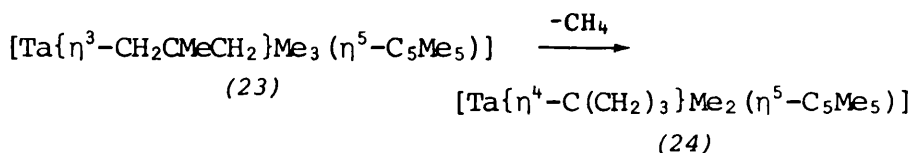


A similar elimination process was observed for the complex bromo-tris(carbonyl)-2-bromomethylallyliron(II) (21) which afforded the iron trimethylenemethane complex (7) via a thermal reaction or in the presence of $[\text{Fe}_2(\text{CO})_9]$.¹² This reaction is of interest because, although the mechanism for the dehalogenation of 2-halomethyl-3-halo-prop-1-ene by $[\text{Fe}_2(\text{CO})_9]$ has not been rigorously determined, it probably involves the elimination of $[\text{FeBr}_2(\text{CO})_4]$ from an η^3 -allyl intermediate (22) and can be viewed as a thermal extrusion type reaction, Scheme 4.¹²



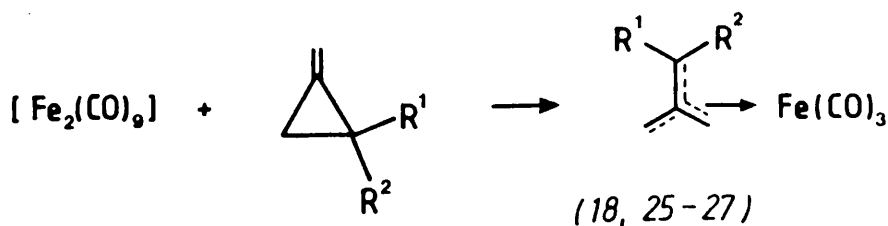
Scheme 4

Another example of a thermal elimination reaction was observed for the η^3 -2-methylallyl tantalum complex (23), obtained from the reaction of $[\text{TaClMe}_3(\eta^5\text{-C}_5\text{Me}_5)]$ with methylallyl magnesium chloride, which eliminates methane at ambient temperatures to afford the trimethylenemethane complex (24).¹⁹



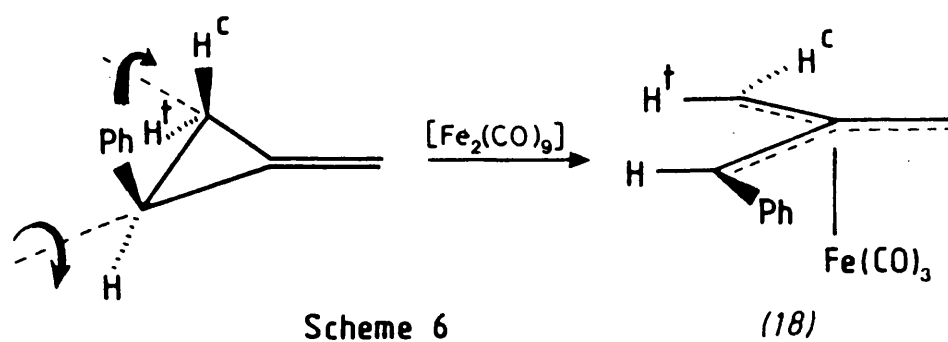
(iii) Ring opening of alkylidenecyclopropanes

The ring opening of 2-substituted methylenecyclopropanes in the presence of $[\text{Fe}_2(\text{CO})_9]$ afforded the η^4 -trimethylenemethane complexes (18, $\text{R}^1=\text{H}$, $\text{R}^2=\text{Ph}$), (25, $\text{R}^1=\text{Me}$, $\text{R}^2=\text{Ph}$), (26, $\text{R}^1=\text{R}^2=\text{Ph}$) and (27, $\text{R}^1=\text{H}$, $\text{R}^2=\text{CH}=\text{CH}_2$), see Scheme 5.^{20,21}



Scheme 5

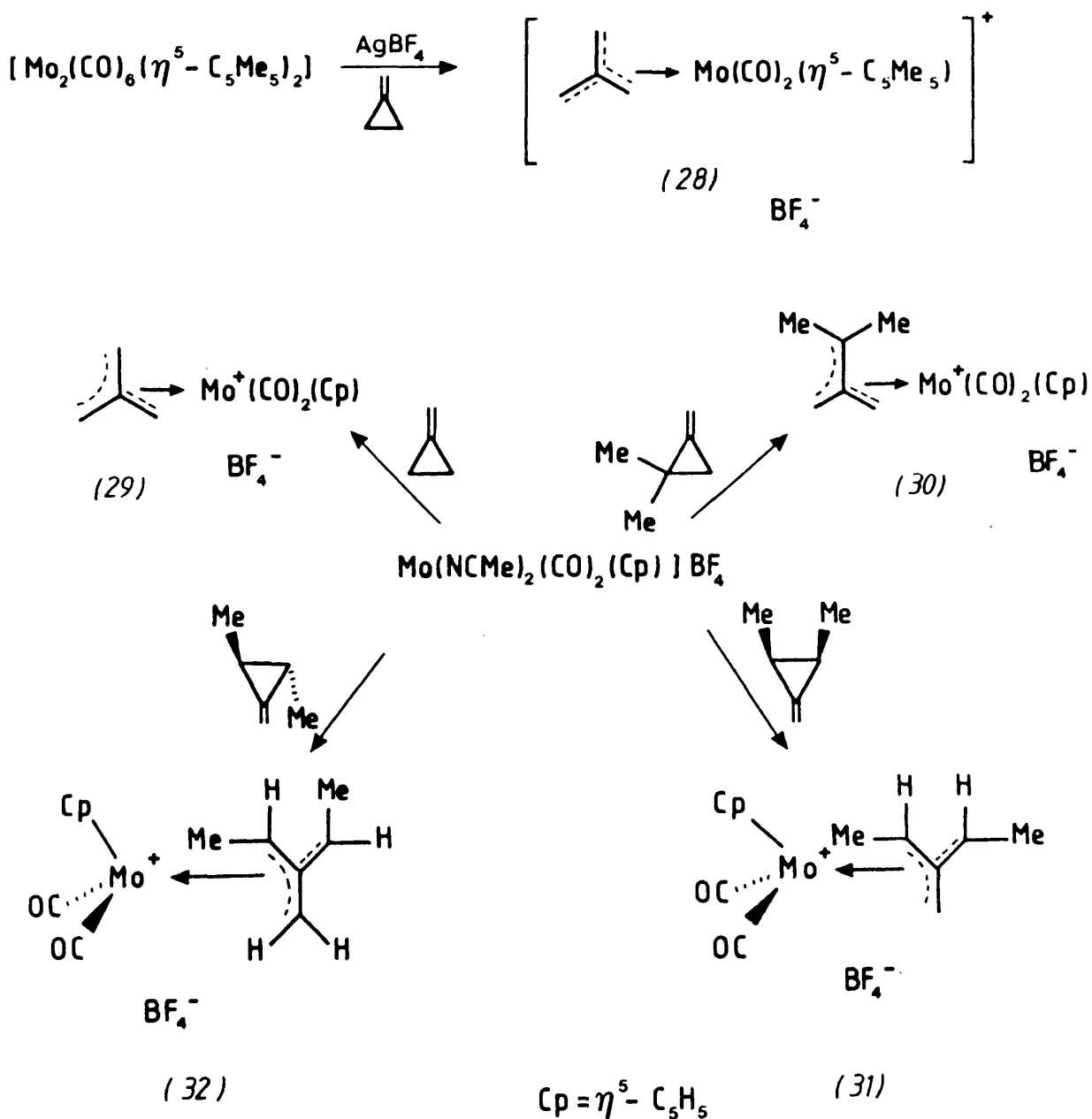
The stereochemistry of the ring opening of 2-phenylmethylenecyclopropane to give the (η^4 -phenyltrimethylenemethane)iron complex (18) has been elucidated by stereospecific deuterium labelling experiments and shows that a specific disrotatory mode of ring opening occurs, as predicted by frontier molecular orbital diagrams, Scheme 6.²²⁻²⁵



The reaction of $[\text{Mo}_2(\text{CO})_6(\eta^5\text{-C}_5\text{Me}_5)_2]$ with methylenecyclopropane and AgBF_4 afforded the cationic trimethylenemethane complex (28).²⁶ Methylenecyclopropane and 2,2-dimethylmethylenecyclopropane also ring open in the presence of $[\text{Mo}(\text{NMe})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]\text{BF}_4$ to give the cationic trimethylenemethane complexes (29) and (30) respectively. The mode of ring opening was verified by the use of cis and trans-2,3-dimethylmethylenecyclopropane to afford respectively syn, syn and the syn, anti-dimethyltrimethylenemethane complexes (31) and (32), which are consistent with a disrotatory-out ring opening reaction where the breaking 2,3- σ bond bends away from the metal, Scheme 7.^{26,27}

1.3 REACTIONS OF TRIMETHYLENEMETHANE METAL COMPLEXES

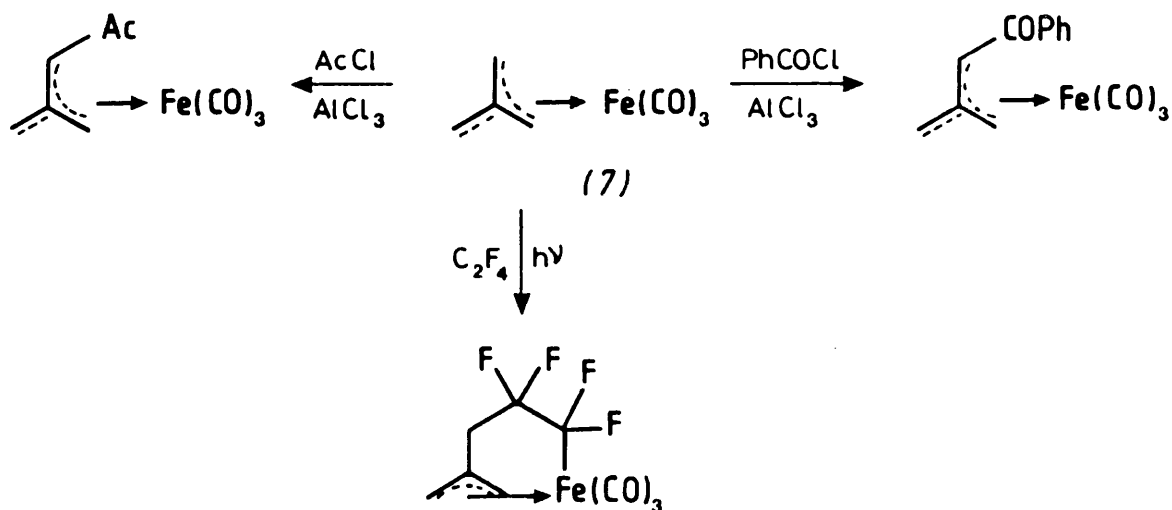
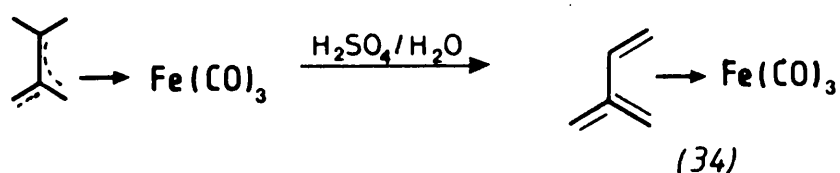
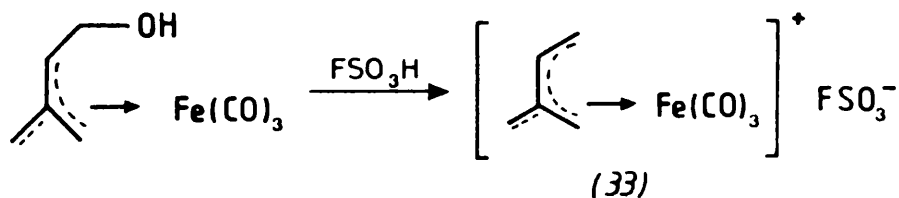
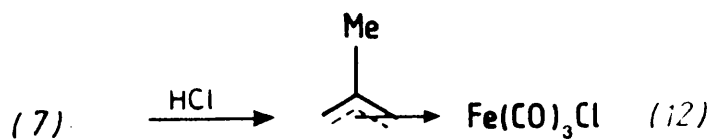
Initial studies have shown that iron trimethylenemethane complexes are susceptible to electrophilic attack. Addition of hydrochloric acid to tris(carbonyl)- η^4 -trimethylenemethaneiron(0) (7) gives chlorotris(carbonyl)-2-methylallyliron(II) (12)¹² whilst substituted trimethylenemethane iron complexes react with strong acids to afford cross-conjugated dienyl iron cations (33) and η^4 -diene complexes (34).^{12,14,28} The



Scheme 7

addition of bromine to the iron complex (7) gives bromotris(carbonyl)-2-bromomethylallyliron(II) (21),¹² and Friedel-Crafts acylation of the trimethylenemethane ligand of complex (7) is also possible.¹² Photolysis of (7) in the presence of tetrafluoroethylene affords an η^3 -allyl complex (35) where addition across the metal and the trimethylenemethane ligand occurs,²⁹ while photolysis of (7) with trifluorophosphine afforded all three substituted complexes $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_{3-x}(\text{PF}_3)_x]$, where $x = 1$,

2 and 3.³⁰ Scheme 8 summarises these reactions.

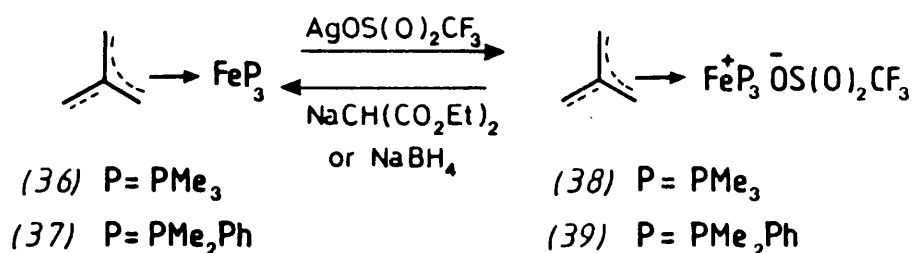


Scheme 8

(35)

The electron-rich trimethylenemethane complexes (36) and (37) are oxidised with one equivalent of silver trifluoromethanesulphonate to afford the cationic seventeen electron complexes (38) and (39) respectively. The oxidised complexes react with sodium diethylmalonate or sodium borohydride to reform the original neutral trimethylenemethane complexes (36) and (37), Scheme 9.¹⁵

The cationic molybdenum trimethylenemethane complex (28) is susceptible

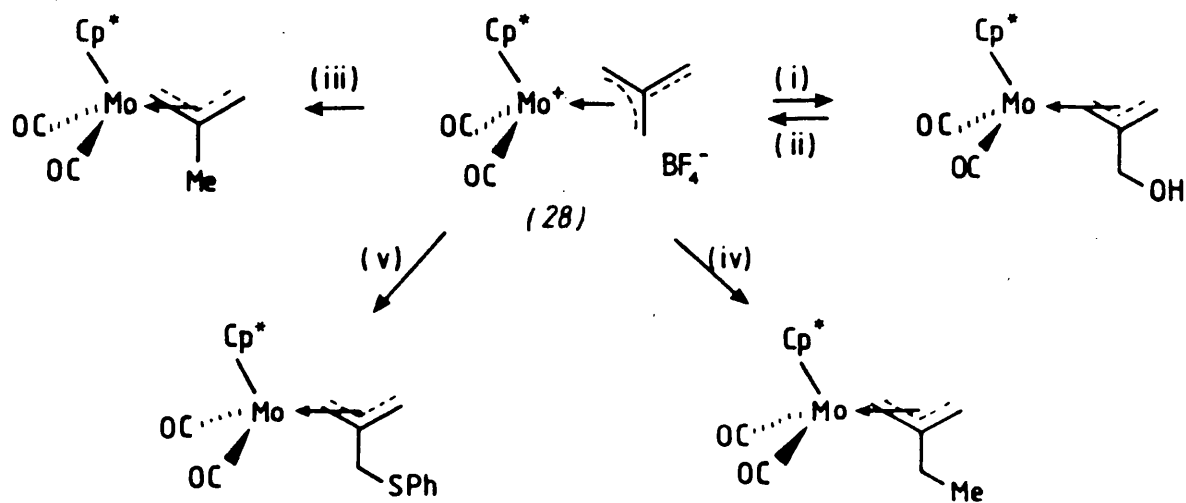


Scheme 9

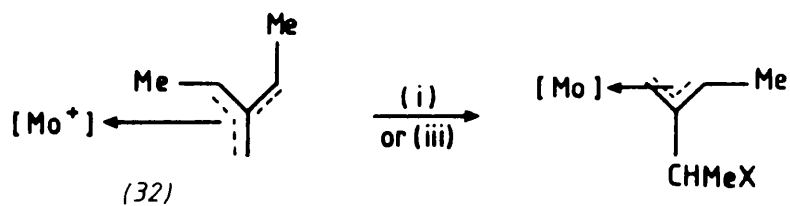
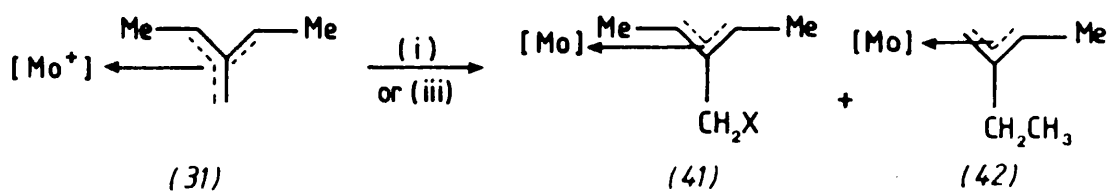
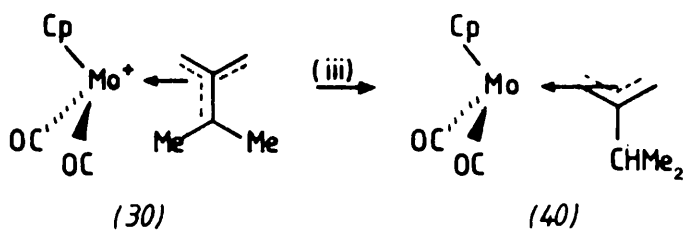
to nucleophilic attack at the trimethylenemethane ligand forming neutral η^3 -allyl complexes, Scheme 10.²⁷ The methyl-substituted trimethylenemethane cationic complexes also react readily with nucleophiles. Thus complex (30) reacted with sodium borohydride to give the η^3 -allyl (40) where attack of the nucleophile occurred at the methyl substituted carbon. However, attack of borohydride ion on the complexes (31) and (32) gave the products (41, X=H) and (42) due to attack of the nucleophile at both unsubstituted and substituted carbons. Similar results were obtained with hydroxide ion as the nucleophile. Thus the cation (31) reacts regioselectively at the unsubstituted carbon to give the alcohol (41, X=OH), whereas the reaction of (32) with hydroxide ion gave the product (43) where attack has occurred at a substituted carbon atom. A combination of steric and electronic effects are thought to control the position of nucleophilic attack on the trimethylenemethane ligand.²⁷

1.4 THE RÔLE OF TRIMETHYLENEMETHANE IN ORGANIC SYNTHESIS

The cycloaddition of trimethylenemethane to alkenes can be envisaged as the Diels-Alder ($4\pi + 2\pi$) reaction for the synthesis of five-membered rings. This is an attractive ring system to synthesise due to the abundance of five-membered rings found in natural products such as the prostaglandins.³¹ Cycloaddition reactions also have the advantage of multibond formation occurring almost simultaneously resulting in



(i) OH^- ; (ii) HBF_4 , Propionic anhydride; (iii) BH_4^- ; (iv) CuMe_2^- ;
 (v) SPh^- . $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$.

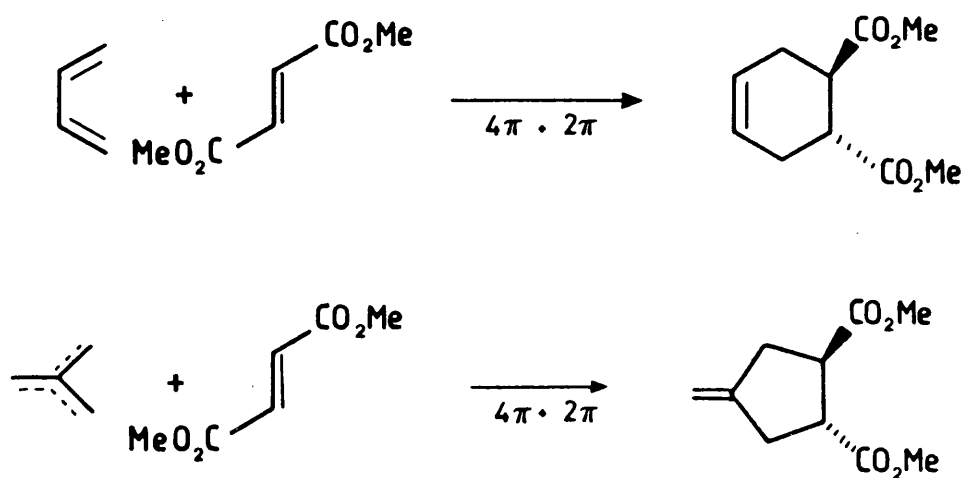


$\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ (42) $\text{X} = \text{H}$
 $\text{X} = \text{H or OH}$ (43) $\text{X} = \text{OH}$

$[\text{Mo}^+] = [\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]^+$

Scheme 10

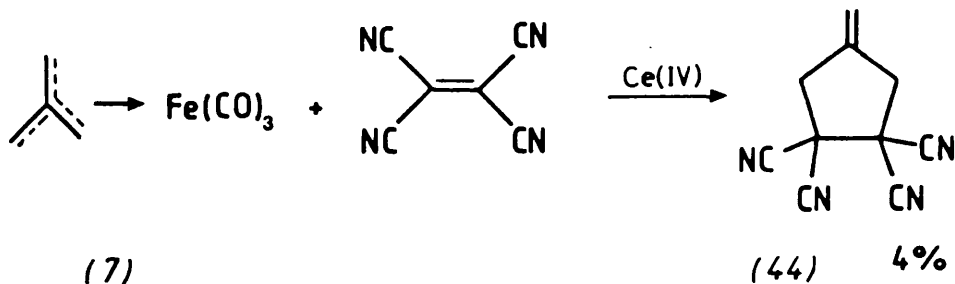
structural complexity.³² The strength of the Diels-Alder reaction in cyclohexene chemistry is due to the stereochemical consequences of such a concerted process and similar stereochemical control may be expected in the related cycloaddition of trimethylenemethane to alkenes, Scheme 11.³³



Scheme 11

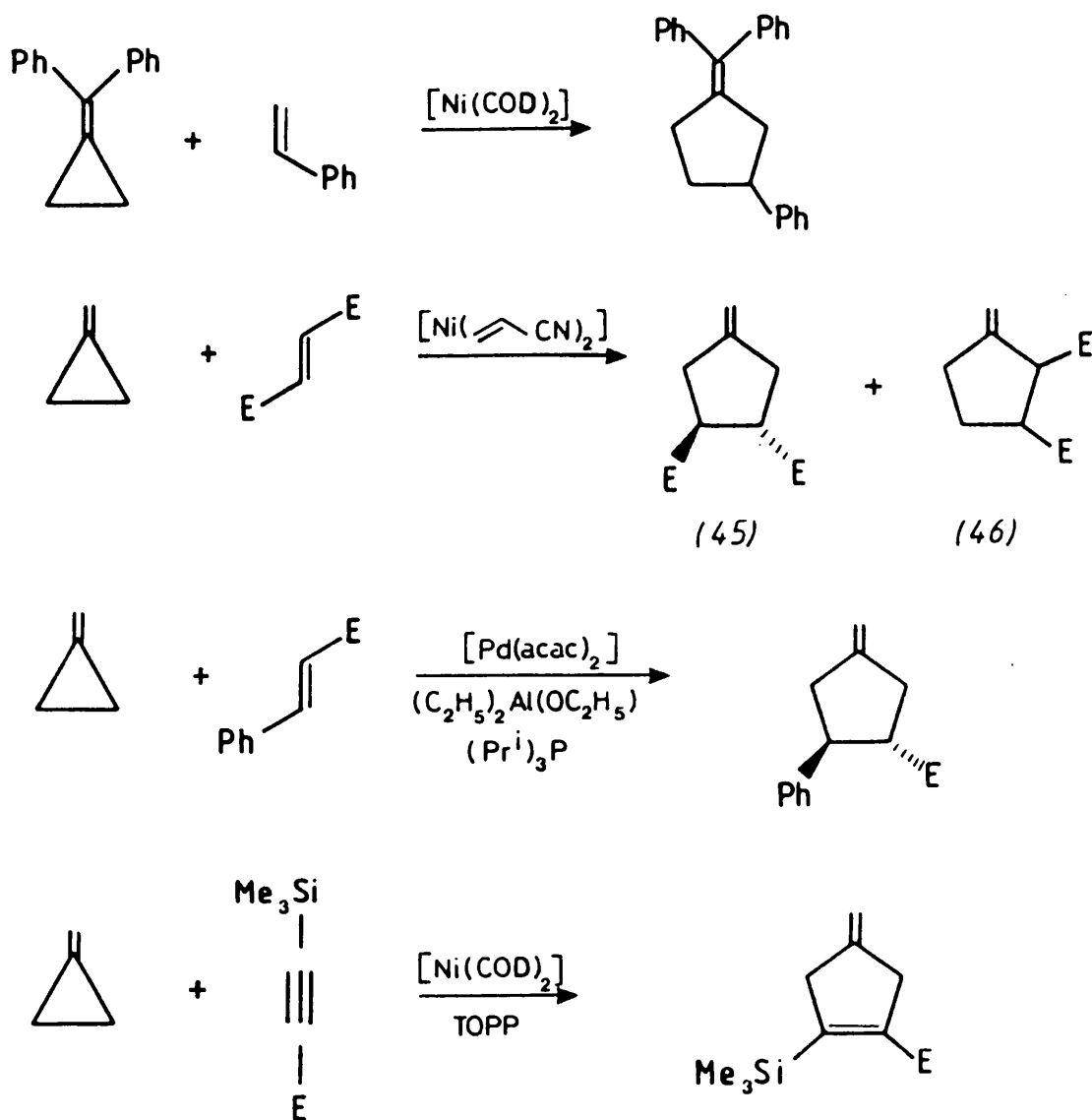
A potential source of trimethylenemethane is by the oxidative degradation of a trimethylenemethane metal complex. However this route has met with limited success; the cerium(IV) oxidation of the iron complex (7) in the presence of tetracyanoethylene gave the cycloadduct (44) in very poor yield.¹³ The photolysis of (7) afforded methylenecyclopropane and related products, while in the presence of trapping agents like cyclopentadiene and cyclopentene the expected cycloaddition products were obtained but in low yields.³⁴

The disrotatory ring opening of substituted methylenecyclopropanes



in the presence of $[\text{Fe}_2(\text{CO})_9]$, to give stable η^4 -trimethylenemethane complexes,²⁰⁻²⁴ led to the investigation of the transition metal mediated cycloaddition reactions of methylenecyclopropane. Low-valent nickel and palladium complexes catalyse the co-dimerisation of methylenecyclopropane with both electron-rich and electron-deficient alkenes or alkynes, Scheme 12.³⁵⁻⁴⁵

The mechanisms of these co-dimerisation reactions are uncertain.



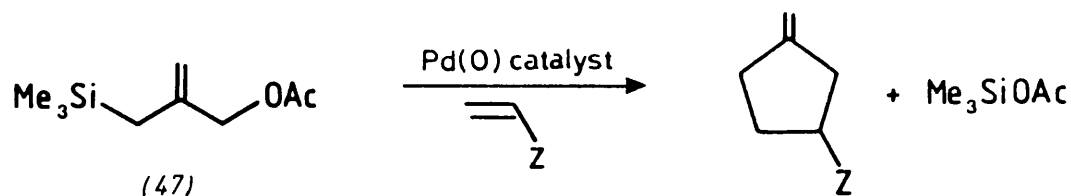
$\text{E} = \text{CO}_2\text{Me}$

TOPP = tris(o-biphenyl) phosphite

Scheme 12

Trimethylenemethane metal complexes have been postulated as intermediates in the palladium mediated reactions but in the nickel catalysed reactions other intermediates may be involved.^{36,43} Thus the cycloadduct (45) can be derived from a trimethylenemethane metal complex but the other product (46) cannot. It is presumably formed from an intermediate generated by cleavage of the C(1)-C(2) bond of methylenecyclopropane.³⁸

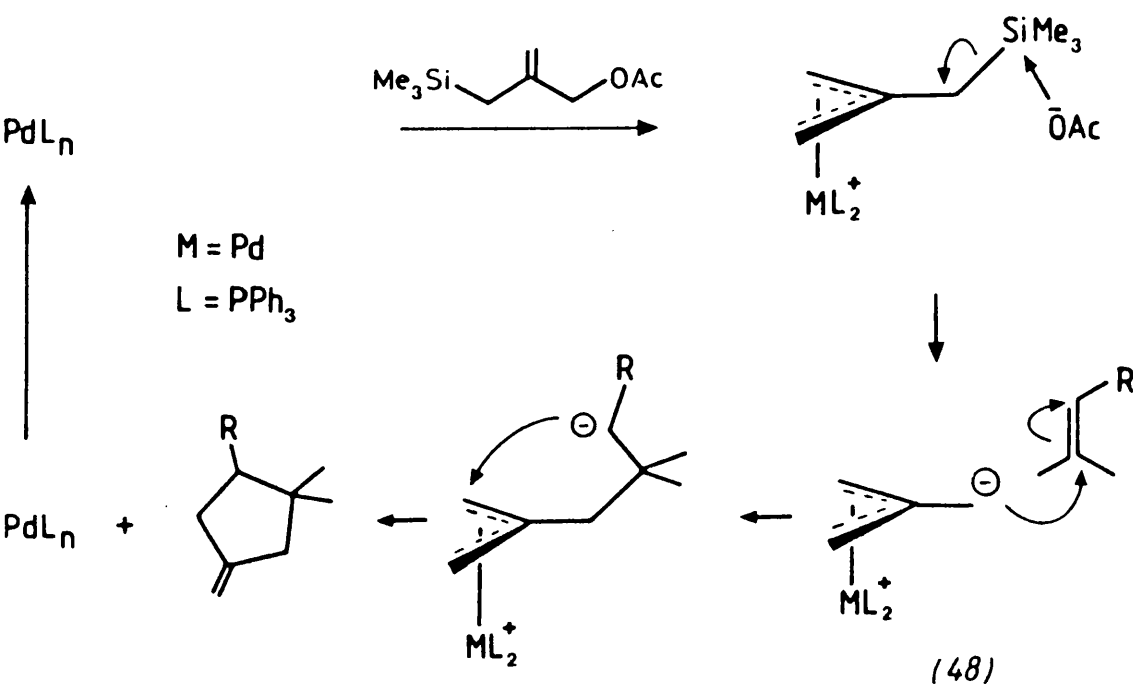
The ability of palladium(0) catalysts to generate η^3 -allyl complexes by the ionisation of allylic acetates,^{46,47} led Trost *et al.* to introduce the functionalised allylic-acetate, 3-trimethylsilyl-2-(acetoxymethyl)-prop-1-ene (47) as a precursor to a palladium trimethylenemethane complex.^{48,49} Heating the silyl-acetate (47) in the presence of a catalytic amount of a palladium(0) complex and an electron-deficient alkene results in a cycloaddition of trimethylenemethane to the carbon-carbon double bond, Scheme 13.^{48,49}



Z = electron withdrawing group

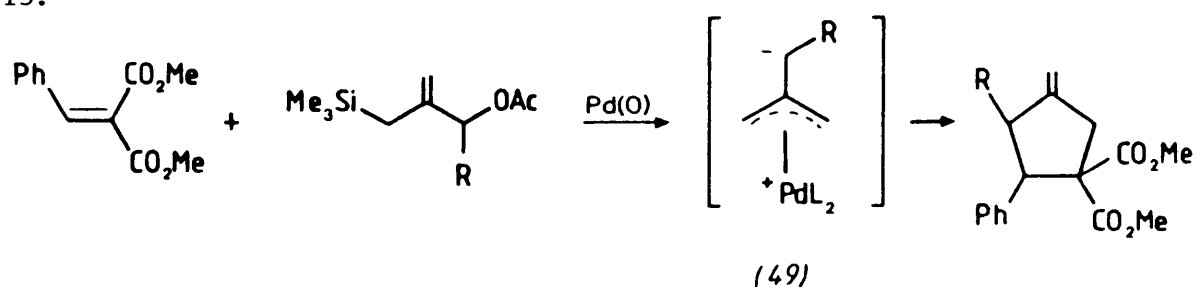
Scheme 13

The proposed mechanism for this reaction is thought to proceed via a zwitterionic η^3 -trimethylenemethane intermediate (48).⁴⁹ Theoretical calculations on $[\text{Pd}(\text{trimethylenemethane})\text{L}_2]$ have demonstrated that the η^3 -trimethylenemethane structure (48) is electronically favoured over an η^4 -trimethylenemethane geometry.^{50,51} Scheme 14 summarises the presumed mechanism for the formation of this intermediate (48). The nucleophilic character of (48) was verified by simple allylic alkylation reactions and deuterium labelling of the allylic acetate showed that the trimethylenemethane fragment was fluxional and that all three methylene

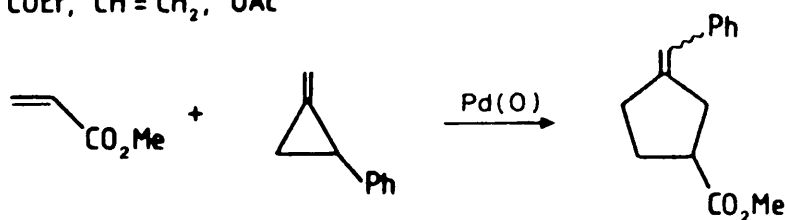


Scheme 14

carbons were rapidly interconverting.⁴⁹ Interestingly, when substituted derivatives of (47) were used in the cycloaddition reactions, a single regioisomer was isolated, presumably due to preferential reaction via an intermediate (49).⁵²⁻⁵⁵ This regioselectivity is in contrast to the ring opening reactions of phenyl- and vinyl-substituted methylenecyclopropanes which gave cyclopentane derivatives bearing the substituent almost exclusively on the exocyclic methylene carbon, as shown in Scheme 15.^{42, 56}



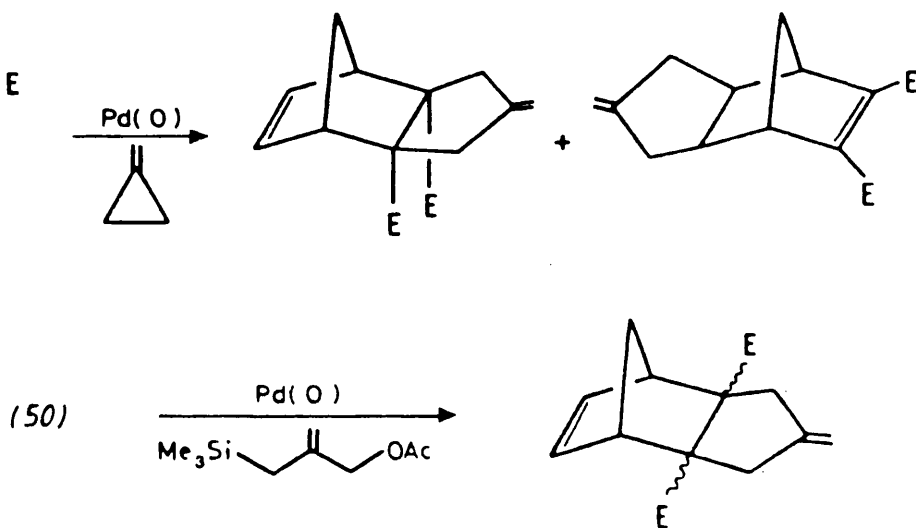
$\text{R} = \text{Ph}, \text{CN}, \text{COEt}, \text{CH}=\text{CH}_2, \text{OAc}$



Scheme 15

(50)

Chemical reaction scheme (50) showing the hydrogenation of a bicyclic diene with two substituents (E) using Pd(0) and cyclopropane as a hydrogen source. The reaction yields two bicyclic products: one with two saturated rings and two E substituents, and another with one saturated ring and one ring containing a double bond and two E substituents.

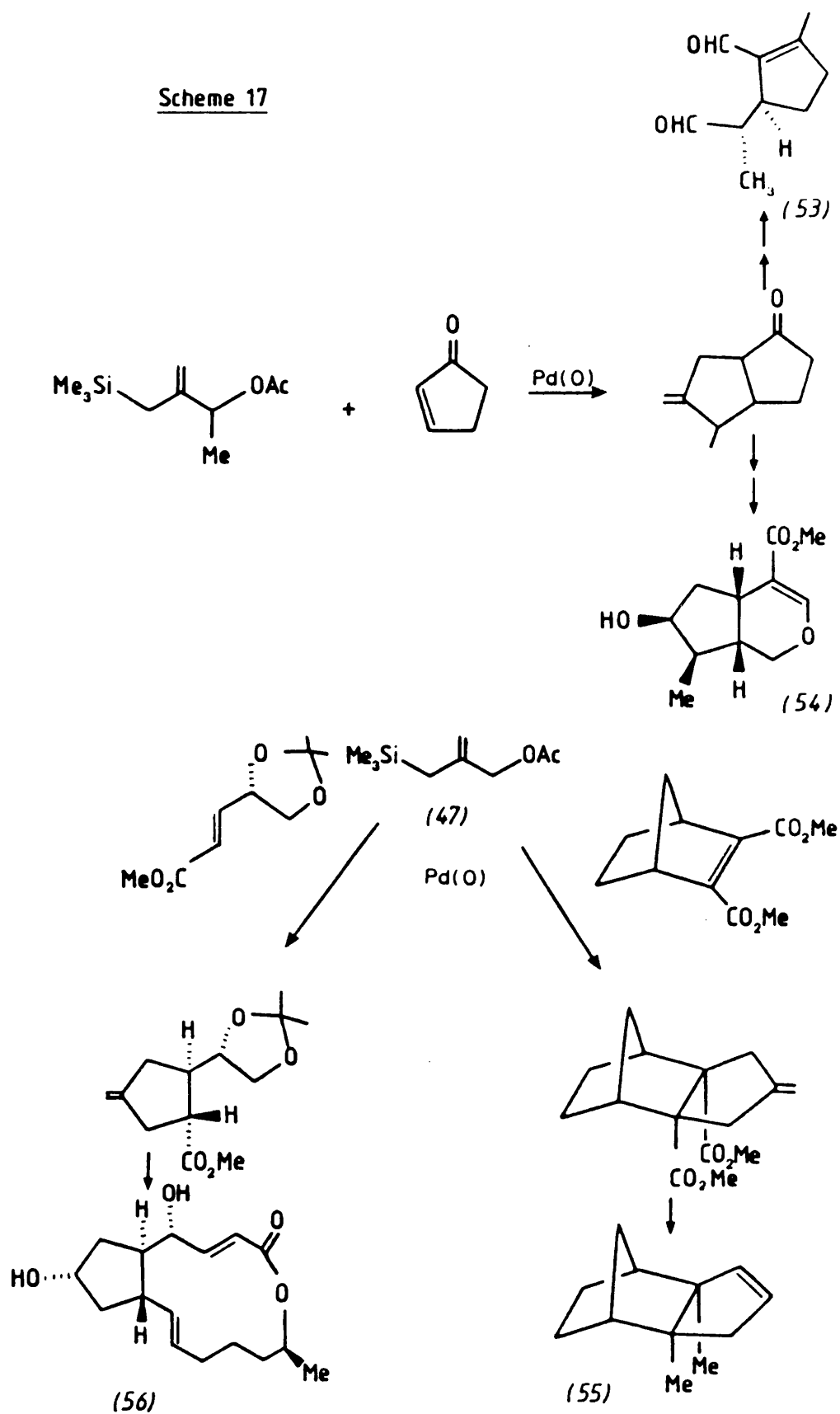


exo and endo

$$\text{Me}_3\text{Sn}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OAc} + \text{R}-\text{CH}=\text{O} \xrightarrow{\text{Pd}(0)} \text{R}-\text{CH}(\text{O})-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OAc} \quad (51)$$
 $+ \text{Me}_3\text{SnOAc}$

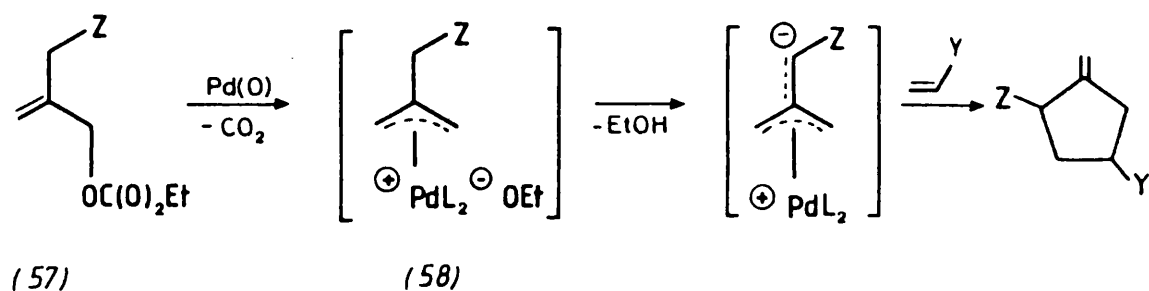
- 17 -

Scheme 17



for retrosynthetic analysis of complex molecules. The synthesis of the natural products, chrysomelidial (53),⁵⁴ loganin aglucone (54),⁵⁵ albene (55),⁵⁹ and brefeldin (56)⁶⁰ use the cycloaddition of trimethyl-enemethane to alkenes as a means of constructing the five-membered ring. The exocyclic methylene group acts as a versatile functionality for further modifications. Scheme 17 illustrates the principle cycloaddition steps used for the synthesis of these products.

In the special cases of substituents that are good anion-stabilising groups the allyl carbonate (57, Z=CN) serves as a suitable trimethylenemethane precursor. The leaving group generates a sufficiently strong base to effect deprotonation of the η^3 -allyl intermediate (58) generating a trimethylenemethane complex which reacts with electron-deficient alkenes,⁶¹ Scheme 18.



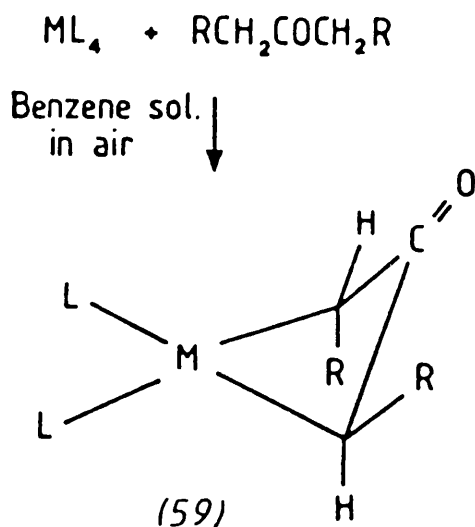
Y, Z = electron withdrawing groups

Scheme 18

The forthcoming chapters will examine the reactivity of the silyl-acetate (47) and its derivatives with various platinum group metals to prepare stable η^4 -trimethylenemethane complexes. The nickel catalysed cycloaddition of trimethylenemethane to alkenes and imines is also investigated. The latter affords a high yield one-step synthesis of the pyrrolidine ring system.

1.5 SYNTHESIS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

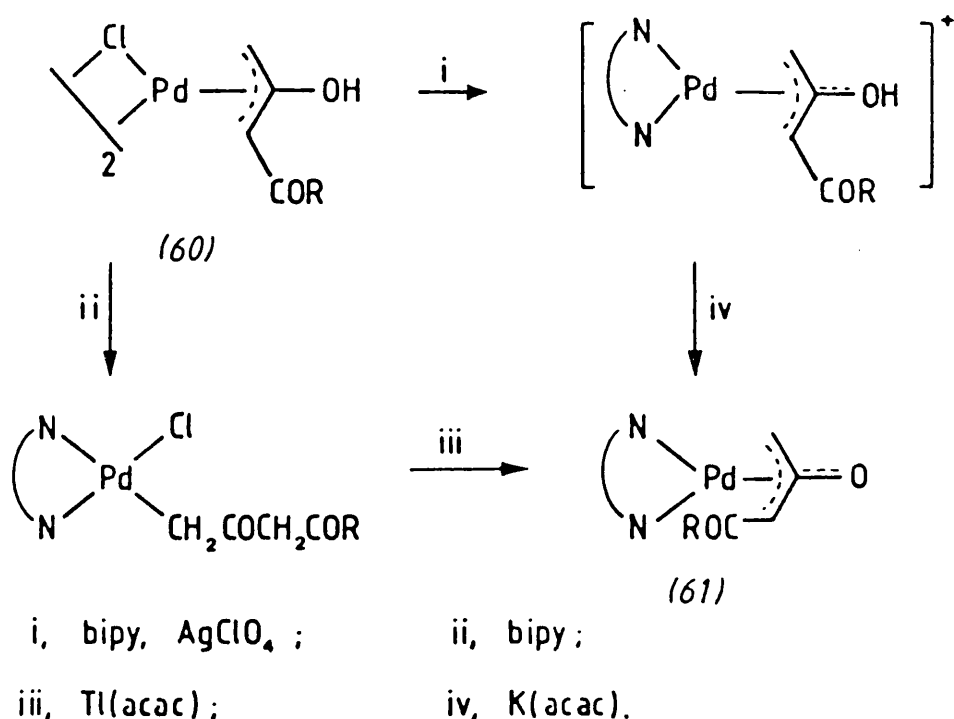
The first oxodimethylenemethane metal complexes (59, M=Pt or Pd; L=PPh₃, AsPh₃, PMePh₂, or PMe₂Ph; R=CO₂Me or CO₂Et) were obtained from the reaction of a metal(0) complex, [Pt(PPh₃)₄], [Pt(PMePh₂)₄], [Pt(PMe₂Ph)₄], [Pt(AsPh₃)₄], [Pd(PPh₃)₄], or [Pd(AsPh₃)₄], with either the methyl or ethyl ester of 3-oxopentanedioic acid in the presence of air, Scheme 19.⁶²⁻⁶⁵



Scheme 19

A high yield synthesis of a variety of palladium derivatives (59, M=Pd) were obtained via the palladium(0) precursor [Pd₂dba₃].CHCl₃ in the presence of oxygen and the dialkyl ester of 3-oxopentanedioic acid with an excess of a donor ligand.^{63,65} These reactions are believed to proceed via the dioxygen complexes of type [M(O₂)(L)₂] since the reaction of [Pd(O₂)(PPh₃)₂] with MeO₂CCH₂COCH₂CO₂Me gave the complex (59, M=Pd, L=PPh₃, R=CO₂Me).⁶⁵ Treatment of the carbonate complexes [Pt(CO₃)L₂], (L = phosphine or arsine donor ligand), with the esters RCH₂COCH₂R (R = CO₂Me, CO₂Et, or CO₂Prⁿ), and with heptane-2,4,6-trione, gave a high yield of the respective platinum oxodimethylenemethane complexes.⁶⁶

$[\text{PdCl}_2]$ reacts with mono-substituted acetones in water to afford the 2-hydroxyallyl dimer complexes (60, $\text{R}=\text{Me}$ or OEt) which are transformed into the oxodimethylenemethane complexes (61, $\text{R}=\text{Me}$ or OEt) on addition of nitrogen donor ligands, Scheme 20.⁶⁷ The bipy ligand in (61) can be displaced by phosphine ligands to afford a new series of oxodimethylenemethane complexes.^{68,69} The reaction of $[\text{Pt}(\text{acac})_2]$ with tri-*p*-chlorophenylphosphine afforded the oxodimethylenemethane complex (62, $\text{L} = \text{tri-}p\text{-chlorophenylphosphine}$).⁷⁰



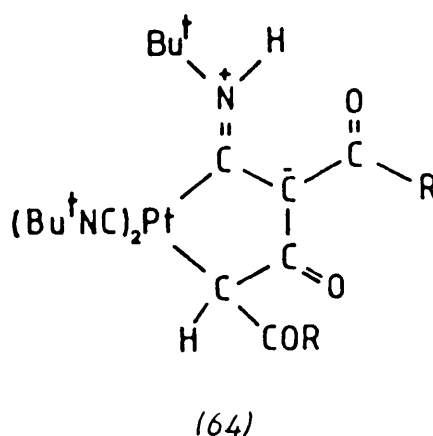
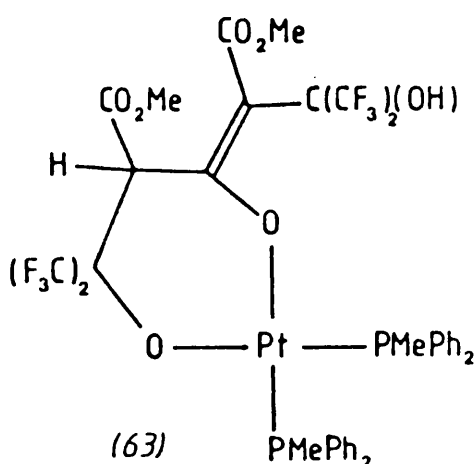
Scheme 20

Treatment of $[\text{Ir}(\text{L})_4]\text{Cl}$, ($\text{L}=\text{PMe}_3$ or AsMe_3) with the enolate salt of acetone affords the iridaoxodimethylenemethane complex $[\text{Ir}(\eta^3\text{-CH}_2\text{-COCH}_2)(\text{H})(\text{L})_3]$ ($\text{L}=\text{PMe}_3$ or AsMe_3) formed via the oxidative addition of a distal C-H bond.⁷¹ These complexes are the first examples of an oxodimethylenemethane ligand co-ordinated to a $\underline{d}^8\text{-ML}_4$ fragment.

1.6 REACTIONS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

Preliminary studies of platinum oxodimethylenemethane complexes have shown that they are susceptible to electrophilic attack. Thus the oxodimethylenemethane complex (59, $M = \text{Pt}$, $L = \text{PPh}_3$, $R = \text{CO}_2\text{Me}$) reacts with concentrated hydrochloric acid, iodine, and trifluoroacetic acid to give cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{PtI}_2(\text{PPh}_3)_2]$, and cis- $[\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2]$ respectively.^{63,72} The reaction of (59, $M = \text{Pt}$, $L = \text{PMePh}_2$, $R = \text{CO}_2\text{Me}$) with hexafluoroacetone gave the oxygen bonded σ -heteroallyl complex (63).⁶²

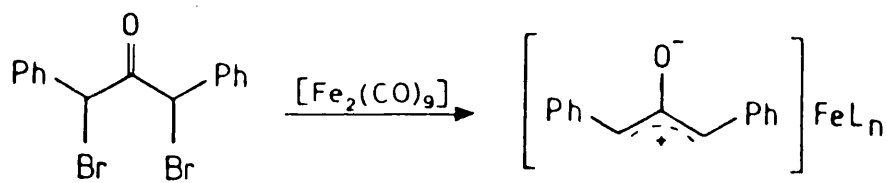
Simple ligand substitution reactions of oxodimethylenemethane complexes occurs readily. In particular, a variety of tertiary phosphines displace triphenylarsine from the complex (59, $M = \text{Pt}$, $L = \text{AsPh}_3$, $R = \text{CO}_2\text{Me}$).⁶³ Similarly, *t*-butylisocyanide is able to displace one of the tertiary arsine or phosphine ligands from the oxodimethylenemethane platinum complex to afford a monosubstituted complex. An excess of *t*-butylisocyanide results in the insertion of a molecule of *t*-butylisocyanide into one of the platinum-carbon bonds and formation of a zwitterion complex (64).⁶³



1.7 THE RÔLE OF OXODIMETHYLENEMETHANE IN ORGANIC SYNTHESIS

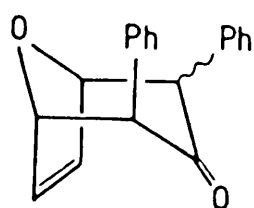
There has been considerable interest in the cyclocoupling of oxodimethylenemethane with alkenes and 1,3-dienes as a synthetic route to five- and seven-membered rings.⁷³ The reaction of the α,α' -dibromo-ketone (65) with $[\text{Fe}_2(\text{CO})_9]$ generates an oxodimethylenemethane intermediate (66) which, in the presence of furan, undergoes a [3+4] cyclo-coupling reaction to give the bicyclic ketone (67).⁷⁴ The intermediate (66) could not be isolated, in the absence of furan, an intramolecular cycloaddition product (68) is formed.^{74,75} The oxodimethylenemethane iron intermediate cycloadds across aryl-substituted alkenes in a [3+2] type manner producing 3-arylcyclopentanones (69),⁷⁶⁻⁷⁸ although in certain cases the 2-alkylidenetetrahydrofurans (70) were isolated as well.⁷⁸ A study of the reactivity of these oxodimethylenemethane intermediates with labelled styrene demonstrated that the [3+2] cycloaddition reaction proceeds in a stereospecific manner.⁷⁹ These cycloaddition reactions have been extensively used by Noyori as an entry into various cyclic natural products such as the tropane alkaloid system.⁷³

The iron carbonyl mediated cycloaddition reactions require a stoichiometric amount of the $[\text{Fe}_2(\text{CO})_9]$ relative to the α,α' -dibromo ketone and so there has been continued interest in the use of other metal systems as catalysts for these reactions. The [3+4] cycloaddition of oxodimethylenemethane to cyclic 1,3-dienes results from the copper/sodium iodide dehalogenation of α,α' -dibromo ketones.⁸⁰ A zinc-copper couple also promotes this [3+4] reaction,⁸¹ Scheme 21, although the yields were poor on comparison with the iron carbonyl mediated reactions.⁸²⁻⁸⁴ However, it was recently discovered that the yields of these zinc-copper couple mediated reactions were dramatically improved if the reactions were conducted in the presence of ultrasound.⁸⁵

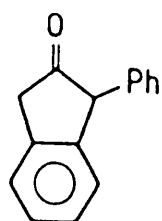


(65)

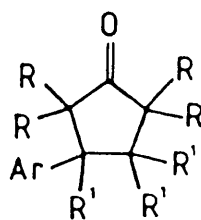
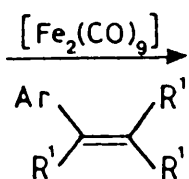
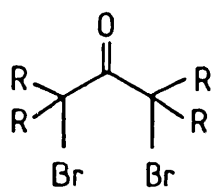
(66)



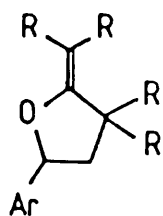
(67)



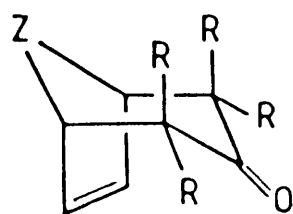
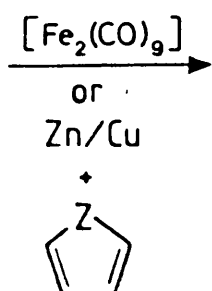
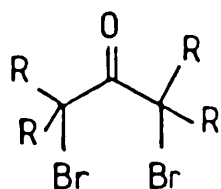
(68)



(69)



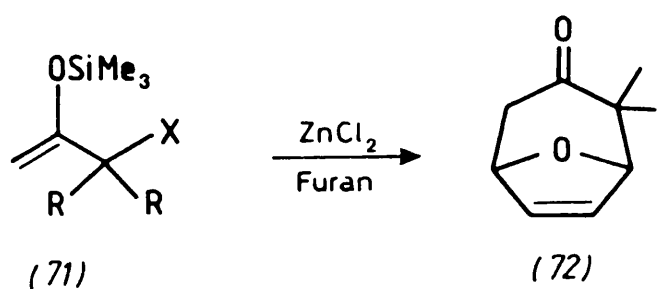
(70)



Z = O, CH₂, NR

Scheme 21

The silylenol ether (71, R=Me, X=Br) is a useful reagent for the synthesis of seven- and five-membered cyclic ketones from 1,3-dienes and alkenes respectively.⁸⁶ Thus in the presence of zinc(II) chloride in furan the bicyclic product (72) is obtained in almost quantitative yield.⁸⁶ Chapter 5 investigates the reactions of 3-chloro-2-(trimethylsiloxy)prop-1-ene (71, R=H, X=Cl) with low-valent metal centres to afford a synthetic route to stable oxodimethylenemethane metal complexes.





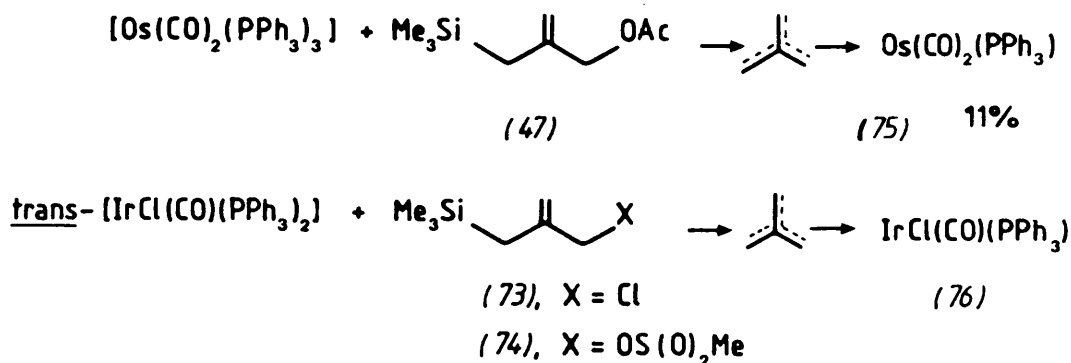
CHAPTER 2

Synthesis of η^4 -Trimethylenemethane Complexes
of Iridium, Rhodium, Osmium and Ruthenium

2.1 PREPARATION OF TRIMETHYLENEMETHANE METAL COMPLEXES

The allylic acetate, 3-trimethylsilyl-2-(acetoxymethyl)prop-1-ene (47), eliminates trimethylsilylacetate in the presence of palladium(0) catalysts and generates a highly reactive η^3 -trimethylenemethane palladium intermediate (48).^{48,49} As part of this thesis the reactions of the allylic acetate (47), chloride (73), and methanesulphonate (74) with various d^8 -metal complexes have been investigated.

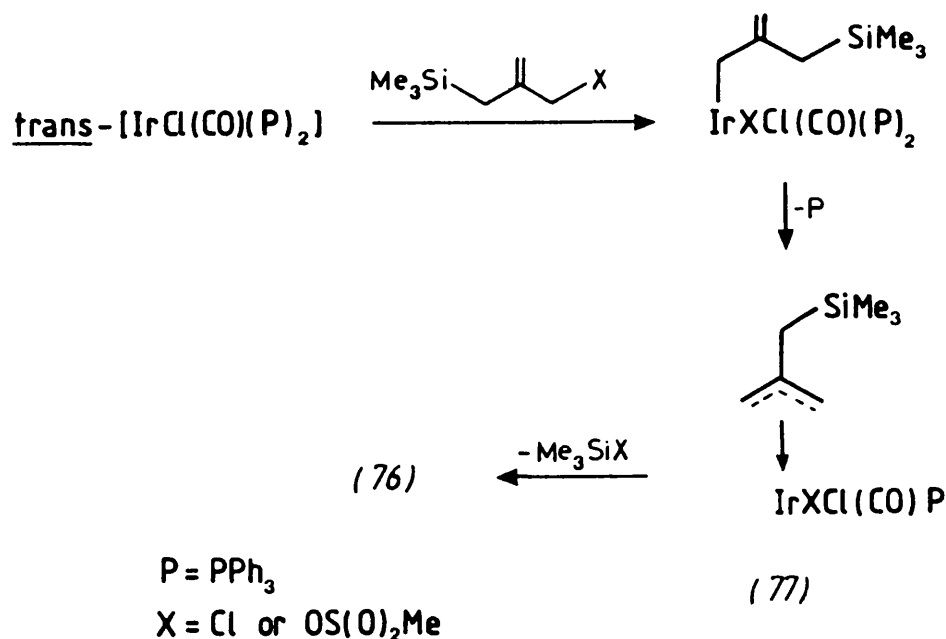
The η^4 -trimethylenemethane osmium complex (75) was isolated in low yield from the reaction of $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ with the allylic acetate (47). Similarly, trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and the allylic chloride (73), in refluxing toluene, afforded the η^4 -trimethylenemethane complex (76) in poor yield, Scheme 22.



Scheme 22

Following the pathway proposed for the formation of the η^3 -trimethylenemethane palladium intermediate (48)^{48,49} (see Chapter 1) a plausible route to the complex (76) may involve oxidative addition of the allylic chloride (73) to the iridium(I) centre to give an η^1 -allyl intermediate, formation of an η^3 -allyl (77) by dissociation of a co-ordinated ligand, and elimination of trimethylsilylchloride to generate the η^4 -trimethylenemethane metal complex (76), Scheme 23. A crucial step in this mechanism is believed to be the ionisation of chloride from the metal centre followed by attack of chloride ion at the silicon to effect desilylation

of the η^3 -allyl intermediate (77). A detailed study has been made of the oxidative addition reactions of allylic chlorides and allylic methanesulphonates to iridium(I) centres which shows that allylic methanesulphonates oxidatively add rapidly to iridium(I) complexes and that the methanesulphonate ion is a poor co-ordinating ligand.⁸⁷ This suggested that the allylic methanesulphonate (74) might be an attractive precursor to trimethylenemethane metal complexes. Accordingly, the reactions of (74) with a number of iridium(I) complexes were investigated. These reactions afforded much improved yields of a variety of η^4 -trimethylenemethane complexes. Thus refluxing a solution of the methanesulphonate (74) in toluene or benzene with the complexes trans-[IrX(CO)(P)₂] (X = Cl or Br, L = PPh₃; X = Cl, L = AsPh₃), and [Ir₂Cl₂(COT)₄]/(4PPh₃) afforded high yields of the η^4 -trimethylenemethane complexes [Ir(η^4 -C(CH₂)₃)X(CO)L] (76, X = Cl, L = PPh₃), (78, X = Br, L = PPh₃), (79, X = Cl, L = AsPh₃), and [Ir(η^4 -C(CH₂)₃)Cl(PPh₃)₂] (80) respectively. Trimethylsilylmethanesulphonate was isolated from the volatile components.

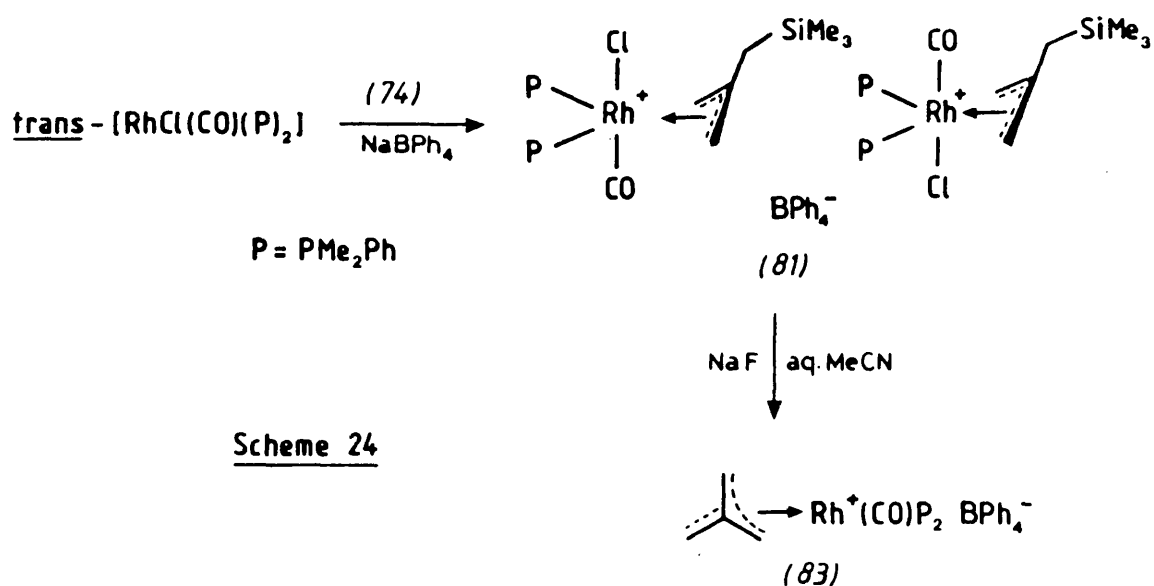


Scheme 23

Evidence for the existence of trimethylsilylmethylallyl complexes of the type (77) as intermediates in the synthesis of these trimethylene-methane metal complexes was obtained by the isolation of the η^3 -2-trimethylsilylmethylallyl rhodium complex (81) from the reaction of trans-[RhCl(CO)(PMe₂Ph)₂] with the methanesulphonate (74) in the presence of NaBPh₄. The ¹H, ¹³C-{¹H}, and ³¹P-{¹H} n.m.r. spectra confirms the presence of mutually cis phosphine ligands which are trans to the symmetrical η^3 -allyl fragment although the relative arrangement of the chloride and carbonyl ligands to the η^3 -allyl is uncertain, Scheme 24. The complex [Rh{ η^3 -CH₂C(CH₂SiMe₃)CH₂}Cl(CO)(PMe₃)₂]BPh₄ (82) was obtained from the reaction of trans-[RhCl(CO)(PMe₃)₂] with (74) and NaBPh₄ in methanol. Similar η^3 -allyl complexes of the type [Ir(η^3 -C₃H₅)Cl(CO)(P)₂]-BPh₄ (P = PMe₂Ph or PMePh₂) have been isolated from the reaction of 3-chloroprop-1-ene with trans-[IrCl(CO)(P)₂] and NaBPh₄ in methanol.⁸⁸ The initial step in the reactions of (74) with low-valent metal centres is presumably the formation of an η^1 -allyl complex.^{88,89} However, the η^1 -trimethylsilylmethylallyl rhodium complex could not be isolated. Treatment of trans-[RhCl(CO)(PMe₂Ph)₂] with (74), in the absence of NaBPh₄, afforded a yellow solid which became oily after a short length of time. The ¹H n.m.r. spectrum showed the presence of (74) and trans-[RhCl(CO)(PMe₂Ph)₂] in solution. This indicates that the oxidative addition reaction of (74) to the rhodium(I) complex is reversible. A similar reversible reaction was observed between trans-[IrCl(CO)(PPh₃)₂] and 3-methanesulphonateprop-1-ene.⁸⁷

The η^3 -2-trimethylsilylmethylallyl rhodium complex (81) was desilylated by sodium fluoride in aqueous methyl cyanide to afford the rhodium trimethylenemethane complex (83) in high yield, Scheme 24.

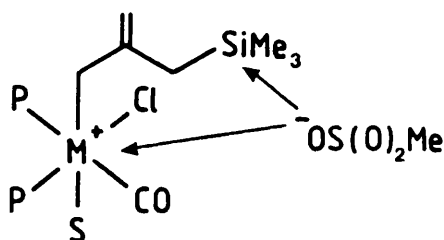
Fluoride ions are good silylophiles⁹⁰ and attack at silicon would be



expected rather than attack at the metal centre. Thus elimination of trimethylsilylfluoride and sodium chloride transforms the η^3 -allyl complex (81) to the trimethylenemethane complex (83). However, elimination of trimethylsilylfluoride from an η^1 -allyl complex, formed by prior attack of a fluoride ion at the metal, is also possible.

The analogous η^3 -2-trimethylsilylmethylallyl iridium complex could not be isolated. The reaction of the methanesulphonate (74) with trans-[IrCl(CO)(PMe₂Ph)₂] and NaBPh₄ in methanol gave the protodesilylated product [Ir(η^3 -CH₂CMeCH₂)Cl(CO)(PMe₂Ph)₂]BPh₄. A possible explanation for this differing reactivity of the rhodium and iridium complexes is that in a co-ordinating solvent such as methanol, a solvato complex (84) is initially formed during the oxidative addition reaction.⁸⁷ Attack by the methanesulphonate anion at the metal, displacing the solvent molecule (S), will form an η^1 -allyl intermediate which, on addition of NaBPh₄, will lead to an η^3 -2-trimethylsilylmethylallyl complex (81).⁸⁸ However, attack of the methanesulphonate anion at the trimethylsilyl group in the solvato complex (84) will result in protodesilylation,⁹⁰ a proton being abstracted from the solvent. Addition of NaBPh₄ affords an η^3 -2-methylallyl complex. The attack of the methanesulphonate anion at the metal

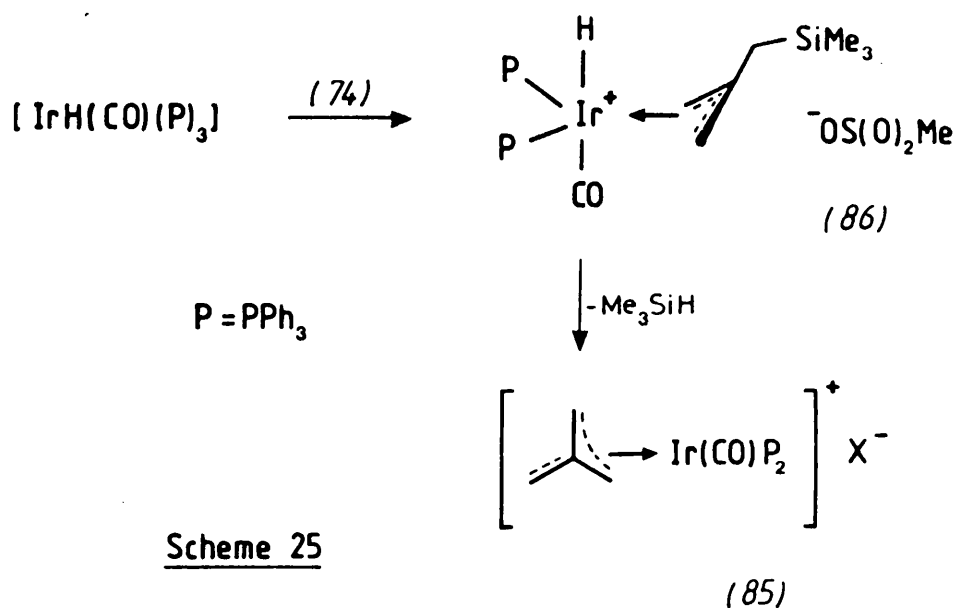
centre requires prior dissociation of the co-ordinated solvent molecule (S). Such a dissociative step is many times slower at an iridium(III) centre compared to the corresponding rhodium(III) centre.⁹¹ The methanesulphonate anion is also a poor ligand for iridium(III) centres.⁸⁷ Thus in the iridium solvato complex (84, M=Ir) the methanesulphonate anion attacks the trimethylsilyl group, leading to a protodesilylated product, rather than the slower attack at the metal centre.



(84)

A reaction of interest is that of the methanesulphonate (74) with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ which affords the cationic η^4 -trimethylenemethane complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{OS}(\text{O})_2\text{Me}$ (85, $\text{X} = \text{OS}(\text{O})_2\text{Me}$) in high yield. The elimination of trimethylsilane from an η^3 -allyl intermediate (86) provides an attractive route to this complex although attempts to detect trimethylsilane were unsuccessful, Scheme 25. The iridium complex (85, $\text{X} = \text{PF}_6$) was obtained from the reaction of the allylic chloride (73) with trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and KPF_6 .

The allylic methanesulphonate (74) reacted with the ruthenium, osmium and rhodium complexes $[\text{MCl}(\text{NO})(\text{PPh}_3)_n]$ ($\text{M} = \text{Ru}$, $n = 2$; $\text{M} = \text{Os}$, $n = 3$), $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$, and $[\text{RhCl}(\text{PPh}_3)_3]$ to afford the η^4 -trimethylenemethane complexes $[\text{M}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{NO})(\text{PPh}_3)]$ (87, $\text{M} = \text{Ru}$), (88, $\text{M} = \text{Os}$), $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (75), and $[\text{Rh}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{PPh}_3)_2]$ (89) respectively. The complexes which react with the methanesulphonate (74) are electron-rich and readily undergo oxidative addition reactions.⁹²⁻⁹⁴ No reaction was observed between trans- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ and (74) in



refluxing toluene although under analogous conditions the iridium complex trans-[IrCl(CO)(PPh₃)₂] afforded the trimethylenemethane complex (76). This indicates that oxidative addition to the metal centre is an important step in the reactions of (74) and that complexes which are slow to undergo oxidative addition reactions, such as trans-[RhCl(CO)-(PPh₃)₂],⁹⁵ will not react with (74). This problem could possibly be overcome by using a more reactive trimethylenemethane precursor. Trifluoromethanesulphonate is a much better leaving group than methanesulphonate⁹⁶ but attempts to generate the trifluoromethanesulphonate derivative of (74) were thwarted by its thermal instability. 3-Trimethylsilyl-2-(hydroxymethyl)prop-1-ene reacted with trifluoromethanesulphonic anhydride in the presence of a base. However, on warming above 0°C a dark brown solution formed and no pure products could be isolated.

The ring opening of methylenecyclopropane has been used with great success in the synthesis of η^4 -trimethylenemethane complexes²⁰⁻²⁷ and so the reactions of methylenecyclopropane with [Os(CO)₂(PPh₃)₃] and trans-[IrCl(CO)(PPh₃)₂] were investigated to see if this route afforded the same trimethylenemethane complexes as were obtained using the methanesulphonate (74).

A benzene solution of $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ and an excess of methylenecyclopropane was sealed in a Carius tube and heated to 90°C . The yellow colour associated with the starting material faded and an η^2 -methylenecyclopropane complex $[\text{Os}(\eta^2\text{-CH}_2\text{:}\overline{\text{CCH}_2\text{CH}_2})(\text{CO})_2(\text{PPh}_3)_2]$ (90) was isolated from the solution. Similar η^2 -bonded methylenecyclopropane complexes have been isolated on iron(0), rhodium(I), iridium(I), platinum(II) and platinum(0).⁹⁷⁻⁹⁹ The spectroscopic data for the complex (90) are fully compatible with the formulation as an η^2 -bonded methylenecyclopropane complex in which the three-membered ring has remained intact. The ^1H n.m.r. spectrum exhibits a triplet due to the co-ordinated methylene group at δ 0.09, establishing the presence of two phosphorus ligands [$J(\text{HP}) = 7\text{ Hz}$]. Similar values were obtained for the closely related η^2 -ethylene complex $[\text{Os}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2]$.¹⁰⁰ There are two other multiplets at δ -0.29 and 0.3 p.p.m. assigned to the protons of the cyclopropyl ring. The i.r. spectrum exhibits two strong bands of equal intensity at 1885 and 1955 cm^{-1} , at the same positions as observed for the ethylene complex $[\text{Os}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2]$, indicative of cis carbonyl groups.¹⁰⁰

No reaction was observed between trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and methylenecyclopropane after heating in a sealed tube for three days at 90°C . These results illustrate that although high yield syntheses of η^4 -trimethylenemethane complexes of iridium, rhodium, osmium, and ruthenium can be obtained from the reaction of the methanesulphonate (74) with low-valent metal complexes these trimethylenemethane complexes are not obtained from the reaction of methylenecyclopropane with iridium(I) or osmium(0) centres.⁹⁷

2.2 STRUCTURAL PROPERTIES OF TRIMETHYLENEMETHANE METAL COMPLEXES

Single-crystal X-ray diffraction studies for a number of these trimethylenemethane metal complexes have been carried out to establish the nature of the bonding of the trimethylenemethane fragment. The osmium complex (75), the iridium complex (76), and the cationic iridium complex (85, $X = PF_6$) have had their molecular structures determined, and a summary of the important bond lengths and angles are given in Tables 1 and 2.

The general molecular structure for these trimethylenemethane metal complexes is summarised in Scheme 26, which also gives the crystallographic numbering system. The co-ordination around the metal atom in all three complexes is essentially a distorted octahedral arrangement with the methylene carbon atoms of the trimethylenemethane occupying three facial vertices and the metal atom is located directly beneath the central carbon atom C(1). This staggered conformation is predicted by theoretical considerations.^{101,102} The metal to the central carbon C(1) is the shortest distance to the trimethylenemethane fragment but the three methylene carbons C(2), C(3), and C(4), although at a greater distance, are tipped towards the metal so that the trimethylenemethane ligand adopts the usual umbrella arrangement. The reason for this bending action in η^4 -trimethylenemethane- ML_3 complexes has been well documented¹⁰¹ and is quantified by the two angular parameters θ and β shown in Scheme 26, where β is the angle between the line C(1)-C(2) and the plane H-C(2)-H. For the complex $[Fe\{\eta^4-C(CH_2)_3\}(CO)_3]$ ¹⁰³ $\theta = 13.6^\circ$ and $\beta = 14.4^\circ$, and in the case of $[Fe\{\eta^4-C(CH_2)_2CHPh\}(CO)_3]$ θ values of 13.9 , 13.0 , and 11.7° are recorded.¹⁰⁴ Tris(carbonyl)-(η^4 -7-methylene-cyclohepta-1,3,5-triene)iron also contains a trimethylenemethane ligand, with $\theta = 11.0$, 10.1 , and 10.1° and $\beta = 14.8$, 15.9 , and 23.4° .¹⁰⁵ For the

TABLE 1^aBond lengths for the complexes $[M\{\eta^4-C(CH_2)_3\}L_3]$

Bond Length ° (Å)	Complex		
	(75) M = Os, L(1) = PPh ₃ , L(2) = L(3) = CO	(76) M = Ir, L(1) = PPh ₃ , L(2) = Cl, L(3) = CO	(85) M = Ir, L(1) = PPh ₃ , L(2) = PPh ₃ , L(3) = CO
M-L(1)	2.343 (2)	2.330 (3)	2.367 (5)
M-L(2)	1.895 (7)	2.448 (3)	2.362 (5)
M-L(3)	1.86 (1)	1.90 (2)	1.84 (2)
M-C(1)	2.09 (1)	2.05 (1)	2.05 (2)
M-C(2)	2.25 (1)	2.29 (1)	2.29 (2)
M-C(3)	2.25 (1)	2.17 (1)	2.21 (2)
M-C(4)	2.24 (1)	2.20 (1)	2.23 (2)
C(1)-C(2)	1.45 (1)	1.51 (2)	1.52 (3)
C(1)-C(3)	1.39 (1)	1.43 (2)	1.52 (3)
C(1)-C(4)	1.42 (1)	1.46 (2)	1.52 (3)

^a See Scheme 26 for crystallographic numbering system.

TABLE 2^aBond angles for the complexes $[M(\eta^4-C(CH_2)_3)L_3]$

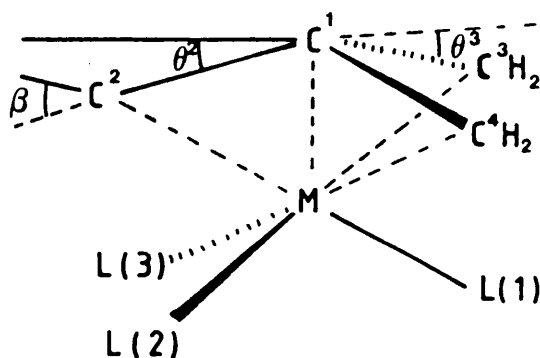
Angle (°)	Complex		
	(75) M = Os, L(1) = PPh ₃ , L(2) = L(3) = CO	(76) M = Ir, L(1) = PPh ₃ , L(2) = Cl, L(3) = CO	(85) M = Ir, L(1) = PPh ₃ , L(2) = PPh ₃ , L(3) = CO
L(1)-M-L(2)	94.1 (0.3)	91.8 (0.1)	102.8 (0.2)
L(1)-M-L(3)	93.4 (0.2)	94.6 (0.4)	98.9 (0.6)
L(2)-M-L(3)	96.1 (0.4)	95.5 (0.3)	94.5 (0.6)
C(1)-M-C(2)	38.8 (0.4)	40.0 (0.6)	40.5 (0.8)
C(1)-M-C(3)	37.1 (0.3)	39.3 (0.6)	41.7 (0.7)
C(1)-M-C(4)	38.1 (0.4)	40.1 (0.6)	41.1 (0.7)
C(2)-M-C(3)	64.8 (0.4)	66.7 (0.7)	69.5 (0.8)
C(2)-M-C(4)	65.4 (0.5)	68.6 (0.6)	71.2 (0.7)
C(3)-M-C(4)	63.3 (0.4)	66.7 (0.6)	67.2 (0.7)
M-C(2)-C(1)	65.0 (0.5)	61.5 (0.7)	61.4 (1.1)
M-C(3)-C(1)	65.4 (0.4)	65.8 (0.8)	63.8 (1.1)
M-C(4)-C(1)	65.5 (0.6)	64.5 (0.7)	62.8 (1.1)
C(2)-C(1)-C(3)	115.8 (1.2)	113.8 (1.6)	115.0 (1.9)
C(2)-C(1)-C(4)	115.0 (1.0)	117.2 (1.5)	120.6 (1.9)
C(3)-C(1)-C(4)	113.8 (1.0)	112.6 (1.5)	108.1 (1.2)
θ^2	13.8 (0.5)	11.6 (0.8)	11.9 (1.3)
θ^3	12.5 (0.5)	15.1 (0.8)	15.4 (1.1)
θ^4	13.6 (0.5)	14.6 (0.8)	13.9 (1.2)

^a See Scheme 26 for crystallographic numbering system.

complexes (75), (76), and (85) θ values are in the range 11.6 (0.8) to 15.4 (1.1)°. In all of these complexes the puckering of the trimethylenemethane fragment is not sufficient to cause the methylene carbon atoms to approach closer to the metal than the central carbon C(1). Thus in the complexes (75), (76), and (85) the M-C(1) distances are 2.09(1), 2.05(1), and 2.05(2) Å respectively while the M-CH₂ distances are in the range 2.17(1) to 2.29(2) Å. For the iron complexes the Fe-C(CH₂)₃ distances are shorter than those distances in the osmium and iridium complexes due to the smaller iron atom. Thus the Fe-C (central) distances lie within the range 1.93-1.95 Å while Fe-C (outer) values span 2.10-2.175 Å.^{15,103-105} In the cationic molybdenum complex [Mo{ η^4 -C(CH₂)₃}(CO)₂(η^5 -C₅Me₅)]BF₄ (28)²⁷ θ values are 14.6(5), 12.0(6), and 10.6(6)° and, while the Mo-C(CH₂)₃ distances are longer, the puckering is essentially the same, Mo-C (central) being 2.21(1) Å whilst Mo-CH₂ lie within the range 2.31(1)-2.39(1) Å. Interestingly, the trimethylenemethane ligand in the iridium complex (76) is not symmetrically bound to the metal, the Ir-CH₂ distances reflecting the markedly differing trans-influences of chloride, carbonyl, and triphenylphosphine ligands.^{106,107} Thus Ir-C(2), trans to phosphorus, is 2.29(2) Å while Ir-C(3), trans to chloride, is 2.17(2) Å. Some asymmetry in the C-C bonds of the trimethylenemethane ligand in the complex (76) is evident, there being a slight difference in the C(1)-C(2) and C(1)-C(3) distances, presumably due to the differing trans-influences of triphenylphosphine and chloride ligands. These C-C bond lengths extend the previous range of 1.405(4)-1.45(2) Å found in other η^4 -trimethylenemethane-FeL₃ complexes^{15,103-105} and also the distances of 1.39(1)-1.46(2) Å seen in the cationic complex [Mo{ η^4 -C(CH₂)₃}(CO)₂(η^5 -C₅Me₅)]BF₄.²⁷

The hydrogen atoms of the trimethylenemethane ligand were located in

the osmium complex (75) and, although the positions of the hydrogen atoms are subject to relatively large errors, the bend-back angles β at C(2), C(3), and C(4) are 28, 12, and 41° respectively. This shows that the H-C-H plane is tipped away from the metal atom, as seen in other η^4 -trimethylenemethane metal complexes.¹⁰³



Scheme 26

Figures 1, 2, and 3 show the molecular structures of the trimethylenemethane complexes (75), (76), and (85) respectively. The iridium atom in the complex (76) is chiral and the two enantiomers co-crystallise from solution in a centrosymmetric space group.

In all these complexes trimethylenemethane can be considered as a neutral 4π -donor co-ordinated to iridium(I) and osmium(0), or as a dianionic 6π -donor co-ordinated to iridium(III) and osmium(II). Although these are the two limiting extremes, a number of features of these complexes indicates that there is a contribution from the higher metal oxidation state. Iridium(III) complexes usually adopt an octahedral arrangement about the metal as in $[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{PF}_6$ ^{88,108} and this is in line with the observed geometry of the trimethylenemethane complexes in which the trimethylenemethane ligand occupies three vertices of a distorted octahedron. Iridium(I) complexes are usually four or five co-ordinate as in trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ ¹⁰⁹ or $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$.

The variation of $\nu(\text{CO})$ values has been correlated with the relative

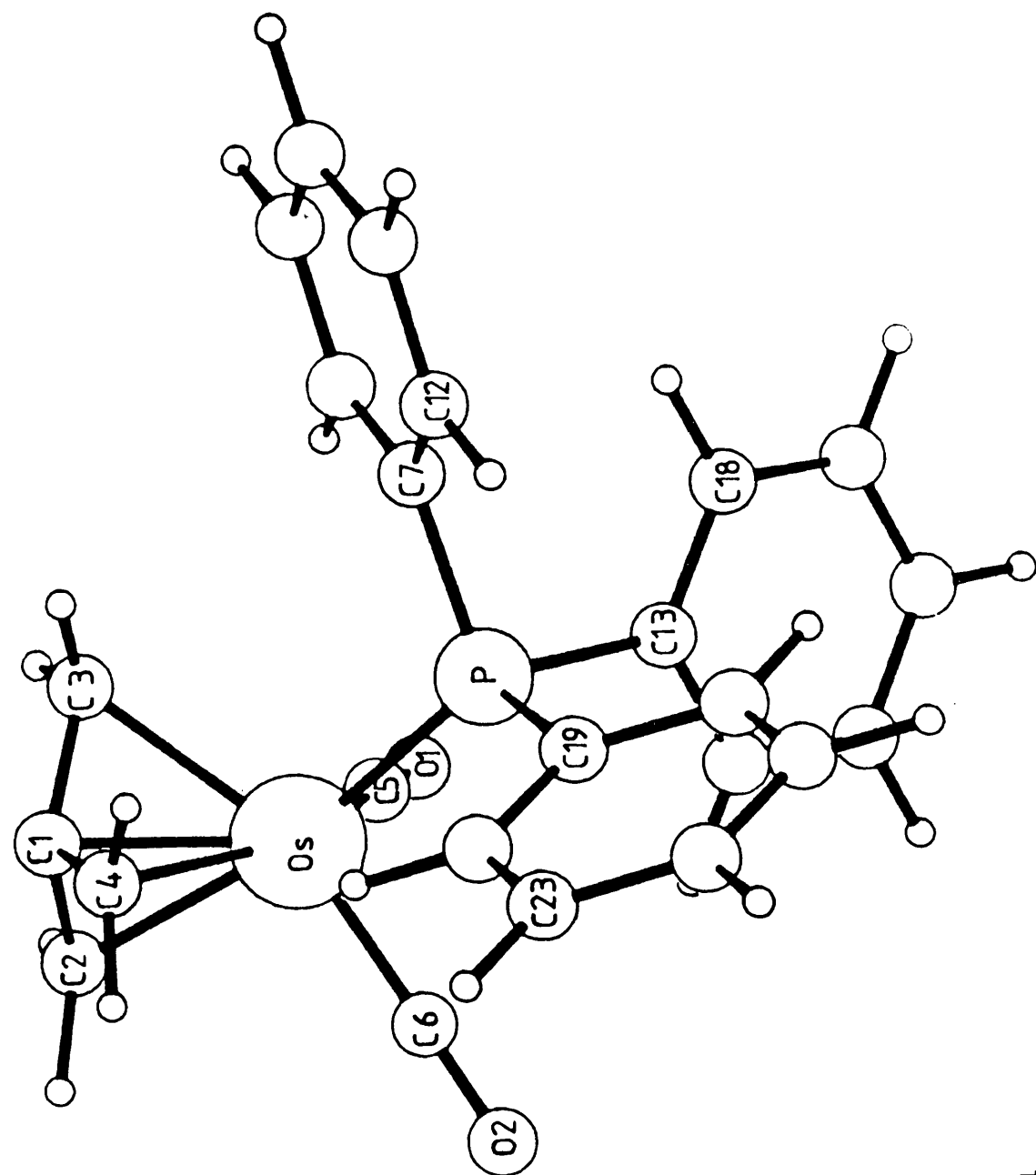


FIGURE 1
Molecular structure of the complex $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (75).

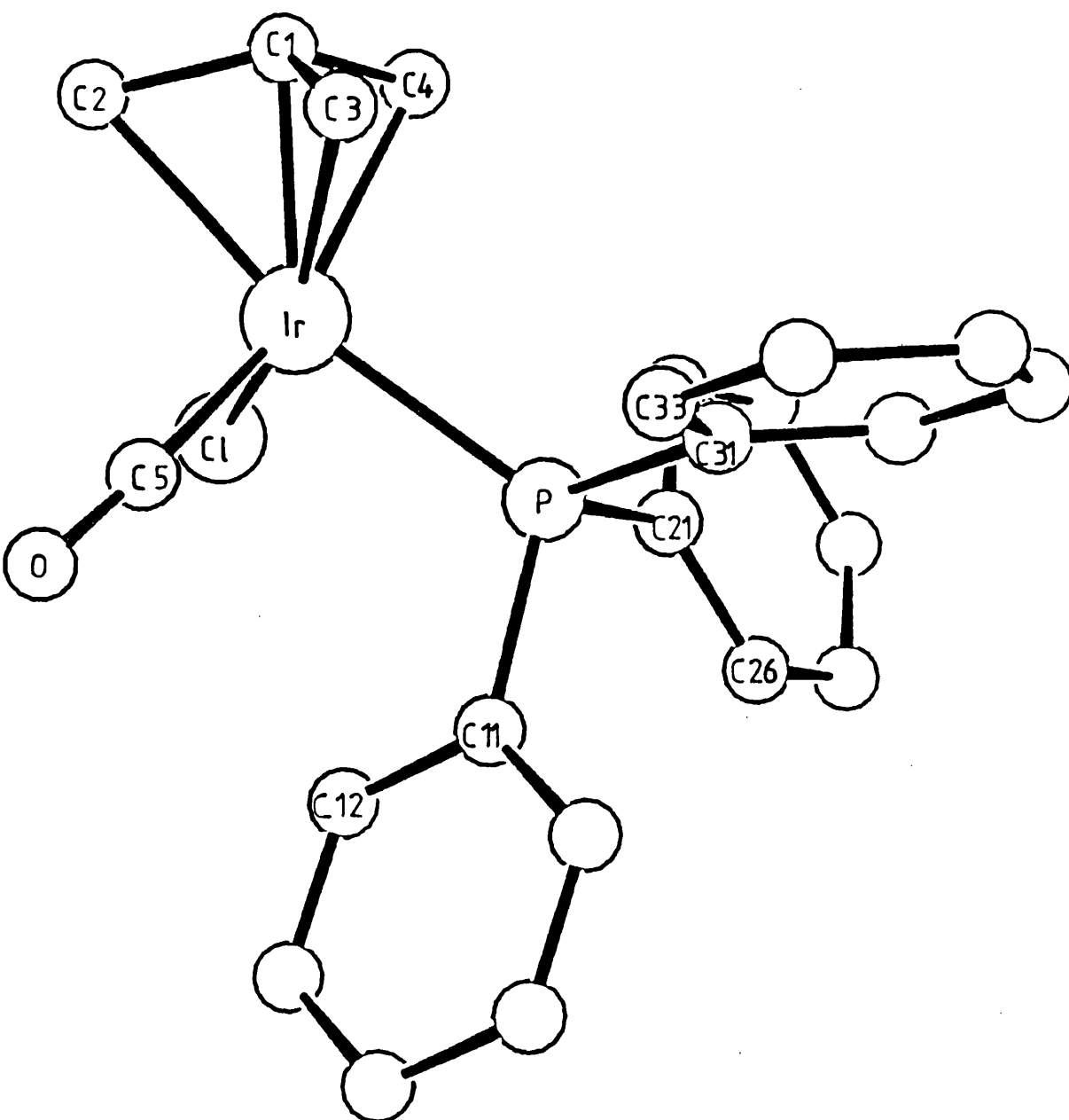


FIGURE 2

Molecular structure of the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76), with hydrogen atoms of phenyl rings and methylene groups omitted.

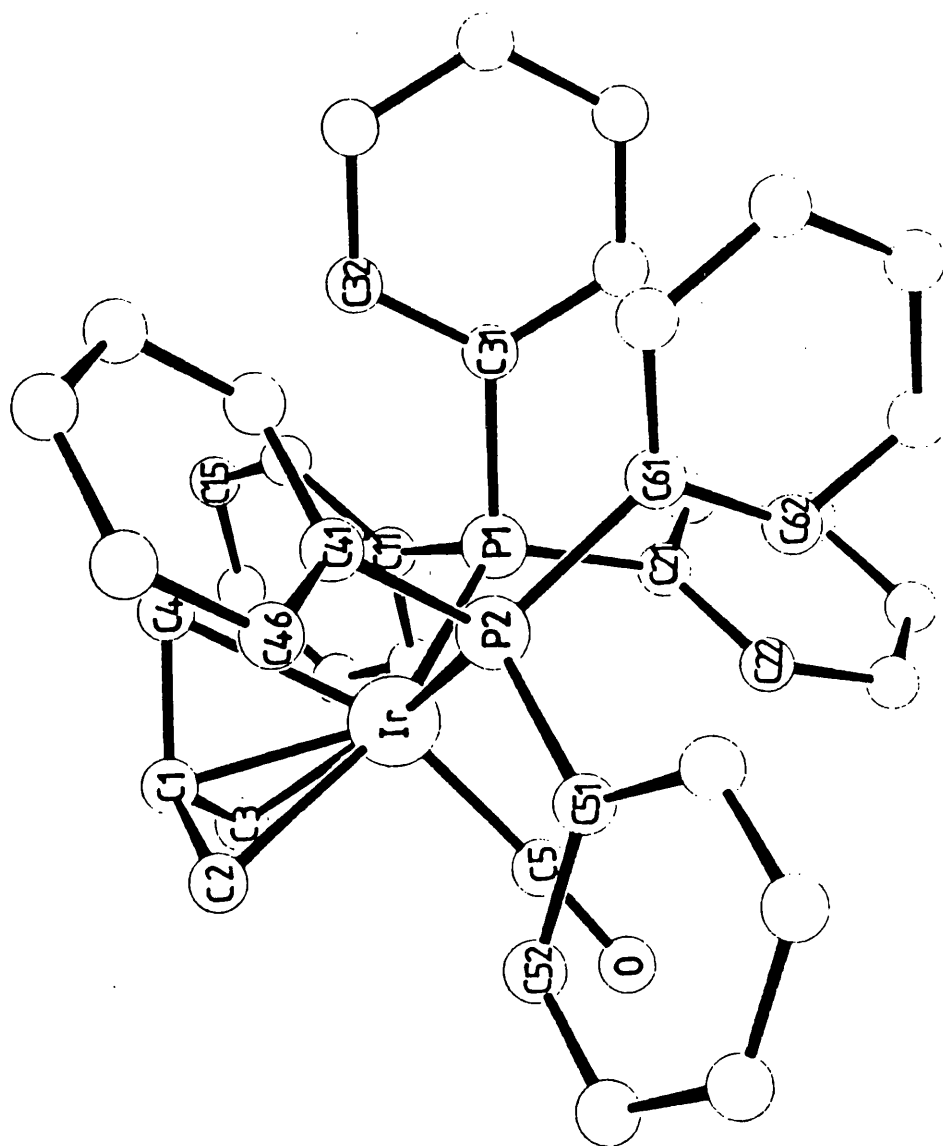
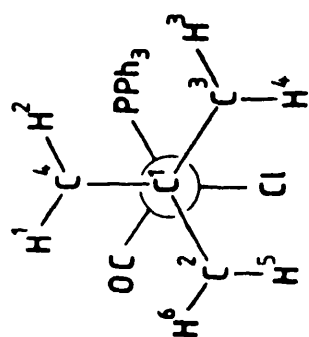


FIGURE 3
Molecular structure of the complex $[\text{Ir}\{\eta^3\text{-C}(\text{CH}_2)_3\}\{\text{CO}(\text{PPh}_3)_2\}]\text{PF}_6$ (85), with hydrogen atoms of phenyl rings and methylene groups omitted.

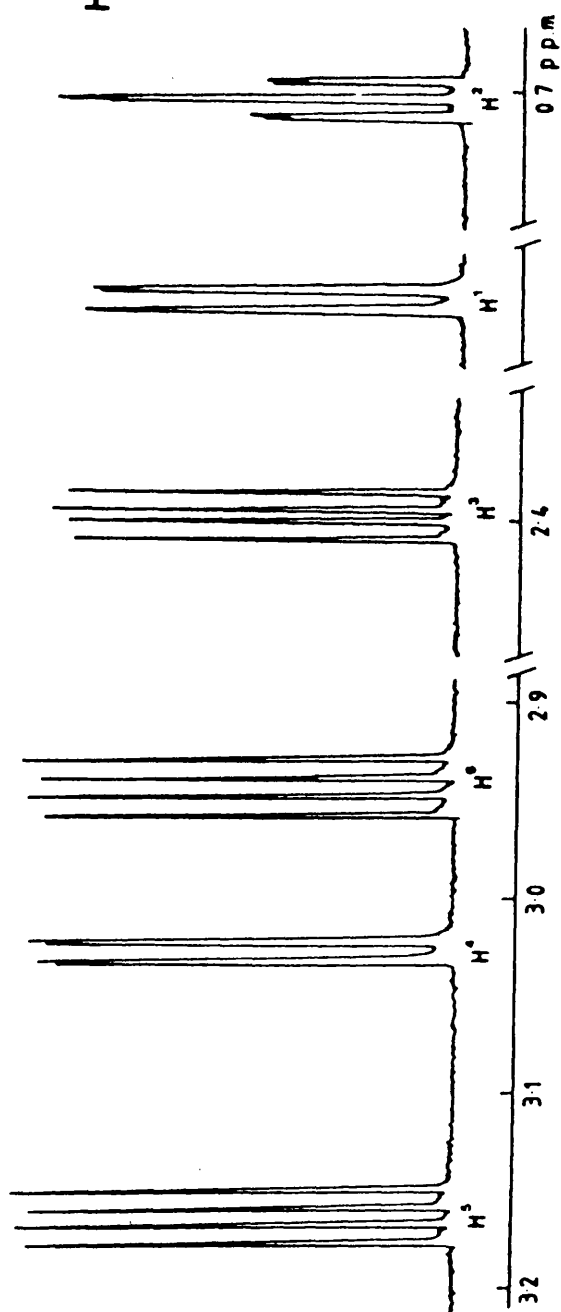
oxidation state of iridium for various adducts of trans-[IrCl(CO)-(PPh₃)₂].¹¹⁰ The $\nu(\text{CO})$ values observed in the iridium trimethylenemethane complexes are consistent with a contribution from an iridium(III) centre which have $\nu(\text{CO})$ values above 2000 cm^{-1} whereas iridium(I) complexes have $\nu(\text{CO})$ values below 2000 cm^{-1} .¹¹¹ Thus in the complex trans-[IrCl(CO)(PPh₃)₂] the $\nu(\text{CO})$ value of 1965 cm^{-1} contrasts with the iridium complex (76), $\nu(\text{CO})$ 2030 cm^{-1} , and the cationic complex (85), $\nu(\text{CO})$ 2040 cm^{-1} . This indicates that the iridium carries a higher positive charge in the trimethylenemethane complexes relative to the complex trans-[IrCl(CO)(PPh₃)₂].

2.3 ROOM TEMPERATURE ¹H AND ¹³C NMR SPECTRA OF TRIMETHYLENEMETHANE METAL COMPLEXES

The ¹H and ¹³C-{¹H} n.m.r. spectra of all of the η^4 -trimethylenemethane metal complexes synthesised are consistent with a staggered conformation of the trimethylenemethane ligand relative to the ML₃ fragment creating a distorted octahedral arrangement about the metal. The ¹H n.m.r. spectrum of the complex [Ir(η^4 -C(CH₂)₃)Cl(CO)(PPh₃)] (76), measured at room temperature, shows six resonances due to the methylene protons of the co-ordinated trimethylenemethane ligand, Scheme 27. This indicates that the trimethylenemethane ligand is rigid and no rotation occurs on the n.m.r. time scale at room temperature since rotation of the trimethylenemethane ligand would equilibrate the protons. Each proton of the trimethylenemethane ligand shows a long range proton-proton "W coupling"; thus in the complex (76) H² couples strongly to H⁵, while H¹ couples strongly to H⁴. In addition to this coupling, H², H³, H⁵, and H⁶ show additional coupling to phosphorus-31. The protons H⁵ and H⁶, which are in a pseudo trans orientation with respect to the tertiary phosphine ligand exhibit the larger phosphorus-31 coupling, although H¹ and H⁴ show

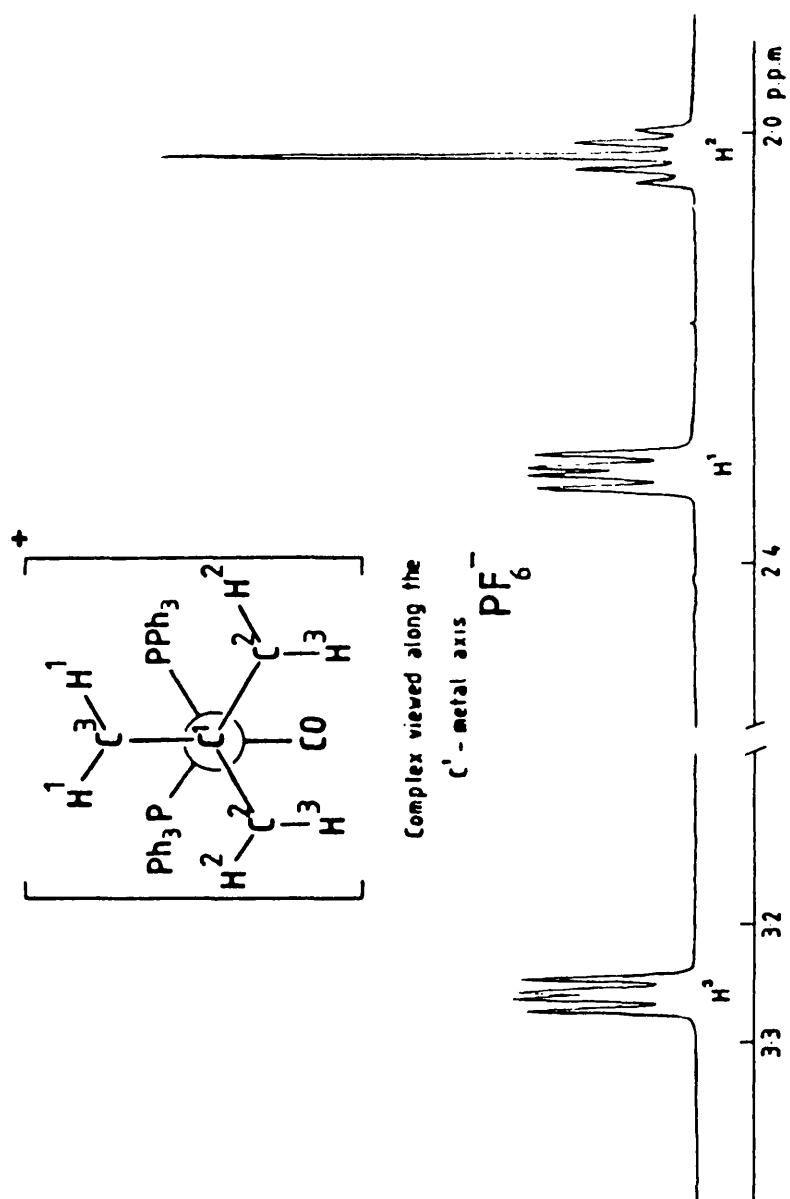


Complex viewed along the
C' - metal axis



SCHEME 27

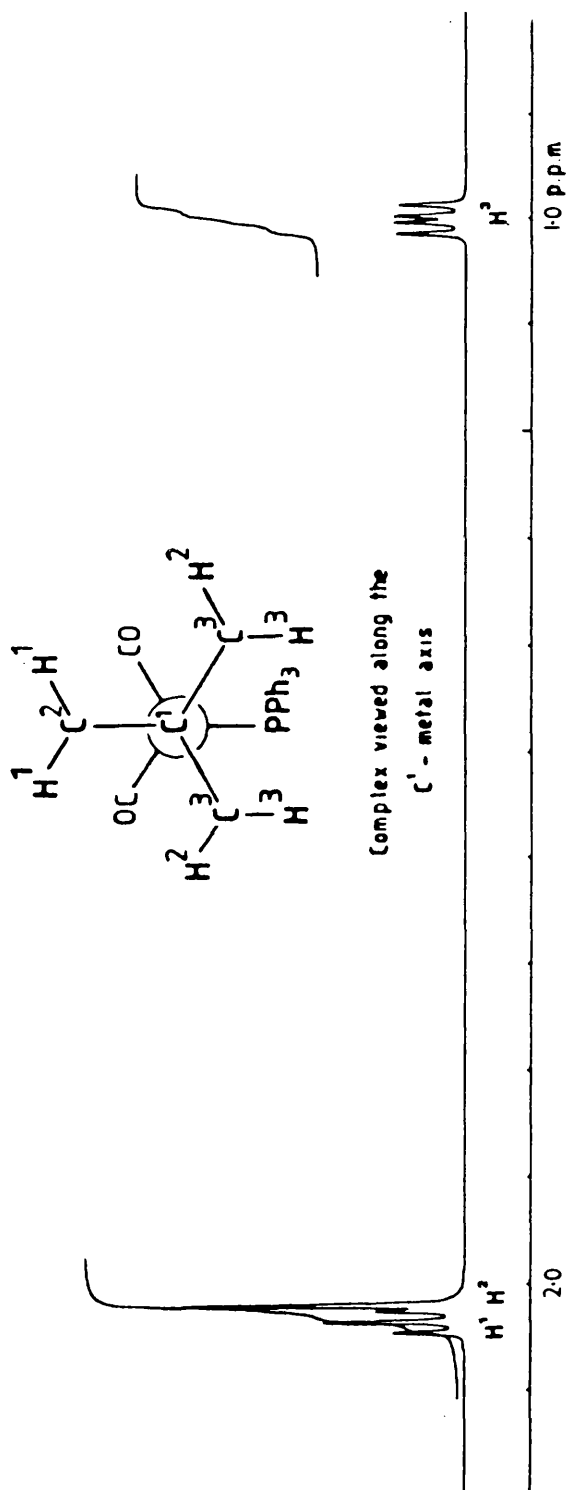
no coupling to phosphorus-31. This variation in the magnitude of the coupling of the trimethylenemethane protons to phosphorus-31 nuclei suggests that the "three-bond" coupling (P-M-C-H) may be under dihedral angle control as in the well-known Karplus relations for vicinal (H-C-C-H) couplings.^{112,113} This full analysis of the ¹H-n.m.r. spectrum has been obtained from selective decoupling experiments and nuclear Overhauser effect (n.O.e.) difference spectra.¹¹³ The nuclear Overhauser effect is a dipole-dipole interaction¹¹⁴ leading to relaxation and varies inversely with the cube of the distance between the dipoles allowing information about the spatial orientation of the nuclei to be obtained.¹¹³ Thus n.O.e. enhancement of about 30% is observed between the pairs of protons which are geminally related, e.g. H¹ and H² in Scheme 27, along with a weaker enhancement of about 5% between H¹ and H⁶.²⁴ The n.O.e. technique not only allows a full analysis of the ¹H n.m.r. spectrum of the η⁴-trimethylenemethane fragment but, due to the proximity of H² and H³ with the ortho protons of the triphenylphosphine aromatic rings, it is also possible to obtain the arrangement of the phosphine ligand relative to the trimethylenemethane protons. The relative arrangement of the chloride and carbonyl ligands to the various trimethylenemethane protons is uncertain but the arrangement shown in Scheme 27 is based on the effect of these ligands on the chemical shift of the trimethylenemethane protons, as discussed below. When two triphenylphosphine ligands are present as in the complex [Ir{η⁴-C(CH₂)₃}(CO)(PPh₃)₂](PF₆) (85), there are only three resonances associated with the trimethylenemethane ligand due to the symmetry of the complex, Scheme 28. The two protons H² are readily assigned because they appear as a second order multiplet, being the A part of an AA'XX' spin-system (X = ³¹P). A full analysis of this spin-system can be carried out and was verified by



SCHEME 28

computer simulation experiments.¹¹⁴ The large central peak in the multiplet is a result of the $J(H^2P)$ coupling being equal but opposite in sign relative to $-J(H^2'P)$.

The wide range of chemical shifts seen for the 1H n.m.r. spectra of these trimethylenemethane complexes is presumably a result of the other ligands co-ordinated to the metal. In the cationic complex (85) the protons H^1 and H^2 have similar chemical shifts whereas H^3 , which is attached to the same carbon atom as H^2 , is deshielded by over 1 p.p.m. relative to H^2 , Scheme 28. Aromatic rings can shield protons¹¹⁴ and it seems reasonable that the triphenylphosphine ligand is shielding H^1 and H^2 , which are relatively close to the aromatic rings, but not H^3 which is at a greater distance away. A similar trend is seen for the osmium complex $[Os\{\eta^4-C(CH_2)_3\}(CO)_2(PPh_3)]$ (75), and the 1H n.m.r. spectrum of the trimethylenemethane ligand is shown in Scheme 29. The n.O.e. technique verified that H^2 and H^3 were attached to the same carbon atom. H^2 shows no proton-proton or proton-phosphorus-31 coupling and is deshielded by 1 p.p.m. relative to H^3 . Presumably the phenyl rings are shielding the protons H^3 but not H^1 and H^2 . Carbonyl double bonds exhibit anisotropic deshielding effects in organic systems¹¹⁴ and so it is possible that the metal carbonyl group could be deshielding H^1 and H^2 but not H^3 . An interesting comparison can be made between the cationic complex (85), Scheme 28, and the neutral complex $[Ir\{\eta^4-C(CH_2)_3\}Cl(PPh_3)_2]$ (80). The protons H^1 trans to chloride resonate at δ 0.81 p.p.m. in the neutral complex (80) whereas the protons H^1 trans to carbonyl in the complex (85) resonate at δ 2.27 p.p.m. This is not purely a result of the overall charge difference between the two complexes because the protons H^2 and H^3 in the neutral complex (80) resonate at δ 2.1 and δ 2.9 p.p.m. respectively and are therefore at very similar chemical shifts to



SCHEME 29

that seen for the protons H^2 and H^3 in the cationic complex (85). This would therefore indicate that there is also a trans-ligand influence on the chemical shifts of the trimethylenemethane protons. On comparing the 1H n.m.r. spectra of the complexes $[Ir\{\eta^4-C(CH_2)_3\}Cl(CO)(PPh_3)]$ (76) and $[Ir\{\eta^4-C(CH_2)_3\}Br(CO)(PPh_3)]$ (78) the protons assigned to H^1 and H^2 , trans to the halide, move to low field in the complex (78) relative to the complex (76) whereas the protons H^3 , H^4 , H^5 , and H^6 have similar chemical shifts in both complexes. These observations have been used to establish the relative arrangement of the halogen and carbonyl ligands to the trimethylenemethane protons in the complexes (76), (78), and (79).

The $^{13}C\{-^1H\}$ n.m.r. spectra of these complexes exhibit the expected features for a static trimethylenemethane ligand. The characteristic feature is a resonance due to the central carbon C^1 in the region 104-118 p.p.m.^{11,26} and this assignment was confirmed by an off-resonance decoupled ^{13}C spectrum. The terminal carbon atoms have shifts in the range of 37 to 77 p.p.m. The central carbon C^1 exhibits a small coupling to the co-ordinated tertiary phosphine ligand of the order of 1-3 Hz. A larger phosphorus coupling is observed for the methylene carbon C^2 trans to the phosphorus nuclei. Thus the carbon C^2 in the complex $[Ir\{\eta^4-C(CH_2)_3\}Cl(CO)(PPh_3)]$ (76), Scheme 27, exhibits a phosphorus-31 coupling of 38 Hz whilst C^3 and C^4 in this complex show no phosphorus-31 coupling. The $^{13}C\{-^1H\}$ n.m.r. spectra of the trimethylenemethane complexes with two triphenylphosphine ligands present exhibit second order spectra. In the complex $[Ir\{\eta^4-C(CH_2)_3\}Cl(PPh_3)_2]$ (80) the resonance assigned C^2 , trans to phosphorus appears as the A part of an AXX' spin system ($X = ^{31}P$) and a doublet of doublets is observed. The $^{13}C\{-^1H\}$ n.m.r. spectra for the rhodium trimethylenemethane complexes exhibit an additional rhodium coupling. Thus in the complex $[Rh\{\eta^4-C(CH_2)_3\}Cl(PPh_3)_2]$ (89), the central

carbon C¹ appears as a doublet of triplets coupling to two equivalent phosphorus nuclei and to the rhodium-103 nucleus. C³, trans to chloride, appears as a doublet coupling only to rhodium-103, whereas C² appears as the A part of an AMXX' spin-system (M = ¹⁰³Rh, X = ³¹P) and a 1:3:1:0.5:0.5:1:3:1 multiplet is observed.

2.4 VARIABLE TEMPERATURE NMR STUDY OF SOME TRIMETHYLENEMETHANE METAL COMPLEXES

The trimethylenemethane ligand is rigid at room temperature on the n.m.r. time scale, any sign of rotation would interconvert the protons. Variable temperature ¹H n.m.r. studies were carried out at elevated temperatures to see if any rotation could be observed. The iridium complex (76) was heated to 70°C but no spin-magnetisation transfer could be detected at 400 MHz. The complex was heated to 105°C in a sealed tube at 100 MHz but the ¹H n.m.r. spectrum showed no sign of rotation of the trimethylenemethane ligand. The Gutowsky-Holm equation¹¹⁵⁻¹¹⁶ sets a lower limit for the barrier to rotation at $\Delta G^\ddagger > 84 \text{ kJ mol}^{-1}$. The osmium complex (75) was heated to 140°C in [²H₆]-dimethylsulphoxide but no sign of rotation of the trimethylene-methane ligand was detected setting $\Delta G^\ddagger > 95 \text{ kJ mol}^{-1}$. Both of these values are higher than the values of 71-79 kJ mol⁻¹ found for the rotational barriers of substituted trimethylenemethane complexes [Fe{η⁴-C(CH₂)₂(CHR)}(CO)₃], [R = COMe, MeCH(OH), MeCH(OAc), and Et].¹¹⁷ The origins of the barrier to rotation of the trimethylenemethane ligand in [Fe{η⁴-C(CH₂)₃}(CO)₃] have been well documented and indicate that a large increase in the barrier of rotation would be expected on replacing carbonyl ligands with tertiary phosphine or chloride ligands.¹⁰¹ A very low barrier to rotation has been observed for the complex [Mo{η⁴-C(CH₂)₃}(CO)₂(η⁵-C₅H₅)]BF₄ (29)²⁷ and the estimated barrier to rotation afforded a

value of $\Delta G^\ddagger = 41.2 \text{ kJ mol}^{-1}$. However, a different process for the interconversion of the trimethylenemethane protons was invoked because the theoretical barrier to rotation of the trimethylenemethane ligand in this complex was calculated at $\Delta G^\ddagger = 202.9 \text{ kJ mol}^{-1}$. This interconversion process involves slipping of the η^4 -trimethylenemethane ligand to an η^1 -trimethylenemethane arrangement followed by rotation about a Mo-C bond.²⁷ This rearrangement path is similar to that proposed for the syn-anti exchange process observed for η^3 -allyl complexes.^{118,119} Hindered rotation of the trimethylenemethane ligand has been observed for the complex $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PF}_3)]$.³⁰

2.5 CONCLUSION

3-Trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74) serves as a new entry into trimethylenemethane metal complexes.¹²⁰ Reaction with low-valent metal complexes afford trimethylenemethane complexes of iridium, rhodium, osmium, and ruthenium. Trimethylenemethane metal complexes are obtained from the reaction of the allylic acetate (47) and chloride (73) with d^8 -metal complexes but in poorer yield.¹²¹ Single-crystal X-ray diffraction studies confirm the presence of an η^4 -trimethylenemethane fragment co-ordinated in a staggered geometry relative to the ML_3 -fragment.

2.6 EXPERIMENTAL

Microanalytical results, m.p.s., and i.r. and n.m.r. spectroscopic data are presented for newly isolated compounds. The microanalyses were carried out by C.H.N. Analysis Ltd., Alpha House, Countesthorpe Road, South Wigston, Leicester. M.p.s. were recorded on a Reichart hot-stage apparatus and are uncorrected. A Perkin-Elmer 580 spectrophotometer was used to record i.r. spectra as CsCl discs. The ^1H n.m.r. spectra were

recorded at room temperature, unless otherwise stated, on a Bruker Spectrospin WH 400 spectrometer at 400.13 MHz, a JEOL EM 390 spectrometer at 90 MHz, a JEOL PS 100 spectrometer at 100 MHz, and a Bruker AM 300 spectrometer at 300.13 MHz with SiMe₄ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low-field), coupling constants are in Hz. The ¹³C-{¹H} n.m.r. spectra were recorded at room temperature, unless otherwise stated, on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz, and on a Bruker AM 300 spectrometer at 75.47 MHz with SiMe₄ (0.0 p.p.m.) as internal reference. The ¹³C-{¹H} data for the aromatic region between δ 125 and 140 p.p.m. have been omitted for clarity. The ³¹P-{¹H} n.m.r. spectra were recorded on either a JEOL JNM-FX 60 or a Bruker WH 400 spectrometers operating at 24 and 162 MHz respectively. ³¹P chemical shifts are reported relative to external [P(OH)₄]⁺¹²² in [D₂O]-water (0.0 p.p.m.) unless otherwise stated, with positive values to high frequency (low-field). Mass spectra were obtained using an A.E.I. MS9 spectrometer operating at 70 eV; output was tabulated and calibrated by a linked computer. Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction boiling in the range 40-60°C. The compounds trans-[IrCl(CO)(PPh₃)₂],¹⁰⁹ trans-[IrCl(CO)(AsPh₃)₂],¹²³ trans-[IrBr(CO)(PPh₃)₂],¹²⁴ trans-[RhCl(CO)(PMe₂Ph)₂],¹²⁵ trans-[IrCl(CO)(PMe₂-Ph)₂],¹²⁶ [IrH(CO)(PPh₃)₃],¹²⁷ trans-[RhCl(CO)(PMe₃)₂],⁸⁹ [Ir₂Cl₂(COT)₄],¹²⁸ [RhCl(PPh₃)₃],¹²⁹ [Os(CO)₂(PPh₃)₃],⁹⁴ [OsCl(NO)(PPh₃)₃],¹³⁰ [RuCl(NO)-(PPh₃)₂],¹³¹ 3-trimethylsilyl-2-(hydroxymethyl)prop-1-ene,¹³² and 3-trimethylsilyl-2-(acetoxymethyl)prop-1-ene (47)⁴⁸ were prepared as in the literature. The platinum metal salts were obtained on loan from Johnson Matthey, p.l.c.

Preparation of 3-Trimethylsilyl-2-(chloromethyl)prop-1-ene (73)

Thionyl chloride (1.7 g, 14 mmol) in dichloromethane (100 cm³) was added dropwise to a stirred solution of 3-trimethylsilyl-2-(hydroxymethyl)prop-1-ene (2.0 g, 13.8 mmol) and pyridine (1.5 g, 19 mmol) in dichloromethane (100 cm³) at 0°C. The solution was stirred for 0.5h at 0°C and then allowed to warm to room temperature and stirred for a further 0.5h. The solution was washed with dilute sulphuric acid (0.1M, 3 × 100 cm³) and dried over anhydrous potassium carbonate. The solvent was removed in vacuo and the residue distilled (40°C, 0.005 mmHg) into a trap cooled to -78°C to give a clear oil (2.2 g, 98%). The product must be stored at 0°C to avoid decomposition. I.r. (film): 2960s, 2900m, 1640m, 1450m, 1420m, 1250s, 1210m, 960s, 910s, 850s cm⁻¹. N.m.r. (CDCl₃): ¹H (90 MHz), δ 0.1 (s, 9H, SiMe₃), 1.7 (s, 2H, CH₂-SiMe₃), 4.4 (br s, 2H, CH₂-Cl), 4.85 (br s, 1H), 5.0 p.p.m. (m, 1H).

This compound has been previously synthesised via an alternative route.¹³³

Preparation of 3-Trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74)

Methanesulphonyl chloride (1.7 g, 0.0144 mol) in dichloromethane (15 cm³) was added dropwise over 0.5h to a stirred solution of 3-trimethylsilyl-2-(hydroxymethyl)prop-1-ene (2.0 g, 0.0138 mol) and triethylamine (3.0 g, 0.03 mol) in dichloromethane (10 cm³) at 0°C. The resultant cloudy solution was stirred at 0°C for a further 0.5h. The reaction was diluted with diethyl ether (50 cm³), washed successively with saturated sodium bicarbonate (2 × 25 cm³), saturated copper sulphate (3 × 25 cm³), water (25 cm³), and brine (25 cm³), and dried over anhydrous potassium carbonate. The solvent was removed at water pump pressure and the residue distilled (80°C, 0.5 mmHg) to give 2.76 g, (90%) of the title compound as a colourless liquid.¹³⁴ I.r. (film): 3080w, 3030w, 2950m,

2920m, 1640m, 1460m, 1420m, 1360s, 1255s, 1175vs, 1010s, 970s, 935s and 855 vs, cm^{-1} ; mass spectrum, m/e (%) M^+ 222(6), 169(10), 155(5), 154(6), 153(100), 110(10). N.m.r. (CDCl_3): ^1H (90 MHz), δ 0.1 (s, 9H), 1.6 (s, 2H), 3.0 (s, 3H), 4.5 (br s, 2H), 4.8 (br s, 1H), and 5.0 p.p.m. (m, 1H).

Preparation of Trimethylenemethane metal complexes

$[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76)

Trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (1.0 g, 1.28 mmol) and 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74) (0.85 g, 3.8 mmol) in toluene (20 cm^3) were refluxed for 12h, (the reaction appeared to be complete after the disappearance of the yellow colour within 3h). The solvent was removed in vacuo and ethanol (5 cm^3) was added to the residue. The white product was filtered and washed with ethanol and diethyl ether and dried in vacuo to give the title complex (0.55 g, 75%), m.p. 180°C (decomp.) (Found: C, 48.2; H, 3.6. $\text{C}_{23}\text{H}_{21}\text{ClIrOP}$ requires C, 48.3; H, 3.7%); i.r. ν_{CO} 2030, ν_{IrCl} 282 cm^{-1} ; n.m.r. (C_6D_6): ^1H (400 MHz), δ 0.70 [dt, 1H, H^2 , $J(\text{H}^2\text{H}^5) = J(\text{H}^2\text{P}) = 3.8$, $J(\text{H}^2\text{H}^1) 0.7$], 1.66 [br d, 1H, H^1 , $J(\text{H}^1\text{H}^4) 4.1$], 2.40 [dd, 1H, H^3 , $J(\text{H}^3\text{H}^6) 3.9$, $J(\text{H}^3\text{P}) 6.4$], 2.94 [dd, 1H, H^6 , $J(\text{H}^6\text{H}^3) 3.9$, $J(\text{H}^6\text{P}) 7.5$], 3.03 [dd, 1H, H^4 , $J(\text{H}^4\text{H}^1) 4.1$, $J(\text{H}^4\text{H}^3) \text{ or } J(\text{H}^4\text{P}) 0.5$], 3.16 [dd, 1H, H^5 , $J(\text{H}^5\text{H}^2) 3.8$, $J(\text{H}^5\text{P}) 7.0$], and 7.55 [m, 15H, PPh_3]; ^{13}C - $\{^1\text{H}\}$ (100 MHz), δ 40.2 (s, C^4), 54.0 [d, C^2 , $J(\text{C}^2\text{P}) 37.7$], 57.8 (s, C^3), 108.8 [d, C^1 , $J(\text{C}^1\text{P}) 3.1$], and 175.0 [d, CO, $J(\text{CP}) 4.4$]; ^{31}P - $\{^1\text{H}\}$ (CDCl_3), δ 6.25 p.p.m. Figure 4, $M=\text{Ir}$, $X=\text{Cl}$, $L=\text{PPh}_3$. Complex viewed along the C^1 -metal axis.

Inspection of the volatile components confirmed the presence of trimethylsilylmethanesulphonate by comparison of its ^1H n.m.r. spectrum with an authentic sample.¹³⁵

3-Trimethylsilyl-2-(chloromethyl)prop-1-ene (73) (0.2 g, 1.23 mmol) and trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (0.25 g, 0.32 mmol) under analogous conditions

gave the title complex (76) (0.045 g, 25%) and unreacted trans-
[IrCl(CO)(PPh₃)₂] (0.05 g).

[Ir{η⁴-C(CH₂)₃}Br(CO)(PPh₃)₂] (78)

Trans-[IrBr(CO)(PPh₃)₂] (0.5 g, 0.6 mmol) and (74) (0.4 g, 1.82 mmol) were refluxed in toluene (10 cm³) for 6h. The solvent was removed in vacuo and ethanol (5 cm³) was added to the residue. The white precipitate was filtered and washed with ethanol and diethyl ether, and dried in vacuo to give the title complex (0.28 g, 76%), m.p. 170°C (decomp.) (Found: C, 44.9; H, 3.5. C₂₃H₂₁BrIrOP requires C, 44.8; H, 3.4%); i.r. ν_{CO} 2030 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 1.14 [t, 1H, H², J(H²H⁵) = J(H²P) = 3.7], 2.29 [br d, 1H, H¹, J(H¹H⁴) 4.1], 2.42 [dd, 1H, H³, J(H³H⁶) 3.9, J(H³P) 6.2], 2.99 [d, 1H, H⁴, J(H⁴H¹) 4.1], 3.08 [dd, 1H, H⁵, J(H⁵H²) 3.7, J(H⁵P) 6.8], 3.18 [dd, 1H, H⁶, J(H⁶H³) 3.9, J(H⁶P) 7.3], and 7.55 [m, 15H, PPh₃]; ¹³C-{¹H} (100 MHz), δ 43.8 (s, C⁴), 52.9 [d, C², J(C²P) 36.5], 57.0 (s, C³), 107.8 (s, C¹), and 173.9 p.p.m. (s, CO). Figure 4, M=Ir, X=Br, L=PPh₃. Complex viewed along the C¹-metal axis.

[Ir{η⁴-C(CH₂)₃}Cl(CO)AsPh₃] (79)

Trans-[IrCl(CO)(AsPh₃)₂] (0.33 g, 0.37 mmol) and (74) (0.25 g, 1.14 mmol) in toluene (15 cm³) were warmed to reflux for 0.5h. After cooling the solvent was removed in vacuo and diethyl ether (10 cm³) was added. The cream coloured compound was filtered off and washed with diethyl ether and dried in vacuo to give the title complex (0.18 g, 77%), m.p. 138°C (decomp.) (Found: C, 44.6; H, 3.4. C₂₃H₂₁AsClIrO requires C, 44.8; H, 3.4%); i.r. ν_{CO} 2020, ν_{IrCl} 285 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 1.54 [d, 1H, H², J(H²H⁵) 3.4], 2.11 [d, 1H, H¹, J(H¹H⁴) 4.1], 2.72 [d, 1H, H³, J(H³H⁶) 3.9], 2.88 [d, 1H, H⁴, J(H⁴H¹) 4.1], 3.12 [d, 1H, H⁵, J(H⁵H²) 3.4], 3.19 [d, 1H, H⁶, J(H⁶H³) 3.9], and 7.5 [m, 15H, AsPh₃];

$^{13}\text{C}-\{^1\text{H}\}$ (100 MHz), δ 37.4 (s, C^4), 52.0 (s, C^2), 57.2 (s, C^3), 106.0 (s, C^1), and 174.4 p.p.m. (s, CO). Figure 4, $\text{M}=\text{Ir}$, $\text{X}=\text{Cl}$, $\text{L}=\text{AsPh}_3$.

$[\text{Ir}\{\eta^4-\text{C}(\text{CH}_2)_3\}\text{Cl}(\text{PPh}_3)_2]$ (80)

A solution of $[\text{Ir}_2(\text{COT})_4\text{Cl}_2]$ (0.5 g, 0.56 mmol) and PPh_3 (0.58 g, 2.2 mmol) was stirred under N_2 in benzene (40 cm^3). After five minutes (74) (0.38 g, 1.7 mmol) was added under N_2 . The solution was heated to reflux for 1.5h. The solvent was removed in vacuo and the residue was washed with light petroleum and chromatographed on alumina. Elution with dichloromethane gave a pale yellow band. Recrystallisation from CH_2Cl_2 /light petroleum gave large crystals of the title complex (0.41 g, 45%), m.p. 200°C (decomp.) (Found: C, 59.3; H, 4.9. $\text{C}_{40}\text{H}_{36}\text{ClIrP}_2$ requires C, 59.6; H, 4.5%); i.r. ν_{IrCl} 260 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 0.81 [t, 2H, H^1 , $\text{J}(\text{H}^1\text{H}^3) = \text{J}(\text{H}^1\text{P}) = 3.8$], 2.1 [1:2:4:4:2:1 sextet 2H, H^2 , AA'XX' system, $\text{J}(\text{H}^2\text{H}^{2'})$ 3.7, $\text{J}(\text{PP}')$ 0.0, $\text{J}(\text{H}^2\text{P})$ 6.65, $\text{J}(\text{H}^{2'}\text{P})$ -5.3], 2.9 [dd, 2H, H^3 , $\text{J}(\text{H}^3\text{H}^1)$ 3.8, $\text{J}(\text{H}^3\text{P})$ 6.9], and 7.55 [m, 30H, PPh_3]; $^{13}\text{C}-\{^1\text{H}\}$ (100 MHz), δ 39.0 [s, C^3], 55.3 [dd, C^2 , AXX', $|\text{J}(\text{C}^2\text{P}) + \text{J}(\text{C}^2\text{P}')|$ 42.6, $\text{J}(\text{PP}')$ 0], and 104.5 [t, C^1 , $\text{J}(\text{C}^1\text{P})$ 3.0]; $^{31}\text{P}-\{^1\text{H}\}$, δ 0.20 p.p.m.

Figure 5, $\text{M}=\text{Ir}$, $\text{L}=\text{PPh}_3$.

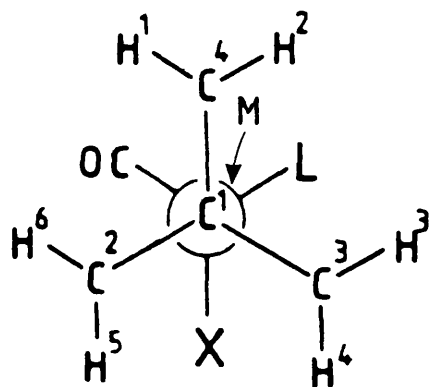


FIGURE 4

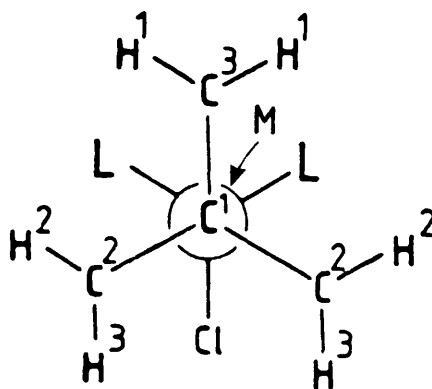


FIGURE 5

[Rh{ η^3 -CH₂C(CH₂SiMe₃)CH₂}Cl(CO)(PMe₂Ph)₂]BPh₄ (81)

(74) (0.75 g, 3.38 mmol) was added to a stirred suspension of trans-[RhCl(CO)(PMe₂Ph)₂] (0.5 g, 1.14 mmol) in methanol (5 cm³). The suspension immediately dissolved leaving a dark red-brown solution.

NaBPh₄ (0.4 g, 1.17 mmol) in methanol (2 cm³) was added and immediately a yellow precipitate formed which was filtered and washed with water, methanol, and diethyl ether, and dried in vacuo to give the title complex (0.81 g, 80%), m.p. 114-115°C (Found: C, 65.3; H, 6.4.

C₄₈H₅₇BClOP₂RhSi requires C, 64.8; H, 6.5%); i.r. ν_{CO} 2070 cm⁻¹; n.m.r.

(CD₂Cl₂): ¹H (400 MHz), δ 0.38 (s, 9H, SiMe₃), 1.80 [d, 6H, PMe₂Ph, |²J(PH) + ⁴J(PH)|11.2], 1.86 [br s, 2H, CH₂-SiMe₃], 1.88 [d, 6H, PMe₂Ph, |²J(PH) + ⁴J(PH)|7.3], 3.52 [d, 2H, H², J(H²P) 9.4], 4.12 [d, 2H, H¹, J(H¹P) 3.3], 7.13 (m, 10H, PPhMe₂), and 7.6 (m, 20H, BPh₄); ¹³C-{¹H} (100 MHz), δ 2.1 (s, SiMe₃), 13.9 [d, second order, Me, PMe₂Ph, |¹J(PC) + ³J(PC)|35.5], 17.0 [d, second order, Me, PMe₂Ph, |¹J(PC) + ³J(PC)|35.5], 31.9 (s, C³), 69.3 (m, C², AMXX' system), 145.3 (m, C¹), and 182.7 [dt, CO, J(CRh) 62.3, J(CP) 10.1]; ³¹P-{¹H} (162 MHz), δ -2.48 p.p.m. [d, J(PRh) 101]. Figure 6.

[Rh{ η^3 -CH₂C(CH₂SiMe₃)CH₂}Cl(CO)(PMe₃)₂]BPh₄ (82)

(74) (0.75 g, 3.38 mmol), trans-[RhCl(CO)(PMe₃)₂] (0.33 g, 1.3 mmol), and NaBPh₄ (0.6 g) in methanol (5 cm³), under analogous conditions, gave the title complex (0.64 g, 64%), m.p. 118°C (decomp.) (Found: C, 59.7; H, 7.0. C₃₈H₅₃BClOP₂RhSi requires C, 59.7; H, 7.0%); i.r. ν_{CO} 2080 cm⁻¹; n.m.r. (CDCl₃): ¹H (300 MHz), δ 0.23 (s, 9H, SiMe₃), 1.31 [d, 18H, PMe₃, |²J(PH) + ⁴J(PH)|11.3], 1.67 (s, 2H, CH₂-SiMe₃), 3.16 [d, 2H, H², J(H²P) 9.5], 3.93 [br d, 2H, H¹, J(H¹P) 3.5], and 7.3 (m, 20H, BPh₄); ³¹P-{¹H} (24 MHz), δ -6.55 p.p.m. [d, J(PRh) 102.5].

Reaction of trans-[RhCl(CO)(PMe₂Ph)₂] with (74)

(74) (0.75 g, 3.38 mmol) was added to a stirred suspension of trans-[RhCl(CO)(PMe₂Ph)₂] (0.5 g, 1.14 mmol) in methanol (5 cm³). The suspension immediately dissolved. After stirring for 0.5h the solvent was removed in vacuo. The residue was washed with light petroleum and a yellow solid formed. The solution was filtered and the yellow solid washed with light petroleum. After about five minutes under nitrogen the yellow solid became oily and the ¹H and ³¹P-{¹H} n.m.r. indicated that both (74) and trans-[RhCl(CO)(PMe₂Ph)₂] were present in solution.

[Rh{η⁴-C(CH₂)₃} (CO)(PMe₂Ph)₂]BPh₄ (83)

Sodium fluoride (0.06 g, 1.4 mmol) was added to a solution of complex (81) (0.05 g, 0.056 mmol) in aqueous methyl cyanide (5 cm³). After standing for 12h at room temperature the solvent was removed in vacuo and the residue extracted with dichloromethane (15 cm³) and dried over anhydrous potassium carbonate. The solvent was removed in vacuo and ¹H and ³¹P n.m.r. spectra showed complete reaction. Recrystallisation from dichloromethane/diethyl ether afforded pale yellow needles of the title complex (0.035 g, 80% recovered), m.p. 108-109°C (Found: C, 68.7; H, 6.2. C₄₅H₄₈BOP₂Rh requires C, 69.2; H, 6.2%); i.r. ν_{CO} 2058 cm⁻¹; n.m.r. (CDCl₃): ¹H (300 MHz), δ 1.22 [m, second order, 6H, PMe₂Ph, |²J(PH) + ⁴J(PH)| 8.8], 1.32 [m, second order, 6H, PMe₂Ph, |²J(PH) + ⁴J(PH)| 8.5], 1.86 [br d, 2H, second order AA'XX', H², |J(H²P) + J(H²P')| 1.6], 2.13 [dd, 2H, H¹, J(H¹H³) 4.2, J(H¹P) 6.3], 2.65 [dd, 2H, H³, J(H³H¹) 4.2, J(H³P) 6.7], and 7.5 [m, 30H, PPhMe₂ and BPh₄⁻]; ¹³C-{¹H} (75 MHz), δ 17.0 to 19.0 [m, PMe₂Ph, AMXX' system], 60.6 [1:1:3:3:3:3:3:-3:1:1, dectet, AMXX', C², J(CP) -28, J(CP') 5, J(CRh) 5.7, J(PRh) 132, J(P'Rh) 132, J(PP') 17], 62.7 [d, C³, J(C³Rh) 7.5], 112.3 [dt, C¹, J(C¹Rh) 3.3, J(C¹P) 5.0], and 190.0 [dt, CO, J(CRh) 63.3, J(CP) 10.7];

$^{31}\text{P}-\{^1\text{H}\}$, δ 4.13 p.p.m. [d, $J(\text{PRh})$ 131.8]. Figure 7, $\text{M} = \text{Rh}$, $\text{L} = \text{PMe}_2\text{Ph}$, $\text{X} = \text{BPh}_4$.

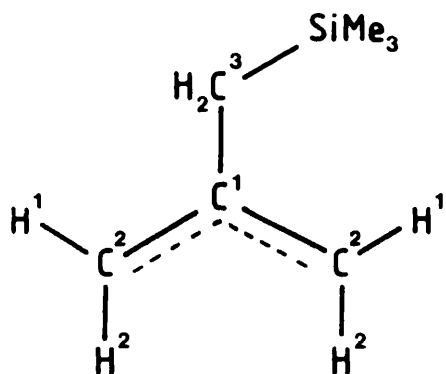


FIGURE 6

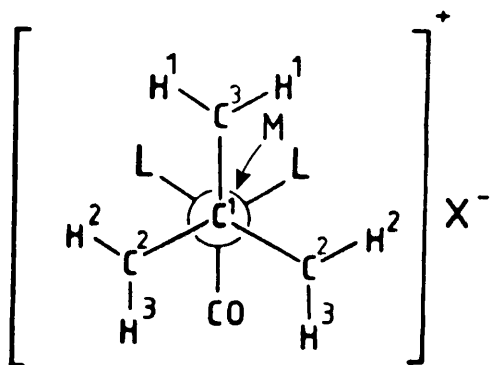


FIGURE 7

Reaction of $\text{trans-}[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ with (74)

(74) (0.6 g, 2.8 mmol) was added to a stirred solution of trans-
 $[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ (0.5 g, 0.94 mmol) in methanol (7 cm^3). After two
minutes NaBPh_4 (0.35 g, 1.02 mmol) in methanol (5 cm^3) was added to the
pale yellow solution. The white precipitate was filtered and washed
with methanol and dried in vacuo (0.6 g, 70%), m.p. 168-170°C (decomp.)
i.r. ν_{CO} 2050 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (90 MHz), δ 1.7 [d, PMe_2Ph ,
 $|^2J(\text{PH}) + ^4J(\text{PH})| 10.5]$, 1.85 [d, PMe_2Ph , $|^2J(\text{PH}) + ^4J(\text{PH})| 10.5]$, 2.2 [s,
3H, CH_3], 3.0 [d, 2H, CH (anti) $J(\text{HP})$ 6.8], 3.8 [br s, 2H, CH (syn)],
and 7.5 p.p.m. [m, 30H, BPh_4 , PPhMe_2].

The hydrogen-1 n.m.r. is identical to that of $[\text{Ir}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2\}\text{-(Cl)(CO)(PMe}_2\text{Ph})_2]\text{BPh}_4$.⁸⁸

$[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{OS}(\text{O})_2\text{Me}$ (85)

$[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ (0.46 g, 0.45 mmol) and (74) (0.31 g, 1.4 mmol) were
warmed in toluene (15 cm^3) until complete formation of the white solid
had occurred (ca. 1h). The solution was cooled and the product was
filtered and washed with light petroleum to give the title complex
(0.36 g, 90%). Recrystallisation from dichloromethane and light
petroleum afforded white needles which crystallised with 0.75 mol.

equivalents of dichloromethane (as seen by ^1H n.m.r.), m.p. 107-109°C (Found: C, 53.4; H, 4.6. $\text{C}_{42}\text{H}_{39}\text{IrO}_4\text{P}_2\text{S}$. 0.75 CH_2Cl_2 requires C, 53.6; H, 4.3%); i.r. ν_{CO} 2040 cm^{-1} ; n.m.r. (CDCl_3): ^1H (90 MHz), δ 2.0 [1:2:6:2:1 quintet, 2H, H^2 , AA'XX' system, $J(\text{H}^2\text{H}^{2'})$ 4.1, $J(\text{PP}')$ 0.0, $J(\text{H}^2\text{P}) = -J(\text{H}^{2'}\text{P}) = \pm 5.8$], 2.3 [dd, 2H, H^1 , $J(\text{H}^1\text{H}^3)$ 4.1, $J(\text{H}^1\text{P})$ 6.5], 2.8 [s, 3H, MeSO_3], 3.3 [dd, 2H, H^3 , $J(\text{H}^3\text{H}^1)$ 4.1, $J(\text{H}^3\text{P})$ 6.4], and 7.5 [m, 30H, PPh_3]; ^{31}P - $\{^1\text{H}\}$, δ -2.42 p.p.m. Figure 7, M=Ir, L= PPh_3 , X= $\text{OS}(\text{O})_2\text{Me}$.

$[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85, X= PF_6)

Trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, (1.0 g, 1.28 mmol), KPF_6 (0.4 g, 2.0 mmol) and (73) (0.6 g, 3.7 mmol) in methylcyanide (20 cm^3) and toluene (20 cm^3) were refluxed for 12h. The solvent was removed in vacuo and the residue dissolved in methyl cyanide (30 cm^3) and unchanged trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ (0.16 g) was filtered off. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and the potassium salts were filtered off. The solvent was removed in vacuo and the product recrystallised from hot ethanol to give the title complex (0.7 g, 58%) (Found: C, 51.7; H, 4.0. $\text{C}_{41}\text{H}_{36}\text{F}_6\text{IrOP}_3$ requires C, 52.2; H, 3.8%); i.r. ν_{CO} 2040 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 2.02 [1:2:6:2:1 quintet, 2H, H^2 , AA'XX' system, $J(\text{H}^2\text{H}^{2'})$ 4.1, $J(\text{PP}')$ 0, $J(\text{H}^2\text{P}) = -J(\text{H}^{2'}\text{P}) = \pm 5.8$], 2.27 [dd, 2H, H^1 , $J(\text{H}^1\text{H}^3)$ 4.1, $J(\text{H}^1\text{P})$ 6.5], 3.26 [dd, 2H, H^3 , $J(\text{H}^3\text{H}^1)$ 4.1, $J(\text{H}^3\text{P})$ 6.4], and 7.5 [m, 30H, PPh_3]; ^{13}C - $\{^1\text{H}\}$ (100 MHz), δ 54.9 [d, C^2 , $J(\text{C}^2\text{P})$ 29.8], 58.5 (s, C^3), 108.2 [s, C^1], and 172.2 p.p.m. (s, CO). Figure 7, M=Ir, L= PPh_3 , X= PF_6 .

$[\text{Ru}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{NO})(\text{PPh}_3)]$ (87)

$[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ (0.6 g, 0.58 mmol) suspended in benzene was reduced using a Zn/Cu couple.¹³¹ The solution containing $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$ (0.58 mmol) was filtered and (74) (0.39 g, 1.7 mmol) was added. The

green colour gradually disappeared. After stirring for 14h the solvent was removed in vacuo. The residue was washed with light petroleum and diethyl ether. The residue was chromatographed on an alumina column.

Elution with dichloromethane produced an orange band which on addition of light petroleum gave the title complex (0.06 g, 20%), m.p. 129°C

(decomp.) (Found: C, 54.2; H, 4.4; N, 2.9. $C_{22}H_{21}ClNOPRu$ requires C, 54.7; H, 4.4; N, 2.9%); i.r. ν_{NO} 1775, ν_{RuCl} 280 cm^{-1} ; n.m.r.

(CD_2Cl_2): 1H (400 MHz), δ 2.13 [d, 1H, H^1 , $J(H^1H^4)$ 5.2], 2.18 [t, 1H, H^2 , $J(H^2H^5) = J(H^2P) = 3.5$], 2.34 [dd, 1H, H^3 , $J(H^3H^6)$ 4.4, $J(H^3P)$ 9.2], 2.49 [d, 1H, H^4 , $J(H^4H^1)$ 5.2], 3.38 [dd, 1H, H^6 , $J(H^6H^3)$ 4.4, $J(H^6P)$ 6.7], 3.44 [dd, 1H, H^5 , $J(H^5H^2)$ 3.5, $J(H^5P)$ 5.1], and 7.5 [m, 15H, PPh_3]; ^{13}C - $\{^1H\}$ (100 MHz), δ 58.9 (s, C^3 or C^4), 67.4 [d, C^2 , $J(C^2P)$ 28.8], 77.2 (s, C^3 or C^4), and 117.8 p.p.m. (s, C^1). Figure 8, M=Ru, either X=Cl, Y=NO or X=NO, Y=Cl.

$[Os\{\eta^4-C(CH_2)_3\}Cl(NO)(PPh_3)]$ (88)

$[OsCl(NO)(PPh_3)_3]$ (~0.94 g, 0.9 mmol) and (74) (0.6 g, 2.7 mmol) were stirred in benzene (20 cm^3). The green suspension dissolved after twenty minutes to give an orange solution. The solvent was reduced in vacuo to about 1 cm^3 . Light petroleum (35 cm^3) was added and the suspension was filtered to give an orange solution. The solvent was removed in vacuo and the residue stirred with light petroleum. The crude solid obtained was chromatographed on a short alumina column. Elution with dichloromethane gave an orange band which on addition of light petroleum gave the title complex (0.1 g, 20%), m.p. 187-189°C (decomp.) (Found: C, 46.9; H, 3.9; N, 2.1. $C_{22}H_{21}ClNOOsP$ requires C, 46.2; H, 3.7; N, 2.4%); i.r. ν_{NO} 1770, ν_{OsCl} 290 cm^{-1} ; n.m.r. ($CDCl_3$): 1H (300 MHz), δ 1.85 [dd, 1H, H^3 , $J(H^3H^6)$ 5.0, $J(H^3P)$ 9.4], 1.99 [d, 1H, H^4 , $J(H^4H^1)$ 5.5], 2.09 [d, 1H, H^1 , $J(H^1H^4)$ 5.5], 2.68 [br t, 1H, H^2 , $J(H^2H^5) = J(H^2P) = 3.0$], 3.26 [t,

1H , H^6 , $J(\text{H}^6\text{H}^3) = J(\text{H}^6\text{P})$ 5.0], 3.61 [t, 1H , H^5 , $J(\text{H}^5\text{H}^2) = J(\text{H}^5\text{P}) = 3.0$], and 7.5 [m, 15H , PPh_3]; $^{13}\text{C}\{-^1\text{H}\}$ (75 MHz), δ 46.3 (s, C^3 or C^4), 60.1 [d, C^2 , $J(\text{C}^2\text{P})$ 27.6], 66.9 (s, C^3 or C^4), and 114.6 p.p.m. (s, C^1).

Figure 8, $\text{M}=\text{Os}$, either $\text{X}=\text{Cl}$, $\text{Y}=\text{NO}$ or $\text{X}=\text{NO}$, $\text{Y}=\text{Cl}$.

$[\text{Rh}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{PPh}_3)_2]$ (89)

A solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.29 g, 0.31 mmol) and (74) (0.5 g, 2.25 mmol) was heated in benzene (5 cm^3) until there was complete dissolution of the starting material. The solvent was removed in vacuo and the residue washed with light petroleum. Addition of methanol (10 cm^3) caused a yellow solid to precipitate out which was washed with light petroleum to give the title complex (0.11 g, 50%); n.m.r. (CD_2Cl_2): ^1H (300 MHz), δ 0.94 [t, 2H , H^1 , $J(\text{H}^1\text{H}^3) = J(\text{H}^1\text{P}) = 3.6$], 2.23 [br d, $\text{AA}'\text{XX}'$, 2H , H^2 , $|J(\text{H}^2\text{P}) + J(\text{H}^2\text{P}')|$ 3.3], 3.10 [dd, 2H , H^3 , $J(\text{H}^3\text{H}^1)$ 3.6, $J(\text{H}^3\text{P})$ 9.6], and 7.55 [m, 30H , PPh_3]; $^{13}\text{C}\{-^1\text{H}\}$ (75 MHz), δ 56.7 [d, C^3 , $J(\text{C}^3\text{Rh})$ 13.4], 64.4 [1:3:1:0.5:0.5:1:3:1 octet, AMXX' , C^2 , $J(\text{CP})$ -26, $J(\text{CP}')$ 5, $J(\text{CRh})$ 7, $J(\text{PRh})$ 151, $J(\text{P}'\text{Rh})$ 151, $J(\text{PP}')$ 5], and 111.1 [dt, C^1 , $J(\text{C}^1\text{Rh})$ 3.7, $J(\text{C}^1\text{P})$ 5.4]; $^{31}\text{P}\{-^1\text{H}\}$, δ 28.7 p.p.m. [d, $J(\text{PRh})$ 151.4]. Figure 5, $\text{M}=\text{Rh}$, $\text{L}=\text{PPh}_3$.

$[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (75)

A suspension of $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ (0.8 g, 0.77 mmol) in benzene (15 cm^3) and (74) (0.57 g, 2.56 mmol) were refluxed for 12h. A white solid was filtered off (0.18 g) (which has yet to be identified). The solvent was removed in vacuo from the mother liquor and methanol (5 cm^3) was added to the oily residue. The white product was filtered and washed with methanol and light petroleum to give the title complex (0.16 g, 35%), m.p. 145°C (Found: C, 50.8; H, 3.6. $\text{C}_{24}\text{H}_{21}\text{O}_2\text{OsP}$ requires C, 51.2; H, 3.7%); i.r. ν_{CO} 2000, 1935 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 1.04 [dd, 2H , H^3 , $J(\text{H}^3\text{H}^1)$ 4.2, $J(\text{H}^3\text{P})$ 6.6], 2.06 [s, 2H , H^2], 2.07 [t, 2H , H^1 , $J(\text{H}^1\text{H}^3) = J(\text{H}^1\text{P}) = 4.2$], and 7.5 [m, 15H , PPh_3]; $^{13}\text{C}\{-^1\text{H}\}$

(100 MHz), δ 34.4 [d, C², J(C²P) 23.2], 44.1 [d, C³, J(C³P) 2.4], 107.5 (s, C¹), and 185.2 p.p.m. [d, CO, J(CP) 2.4]. Figure 9, M=Os, L=PPh₃.

The title complex (75) was obtained in 11% yield from the reaction of [Os(CO)₂(PPh₃)₃] and (47) under analogous conditions used in the above preparation.

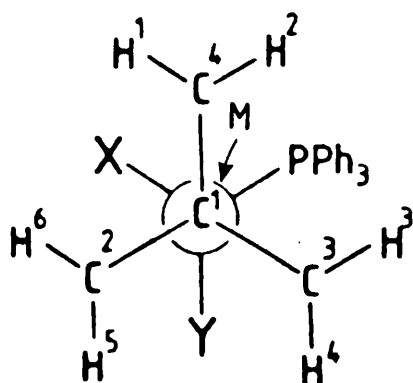


FIGURE 8

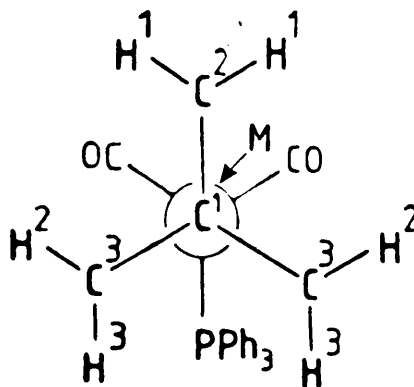


FIGURE 9

Reactions of methylenecyclopropane

(i) A solution of [Os(CO)₂(PPh₃)₃] (0.5 g, 0.5 mmol) and methylenecyclopropane (0.2 g, 3.7 mmol) in benzene (10 cm³) was sealed in a Carius tube and heated to 95°C for 2h. The solvent was removed in vacuo and washed with diethyl ether. The residue was recrystallised from dichloromethane/diethyl ether to give white microcrystals of [Os{η²-CH₂:CCH₂CH₂} (CO)₂(PPh₃)₂] (90) (0.32 g, 76%), m.p. 140°C (Found: C, 61.7; H, 4.7. C₄₂H₃₆OsO₂P₂ requires C, 61.2; H, 4.4%); i.r. ν_{CO} 1955, 1885 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ -0.29 [br t, 2H, J(HH) 3.9], 0.08 [t, 2H, CH₂:C, J(HP) 7.0], 0.31 [br t, 2H, J(HH) 3.9], and 7.4 p.p.m. (m, 30H, PPh₃).

(ii) Trans-[IrCl(CO)(PPh₃)₂] (0.44 g, 0.56 mmol) and methylenecyclopropane (0.17 g, 3.1 mmol) in benzene (15 cm³) were heated to 90°C for 72h in a sealed tube. Addition of light petroleum gave yellow crystals identified as trans-[IrCl(CO)(PPh₃)₂] (0.4 g, 91%).



CHAPTER 3

Reactions of η^4 -Trimethylenemethane
Metal Complexes: An Initial Study

3.1 INTRODUCTION

Many new trimethylenemethane iridium complexes can be prepared by modifying those that have been synthesised in Chapter 2. Strictly this comes under the heading of reactivity. This Chapter describes the reaction of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) with silver hexafluorophosphate which, in the presence of various donor ligands, yields a series of cationic trimethylenemethane complexes. The reactions of trimethylenemethane complexes with neutral and anionic nucleophiles, and with electrophiles are also investigated.

3.2 REACTIONS OF $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) WITH SILVER HEXAFLUOROPHOSPHATE

The ability of silver(I) salts to abstract chloride ions from platinum group metal compounds has found extensive use, particularly in the synthesis of cationic complexes.¹³⁶⁻¹³⁸ The iridium complex (76) reacts with silver hexafluorophosphate to give the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{-(solvent)}(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (91, solvent = acetone), (92, solvent = methyl cyanide), and silver chloride is precipitated. The methyl cyanide solvate (92) could be isolated and characterised but the acetone solvate (91) was too unstable to isolate. On removal of the solvent metallic deposits were formed indicating that the solvate (91) was decomposing. Evidence for the presence of (91) was obtained by carrying out the reaction in $[\text{}^2\text{H}_6]\text{-acetone}$. The $^1\text{H-n.m.r.}$ spectrum showed complete reaction of the starting $\eta^4\text{-trimethylenemethane}$ complex (76) and the presence of a new $\eta^4\text{-trimethylenemethane}$ complex (91).

The i.r. spectrum of the methyl cyanide complex (92) exhibits a weak carbon-nitrogen stretching frequency at 2340 cm^{-1} . This is higher than the value of 2250 cm^{-1} found for the free ligand and is similar to the

values observed for other methyl cyanide complexes.^{136,139} The carbonyl stretching frequencies of the complexes (91) and (92) are 2045 and 2060 cm^{-1} respectively and are slightly higher than the value of 2030 cm^{-1} seen for the complex (76). The ^1H n.m.r. spectra of (91) and (92) showed the expected features for a static η^4 -trimethylenemethane ligand. The ^1H n.m.r. of the complex (92) also exhibited a singlet at δ 2.25 p.p.m. attributed to the co-ordinated methyl cyanide ligand.

The presence of both a positive charge and a weakly co-ordinated solvent ligand would be expected to enhance ligand substitution reactions at the metal centre of the solvate complexes (91) and (92). Thus treatment of (76) with silver hexafluorophosphate in acetone under an atmosphere of carbon monoxide afforded the cationic complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (93) in high yield. Similarly treating a solution of the acetone solvate (91) with ethene gave the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (94). No complex could be isolated from the reaction of ethyne with the solvate complex (91). However, 3-butyne-1-ol reacted with a solution of the acetone solvate (91) and afforded the carbene complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^1\text{-}\overline{\text{C}(\text{CH}_2)_3\text{O}})(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (95). Platinum(II), rhodium(III), and iridium(III) complexes of this cyclic alkoxy carbene ligand have previously been generated from 3-butyne-1-ol.^{137,138} A single-crystal X-ray diffraction study of (95) confirmed the presence of a cyclic carbene ligand together with an η^4 -trimethylenemethane fragment. The molecular structure of complex (95) is depicted in Figure 10 but, due to disorder of the PF_6 and slow decomposition of the crystal, the data is not of sufficient accuracy to quote any bond lengths or angles. However, Figure 10 indicates that the trimethylenemethane fragment adopts the usual staggered 'umbrella' arrangement about the metal atom.^{27,121} Scheme 30 summarises these reactions.

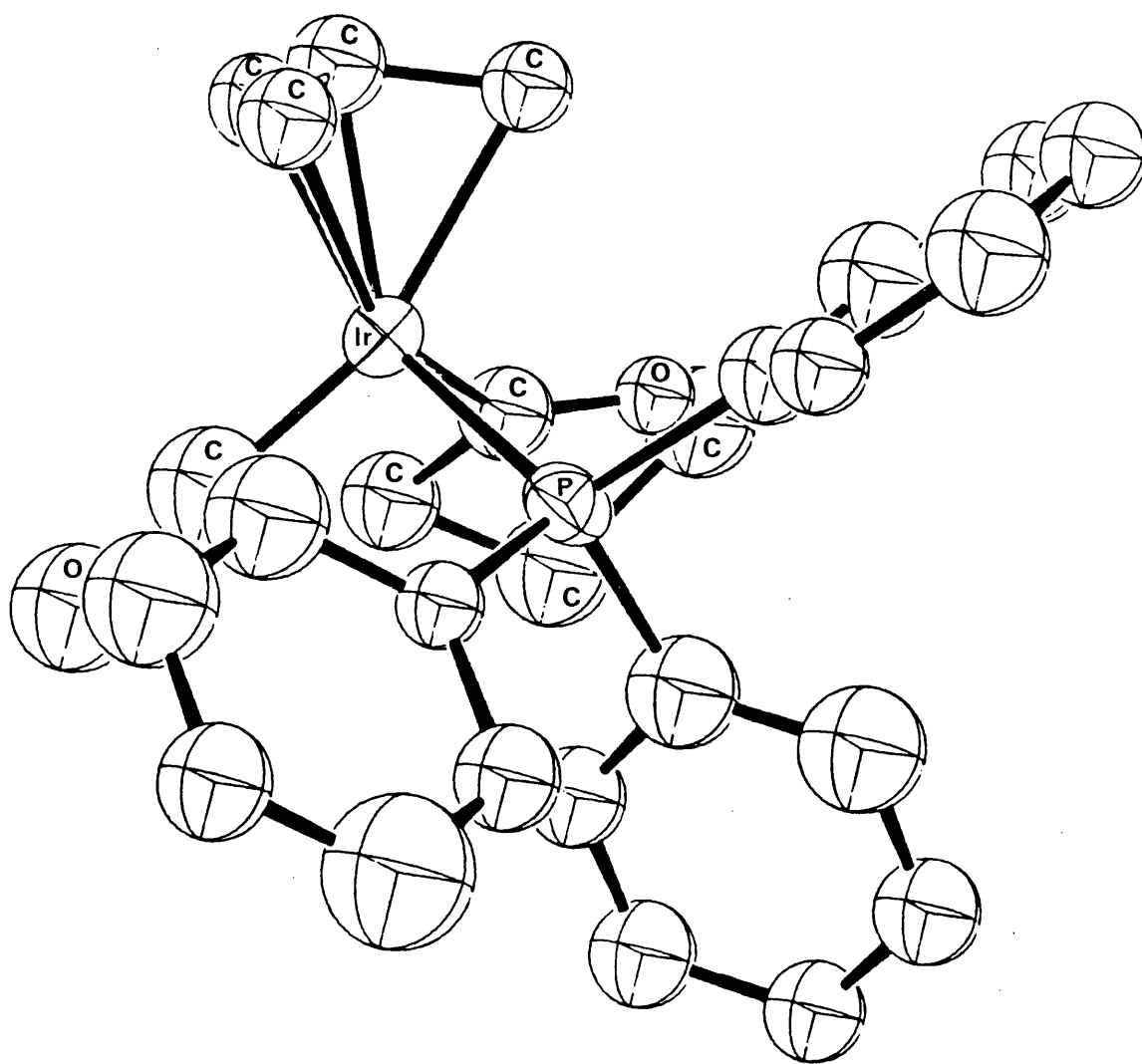
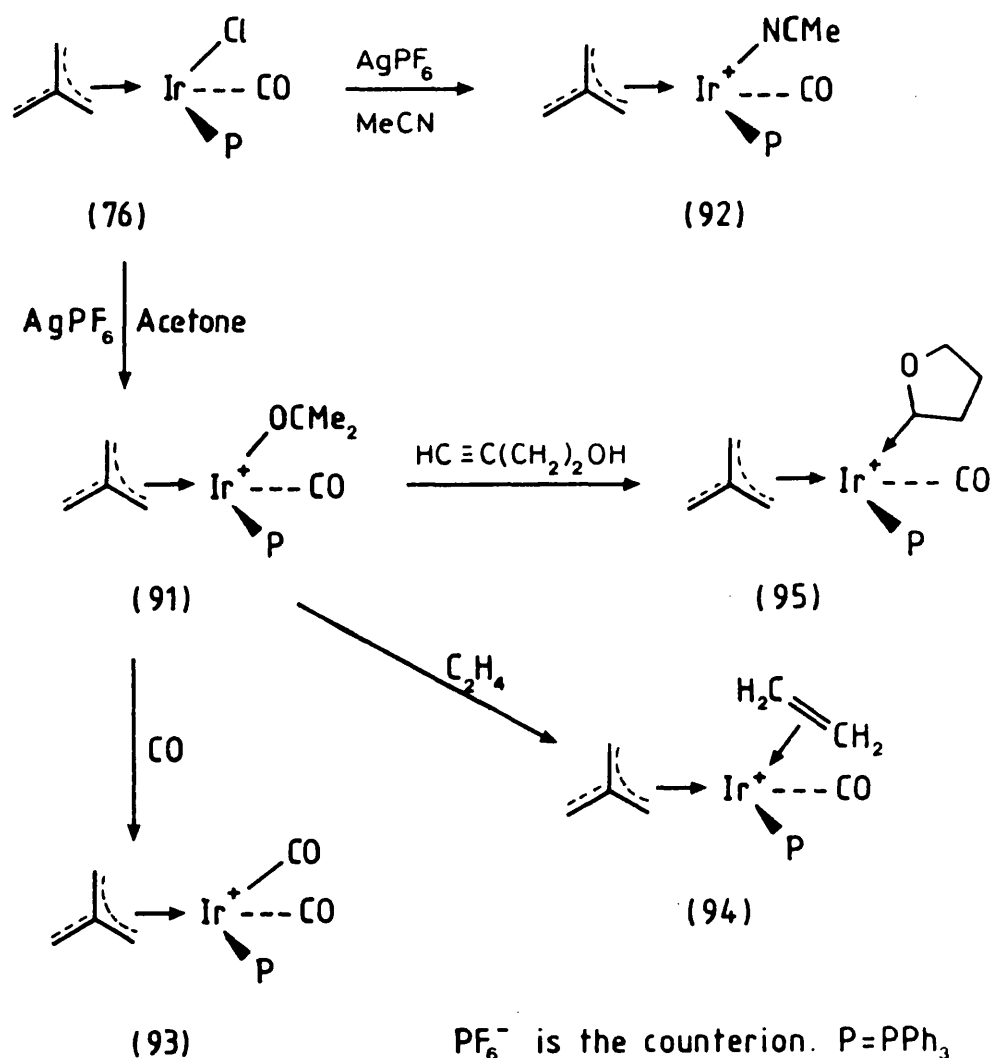


FIGURE 10

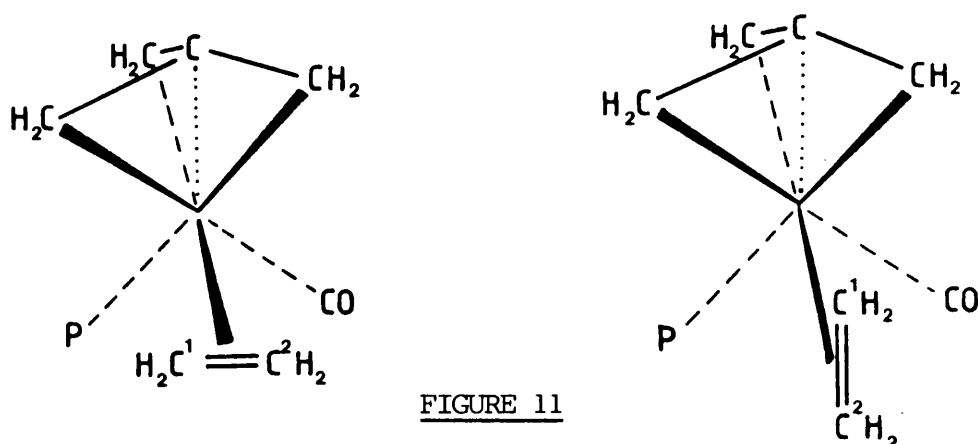
Molecular structure of (95) with hydrogens omitted for clarity.



Scheme 30

All of these complexes gave the characteristic ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra expected for a static η^4 -trimethylenemethane fragment. The ^1H n.m.r. spectrum of the ethene complex (94) exhibited a complex multiplet due to the co-ordinated ethene ligand. Figure 11 shows two possible orientations of the ethene fragment relative to the other ligands. These orientations are similar to those considered for the arrangement of the alkene in the cation $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-C}_2\text{H}_4)(\text{CO})_2]^+$.¹⁴⁰ In both arrangements the two carbon atoms of the ethene fragment are inequivalent. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum of (94) exhibited a singlet assigned to the ethene fragment and this would suggest that the ethene ligand is rapidly

rotating on the n.m.r. time scale.¹¹⁸



The ^1H n.m.r. spectrum of (94) was recorded at -90°C but, apart from a temperature shift, remained unchanged indicating a low barrier to rotation of the η^2 -ethene ligand.

The methyl cyanide ligand in the complex (92) is readily displaced. Thus treatment of (92) with triphenylphosphine or triphenylarsine afforded the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{L})(\text{PPh}_3)]\text{PF}_6$ (85, $\text{L} = \text{PPh}_3$), (96, $\text{L} = \text{AsPh}_3$), whilst the reaction of (92) with phenylethyne in the presence of triethylamine gave the neutral phenylacetylide complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^1\text{-C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)]$ (97). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of (97) exhibited the expected features of a static η^4 -trimethylenemethane fragment and the i.r. spectrum shows a strong band at 2125 cm^{-1} due to the carbon-carbon stretching frequency of the acetylide ligand.¹⁴¹ Phenylethyne did not react with (92) in the absence of triethylamine, the methyl cyanide complex (92) was recovered unchanged.

Similar reactions of silver(I) salts with other η^4 -trimethylenemethane metal complexes which contain a halide ligand may be expected to yield cationic trimethylenemethane complexes. Thus the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{PPh}_3)_2]$ (80) reacted rapidly with silver hexafluorophosphate in methyl cyanide to afford the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{NCMe})(\text{PPh}_3)_2]\text{PF}_6$ (98) in high yield.

3.3 REACTIONS OF CATIONIC η^4 -TRIMETHYLENEMETHANE METAL COMPLEXES

The cationic complex $[\text{Mo}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]\text{BF}_4$ (28) has been shown to react with nucleophiles. Nucleophilic attack at the coordinated η^4 -trimethylenemethane ligand occurs and results in the formation of neutral η^3 -allyl complexes,²⁷ see Chapter 1. It was therefore of interest to investigate the reactions of various neutral and anionic nucleophiles with the cationic η^4 -trimethylenemethane metal complexes prepared in the present studies and compare the results with the reactions of molybdenum trimethylenemethane complexes.

Reactions with neutral nucleophiles

The cationic complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) reacted rapidly at room temperature with various tertiary phosphine ligands. Treatment of (85) with 1 mole equivalent of methyldiphenylphosphine afforded an inseparable 1:1:1 mixture of the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)_2]\text{PF}_6$ (99), $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)(\text{PPh}_3)]\text{PF}_6$ (100), and $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85). The presence of the three complexes was confirmed by the ^1H , $^{13}\text{C}\{-^1\text{H}\}$ and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum of the mixture revealed three triplets associated with the central carbon of the trimethylenemethane fragment each coupling to two phosphorus-31 nuclei. The complex (85) reacted rapidly with 2 mole equivalents of methyldiphenylphosphine to afford the complex (99) in high yield. The complex (99) did not react with an excess of methyldiphenylphosphine even on prolonged reflux in ethanol. In a similar manner the complex (85) reacted with 1,2-bis-(diphenylphosphino)ethane (dppe) to afford $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{dppe})]\text{PF}_6$ (101). The complex (85) did not react with nitrogen nucleophiles such as pyridine or N,N'-dimethylaniline even after prolonged reflux in methyl

cyanide.

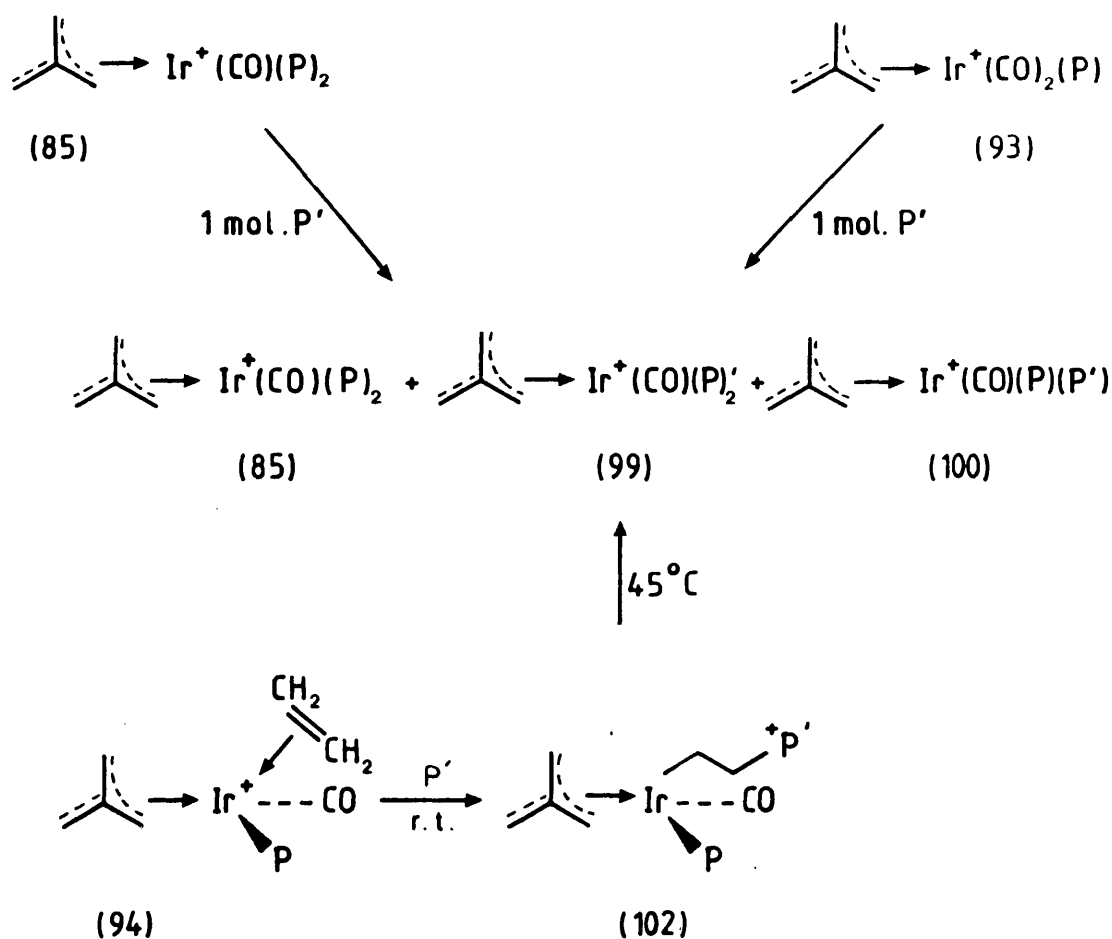
The bis-carbonyl complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (93) also reacted rapidly with tertiary phosphines with the displacement of a carbonyl ligand. Thus treatment of (93) with 1 mole equivalent of methyldiphenylphosphine afforded a 1:1:1 mixture of the complexes (85), (99), and (100). This suggests that the phosphine ligands in these complexes are labile in the presence of a free tertiary phosphine. However, four singlet resonances in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of the mixture of (85), (99), and (100) indicates that there is not rapid exchange of the phosphine ligands in solution. Triphenylphosphine also displaced a carbonyl ligand from (93) and afforded (85) in high yield although triphenylarsine did not react with (93) presumably due to the bulk of the arsine donor.

The ethene complex (94) reacted with methyldiphenylphosphine. The reaction was followed by ^1H n.m.r. and showed the disappearance of the multiplet associated with the η^2 -ethene fragment and the appearance of two complex multiplets centred at δ 1.2 and 2.76 assignable to the IrCH_2 and CH_2P protons of the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CH}_2\text{CH}_2\text{PMePh}_2)(\text{CO})(\text{PPh}_3)]\text{-PF}_6$ (102). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum confirmed the presence of two phosphorus nuclei. The resonance at δ 0.4 has been assigned to the triphenylphosphine ligand co-ordinated to the iridium since similar values were observed for the triphenylphosphine ligand in the ethene complex (94) and the acetylide complex (97) and is considerably different to the shifts observed for the methyldiphenylphosphine ligand in the complex (99). The resonance at δ 11.5 is consistent with the presence of a quaternised methyldiphenylphosphine fragment.¹⁴² The ^1H n.m.r. of (102) showed the characteristic features of an η^4 -trimethylenemethane ligand. Two of the trimethylenemethane hydrogens appear as doublets due to

proton-proton coupling. The absence of phosphorus coupling to these two protons confirms that there is only one phosphine ligand co-ordinated to the iridium, see Chapter 2.

The formation of (102) from (94) may be regarded as proceeding via nucleophilic attack on the co-ordinated ethene. This attack on the ethene fragment is predicted by the 'rules' laid out for nucleophilic addition to organo-transition metal cations containing unsaturated hydrocarbon ligands.¹⁴³ Although ethene and trimethylenemethane are even open polyenes, trimethylenemethane has unpaired electrons in its HOMO and therefore, according to these 'rules', nucleophilic addition to other even polyenes is preferred hence the phosphine attacks the ethene ligand rather than the trimethylenemethane fragment. Similar reactions of co-ordinated ethene with phosphine nucleophiles have been observed previously.¹⁴⁴ On warming a solution of the complex (102) to 45°C a 1:1:1 mixture of the three trimethylenemethane complexes (85), (99), and (100) formed, presumably with the evolution of ethene, Scheme 31.

These reactions of neutral nucleophiles with various η^4 -trimethylenemethane complexes show that the trimethylenemethane ligand is strongly co-ordinated to the metal. Thus, displacement of other co-ordinated ligands such as triphenylphosphine, carbon monoxide, and ethene occurs in preference to attack at, or displacement of the trimethylenemethane ligand. This is in contrast to the work of Kane-Maguire who studied a wide range of organometallic substrates which appeared to undergo nucleophilic attack by tertiary phosphines at the π -hydrocarbon ligand in preference to attack at the metal unless a particularly labile ligand such as acetone was present.¹⁴⁵ However in certain cases, such as the reactions of trialkylphosphines with the cations $[\text{Mn}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]^+$ ¹⁴⁶



$\text{P} = \text{PPh}_3$ PF_6^- is the counterion
 $\text{P}' = \text{PMePh}_2$

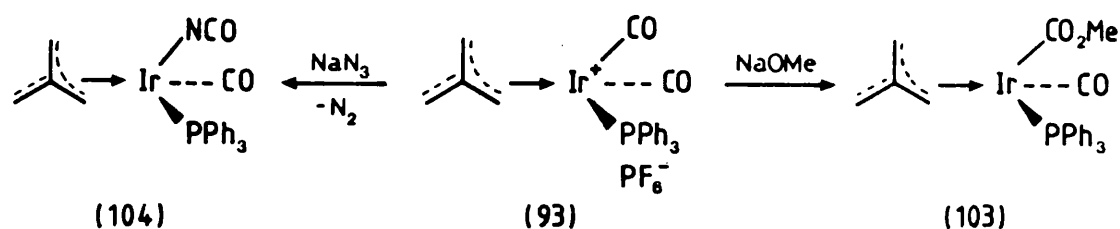
Scheme 31

and $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+$,^{147,148} where only carbonyl or π -hydrocarbon displaced products were isolated, it has been shown that a reversible and rapid ring addition is the initial reaction¹⁴⁹⁻¹⁵¹ and this may be the case for nucleophilic attack by tertiary phosphines on cationic η^4 -trimethylenemethane complexes.

Reactions with anionic nucleophiles

The addition of sodium methoxide to a solution of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (93) resulted in nucleophilic attack of the methoxide

anion at the carbonyl group to afford the alkoxycarbonyl complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO}_2\text{Me})(\text{CO})(\text{PPh}_3)]$ (103), Scheme 32. The i.r. spectrum exhibited a strong band at 1618 cm^{-1} assigned to the CO_2Me group¹⁵² and a single band at 2020 cm^{-1} due to the metal carbonyl ligand. The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra showed the characteristic features of a static η^4 -trimethylenemethane ligand and the ^1H n.m.r. spectrum also exhibited a singlet at $\delta\ 3.15$ p.p.m. attributed to the CO_2Me group. No elemental analysis could be obtained for this complex due to its thermal instability. Nucleophilic attack at the co-ordinated carbonyl ligand also occurred on treating (93) with sodium azide which gave the isocyanate complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{NCO})(\text{CO})(\text{PPh}_3)]$ (104). Attack by azide ion at the carbonyl ligand followed by loss of nitrogen and a rearrangement accounts for the formation of the product (104). Similar isocyanate complexes, derived from attack by azide ion at a carbonyl ligand, have been isolated previously.¹⁵² The i.r. spectrum of (104) exhibits a strong band at 2240 cm^{-1} which is characteristic of a co-ordinated isocyanate ligand¹⁵² and a band at 2020 cm^{-1} attributed to the metal carbonyl. The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra show the distinctive features of a static η^4 -trimethylenemethane ligand.



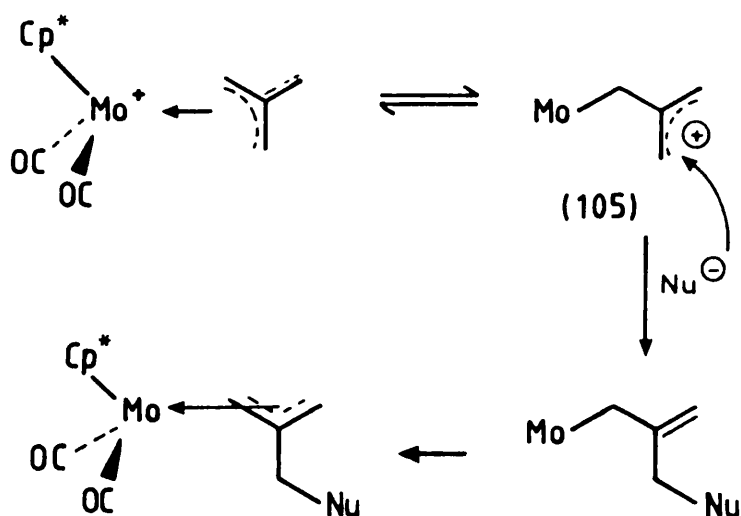
Scheme 32

In contrast to the bis-carbonyl complex (93) the bis-phosphine complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) did not react with either sodium methoxide or sodium azide under analogous conditions, the starting material being recovered unchanged. A combination of steric and

electronic effects resulting from two triphenylphosphine ligands in (85) accounts for the lack of reactivity of the carbonyl ligand to nucleophilic attack. Similarly $[\text{Rh}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BPh}_4$ (83) did not react with sodium azide. These results also illustrate that the trimethylenemethane ligand is not susceptible to nucleophilic attack and that attack at the co-ordinated carbonyl ligand is preferential. This is in marked contrast with the reactivity of the cationic molybdenum trimethylenemethane complexes in which attack by a series of anionic nucleophiles occurred at the η^4 -trimethylenemethane ligand. The differing reactivity of the iridium and molybdenum complexes may be due to fluxionality of the trimethylenemethane ligand in the molybdenum complexes (28) and (29), see Chapter 1, the protons of the trimethylenemethane fragment are interconverted at room temperature on the n.m.r. time scale.²⁷ To explain this proton equivalence of the η^4 -trimethylenemethane hydrogens Green *et al.* proposed that slippage ($\eta^4 \rightarrow \eta^1$) of the trimethylenemethane fragment occurs.²⁷ It is possible that the nucleophile is intercepting the postulated intermediate (105), Scheme 33. The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra of all of the cationic iridium complexes synthesised indicate that the trimethylenemethane ligand is firmly co-ordinated to the metal atom with no sign of rotation on the n.m.r. time scale at room temperature.

3.4 REACTIONS OF η^4 -TRIMETHYLENEMETHANE METAL COMPLEXES WITH ELECTROPHILES

The neutral iron complex $[\text{Fe}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_3]$ (7) reacts with electrophiles, see Chapter 1.¹² Similarly the osmium complex $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (75) reacts with concentrated hydrochloric acid to afford the η^3 -allyl complex $[\text{Os}(\eta^3\text{-CH}_2\text{CMeCH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)]$ (106).



$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$
 ligands omitted for clarity

Scheme 33

This complex was also isolated from the reaction of $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ with 3-chloro-2-methylprop-1-ene. The osmium complex (75) also reacts with fluoroboric acid in methyl cyanide to give the solvate complex $[\text{Os}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{NCMe})(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$ (107). The iridium complex $[\text{Ir}(\eta^4\text{-C}(\text{CH}_2)_3)\text{Cl}(\text{CO})\text{PPh}_3]$ (76) did not react with concentrated hydrochloric acid after 24h at room temperature, the starting complex (76) was recovered unchanged. Some indication of the stability of the iridium complexes can be gained by the observation that the cationic iridium complex $[\text{Ir}(\eta^4\text{-C}(\text{CH}_2)_3)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) was recovered unchanged from a refluxing solution of toluene and methyl cyanide containing an excess of concentrated hydrochloric acid.

3.5 CONCLUSION

This initial study of the reactions of η^4 -trimethylenemethane complexes shows that a wide range of cationic trimethylenemethane complexes

are available from the reaction of the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) with silver hexafluorophosphate in the presence of a neutral donor ligand. The cationic complexes synthesised contain an η^4 -trimethylenemethane fragment which is firmly bound to the metal centre. The reactions with tertiary phosphine nucleophiles gave ligand substitution products whilst anionic nucleophiles afforded complexes where nucleophilic attack at the co-ordinated carbonyl ligand occurred. These results are in contrast with the reactions of the cationic molybdenum trimethylenemethane complexes in which the trimethylenemethane ligand was susceptible to nucleophilic attack.

3.6 EXPERIMENTAL

Experimental techniques were as described in Chapter 2. Reagents were used as supplied from commercial sources: carbon monoxide, ethene (B.O.C), 3-butyne-1-ol, phenylethyne, sodium methoxide, sodium azide, silver hexafluorophosphate (Aldrich), methyldiphenylphosphine (Strem), 1,2-bis-(diphenylphosphino)ethane (Lancaster), and fluoroboric acid etherate (Fluka). The $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. data of PF_6^- is omitted for clarity.

Reactions of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) with silver hexafluorophosphate in donor solvents

(i) In acetone

A solution of (76) (0.12 g, 0.21 mmol) and AgPF_6 (0.009 g, 0.36 mmol) in dichloromethane (3 cm^3) and acetone (2 cm^3) was stirred for 0.5h. AgCl precipitated from the solution almost immediately. The solution was filtered through Florisil and the solvent was removed in vacuo. On addition of dichloromethane a metallic deposit formed. No complex could be isolated from this reaction although solutions of the acetone solvate were used without isolation of the complex.

(ii) In $[^2\text{H}_6]$ -acetone/ $[^2\text{H}_6]$ -benzene

A solution of (76) (0.08 g, 0.14 mmol) and AgPF_6 (0.06 g, 0.24 mmol)

was shaken in a 1:1 mixture of $[^2\text{H}_6]$ -acetone/ $[^2\text{H}_6]$ -benzene (2 cm^3).

AgCl was precipitated and the ^1H -n.m.r. spectrum showed complete reaction of (76) and a new complex (91). I.r. (CH_2Cl_2) ν_{CO} 2045 cm^{-1} ; n.m.r.

$[^2\text{H}_6]$ -acetone/ $[^2\text{H}_6]$ -benzene: ^1H (90 MHz), δ 1.5 [t, 1H, $J(\text{HH}) = J(\text{HP})$

4.5], 2.0 [dd, 1H, H, $J(\text{HH})$ 3.7, $J(\text{HP})$ 7.5], 2.3 [dd, 1H, $J(\text{HH})$ 4.5,

$J(\text{HP})$ 6.0], 3.25 (m, 3H), and 7.5 p.p.m. (m, 15H, PPh_3).

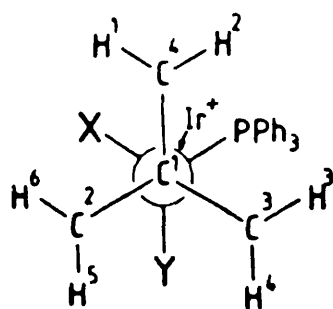


FIGURE 12

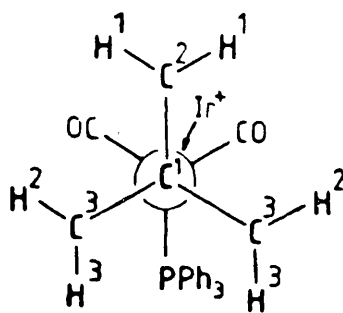


FIGURE 13

(iii) In methyl cyanide

A solution of (76) (0.13 g, 0.22 mmol) and AgPF_6 (0.08 g, 0.3 mmol) in

methyl cyanide (5 cm^3) was stirred for 3h. The solvent was removed

in vacuo, dissolved in dichloromethane (10 cm^3) and filtered through a

short column of Florisil. Recrystallisation from dichloromethane/light

petroleum gave white crystals of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{NCMe})(\text{PPh}_3)]\text{PF}_6$ (92)

(0.15 g, 94%) m.p. 105°C (decomp.), (Found: C, 41.1; H, 3.3; N, 1.96.

$\text{C}_{25}\text{H}_{24}\text{F}_6\text{IrNOP}_2$ requires C, 41.5; H, 3.3; N, 1.94%); i.r. ν_{CN} 2340 , ν_{CO}

2060 , ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 1.54 [t, 1H, H,

$J(\text{HH}) = J(\text{HP})$ 3.9], 2.22 [dd, 1H, H, $J(\text{HP})$ 6.4, $J(\text{HH})$ 4.0], 2.25 (s, 3H,

MeCN), 2.40 [d, 1H, H, $J(\text{HH})$ 3.5], 3.30 (m, 3H), and 7.6 (m, 15H, PPh_3);

$^{13}\text{C}\{-^1\text{H}\}$ (100 MHz), δ 3.1 (s, MeCN), 38.1 (s, C^3 or C^4), 52.8 [d, C^2 ,

$J(\text{C}^2\text{P})$ 31.6], 60.2 (s, C^3 or C^4), 108.9 [d, C^1 , $J(\text{C}^1\text{P})$ 2.9], 124.1 (s,

MeCN), and 170.6 p.p.m. [d, CO, J(CP) 4.3]. A full assignment of the ^1H n.m.r. spectrum was not possible due to the overlap of signals.

Figure 12, X=CO, Y=NCMe, or vice versa.

Reactions of η^4 -trimethylenemethane iridium solvato complexes

(i) With carbon monoxide

A solution of (76) (0.21 g, 0.37 mmol) and AgPF_6 (0.15 g, 0.59 mmol) in dichloromethane (5 cm^3) and acetone (3 cm^3) was stirred under an atmosphere of carbon monoxide (60 p.s.i) at room temperature for 1.5h. The solution was filtered through Florisil and concentrated in vacuo. Addition of light petroleum afforded white crystals of the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (93) (0.2 g, 76%) m.p. 170°C (decomp.), (Found: C, 40.9; H, 3.0. $\text{C}_{24}\text{H}_{21}\text{F}_6\text{IrO}_2\text{P}_2$ requires C, 40.6; H, 3.0%); i.r. ν_{CO} 2110 and 2060, ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (300 MHz), δ 2.1 [dd, 2H, H^3 , J(H^3H^1) 4.2, J(H^3P) 6.6], 3.36 [dd, 2H, H^1 , J(H^1H^3) 4.2, J(H^1P) 6.1], 3.44 (s, 2H, H^2), and 7.6 (m, 15H, PPh_3); ^{13}C - $\{^1\text{H}\}$ (75 MHz), δ 52.1 [d, C^2 , J(C^2P) 25.4], 57.4 (s, C^3), 108.5 [d, C^1 , J(C^1P) 3.3], and 164.3 p.p.m. [d, CO, J(CP) 4.1]. Figure 13.

(ii) With ethene

A solution of (76) (0.22 g, 0.38 mmol) and AgPF_6 (0.1 g, 0.4 mmol) in dichloromethane (5 cm^3) and acetone (3 cm^3) was stirred under an atmosphere of ethene (25 p.s.i) at room temperature for 1.5h. The solution was filtered and the solvent removed in vacuo. Recrystallisation from dichloromethane/light petroleum afforded white crystals of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (94) (0.16 g, 60%) m.p. 130°C (decomp.), (Found: C, 42.1; H, 3.6. $\text{C}_{25}\text{H}_{25}\text{F}_6\text{IrOP}_2$ requires C, 42.3; H, 3.6%); i.r. ν_{CO} 2050, ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 1.76 [ddd, 1H, H^2 , J(H^2H^5) 4.0, J(H^2P) 6.3, J(H^2H^1) 1.1], 2.38 [dd, 1H,

H^3 , $J(H^3H^6)$ 4.1, $J(H^3P)$ 6.5], 2.77 [dd, 1H, H^1 , $J(H^1H^4)$ 4.3, $J(H^1H^2)$ 1.1], 3.11 [dd, 1H, H^6 , $J(H^6H^3)$ 4.1, $J(H^6P)$ 5.8], 3.45 [d, 1H, H^4 , $J(H^4H^1)$ 4.3], 3.49 [dd, 1H, H^5 , $J(H^5H^2)$ 4.0, $J(H^5P)$ 6.4], 3.8 to 4.06 (m, 4H, C_2H_4), and 7.6 (m, 15H, PPh_3); $^{13}C-\{^1H\}$ (100 MHz), δ 54.0 (s, C^3 or C^4), 54.7 [d, C^2 , $J(C^2P)$ 27.0], 60.2 (s, C^3 or C^4), 62.0 (s, C_2H_4), 106.4 [d, C^1 , $J(C^1P)$ 3.0], and 168.1 [d, CO, $J(CP)$ 6.0], $^{31}P-\{^1H\}$ (24 MHz), δ 1.2 p.p.m. Figure 12, $X=CO$, $Y=C_2H_4$ or vice versa.

(iii) With 3-Butyn-1-ol

A solution of (76) (0.21 g, 0.37 mmol) and $AgPF_6$ (0.1 g, 0.4 mmol) in dichloromethane (5 cm^3) and acetone (2 cm^3) was stirred for 0.5h. The solution was filtered through Florisil and 3-butyn-1-ol (0.4 g, 0.57 mmol) was added. After stirring for 2h the solvent was removed in vacuo. Recrystallisation from dichloromethane/light petroleum and ethanol gave white crystals of $[Ir\{\eta^4-C(CH_2)_3\}\{\eta^1-\overline{C(CH_2)_3O}\}(CO)(PPh_3)]PF_6$ (95) (0.2 g, 72%) m.p. 150°C (decomp.), (Found: C, 42.9; H, 3.6. $C_{27}H_{27}F_6IrO_2P_2$ requires C, 43.1; H, 3.6%); i.r. ν_{CO} 2030, ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): 1H (400 MHz), δ 1.6-1.8 (m, 2H, OCH_2CH_2), 1.75 [dd, 1H, H^2 , $J(H^2H^5)$ 4.3, $J(H^2P)$ 7.1], 2.06 [dd, 1H, H^3 , $J(H^3H^6)$ 4.2, $J(H^3P)$ 5.6], 2.67 [dd, 1H, H^6 , $J(H^6H^3)$ 4.2, $J(H^6P)$ 6.2], 2.81 [d, 1H, H^1 , $J(H^1H^4)$ 4.4], 2.83 [d, 1H, H^4 , $J(H^4H^1)$ 4.4], 2.87 [dd, 1H, H^5 , $J(H^5H^2)$ 4.3, $J(H^5P)$ 5.9], 3.08 (m, 2H, CCH_2), 4.82 (m, 2H, OCH_2), and 7.5 (m, 15H, PPh_3); $^{13}C-\{^1H\}$ (100 MHz), δ 11.1 (s, OCH_2CH_2), 35.3 (s, CCH_2), 37.5 [d, C^2 , $J(C^2P)$ 28.9], 47.5 (s, C^3 or C^4), 52.3 (s, C^3 or C^4), 79.3 (s, OCH_2), 101.0 [d, C^1 , $J(C^1P)$ 3.0], 160.4 [d, OCH_2 , $J(CP)$ 3.3], and 179 p.p.m. [d, CO, $J(CP)$ 3.1]. Figure 12, $X=\overline{C(CH_2)_2O}$, $Y=CO$, or vice versa.

Reactions of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{NCMe})(\text{PPh}_3)]\text{PF}_6$ (92)

(i) With triphenylarsine

A solution of (92) (0.06 g, 0.08 mmol) and triphenylarsine (0.03 g, 0.18 mmol) was refluxed in dichloromethane (5 cm³) for 1h. On cooling light petroleum (5 cm³) was added and the white needles filtered and washed with light petroleum to give $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{AsPh}_3)(\text{PPh}_3)]\text{PF}_6$ (96) (0.05 g, 63%) m.p. 205°C (decomp.), (Found: C, 49.8; H, 3.6. $\text{C}_{41}\text{H}_{36}\text{AsF}_6\text{IrOP}_2$ requires C, 49.8; H, 3.7%), i.r. ν_{CO} 2040, ν_{PF} 840 cm⁻¹; n.m.r. (CDCl_3): ¹H (300 MHz), δ 1.85 [dd, 1H, H³, J(H³H⁶) 3.6, J(H³P) 5.4], 2.05 [dd, 1H, H², J(H²H⁵) 4.3, J(H²P) 6.7], 2.30 [dd, 1H, H⁶, J(H⁶H³) 3.6, J(H⁶P) 5.6], 2.67 [d, 1H, H¹, J(H¹H⁴) 4.0], 3.3 (m, 2H, H⁴ and H⁵), and 7.5 (m, 30H, PPh₃, AsPh₃); ¹³C-{¹H} (75 MHz), δ 52.7 [d, C², J(C²P) 30.1], 54.8 (s, C³ or C⁴), 55.5 (s, C³ or C⁴), 106.7 [d, C¹, J(C¹P) 3.0], and 171.3 p.p.m. [d, CO, J(CP) 4.8]. Figure 12, X = AsPh₃, Y = CO, or vice versa.

(ii) With triphenylphosphine

A solution of (92) (0.09 g, 0.12 mmol) and triphenylphosphine (0.04 g, 0.13 mmol) in dichloromethane (1 cm³) was shaken for 24h. Addition of diethyl ether (2 cm³) gave white needles of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) (0.08 g, 71%), which was identified by comparison of the ¹H and ¹³C-{¹H} n.m.r. spectra with an authentic sample.

(iii) With phenylethene/triethylamine

A solution of (92) (0.04 g, 0.06 mmol), phenylethene (0.01 g, 0.1 mmol), and triethylamine (0.02 g, 0.2 mmol) in chloroform (1 cm³) was stirred at room temperature for 1.5h. The solution was filtered and the solvent removed in vacuo. The residue was extracted with light petroleum and the solution filtered. Concentration of the filtrate and

cooling to -78°C gave white crystals of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^1\text{-C}\equiv\text{CPh})(\text{CO})\text{-}(\text{PPh}_3)]$ (97) (0.03 g, 78%) m.p. 165°C (decomp.), (Found: C, 57.8; H, 4.4. $\text{C}_{31}\text{H}_{26}\text{IrOP}$ requires C, 58.4; H, 4.1%); i.r. $\nu_{\text{C}\equiv\text{C}}$ 2125, ν_{CO} 2015 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 1.1 [t, 1H, H^2 , $J(\text{H}^2\text{H}^5) = J(\text{H}^2\text{P}) = 3.6$], 1.83 [dd, 1H, H^3 , $J(\text{H}^3\text{H}^6) 4.2$, $J(\text{H}^3\text{P}) 7.0$], 2.34 [d, 1H, H^1 , $J(\text{H}^1\text{H}^4) 4.3$], 2.53 [d, 1H, H^4 , $J(\text{H}^4\text{H}^1) 4.3$], 2.62 [dd, 1H, H^6 , $J(\text{H}^6\text{H}^3) 4.2$, $J(\text{H}^6\text{P}) 7.3$], 2.62 [dd, 1H, H^5 , $J(\text{H}^5\text{H}^2) 3.6$, $J(\text{H}^5\text{P}) 6.7$], and 6.9 to 7.7 (m, 20H, Ph); ^{13}C - $\{^1\text{H}\}$ (75 MHz), δ 44.6 [d, C^2 , $J(\text{C}^2\text{P}) 37.8$], 48.2 (s, C^3 or C^4), 50.6 (s, C^3 or C^4), 107.5 [d, C^1 , $J(\text{C}^1\text{P}) 3.8$], and 171.2 [d, CO, $J(\text{CP}) 4.1$]. The carbons in the $\text{M-C}\equiv\text{C}$ fragment were not observed and are probably obscured by phenyl resonances. ^{141}P - $\{^1\text{H}\}$ (24 MHz), δ 3.2 p.p.m. Figure 14, $\text{X}=\text{C}\equiv\text{CPh}$, $\text{Y}=\text{CO}$, or vice versa.

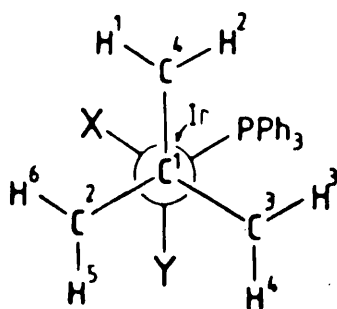


FIGURE 14

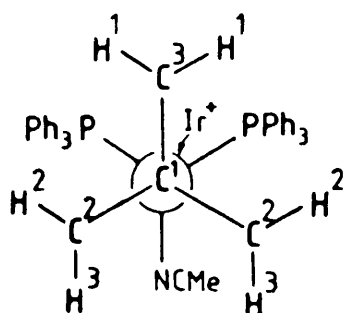


FIGURE 15

Reaction of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{PPh}_3)_2]$ (80) with silver hexafluorophosphate in methyl cyanide

A solution of (80) (0.09 g, 0.11 mmol) and AgPF_6 (0.04 g, 0.15 mmol) in methyl cyanide (10 cm^3) was stirred for 0.5h. The silver chloride was filtered off and the solvent removed in vacuo. The residue was extracted with dichloromethane and filtered through Florisil. Addition of light petroleum gave a white solid identified as $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{NCMe})\text{-}(\text{PPh}_3)_2]\text{PF}_6$ (98) (0.08 g, 76%) m.p. 145°C (decomp.), (Found: C, 52.6; H, 4.2; N, 1.4. $\text{C}_{42}\text{H}_{39}\text{F}_6\text{IrNP}_3$ requires C, 52.7; H, 4.1; N, 1.5%); i.r.

ν_{PF} 835 cm^{-1} ; n.m.r. (CDCl_3): ^1H (90 MHz), δ 1.4 [dd, 2H, H^1 , $J(\text{H}^1\text{H}^3)$ 3.0, $J(\text{H}^1\text{P})$ 6.0], 2.0 (1:2:6:2:1 quintet, AA'XX' system, 2H, H^2), 2.2 (s, 3H, MeCN), 3.2 [dd, 2H, H^3 , $J(\text{H}^3\text{H}^1)$ 3.0, $J(\text{H}^3\text{P})$ 6.0], and 7.4 (m, 30H, PPh_3); ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 3.83 p.p.m. Figure 15.

Reactions of cationic η^4 -trimethylenemethane metal complexes with neutral nucleophiles

(A) Reactions of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) with tertiary phosphines

(i) To a solution of (85) (0.185 g, 0.196 mmol) in dichloromethane (5 cm^3) was added methyldiphenylphosphine (0.04 g, 0.196 mmol) in dichloromethane (2 cm^3). After stirring for 0.5h the solution was concentrated and light petroleum was added. The white solid was filtered and washed with light petroleum. The crude product was chromatographed on alumina. Elution with dichloromethane gave a white solid which was recrystallised from dichloromethane/diethyl ether to give a white crystalline solid, which was dried in vacuo and was identified as a 1:1:1 mixture of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)_2]\text{PF}_6$ (99), $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)(\text{PMePh}_2)]\text{PF}_6$ (100), and (85). The product was characterised as a mixture (0.16 g, 92%), m.p. 104–105°C, (Found: C, 49.1; H, 4.0. The above mixture requires C, 49.0; H, 3.9%); i.r. ν_{CO} 2040, ν_{PF} 830 cm^{-1} ; n.m.r. (CD_2Cl_2): complex (99), see next experiment for ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. data.

Complex (85) was identified by comparison of the ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. spectra with an authentic sample. Complex (100); ^1H (400 MHz), δ 1.76 [dd, 1H, H^6 , $J(\text{H}^6\text{H}^3)$ 4.2, $J(\text{H}^6\text{P})$ 6.2], 1.78 [dd, 1H, H^3 , $J(\text{H}^3\text{H}^6)$ 4.2, $J(\text{H}^3\text{P})$ 6.2], 1.91 [dd, 1H, H^2 , $J(\text{H}^2\text{H}^5)$ 4.2, $J(\text{H}^2\text{P})$ 6.5], 2.02 [d, 3H, PMePh_2 , $|^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})|$ 9.6], 2.25 [dd, 1H, H^1 , $J(\text{H}^1\text{H}^4)$ 4.2, $J(\text{H}^1\text{P})$ 8.3], 3.16 [dd, 1H, H^5 , $J(\text{H}^5\text{H}^2)$ 4.2, $J(\text{H}^5\text{P})$ 6.3], 3.18 [dd, 1H, H^4 , $J(\text{H}^4\text{H}^1)$ 4.2,

$J(H^4P)$ 6.3]; $^{13}C-\{^1H\}$ (100 MHz), δ 16.1 [d, $PMePh_2$, $J(CP)$ 37.7], 53.0 [d, C^2 and C^3 , $J(CP)$ 31.0], 57.5 (s, C^4), 108.5 [t, C^1 , $J(CP)$ 3.0] and 171.7 p.p.m. (t, CO, $J(CP)$ 4.0). Figure 17, $L^1 = PMe_2Ph$, $L^2 = PPh_3$ or vice versa. $^{31}P-\{^1H\}$ (162 MHz) (of mixture), δ -26.1, -22.8, -2.1, and -1.14 p.p.m.

(ii) A solution of (85) (0.185 g, 0.196 mmol) and methyldiphenylphosphine (0.08 g, 0.4 mmol) in dichloromethane (5 cm³) was stirred for 0.5h. The solvent was removed in vacuo, the residue washed with light petroleum, and then recrystallised from dichloromethane/diethyl ether to give white crystals of $[Ir\{\eta^4-C(CH_2)_3\}(CO)(PMePh_2)_2]PF_6$ (99) (0.15 g, 93%) m.p. 140°C, (Found: C, 45.4; H, 4.0. $C_{31}H_{32}F_6IrOP_3$ requires C, 45.4; H, 3.9%); i.r. ν_{CO} 2030, ν_{PF} 830 cm⁻¹; n.m.r. (CD_2Cl_2): 1H (400 MHz), δ 1.95 [1:2:6:2:1 quintet, 2H, H^2 , $AA'XX'$ system, $J(H^2H^{2'})$ 4.1, $J(PP')$ 0, $J(H^2P) = -J(H^{2'}P) = \pm 5.9$], 2.14 [d, 6H, $PMePh_2$, $|^2J(HP) + ^4J(HP)|$ 9.4], 2.46 [dd, 2H, H^1 , $J(H^1H^3)$ 4.2, $J(H^1P)$ 7.0], 3.11 [dd, 2H, H^3 , $J(H^3H^1)$ 4.2, $J(H^3P)$ 6.2], and 7.5 (m, 20H, $PMePh_2$); $^{13}C-\{^1H\}$ (100 MHz), δ 17.0 [d, $PMePh_2$, $J(CP)$ 38.0], 52.7 [d, C^2 , $J(C^2P)$ 30.7], 52.9 (s, C^3), 108.0 (s, C^1), and 171.6 (s, CO); $^{31}P-\{^1H\}$ (24 MHz), δ -22.8 p.p.m. Figure 16, $L^1 = L^2 = PMePh_2$.

(iii) A solution of (85) (0.18 g, 0.19 mmol) and 1,2-bis-(diphenylphosphino)ethane (0.08 g, 0.2 mmol) in dichloromethane (5 cm³) was stirred for 1h. The solvent was removed in vacuo, the residue washed with light petroleum and then chromatographed on alumina. After eluting with dichloromethane the required product was obtained by eluting with dichloromethane/methanol (1:7). The product was recrystallised from dichloromethane/diethyl ether to give the complex $[Ir\{\eta^4-C(CH_2)_3\}(CO)-(dppe)]PF_6$ (101) (0.1 g, 64%) m.p. 216-219°C (decomp.), (Found: C, 45.8;

H, 3.8. $C_{31}H_{30}F_6IrOP_3$ requires C, 45.5; H, 3.7%); i.r. ν_{CO} 2040, ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): 1H (400 MHz), δ 1.37 [dd, H^1 , $J(H^1H^3)$ 4.4, $J(H^1P)$ 7.1], 2.26 (br d, AA'XX' system, H^2), 3.12 [dd, H^3 , $J(H^3H^1)$ 4.4, $J(H^3P)$ 6.1], 3.17 (m, 4H, AA'XX'MM' system, PCH_2CH_2P), and 7.5 (m, 20H, Ph); ^{13}C - $\{^1H\}$ (100 MHz), δ 29.5 (d, AXX' system, PCH_2CH_2P), 48.0 (1:1:1 triplet, AXX' system, C^2), 60.4 (s, C^3), 108.0 [t, C^1 , $J(C^1P)$ 3.0], and 170.8 p.p.m. (s, CO). Figure 16, $L^1L^2 = dppe$.

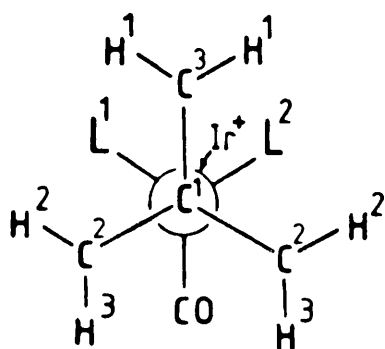


FIGURE 16

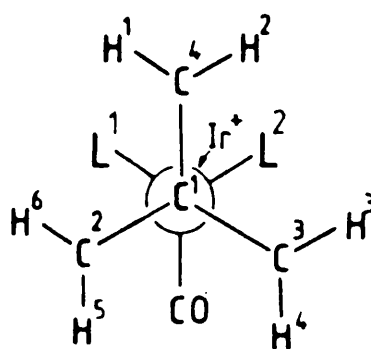


FIGURE 17

(B) Reactions of $[Ir(\eta^4-C(CH_2)_3)(CO)_2(PPh_3)]PF_6$ (93) with tertiary phosphines

(i) To a solution of (93) (0.05 g, 0.07 mmol) in dichloromethane (1 cm^3) was added methyldiphenylphosphine (0.017 g, 0.08 mmol). After stirring for 0.5h the solvent was removed in vacuo, the residue washed with light petroleum, and recrystallised from dichloromethane/diethyl ether to give a 1:1:1 mixture of the complexes (85), (99), and (100) which was identified by comparison of its i.r. and 1H n.m.r. spectra with an authentic sample.

(ii) To a solution of (93) (0.05 g, 0.07 mmol) in $[^2H_2]$ -dichloromethane was added triphenylphosphine (0.019 g, 0.09 mmol). After 2 minutes the 1H n.m.r. spectrum showed no sign of (93). The solvent was removed in vacuo and recrystallisation from dichloromethane/light petroleum gave

white crystals of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) (0.06 g, 91%)

which was identified by comparison with an authentic sample.

(C) Reactions of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (94) with tertiary phosphines

(i) To a solution of (94) (0.05 g, 0.06 mmol) in $[\text{}^2\text{H}_6]\text{-acetone}$ (1 cm^3) was added methyldiphenylphosphine (0.012 g, 0.06 mmol). After stirring for 12h light petroleum was added to give white crystals of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\eta^1\text{-CH}_2\text{CH}_2\text{PMePh}_2)(\text{CO})(\text{PPh}_3)]\text{PF}_6$ (102) (0.04 g, 73%) m.p. 115-117°C, (Found: C, 49.9; H, 4.1. $\text{C}_{38}\text{H}_{38}\text{F}_6\text{IrOP}_3$ requires C, 50.2; H, 4.2%); i.r. ν_{CO} 2000, ν_{PF} 840 cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H (300 MHz), δ 1.2 (m, 2H, IrCH_2), 1.25 [dd, 1H, H^2 , $\text{J}(\text{H}^2\text{H}^5)$ 4.3, $\text{J}(\text{H}^2\text{P})$ 6.8], 1.67 [t, H^3 , $\text{J}(\text{H}^3\text{H}^6) = \text{J}(\text{H}^3\text{P}) = 3.0$], 1.83 [d, 1H, H^1 , $\text{J}(\text{H}^1\text{H}^4)$ 4.1], 1.92 [dd, 1H, H^6 , $\text{J}(\text{H}^6\text{H}^3)$ 3.0, $\text{J}(\text{H}^6\text{P})$ 6.2], 2.03 [d, 3H, PMePh_2 , $\text{J}(\text{PH})$ 12.9], 2.45 [d, 1H, H^4 , $\text{J}(\text{H}^4\text{H}^1)$ 4.1], 2.62 [dd, 1H, H^5 , $\text{J}(\text{H}^5\text{H}^2)$ 4.3, $\text{J}(\text{H}^5\text{P})$ 6.9], 2.76 (m, 2H, CH_2PMe), and 7.4 (m, 25H, Ph); ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 11.5 and 0.4 p.p.m. Figure 14, $\text{X} = \text{CO}$, $\text{Y} = \text{CH}_2\text{CH}_2\text{P}^+\text{MePh}_2$ or vice versa.

(ii) To a solution of (94) (0.06 g, 0.07 mmol) in $[\text{}^2\text{H}_6]\text{-acetone}$ was added methyldiphenylphosphine (0.015 g, 0.07 mmol). The ^1H n.m.r. spectrum confirmed the formation of the complex (102). The solution was heated to 45°C for 5h. The solvent was removed in vacuo and the residue recrystallised from dichloromethane/light petroleum to give a 1:1:1 mixture of the complexes $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85), $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)_2]\text{PF}_6$ (99), and $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMePh}_2)(\text{PPh}_3)]\text{PF}_6$ (100), when compared with an authentic sample.

Reactions of cationic η^4 -trimethylenemethane metal complexes with anionic nucleophiles

(i) A suspension of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ (93) (0.1 g, 0.14

mmol) and sodium methoxide (7.6 mg, 0.14 mmol) in methanol (10 cm³) was stirred at room temperature for 1.5h. The solvent was removed in vacuo and the residue extracted with dichloromethane and the solution filtered. Addition of light petroleum gave a white powder of [Ir{η⁴-C(CH₂)₃} (η¹-CO₂Me)(CO)(PPh₃)] (103) (0.06 g, 72%). The complex decomposed on standing at room temperature after several hours. I.r. (CHCl₃) ν_{CO} 2021, ν_{CO₂Me} 1618 cm⁻¹; n.m.r. (CDCl₃): ¹H (300 MHz), δ 1.25 [t, 1H, H², J(H²H⁵) = J(H²P) = 4.0], 1.60 [dd, 1H, H³, J(H³H⁶) 4.2, J(H³P) 7.4], 2.28 [d, 1H, H¹, J(H¹H⁴) 4.3], 2.39 [d, 1H, H⁴, J(H⁴H¹) 4.3], 2.44 [dd, 1H, H⁵, J(H⁵H²) 4.0, J(H⁵P) 6.5], 2.59 [dd, 1H, H⁶, J(H⁶H³) 4.2, J(H⁶P) 6.5], 3.15 [s, 3H, CH₃CO₂], and 7.3 (m, 15H, PPh₃); ¹³C-{¹H} (75 MHz), δ 42.1 (s, Me), 44.2 [d, C², J(C²P) 34.7], 49.5 (s, C³ or C⁴), 54.7 (s, C³ or C⁴), 110.6 [d, C¹, J(C¹P) 3.0], 173.2 [d, CO₂Me, J(CP) 10.0], and 173.9 p.p.m. [d, CO, J(CP) 4.2]. Figure 14, X=CO₂Me, Y=CO or vice versa.

(ii) A solution of [Ir{η⁴-C(CH₂)₃} (CO)₂ (PPh₃)]PF₆ (93) (0.05 g, 0.08 mmol) and sodium azide (5.0 mg, 0.08 mmol) in acetone (1 cm³) was stirred for 5h. The solvent was removed in vacuo and the residue was extracted with dichloromethane and filtered. Addition of light petroleum gave a white powder of [Ir{η⁴-C(CH₂)₃} (NCO)(CO)(PPh₃)] (104) (0.03 g, 66%) m.p. 126°C (decomp.), (Found: C, 49.8; H, 3.8; N, 2.5. C₂₄H₂₁IrNO₂P requires C, 49.8; H, 3.7; N, 2.4%); i.r. ν_{NCO} 2240, ν_{CO} 2020 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 1.01 [td, 1H, H², J(H²H⁵) = J(H²P) = 3.9, J(H²H¹) 1.0], 2.01 [dd, 1H, H¹, J(H¹H⁴) 4.2, J(H¹H²) 1.0], 2.31 [dd, 1H, H³, J(H³H⁶) 4.0, J(H³P) 6.4], 2.84 [d, 1H, H⁴, J(H⁴H¹) 4.2], 2.96 [dd, 1H, H⁵, J(H⁵H²) 3.9, J(H⁵P) 6.4], 3.09 [dd, 1H, H⁶, J(H⁶H³) 4.0, J(H⁶P) 7.5], and 7.5 (m, 15H, PPh₃); ¹³C-{¹H} (100 MHz), δ 37.0 (s, C³ or C⁴), 51.2 [d, C², J(C²P) 37.0], 57.3 (s, C³ or C⁴),

109.2 [d, C¹, J(C¹P) 3.8], 172.7 (s, NCO), and 178.0 p.p.m. (s, CO).

Figure 14, X=NCO, Y=CO or vice versa.

(iii) A solution of [Ir{ η^4 -C(CH₂)₃} (CO)(PPh₃)₂]PF₆ (85) (0.18 g, 0.19 mmol) and sodium methoxide (10 mg, 0.19 mmol) in methanol (10 cm³) was stirred at room temperature for 24h. The solvent was removed in vacuo and the residue extracted with dichloromethane and the solution filtered.

Addition of light petroleum gave white crystals which were dried in vacuo and identified as starting material [Ir{ η^4 -C(CH₂)₃} (CO)(PPh₃)₂]PF₆ (85) (0.16 g, 89%).

(iv) A solution of [Ir{ η^4 -C(CH₂)₃} (CO)(PPh₃)₂]PF₆ (85) (0.18 g, 0.19 mmol) and sodium azide (12 mg, 0.19 mmol) in acetone (1 cm³) was stirred for 24h. The solvent was removed in vacuo and the residue extracted with dichloromethane and filtered. Addition of light petroleum gave white crystals identified as starting material [Ir{ η^4 -C(CH₂)₃} (CO)(PPh₃)₂]PF₆ (85) (0.17 g, 94%).

Reactions of η^4 -trimethylenemethane metal complexes with electrophiles

(i) To a solution of [Os{ η^4 -C(CH₂)₃} (CO)₂(PPh₃)] (75) (0.05 g, 0.09 mmol) in dichloromethane (1 cm³) was added concentrated hydrochloric acid (1 drop, excess). After 5 minutes the organic layer was separated and dried over sodium carbonate. The solution was filtered and diethyl ether was added to precipitate out white microcrystals of [Os(η^3 -CH₂CCH₃CH₂)Cl(CO)₂(PPh₃)] (106) (0.04 g, 74%), m.p. 135°C (Found: C, 48.5; H, 3.8. C₂₄H₂₂ClO₂OsP requires C, 48.1; H, 3.7%); i.r. ν_{CO} 2020, 1950 cm⁻¹; n.m.r. (CDCl₃): ¹H (400 MHz), δ 2.15 (brm, 1H), 2.32 [d, 3H, Me, J(HP) 0.8], 2.69 (m, 1H), 3.42 (m, 1H), 3.78 (m, 1H), and 7.4 (m, 15H, PPh₃); ³¹P-{¹H} (24 MHz), δ 15.6 p.p.m.

The complex (106) was also obtained from refluxing $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2]$ (1.21 g, 1.17 mmol) and 3-chloro-2-methylprop-1-ene (0.25 g, 2.76 mmol) in benzene (50 cm^3) for 0.5h. The solution was cooled, filtered, and concentrated in vacuo. Addition of diethyl ether gave white crystals of (106) (0.46 g, 66%) which was identified by comparison of the ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra with an authentic sample.

(ii) To a suspension of the osmium complex (75) (0.12 g, 0.22 mmol) in methyl cyanide (5 cm^3) was added HBF_4 (ca. 0.5 mmol) in diethyl ether. After stirring for 1h potassium carbonate was added, the solution filtered, and the solvent was removed in vacuo. The residue was washed with diethyl ether, the white solid filtered, washed with diethyl ether, and dried in vacuo to give $[\text{Os}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{NCMe})(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$ (107) (0.12 g, 79%) (Found: C, 45.3; H, 3.6; N, 1.9. $\text{C}_{26}\text{H}_{25}\text{BF}_4\text{NO}_2\text{OsP}$ requires C, 45.2; H, 3.6; N, 2.0%); i.r. ν_{CN} 2330, ν_{CO} 2050, 1980 cm^{-1} ; n.m.r. (CDCl_3): ^1H (90 MHz), δ 2.0 (s, 3H, MeCN), 2.2 (m, 1H), 2.5 (s, 3H, Me), 2.6 (m, 1H), 3.3 (m, 1H), 3.8 (m, 1H), and 7.5 p.p.m. (15H, PPh_3).

(iii) To a solution of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) (0.06 g, 0.1 mmol) in dichloromethane (1 cm^3) was added concentrated hydrochloric acid (1 drop, excess). The solution was stirred for 24h. The organic layer was separated, dried over sodium carbonate, filtered and diethyl ether was added to precipitate out a white solid identified as starting material (76) (0.04 g, 67%).

(iv) A solution of $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (85) (0.18 g, 0.19 mmol) and concentrated hydrochloric acid (3 drops, excess) in methyl cyanide/toluene (1:1) (20 cm^3) was refluxed for 24h. The solvent was removed in vacuo, the residue extracted with dichloromethane, dried over sodium

carbonate and filtered. Addition of light petroleum gave white crystals identified as starting material (85) (0.14 g, 78%).



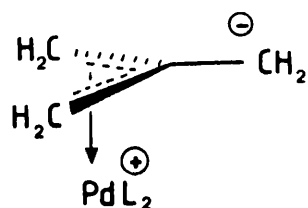
CHAPTER

4

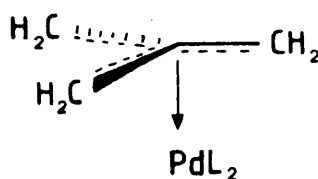
Reactions of 3-Trimethylsilyl-2-(Methyl-
sulphonyloxymethyl)prop-1-ene with
 d^{10} -Metal Complexes

4.1 INTRODUCTION

3-Trimethylsilyl-2-(acetoxymethyl)prop-1-ene (47), in the presence of a catalytic amount of a palladium(0) complex, serves as an equivalent of trimethylenemethane in cycloadditions to electron-deficient carbon-carbon double bonds.^{48,49} These cycloaddition reactions are thought to proceed via the polar trimethylenemethane intermediate $[\text{Pd}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{L})_2]$ (48) ($\text{L} = \text{PPh}_3$) although the presence of the alternative η^4 -co-ordinated form (108) must also be considered.⁵⁷ The isolation of η^4 -trimethylenemethane metal complexes from the reactions of the allylic acetate (47), chloride (73), and methanesulphonate (74) with low-valent metal centres (see Chapter 2) provides support for the formation of an η^3 - or η^4 -trimethylene-methane palladium complex as an intermediate in the palladium mediated cycloaddition approach to cyclopentanoids.^{120,121}



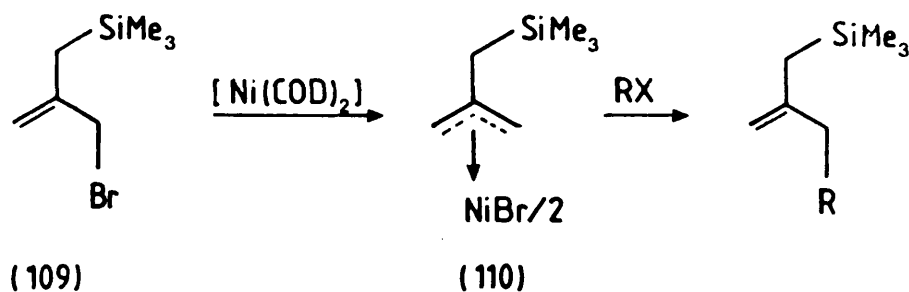
(48)



(108)

The 2-[(trimethylsilyl)methyl]allyl esters and halides introduced by Trost *et al.*^{48,132} have found applications other than in the palladium catalysed [3+2] cycloaddition reactions. Thus treatment of 3-trimethylsilyl-2-(bromomethyl)prop-1-ene (109) with *bis*-(1,5-cyclooctadiene)-nickel(0) in toluene led to a quantitative conversion into the corresponding trimethylsilyl-substituted η^3 -allylnickel halide complex (110).¹⁵³ 3-Trimethylsilyl-2-(iodomethyl)prop-1-ene, as well as the chloride (73), methanesulphonate (74), and trifluoroacetate derivatives, do not work as well as the bromide. The nickel allyl complex (110) retained the same reactivity as the previously reported η^3 -allylnickel bromides¹⁵⁴⁻¹⁵⁶ and

under very mild conditions reacted with organic halides to provide a high yield route to substituted allyl silanes, Scheme 34.¹⁵³

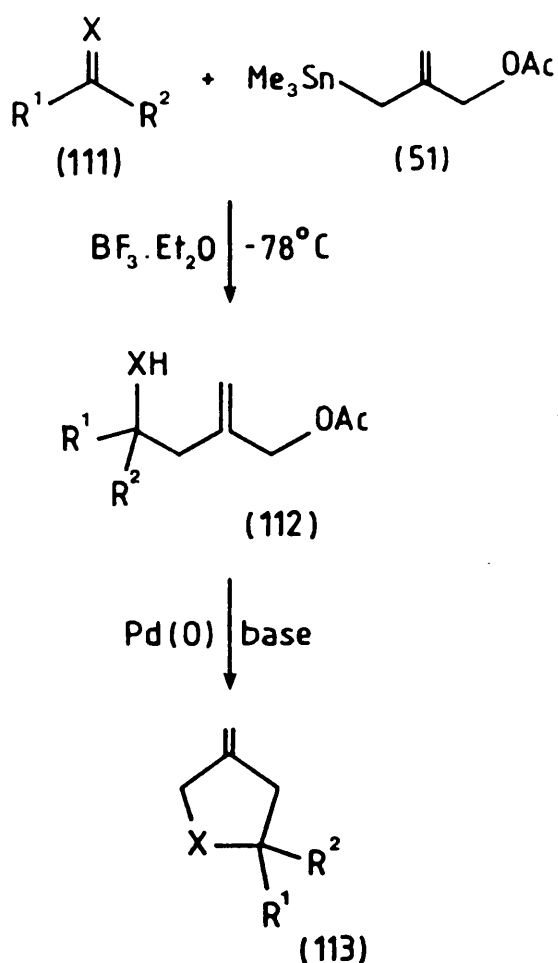


Scheme 34

The tin-acetate (51) introduced by Trost *et al.* is a very effective reagent for the cycloaddition of the trimethylenemethane fragment to aldehydes in the presence of palladium(0) catalysts, see Chapter 1.⁵⁸ However, ketones do not undergo this cycloaddition reaction in satisfactory yields and so a two-step synthesis was developed which involves a Lewis-acid-initiated addition of the allylstannane (51) to the ketone (111, X=O). The adduct (112, X=O) cyclises in the presence of a palladium(0) catalyst to afford the 4-methylenetetrahydrofuran (113, X=O), Scheme 35.¹⁵⁷

A similar Lewis-acid mediated reaction extends this strategy for heterocyclic synthesis of pyrrolidines. Thus the imine (111, X=NR) reacts with the allylstannane (51) in the presence of a Lewis-acid to afford the adduct (112, X=NR) which is readily converted to the 4-methylenepyrrolidine (113, X=NR) using a palladium(0) catalyst, Scheme 35.¹⁵⁷ These two-step reactions are equivalent to a [3+2] cycloaddition of the trimethylenemethane fragment to ketones and imines.

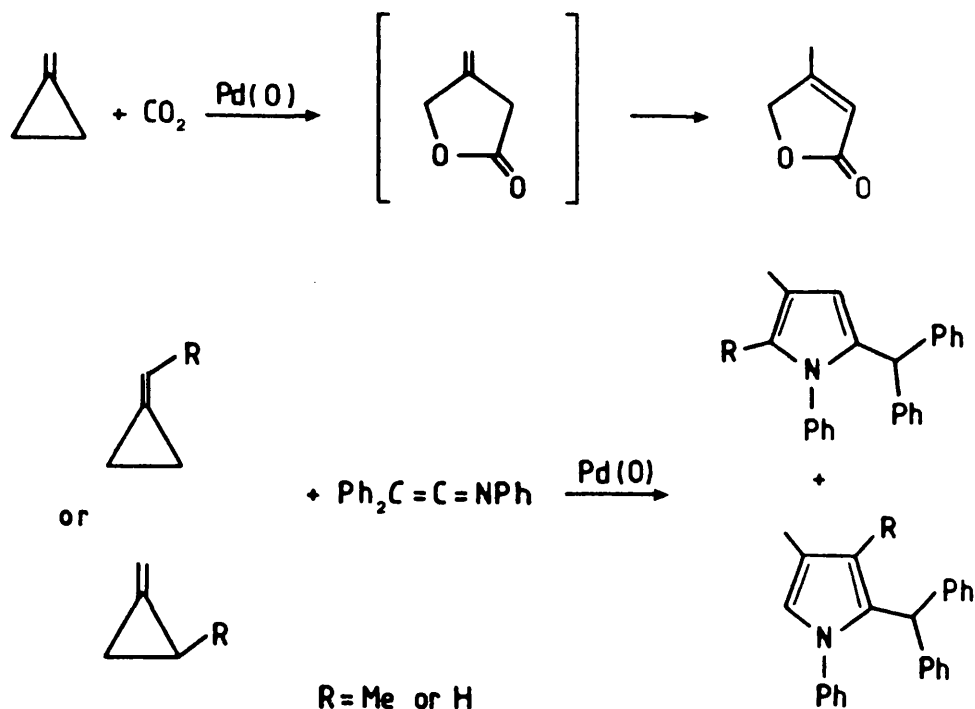
Similar heterocyclic systems have been synthesised from the d^{10} -metal catalysed ring opening reactions of alkylidenecyclopropanes. Thus the co-dimerisation of methylenecyclopropane with carbon dioxide is catalysed



Scheme 35

by a palladium(0) complex and leads to γ -lactones. However, if an easily enolisable proton exists in the initial adduct isomerisation to the γ -butenolide occurs under the reaction conditions, Scheme 36.^{158,159} A similar co-dimerisation of alkylidenecyclopropanes with ketenimines, in the presence of a nickel(0) or palladium(0) catalyst leads to pyrroles, α -methylene- Δ^3 -pyrrolines, or iminocyclopentenones depending on the substituents of the imino group and the alkylidenecyclopropanes, Scheme 36.¹⁶⁰

The high reactivity of the methanesulphonate (74) with d^8 -metal complexes led to an investigation of the reactivity of (74) with various d^{10} -metal centres. This Chapter also describes the cycloaddition of



Scheme 36

the trimethylenemethane fragment, generated from (74), to alkenes and imines in the presence of low-valent metal centres. Thus the d^{10} -complex $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ catalyses the cycloaddition of the trimethylenemethane fragment to the carbon-nitrogen double bond of an imine to afford a high yield synthesis of 4-methylenepyrrolidines.

4.2 PREPARATION OF η^3 -2-TRIMETHYLSILYLMETHYLLYLS OF PALLADIUM(II) AND PLATINUM(II)

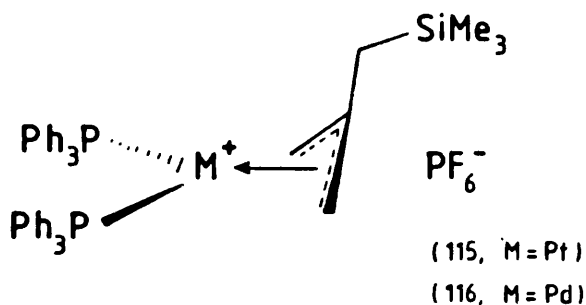
The methanesulphonate (74) reacted rapidly with a benzene solution of $[\text{Pt}(\text{PPh}_3)_4]$. A white solid precipitated from the solution and was identified as $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]\text{OS}(\text{O})_2\text{Me}$ (114). Oxidative addition of the allylic methanesulphonate (74) to platinum(0) is believed to be the initial step in this reaction although whether an intermediate η^3 -trimethylenemethane complex $[\text{Pt}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ is formed is unclear. Attempts to trap a trimethylenemethane complex by carrying out this reaction in the presence of an electron-deficient

alkene led only to isolation of the protodesilylated product (114). However, treatment of the methanesulphonate (74) with a solution of $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ or $[\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2]$ and a large excess of ammonium hexafluorophosphate in acetone afforded the η^3 -2-trimethylsilylmethylallyl complex (115). The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra showed the expected features of an η^3 -allyl complex. The ^1H n.m.r. spectrum is very similar to that of the η^3 -2-methylallyl platinum complex (114) apart from the presence of a singlet at δ 0.0 attributed to the trimethylsilyl group and a singlet at δ 1.58 assigned to the CH_2SiMe_3 fragment. Interestingly the platinum-195 coupling to this CH_2 group is much smaller than the platinum coupling observed to the methyl group of the η^3 -2-methylallyl complex (114) and is presumably a result of the bulky trimethylsilyl group present in (115). The assignment of the syn- and anti- protons of the allyl fragment is based on the previous observations that the anti-protons exhibit larger coupling to the co-ordinated phosphorus-31 nuclei.^{161,162} This was confirmed by a n.O.e. difference spectra which showed that there was a n.O.e. between the CH_2SiMe_3 group and the resonance assigned to the syn-protons but no n.O.e. was observed between the CH_2SiMe_3 group and the resonance attributed to the anti-protons.

The analogous palladium η^3 -2-trimethylsilylmethylallyl complex (116) was isolated from the reaction of the methanesulphonate (74) with $[\text{Pd}(\text{PPh}_3)_4]$ and ammonium hexafluorophosphate in acetone. The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra showed the expected features for an η^3 -allyl complex. The ^1H n.m.r. spectrum of the allyl fragment consists of a broad singlet, assigned to the syn-protons, and a complex multiplet at δ 3.18 due to the anti-protons. This multiplet is very similar to that observed for the related complex $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{dppe})]\text{PF}_6$ and can

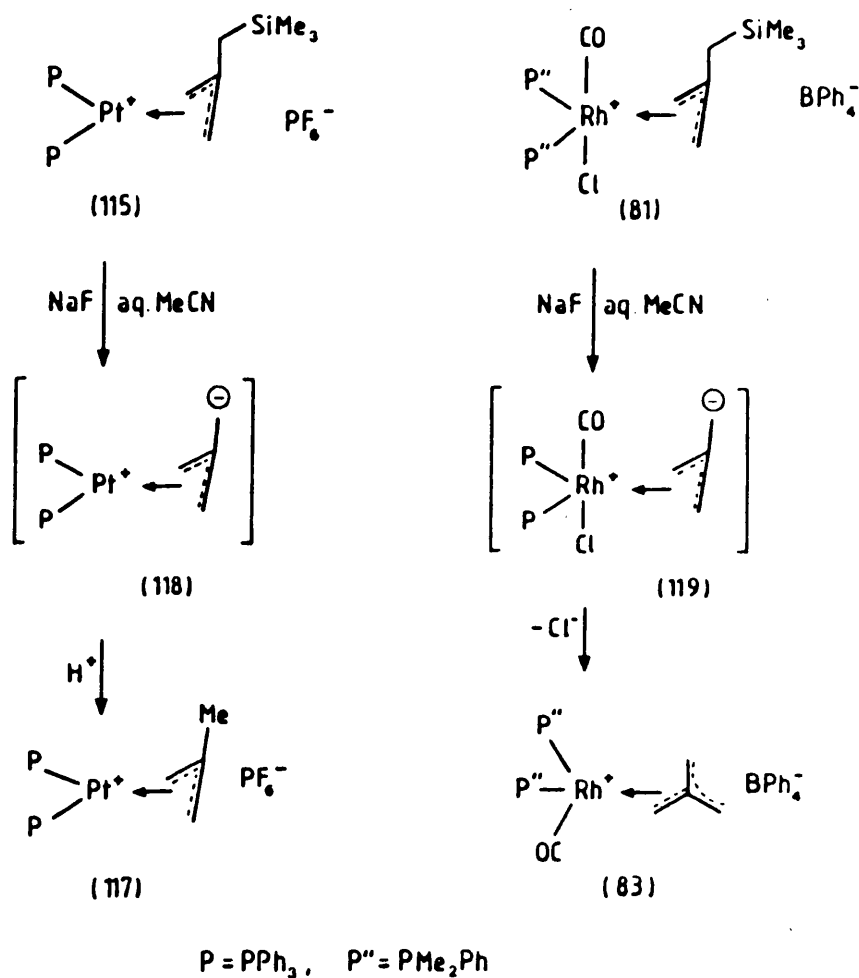
probably be analysed in terms of an AA'XX' spin-system ($X = {}^{31}\text{P}$).¹⁶³

The presumed mechanism for the formation of these two complexes (115) and (116) involves oxidative addition of the allylic methanesulphonate (74) to the low-valent metal centre forming an η^1 -allyl complex. Loss of a co-ordinated ligand converts the η^1 -allyl to an η^3 -allyl and the simple ion-exchange with the large excess of the ammonium hexafluorophosphate effectively removes the silylophilic methanesulphonate ion. The palladium complex (116) is of interest since it is one of the intermediates implicated in the generation of the trimethylenemethane species $[\text{Pd}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ (48), see Chapter 1.^{48,49}



Treatment of the η^3 -2-trimethylsilylmethylallyl platinum complex (115) with sodium fluoride in aqueous methyl cyanide afforded the proto-desilylated product $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]\text{PF}_6$ (117) in high yield. This reaction is in contrast with the rhodium η^3 -2-trimethylsilylmethylallyl complex $[\text{Rh}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{SiMe}_3)\text{CH}_2\}\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BPh}_4$ (81) which reacted with sodium fluoride in aqueous methyl cyanide to give the η^4 -trimethylenemethane complex $[\text{Rh}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BPh}_4$ (83) in quantitative yield, see Chapter 2. These two reactions illustrate the major differences between a trimethylenemethane ligand co-ordinated to a d^8 - and d^{10} -metal centre. Thus the species $[\text{Pt}(\text{trimethylenemethane})-(\text{PPh}_3)_2]$ (118), presumably formed in the desilylation of the platinum complex (115), is susceptible to protonation whereas desilylation of the

rhodium complex (81) may form an η^3 -trimethylenemethane intermediate (119) which rearranges to the observed η^4 -trimethylenemethane product (83) rather than abstract a proton from the solvent, Scheme 37.

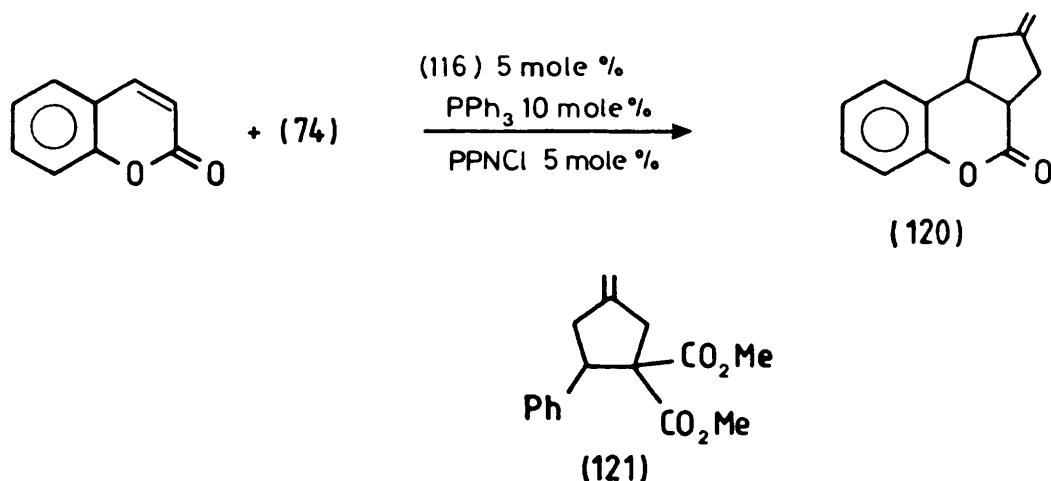


Scheme 37

Attempts to trap a platinum trimethylenemethane intermediate by desilylating the η^3 -allyl complex (115) in the presence of an electron-deficient alkene or alkyne were unsuccessful and only the protodesilylated η^3 -2-methylallyl complex (117) was isolated. Interestingly, a solution of the η^3 -2-trimethylsilylmethylallyl platinum complex (115) in $[^2H_1]$ -chloroform showed no sign of the protodesilylated product (117) after 24h. However, on addition of triphenylphosphine to the solution the η^3 -2-methylallyl product (117) was formed, the reaction being complete

after 12h at room temperature. It would thus appear that the addition of triphenylphosphine enhances desilylation of the platinum complex. This is consistent with the observation that ligand to palladium ratios of >4:1 are the rule for the cycloaddition of trimethylenemethane to electron-deficient alkenes.^{48,49} Although it is unclear what is causing the desilylation of the η^3 -2-trimethylsilylmethylallyl complex (115) it seems likely that the abstraction of a proton from water present in the n.m.r. solvent accounts for the protonation step.

Interestingly the palladium complex (116) is an effective catalyst for the cycloaddition of the trimethylenemethane fragment to alkenes. Thus, on refluxing a toluene solution of 5 mole % of the palladium complex (116) with bis-(triphenylphosphine)iminium chloride as a desilylating agent, triphenylphosphine (10 mole %), the methanesulphonate (74) (1 mole equivalent), and an excess of coumarin the cycloadduct (120) was formed in 23% yield based on (74). This compares favourably with the 42% yield of the adduct (121) which Trost et al. obtained from the reaction of the methanesulphonate (74) with dimethyl benzylidene-malonate in the presence of $[\text{Pd}(\text{PPh}_3)_4]$.⁴⁸ This experiment thus provides support for the mechanism proposed by Trost et al. for the palladium mediated cycloaddition of trimethylenemethane to alkenes. No cycloadduct (120) was obtained when the above experiment was repeated in the absence of the excess triphenylphosphine and again suggests that the excess of triphenylphosphine plays an important rôle in the formation of the trimethylenemethane intermediate in these cycloaddition reactions.



4.3 METAL CATALYSED CYCLOADDITION OF TRIMETHYLENEMETHANE TO ALKENES AND IMINES

It has previously been reported that the methanesulphonate (74) serves as a trimethylenemethane equivalent in the palladium mediated cycloadditions to electron-deficient alkenes, although the yield of the cycloadduct (121) was poorer than that obtained using the allylic acetate precursor (47).⁴⁸

Encouraged by the high reactivity of the methanesulphonate (74) with d^8 - and d^{10} -metal complexes the cycloaddition reactions of the trimethylenemethane precursor (74) were investigated further.

Coumarin was used as a standard trap to assess the activity of various low-valent metal complexes in catalysing the cycloaddition of the trimethylenemethane fragment to an electron-deficient alkene. None of the desired cycloadduct (120) could be isolated from the reactions of the methanesulphonate (74) with the d^8 -metal complexes trans-[IrCl(CO)(PPh₃)₂], [RhH(PPh₃)₄], [RhCl(PPh₃)₃], and [RuH₂(PPh₃)₄], the starting material being recovered unchanged. The conditions for these catalytic reactions involved refluxing the methanesulphonate (74) with an excess of coumarin and about 10 mole % of the metal catalyst in toluene for 16h. These

reactions were also carried out in the presence of additional triphenylphosphine or tri-n-butylphosphine but still no cycloadduct (120) could be isolated. Interestingly, some of these d^8 -metal complexes have been found to be active catalysts for the allylation of carbonucleophiles with allylic carbonates.¹⁶⁴ However, although d^8 -metal complexes did not catalyse the cycloaddition reaction a metal-catalysed cycloaddition of trimethylenemethane to coumarin was achieved using the d^{10} -metal complexes $[Ni\{P(OEt)_3\}_4]$, $[Pd(PPh_3)_4]$, and $[Pt(PPh_3)_4]$. Interestingly, the nickel phosphite catalyst afforded the cycloadduct (120) in 77% yield but the palladium phosphine catalyst afforded (120) in only 27% yield based on (74) as the limiting reagent. The platinum system afforded a very low yield of the desired cycloadduct (120). The yield of the cycloadduct obtained from the $[Pd(PPh_3)_4]$ catalysed reaction is approximately the same as that obtained from the reaction using the η^3 -2-trimethylsilylmethylallyl palladium complex (116) as the catalyst and provides further evidence that (116) is an intermediate in these cycloaddition reactions. The nickel complex $[Ni\{P(OEt)_3\}_4]$ was also an effective catalyst for mediating the cycloaddition of trimethylenemethane to other electron-deficient alkenes and the results are summarised in Table 3.

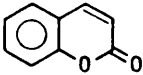
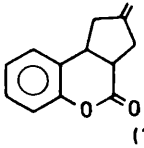
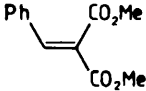
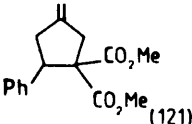
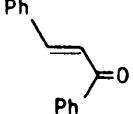
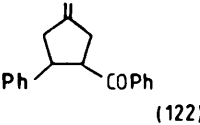
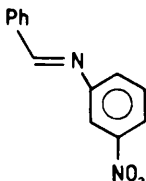
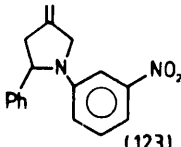
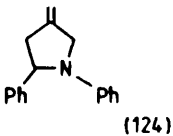
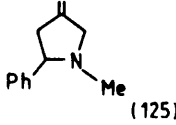
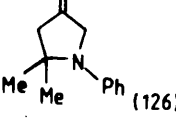
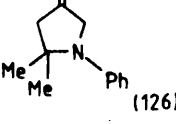
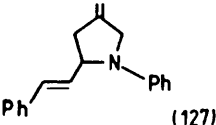
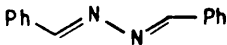
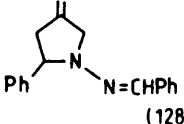
Following the success of the nickel-catalysed cycloaddition of trimethylenemethane to alkenes, it was discovered that $[Ni\{P(OEt)_3\}_4]$ was also very effective in catalysing the cycloaddition of the trimethylenemethane fragment to the carbon-nitrogen double bond of an imine to afford a high-yield one-step synthesis of the 4-methylenepyrrolidine ring system. This reaction is also catalysed by a palladium(0)-triethylphosphite catalyst generated from the reaction of the palladium(0) precursor $[Pd_2(dba)_3 \cdot CHCl_3]$ and an excess of triethylphosphite, but the

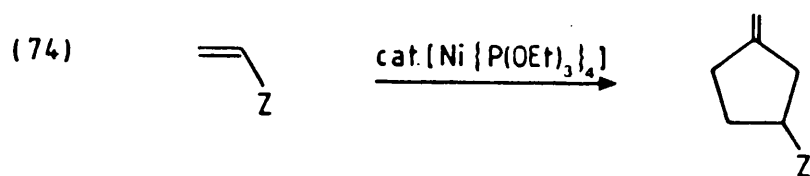
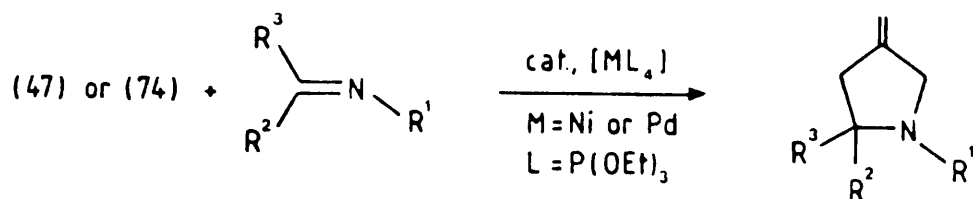
analogous platinum system $[\text{Pt}\{\text{P}(\text{OEt})_3\}_n]$ is not an effective catalyst. The general reaction is shown in Scheme 38 and Table 3 summarises the results. The allylic acetate (47) also serves as a precursor to the trimethylenemethane fragment in the palladium catalysed [3+2] cycloaddition to imines (entries 7 and 8). Surprisingly, $[\text{Pd}(\text{PPh}_3)_4]$, which was a very good catalyst for mediating the cycloaddition of the trimethylenemethane fragment to electron-deficient alkenes, was a poor catalyst for the cycloaddition of trimethylenemethane to imines (entries 8 and 9). This indicates that the choice of ligand is an important factor in these cycloaddition reactions. Trost *et al.* has previously noted that the yields of the cycloadducts of substituted trimethylenemethane with alkenes were improved if the catalyst was switched from $[\text{Pd}(\text{PPh}_3)_4]$ to $[\text{Pd}\{\text{P}(\text{OPr}^i)_n\}]$.^{52,55}

The reaction conditions for all of the examples quoted in Table 3 involved refluxing a toluene solution of the acetate (47) or methane-sulphonate (74) in the presence of 5 mole % of the nickel(0) or palladium(0) catalyst and the acceptor. The isolated yields are based upon results obtained using (47) or (74) as the limiting reagent since 2.5 mole equivalents of the imine acceptor were employed. The reaction mixture was refluxed for 16h under nitrogen and the products were isolated by column chromatography. The pyrrolidine adducts with an N-aryl fragment appear to be oxygen-sensitive and so flash chromatography¹⁶⁵ was performed under nitrogen. To demonstrate that these reactions are metal catalysed, a solution of (74), benzylidene aniline, and triethylphosphite in toluene was refluxed for 16h. No cycloadducts could be isolated and only starting material was recovered.

The adducts (120), (121), and (122) have spectral properties identical with those reported in the literature.⁴⁸ The cycloadducts in Table 3 are

TABLE 3

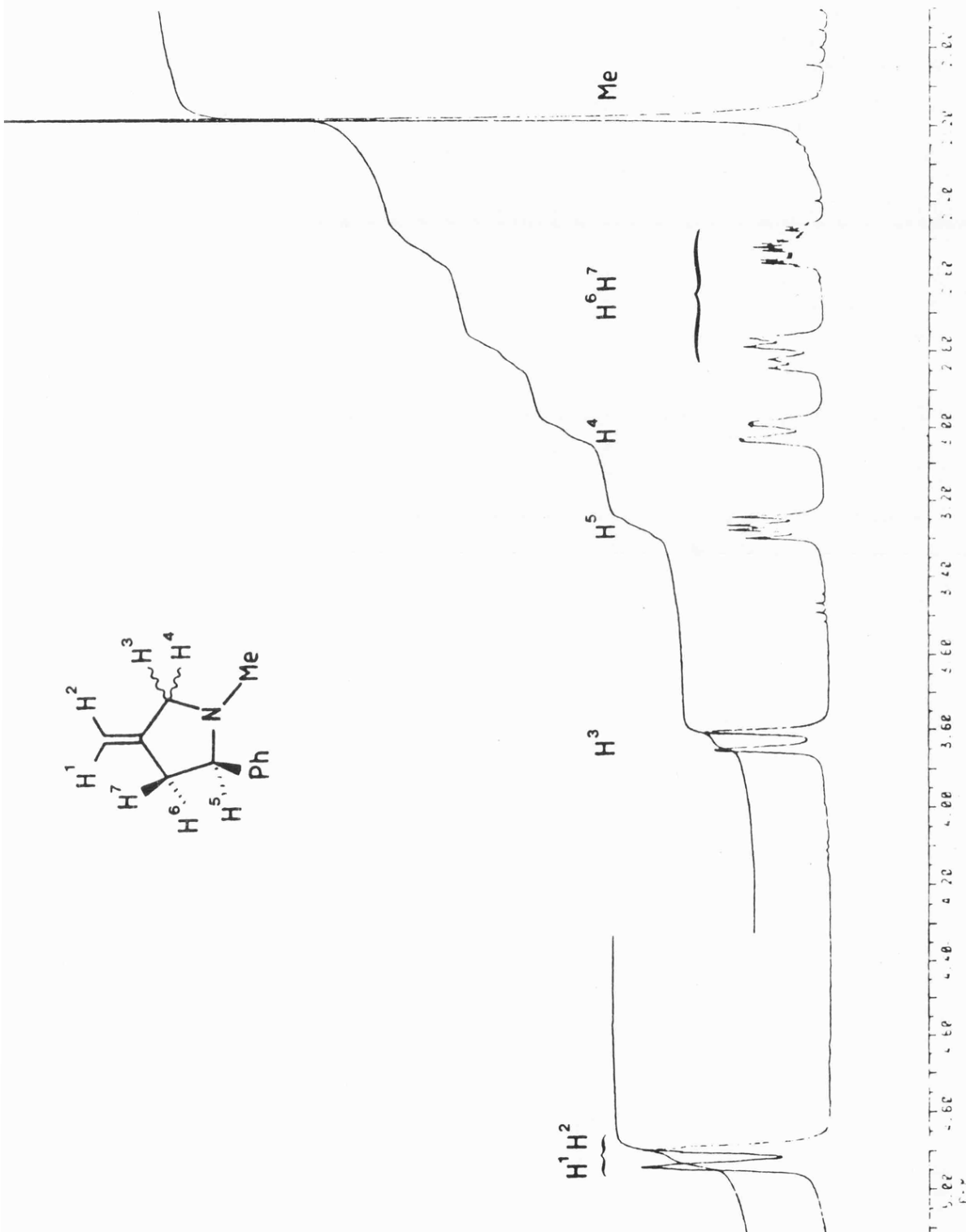
Entry	Acceptor	Reagent	Catalyst	Adduct	Yield, %
1		74	$[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$	 (120)	77
2		74	"	 (121)	87
3		74	"	 (122)	50
4		74	"	 (123)	58
5	$\text{PhCH}=\text{NPh}$	74	"	 (124)	77
6	"	74	$[\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3]$ 8 $\text{P}(\text{OEt})_3$	"	52
7	"	47	"	"	73
8	"	47	$[\text{Pd}(\text{PPh}_3)_4]$	"	27
9	"	74	$[\text{Pd}(\text{PPh}_3)_4]$	"	19
10	$\text{PhCH}=\text{NMe}$	74	$[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$	 (125)	68
11	$\text{PhN}=\text{CMe}_2$	74	$[\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3]$ 8 $\text{P}(\text{OEt})_3$	 (126)	50
12	$\text{PhN}=\text{CMe}_2$	74	$[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$	 (126)	40
13		74	"	 (127)	69
14		74	$[\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3]$ 8 $\text{P}(\text{OEt})_3$	 (128)	55



$\text{Z} = \text{electron-withdrawing group}$

Scheme 38

formulated on the basis of n.m.r. and i.r. spectroscopic data, mass spectra, and elemental analysis. The exocyclic methylene group in both the cyclopentanoid and pyrrolidine adducts is readily characterised by multiplets in the region δ 4.8 to 5.1 p.p.m. in the ^1H n.m.r. spectrum. The ^1H n.m.r. spectrum for the pyrrolidine adduct (125) is shown in Scheme 39 with the aromatic region omitted. The ring protons appear as a series of multiplets consistent with AB and ABX spin-systems. Thus there is a large geminal coupling between H^6 and H^7 and both protons show additional coupling to the vicinal proton H^5 . The ring protons also exhibit a smaller coupling to each other and to the methylene group. The ^1H n.m.r. spectrum of the cycloadduct (126) is much simpler due to the gem-dimethyl substituents creating a symmetrically substituted ring, the ring protons thus appearing as two singlets with a minor coupling to the exocyclic double bond. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra of all of these adducts exhibit resonances at δ 148-150 and 106-107 p.p.m. associated with the quaternary carbon and the methylene alkene carbons respectively. These shifts are in good agreement with methylenecyclopentane itself (δ 152.9 and 104.3 p.p.m.).¹⁶⁶



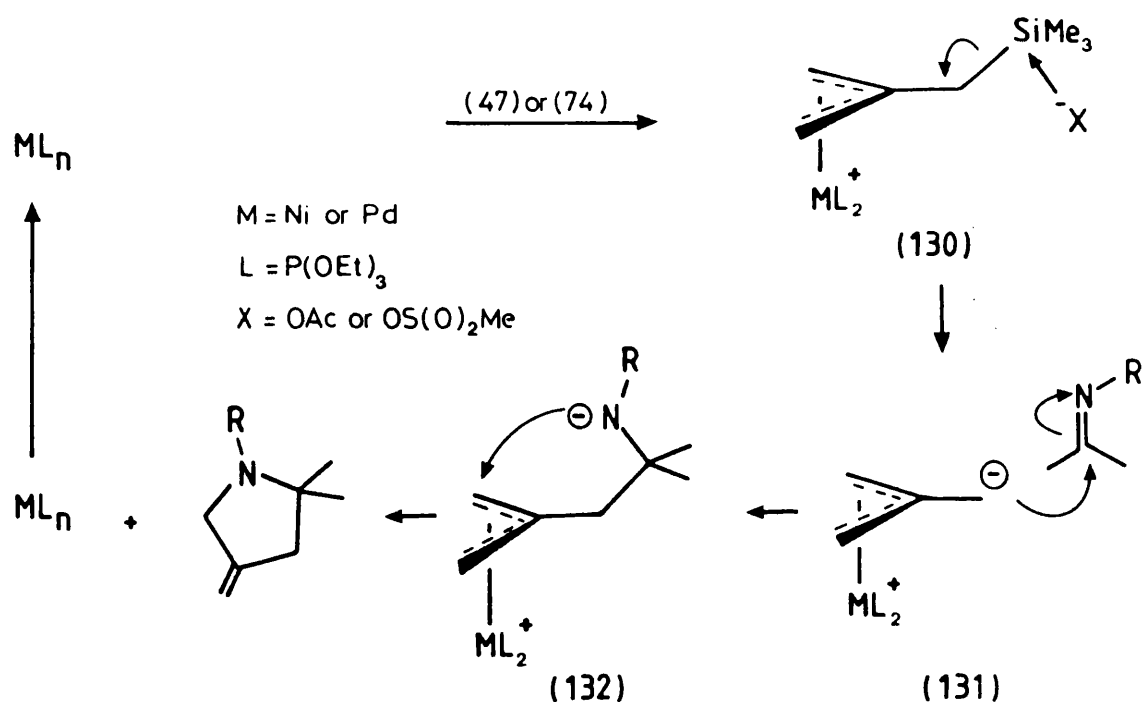
Scheme 39

The cycloaddition of trimethylenemethane to imines shows excellent chemoselectivity. Surprisingly, no cycloaddition of trimethylenemethane to the carbon-carbon double bond of an α,β -unsaturated imine was detected and only the cycloadduct (127), resulting from addition of the trimethylenemethane fragment to the carbon-nitrogen double bond, was isolated (entry 13). The ^1H n.m.r. spectrum of (127) exhibits a doublet of doublets and a doublet at δ 6.11 and 6.44 p.p.m. respectively consistent with the presence of a trans-substituted carbon-carbon double bond with a phenyl substituent [$^3J(\text{HH}) = 15.8$ Hz]. The resonance at δ 6.11 also couples strongly to a multiplet at δ 4.5 p.p.m. assigned to the ring proton attached to C-2 of the pyrrolidine ring. Dibenzylidenehydrazine and the methanesulphonate (74) reacted in the presence of a palladium triethylphosphite catalyst to yield the [3+2] cycloaddition product (128) (entry 14) and no [3+4] adduct was detected. This contrasts with the reactions of the acetate (47) with 1,3-dienes which afforded both [3+2] and [3+4] cycloaddition products.⁴⁸

The exocyclic methylene moiety shows no tendency towards isomerisation under the cycloaddition conditions. In the palladium and nickel catalysed co-dimerisation of alkylidenecyclopropanes with ketenimines double-bond migration occurs.¹⁶⁰ Interestingly, the cycloadduct (124) was not obtained from the co-dimerisation of methylenecyclopropane with benzylidene aniline ($\text{PhCH}:\text{NPh}$) in the presence of $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$. However these co-dimerisation reactions usually favour a ligand to metal ratio of 1:1 whereas the acetate (47) and methanesulphonate (74) reactions usually employ ligand to metal ratios of 4:1.⁵⁷ In fact, addition of small amounts of triethylphosphite prolongs the lifetime of the catalytic system preventing the formation of metallic deposits.

The mechanism for these [3+2] reactions of the acetate (47) and the

methanesulphonate (74) with imines in the presence of a nickel(0) or palladium(0) catalyst is thought to proceed via oxidative addition of the allylic ester to the low-valent metal centre, Scheme 40. Initially, the ester group may be co-ordinated to the metal centre as seen in previous examples of the reactions of allylic halides and esters with d^{10} -metal complexes. Thus $[Pd(PPh_3)_4]$ reacts with 3-chloro-2-methylprop-1-ene to afford the η^1 -allyl complex trans- $[Pd\{\eta^1-CH_2C(Me):CH_2\}Cl-(PPh_3)_2]$ ¹⁶⁷ while treating $[Ni(COD)_2]$ with two mole equivalents of triphenylphosphine and 3-acetoxyp-1-ene gave the η^3 -allyl complex $[Ni(\eta^3-CH_2CHCH_2)(OAc)(PPh_3)]$.¹⁶⁸ It is important to note that in the catalytic reaction the presence of excess of phosphite ligand will effect displacement of the ester group from the metal in an intermediate of the type $[M\{\eta^3-CH_2C(SiMe_3)CH_2\}(X)(L)]$ (129) and form a cationic allyl complex (130) which can then undergo desilylation. However, in an intermediate such as (129) the ester group is not readily available to attack the silicon group. This may explain why these [3+2] cycloaddition reactions favour a ligand to metal ratio of >4:1. Similar η^3 -allyl intermediates to (130) have been postulated in the palladium(0) catalysed allylic alkylation reactions.⁴⁷ The isolation of the η^3 -2-trimethylsilylmethylallyl palladium complex (116) and the observation that it is an active catalyst in these [3+2] cycloaddition reactions lends support to this postulated mechanism. The acetate or methanesulphonate ion is now available to attack the trimethylsilyl group to effect desilylation of the cationic η^3 -2-trimethylsilylmethylallyl complex (130) and form an η^3 -trimethylenemethane intermediate (131). Theoretical calculations have shown that this is the most energetically favoured geometry for a trimethylenemethane ligand co-ordinated to a d^{10} - ML_2 fragment and not the alternative η^4 -trimethylenemethane arrange-



Scheme 40

ment (108).^{50,51,53} These calculations also indicate that there is a large negative charge on the unco-ordinated methylene group and positive charge on the metal, which leads to the zwitterionic formulation (131). The trimethylenemethane intermediate (131) therefore contains a highly nucleophilic carbon atom and so attack at the electro-positive carbon of an imine would be expected resulting in the formation of an η^3 -allyl intermediate (132) which contains a pendant anionic nitrogen centre. Nitrogen nucleophiles readily attack η^3 -allyl palladium complexes⁴⁷ and so a 5-endo-trig ring closure occurs^{169,170} liberating the 4-methylenepyrrolidine product and regenerating the metal(0) catalyst. This mechanism is very similar to that postulated by Trost et al. in the palladium-mediated cycloaddition approach to cyclopentanoids and 4-methylenetetrahydrofurans.^{57,58}

The inability of d^8 -metal complexes to catalyse the addition of

trimethylenemethane to alkenes or imines is presumably due to the formation of stable η^4 -trimethylenemethane complexes of the type $[M\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{L}_3]$ in which all three methylene carbons are strongly co-ordinated to the metal centre, see Chapter 2. Interestingly, heating the complex $[\text{Ir}\{\eta^4\text{-C}(\text{CH}_2)_3\}\text{Cl}(\text{CO})(\text{PPh}_3)]$ (76) in toluene with triphenylphosphine for 50h under nitrogen afforded the complex trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$. However no cycloadducts of the trimethylenemethane fragment with an electron-deficient alkene could be isolated from this reaction. Similar disappointing results were observed when various iron trimethylenemethane complexes were decomposed by oxidative degradation with cerium(IV),¹³ by photolysis,³⁴ or by reaction with trimethylamine-N-oxide.¹⁷¹ These results are in contrast with the closely related η^4 -cyclobutadiene iron complex (2). Decomposition of (2) affords a very convenient source of cyclobutadiene which reacts with alkenes to give Diels-Alder type adducts in high yield.¹ It is interesting to note that the $\underline{d}^8\text{-ML}_4$ and $\underline{d}^{10}\text{-ML}_2$ fragments are isolobal.¹⁷² Thus co-ordination of trimethylenemethane to a $\underline{d}^8\text{-ML}_4$ fragment should give an η^3 -trimethylenemethane arrangement which would be expected to undergo similar reactions to the $[\text{M}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ ($\text{M}=\text{Ni}, \text{Pd}, \text{or Pt}$) intermediates, providing that a rearrangement to an η^4 -trimethylenemethane geometry with dissociation of a co-ordinated ligand does not occur.

The cycloaddition of trimethylenemethane to other acceptors was also investigated. No cycloaddition products could be isolated from the reactions of benzonitrile with the methanesulphonate (74) in the presence of either nickel(0) or palladium(0) catalysts. Similarly, the attempted cycloaddition of the trimethylenemethane fragment to alkynes also failed. Recently a two-step route has been developed by Trost et al. which effectively results in the cycloaddition of the trimethylenemethane

fragment to alkynes. This synthesis of 4-methylene-1-cyclopentenenes involves the cycloaddition of the trimethylenemethane fragment to a substituted bicyclo[2.2.1]hepta-2,5-diene using a palladium(0) phosphite catalyst. Flash vacuum thermolysis of the cycloadduct results in a retro Diels-Alder reaction liberating cyclopentadiene and the required 4-methylene-1-cyclopentene.¹⁷³ The inability of the palladium or nickel complexes to catalyse the cycloaddition of the trimethylenemethane fragment, generated from (47) or (74), to carbon-carbon triple bonds is in marked contrast with the low-valent metal-catalysed co-dimerisation of alkylidenecyclopropanes with alkynes which afforded 4-methylene-1-cyclopentenenes in high yield.⁴¹ This suggests that the alkylidenecyclopropane and the silyl-ester reactions proceed via different intermediates.

The methanesulphonate (74) reacted in the presence of benzaldehyde and $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ to afford a 4-methylenetetrahydrofuran adduct resulting from a [3+2] addition of the trimethylenemethane fragment to the carbon-oxygen double bond although the isolated yield was poorer than that obtained using the tin-acetate reagent (51).⁵⁸

4.4 CONCLUSION

The silicon precursors introduced by Trost et al. have renewed interest in trimethylenemethane metal complexes. The allylic methane-sulphonate (74) not only acts as a precursor to stable η^4 -trimethylenemethane metal complexes but reacts rapidly with d^{10} -metal centres to afford η^3 -2-trimethylsilylmethylallyl complexes of platinum(II) and palladium(II). The isolation of the palladium complex (116) provides support for the generation of the catalytic species $[\text{Pd}\{\eta^3\text{-C}(\text{CH}_2)_3\}(\text{PPh}_3)_2]$ in the [3+2] cycloaddition approach to five-membered rings.^{48,49} The methanesulphonate (74) also acts as an effective reagent for the cyclo-

addition of the trimethylenemethane fragment to electron-deficient alkenes and to imines, the latter reaction affording a high yield synthesis of 4-methylenepyrrolidines in the presence of either nickel(0) or palladium(0) phosphite catalysts.¹⁷⁴ Synthetically, this one-step procedure represents an improvement in yield, cleanliness, and convenience in comparison to the earlier two-step synthesis of 4-methylenepyrrolidines which used a more expensive tin reagent.¹⁵⁷ The ability of a readily available nickel(0) catalyst to mediate these cycloaddition reactions is also attractive in comparison to the more expensive palladium complexes, which are usually employed in these [3+2] cycloaddition reactions.⁵⁷

4.5 EXPERIMENTAL

Experimental techniques were as described in Chapter 2. Flash chromatography was performed according to the method reported by Still *et al.*¹⁶⁵ on Camlab (grade 60, 230-400 mesh) silica gel. Pseudo first-order analysis of second-order ¹H n.m.r. spectra are reported. The compounds, [Pt(PPh₃)₄],¹⁷⁵ [Pd(PPh₃)₄],¹⁷⁶ [Ni{P(OEt)₃}₄],¹⁷⁷ [Pt(η²-C₂H₄)(PPh₃)₂],¹⁷⁸ [Pt(η²-trans-stilbene)(PPh₃)₂],¹⁷⁹ [Pd₂(dba)₃.CHCl₃],¹⁸⁰ PhCH:NPh,¹⁸¹ Me₂C:NPh,¹⁸² dibenzylidenehydrazine,¹⁸³ the other imines,^{184,185} and dimethyl benzylidenemalonate¹⁸⁶ were prepared as in the literature procedures. Dimethylacetylenedicarboxylate, acrylonitrile, and methyl acrylate were obtained from Aldrich and were distilled prior to use. Coumarin (B.D.H.), chalcone (Aldrich), and triethylphosphite (Lancaster) were obtained from commercial sources.

Reactions of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74) with d¹⁰-metal complexes

(i) with [Pt(PPh₃)₄]

To a solution of [Pt(PPh₃)₄] (0.5 g, 0.4 mmol) in benzene (5 cm³) was added (74) (0.18 g, 0.8 mmol). A white solid formed immediately, the solution was filtered, the product washed with light petroleum, dried in vacuo, and identified as [Pt(η³-CH₂CMeCH₂)(PPh₃)₂]OS(O)₂Me (114) (0.26 g, 75%) m.p. 200°C (decomp.), (Found: C, 56.9; H, 4.7. C₄₁H₄₀O₃P₂PtS requires C, 56.6; H, 4.6%); i.r. ν_{SO} 1200 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 2.02 [s, 3H, Me, J(HPt) 63.0], 2.58 (s, 3H, MeSO₃), 3.06 [d, 2H, anti, J(HP) 8.2, J(HPt) 39.7], 3.47 (br s, 2H, syn), and 7.4 p.p.m. (m, 30H, PPh₃).

(ii) with [Pt(PPh₃)₄] and acrylonitrile

The reaction was repeated as in (i) but in the presence of 2 mole equivalents of acrylonitrile. The complex (114) was isolated (0.2 g, 58%).

(iii) with [PtL(PPh₃)₂] (L = η²-C₂H₄ or η²-PhCH:CHPh)

[PtL(PPh₃)₂] (0.53 mmol) was added to a solution of (74) (0.37 g, 0.15 mmol) and NH₄PF₆ (1.5 g) in acetone (10 cm³). After stirring for 1h the solvent was removed in vacuo and the residue extracted with benzene and filtered. The solution was concentrated and addition of diethyl ether gave white crystals which were dried in vacuo and identified as [Pt{η³-CH₂C(CH₂SiMe₃)CH₂}(PPh₃)₂]PF₆ (115) (0.4 g, 76%) m.p. 125°C (decomp.), (Found: C, 52.0; H, 4.5. C₄₃H₄₅F₆P₃PtSi requires C, 52.1; H, 4.6%); n.m.r. (CDCl₃): ¹H (300 MHz), δ 0.0 (s, 9H, SiMe₃), 1.58 [s, 2H, CH₂SiMe₃, J(HPt) 36.5], 2.81 [d, 2H, H², J(HP) 8.2, J(HPt) 42.4], 3.07 (br s, 2H, H¹), and 7.3 (m, 30H, PPh₃); ¹³C-{¹H} (75 MHz), δ -1.7 (s, SiMe₃), 32.2 [s, C³, J(CPt) 27.0], 66.1 (m, AXX' system, C²),

and 141.4 p.p.m. (s, C¹). The Me₃Si group in the sample is set at 0.0 p.p.m. for ¹H n.m.r. shifts. Figure 18.

(iv) with [Pd(PPh₃)₄]

[Pd(PPh₃)₄] (0.5 g, 0.43 mmol) was added to a solution of (74) (0.3 g, 1.35 mmol) and NH₄PF₆ (1.3 g) in acetone (5 cm³). After stirring for 1h the solvent was removed in vacuo, the residue extracted with dichloromethane and filtered. Addition of diethyl ether to the filtrate gave white crystals of [Pd{η³-CH₂C(CH₂SiMe₃)CH₂}(PPh₃)₂]PF₆ (116) (0.3 g, 81%) m.p. 164°C (decomp.), (Found: C, 56.9; H, 5.1. C₄₃H₄₅F₆P₃PdSi requires C, 57.2; H, 5.0%); n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 0.07 (s, 9H, SiMe₃), 1.29 (s, 2H, CH₂SiMe₃), 3.18 (m, 2H, H²), 3.49 (br s, 2H, H¹), and 7.3 (m, 30H, PPh₃); ¹³C-{¹H} (100 MHz), δ -2.18 (s, SiMe₃), 31.0 (s, C³), 74.9 (t, AXX' system, C², J=15.5), and 143.6 p.p.m. (s, C¹). Figure 18.

The multiplet assigned to H² is very similar to that observed in the related η³-allyl complex [Pd(η³-CH₂CMeCH₂)(dppe)]PF₆.¹⁶³

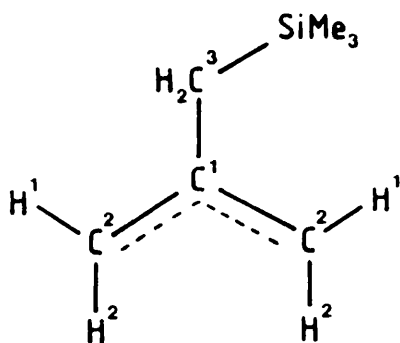


FIGURE 18

Reactions of $[\text{Pt}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{SiMe}_3)\text{CH}_2\}(\text{PPh}_3)_2]\text{PF}_6$ (115)

(i) with NaF in aqueous methyl cyanide

A solution of (115) (0.08 g, 0.08 mmol) and NaF (0.2 g) in aqueous methyl cyanide was stirred for 24h at room temperature. The solvent was removed in vacuo, the residue extracted with dichloromethane, and dried over potassium carbonate. The solution was filtered and addition of light petroleum gave a white powder which was identified as $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]\text{PF}_6$ (117) (0.06 g, 82%) by comparison of its ^1H n.m.r. spectrum with an authentic sample.¹⁶¹

(ii) with NaF and dimethylacetylenedicarboxylate (DMAD)

A solution of (115) (0.08 g, 0.08 mmol), NaF (0.2 g), and DMAD (1 cm³) in tetrahydrofuran (5 cm³) was refluxed for 16h. The solvent was removed in vacuo, dissolved in dichloromethane and filtered. Addition of light petroleum gave a white solid which was identified as $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]\text{PF}_6$ (117) (0.05 g, 68%) by comparison of its ^1H n.m.r. spectrum with an authentic sample.¹⁶¹

(iii) with NaF and methylacrylate

Under analogous conditions to (ii) a solution of (115) (0.08 g, 0.08 mmol), NaF (0.2 g), and methylacrylate (1 cm³) in tetrahydrofuran (5 cm³) was refluxed for 16h. The reaction was worked up as in (ii) and afforded (117) (0.06 g, 82%) which was identified by comparison of its ^1H n.m.r. spectrum with an authentic sample.¹⁶¹

(iv) with triphenylphosphine

To a solution of (115) (0.05 g, 0.05 mmol) in $[\text{}^2\text{H}_1]\text{-chloroform}$ (0.5 cm³) was added triphenylphosphine (0.01 g, 0.04 mmol). After 15 minutes the ^1H n.m.r. spectrum indicated some of the protodesilylated product (117) had formed. The reaction was complete after 12h. Addition of

light petroleum gave a white solid which was identified as (117) (0.03 g, 67%) by comparison of its ^1H n.m.r. spectrum with an authentic sample.¹⁶¹

Reactions of $[\text{Pd}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{SiMe}_3)\text{CH}_2\}(\text{PPh}_3)_2]\text{PF}_6$ (116)

(i) A solution of (74) (0.25 g, 1.1 mmol), triphenylphosphine (0.05 g, 0.2 mmol), bis-(triphenylphosphine)iminium chloride (0.05 g, 0.09 mmol), (116) (0.08 g, 0.09 mmol), and coumarin (0.37 g, 2.5 mmol) in toluene (2 cm³) was refluxed for 18h. The solvent was removed in vacuo (15 mmHg) and the ^1H n.m.r. spectrum indicated that all of (74) had reacted.

Chromatography of the residue gave the cycloadduct (120) (0.05 g, 23%) by comparison of its ^1H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

(ii) The reaction was repeated as in (i) but in the absence of additional triphenylphosphine. The solvent was removed in vacuo (15 mmHg) and the ^1H n.m.r. spectrum indicated that (74) was still present. T.L.C. of the reaction mixture indicated that only starting material was present.

cis-2 Methylene-4,5-benzo-6-oxa-7-oxohydrindan (120)

(i) $[\text{Pd}_2(\text{dba})_3.\text{CHCl}_3]/\text{PPh}_3$ catalyst

(74) (0.25 g, 1.1 mmol), coumarin (0.37 g, 2.5 mmol), $[\text{Pd}_2(\text{dba})_3.\text{CHCl}_3]$ (0.023 g, 0.02 mmol), and triphenylphosphine (0.05 g, 0.19 mmol) in toluene (4 cm³) were refluxed for 14h. The solvent was removed in vacuo and the residue was purified by flash column chromatography (1:2 diethyl ether/light petroleum) to give the title compound (0.06 g, 27%) which was identified by comparison of the ^1H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

(ii) $[\text{Pt}(\text{PPh}_3)_4]$ catalyst

The reaction was repeated as in (i) using $[\text{Pt}(\text{PPh}_3)_4]$ (0.11 g, 0.1

mmol) as the catalyst. The usual work up procedure afforded the title compound (0.04 g, 18%) which was identified by comparison of the ^1H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

(iii) The reactions with trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $\text{RhH}(\text{PPh}_3)_4$, $[\text{RhCl}(\text{PPh}_3)_3]$, and $[\text{RuH}_2(\text{PPh}_3)_4]$ as catalysts were performed as in (i) using 0.01 mmol of the metal catalyst. The reactions were also run with additional triphenylphosphine or tri-n-butylphosphine (0.02 mmol). The solvent was removed from the reaction mixture in vacuo (15 mmHg) and analysed by ^1H n.m.r. spectra and by T.L.C. These reactions afforded none of the required cycloadduct (120). The coumarin and the methane-sulphonate (74) were recovered unchanged.

(iv) $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ catalyst

(74) (0.25 g, 1.1 mmol), coumarin (0.37 g, 2.5 mmol), and $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol) in toluene (4 cm^3) were refluxed for 18h. The solvent was removed in vacuo and the residue was purified by flash column chromatography (1:2 diethyl ether/light petroleum) to give the title compound (0.17 g, 77%) which was identified by comparison of the ^1H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

Methyl 1-(Methoxycarbonyl)-2-phenyl-4-methylenecyclopentane-1-carboxylate (121)

(74) (0.25 g, 1.1 mmol), dimethyl benzylidenemalonate (0.58 g), and $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol) in toluene (4 cm^3) were refluxed for 18h. The solvent was removed in vacuo. Purification of the residue by flash column chromatography (1:5 diethyl ether/light petroleum) gave the title compound (0.26 g, 87%) which was identified by comparison of the ^1H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

trans-3-Benzoyl-4-phenyl-1-methylenecyclopentane (122)

(74) (0.25 g, 1.1 mmol), chalcone (0.52 g, 2.5 mmol), and $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol) in toluene (5 cm³) were refluxed for 20h. The solvent was removed in vacuo and the residue was purified by flash column chromatography (1:3 diethyl ether/light petroleum) to give the title compound (0.15 g, 52%) which was identified by comparison of the ¹H n.m.r. and i.r. spectra with an authentic sample.⁴⁸

The pyrrolidine adducts were obtained by a similar procedure to that used for the isolation of the cyclopentanoid derivatives. Chromatography refers to flash column chromatography. A typical run is illustrated in the synthesis of 4-methylene-2-phenyl-N-(m-nitrophenyl)-pyrrolidine (123). The yields of the cycloadducts have not been optimised.

Synthesis of 4-methylene-2-phenyl-N-(m-nitrophenyl)pyrrolidine (123)

A solution of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74) (0.25 g, 1.1 mmol), $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol), and N-benzylidene-m-nitroaniline (0.54 g, 2.4 mmol) in toluene (5 cm³) was heated to reflux for 15h. The solvent was removed in vacuo and the crude product was purified by chromatography (1:5 diethyl ether/light petroleum) to give (0.18 g, 58%) of the title compound as an orange solid, TLC R_f 0.3 (1:5 diethyl ether/light petroleum), (Found: C, 73.1; H, 6.1; N, 9.4. C₁₇H₁₆O₂N₂ requires C, 72.8; H, 5.8; N, 9.9%); i.r. 3060w, 2960w, 2920w, 1660w, 1610m, 1560w, 1520s, 1490m, 1460m, 1445w, 1425w, 1370s, 1330s, 1230m, 1165m, 1110w, 1030w, 880m, 840m, 760m, 695s, cm⁻¹; mass spectrum, m/e (%): M⁺ 280(100), 203(72), 157(17), 151(25), 143(15), 129(12), 128(15), 106(15), 105(18), 104(18); n.m.r. (CDCl₃): ¹H (300 MHz), δ 2.56 (br d, 1H, J = 15.2), 3.26 (ddm, 1H, J = 15.2, 8.9), 4.25 (AB spin-system,

2H, $J = 13.5$), 4.94 (dd, 1H, $J = 8.9, 2.3$), 5.02 (br s, 1H), 5.16 (br s, 1H), and 7.3 (m, 9H); $^{13}\text{C}-\{^1\text{H}\}$ (75 MHz), δ 42.4, 53.8, 62.7, 106.3, 108.2, 110.7, 117.9, 125.2, 127.2, 128.8, 129.4, 142.9, 143.2, and 146.8 p.p.m.

4-Methylene-2-phenyl-N-phenylpyrrolidine (124)

(i) A solution of 3-trimethylsilyl-2-(acetoxymethyl)prop-1-ene (47) (0.2 g, 1.1 mmol), $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (0.01 g, 0.01 mmol), triethylphosphite (0.04 g, 0.24 mmol), and PhCH:NPh (0.5 g, 2.7 mmol) in toluene (4 cm³) was refluxed for 15h. The solvent was removed in vacuo and the crude product purified by flash column chromatography to give the title compound (0.19 g, 73%): R_f 0.35 (1:40 diethyl ether/light petroleum), (Found: C, 86.3; H, 7.5; N, 5.8. $\text{C}_{17}\text{H}_{17}\text{N}$ requires C, 86.8; H, 7.3; N, 5.9%); i.r. (film): 3060m, 3020m, 2900m, 2850w, 1670m, 1600s, 1500s, 1465m, 1450m, 1360s, 1240w, 1160m, 1070w, 885m, 855m, 745s, 700s, cm⁻¹; mass spectrum, m/e (%): M^+ 235(100), 158(88), 130(20), 106(32), 104(21), 91(16), 77(57), 73(19); n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.5 (dm, 1H, $J = 15.0, 1.5$), 3.2 (ddm, 1H, $J = 15.0, 9.0$), 4.2 (AB spin-system, 2H, $J = 13.4$), 4.88 (dd, 1H, $J = 9.0, 2.0$), 4.96 (br s, 1H), 5.1 (br s, 1H), and 7.0 (m, 10H); $^{13}\text{C}-\{^1\text{H}\}$ (75 MHz), δ 42.6, 53.9, 62.6, 107.3, 112.3, 116.2, 125.7, 126.8, 127.1, 128.6, 129.0, 144.3 and 146.5 p.p.m.

(ii) A solution of (74) (0.25 g, 1.1 mmol), $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (0.01 g, 0.02 mmol), triethylphosphite (0.04 g, 0.24 mmol), and PhCH:NPh (0.5 g, 2.7 mmol) in toluene was refluxed for 15h. The product was isolated as above to give the title compound (0.13 g, 52%) which was identified by comparison of the ^1H and $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectra with an authentic sample.

(iii) A solution of (74) (0.25 g, 1.1 mmol), $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07

mmol), and PhCH:NPh (0.5 g, 2.7 mmol) under analogous conditions to the above gave the title compound (0.2 g, 77%) which was identified by comparison of the ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. with an authentic sample.

(iv) (74) (0.25 g, 1.1 mmol), $[\text{Pd}_2(\text{dba})_3.\text{CHCl}_3]$ (0.01 g, 0.02 mmol), triphenylphosphine (0.06 g, 0.23 mmol), and PhCH:NPh (0.5 g, 2.7 mmol) under analogous conditions to the above gave the title compound (ca. 0.05 g, 19%).

(v) (47) (0.2 g, 1.1 mmol), $[\text{Pd}_2(\text{dba})_3.\text{CHCl}_3]$ (0.01 g, 0.02 mmol), triphenylphosphine (0.06 g, 0.23 mmol), and PhCH:NPh (0.5 g, 2.7 mmol) under analogous conditions to the above gave the title compound (0.07 g, 27%).

Synthesis of 4-methylene-2-phenyl-N-methylpyrrolidine (125)

A solution of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (74) (0.25 g, 1.1 mmol), $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol), and PhCH:NMe (0.3 g, 2.5 mmol) in toluene (3 cm^3) was heated to reflux for 15h. The reaction mixture was acidified with hydrochloric acid (0.1 M, $3 \times 10 \text{ cm}^3$). The aqueous phase was separated and made strongly basic with cold aqueous sodium hydroxide (2.0 M) and extracted with diethyl ether ($5 \times 10 \text{ cm}^3$). The organic layer was dried over potassium carbonate and the solvent removed under a stream of nitrogen and the crude product purified by flash column chromatography (1:3 diethyl ether/light petroleum) to give (0.13 g, 68%) of the title compound as a colourless oil: R_f 0.54 (1:3 diethyl ether/light petroleum), (Found: C, 83.4; H, 8.6; N, 7.9. $\text{C}_{12}\text{H}_{15}\text{N}$ requires C, 83.2; H, 8.7; N, 8.1%); i.r. (film): 3070w, 3030w, 2940s, 2840w, 2780s, 1660w, 1600w, 1490m, 1445s, 1430m, 1320m, 1240w, 1200w, 1150m, 1050m, 950w, 880s, 750s, 700s cm^{-1} ; mass spectrum, m/e (%): M^+ 173(56), 172(35), 158(8), 118(27), 96(89), 91(19),

77(12): n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.17 (s, 3H, CH_3N), 2.52 (ddm, 1H, $J=16.4, 10.3, 2.0$), 2.80 (br dd, 1H, $J=16.4, 6.5$), 3.0 (br d, 1H, $J=13.4$), 3.27 (dd, 1H, $J=10.3, 6.5$), 3.82 (d, 1H, $J=13.4$), 4.89 (br s, 1H), 4.93 (br s, 1H), and 7.3 (m, 5H); $^{13}\text{C}-\{^1\text{H}\}$ (100 MHz), δ 40.3, 42.6, 61.9, 71.6, 104.7, 127.4, 127.5, 128.4, and 146.6 p.p.m.

4-Methylene-2,2'-dimethyl-N-phenylpyrrolidine (126)

(i) (74) (0.25 g, 1.1 mmol), $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ (0.01 g, 0.02 mmol), triethylphosphite (0.04 g, 0.24 mmol), and $\text{Me}_2\text{C:NPh}$ (0.33 g, 2.5 mmol) in toluene (4 cm^3) were heated to reflux for 14h. The solution was concentrated and purified by chromatography (1:20 diethyl ether/light petroleum) to give the title compound (0.11 g, 53%) as an air sensitive colourless oil: R_f 0.45 (1:20 diethyl ether/light petroleum); i.r. (film): 3060w, 3020w, 2960w, 2920w, 2870w, 1670w, 1640m, 1500s, 1460m, 1360m, 1340s, 1280w, 1120m, 1030w, 980w, 880m, 740s cm^{-1} ; mass spectrum; m/e (%) M^+ 187(20), 175(9), 173(15), 172(100), 157(9), 156(8), 134(28), 106(19), 104(10), 77(36); n.m.r. (CDCl_3): ^1H (300 MHz), δ 1.43 (s, 6H), 2.56 (br s, 2H), 3.98 (br s, 2H), 4.97 (m, 2H), and 7.2 (m, 5H); $^{13}\text{C}-\{^1\text{H}\}$ (75 MHz), δ 25.3, 51.1, 55.0, 61.4, 106.0, 114.8, 116.5, 128.0, 144.4, and 146.4 p.p.m.

(ii) (74) (0.25 g, 1.1 mmol), $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol), and $\text{Me}_2\text{C:NPh}$ (0.33 g, 2.5 mmol) in toluene (4 cm^3) under analogous conditions to (i) gave the title compound (0.08 g, 40%).

Synthesis of (127)

(74) (0.22 g, 1.0 mmol), PhCH:CHCH:NPh (0.5 g), and $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol) in toluene (5 cm^3) gave (127) (0.18 g, 69%), R_f 0.4 (1:50 diethyl ether/light petroleum); i.r. 3020m, 2960m, 2900m, 1670w, 1600s, 1500s, 1450w, 1370m, 1250m, 1180w, 970m, 850m, 750s, 700s cm^{-1} ;

mass spectrum, m/e (%): M^+ 261(67), 260(37), 246(16), 206(16), 184(16), 170(36), 158(22), 156(20), 117(22), 115(18), 107(46); n.m.r. ($CDCl_3$): 1H (300 MHz), δ 2.49 (dm, 1H, $J=15.0, 1.2$), 3.0 (ddm, 1H, $J=15.0, 8.6, 1.5$), 4.0 (br s, 2H), 4.5 (tdd, 1H, $J=8.6, 6.6, 2.4$), 5.0 (m, 1H, $J=1.2$), 5.1 (m, 1H), 6.11 (dd, 1H, $J=6.6, 15.9$), 6.44 (d, 1H, $J=15.9$), 6.5 to 7.3 (m, 10H); $^{13}C-\{^1H\}$ (75 MHz), δ 39.8, 52.8, 60.2, 107.1, 112.3, 116.7, 126.3, 127.3, 128.4, 129.0, 129.9, 130.5, 136.7, 144.7, and 146.7 p.p.m.

Synthesis of (128)

(74) (0.25 g, 1.1 mmol), dibenzylidenehydrazine (0.52 g), $[Pd_2(dba)_3 \cdot CHCl_3]$ (0.1 g, 0.02 mmol), triethylphosphite (0.04 g, 0.24 mmol) in toluene (3 cm^3) gave (128) (0.17 g, 58%), R_f 0.55 (1:20 diethyl ether/light petroleum); i.r. 3060m, 3020m, 2960m, 2920s, 2860m, 1670m, 1590m, 1560m, 1495m, 1450s, 1370m, 1300m, 1150s, 1120s, 1070m, 890s, 755s, 700s cm^{-1} ; mass spectrum, m/e (%) M^+ 262(100), 261(37), 185(38), 158(25), 157(27), 156(34), 133(18), 129(45), 128(21), 115(17), 103(20); n.m.r. ($CDCl_3$): 1H (300 MHz), δ 2.57 (ddm, 1H, $J=14.7, 7.7, 2.2$), 3.04 (br dd, 1H, $J=14.7, 7.7$), 3.86 (br d, 1H, $J=13.2$), 4.27 (br d, 1H, $J=13.2$), 4.62 (t, 1H, $J=7.7$), 5.02 (m, 1H, $J=2.2$), 5.07 (m, 1H, $J=2.0$), and 7.0 to 7.5 (m, 12H); $^{13}C-\{^1H\}$ (75 MHz), δ 40.67, 54.9, 67.6, 107.4, 125.5, 126.8, 127.0, 127.3, 128.3, 134.3, 143.0, and 143.3 p.p.m.

Reactions of $[Ir\{\eta^4-C(CH_2)_3\}Cl(CO)(PPh_3)]$ (76)

(i) A solution of (76) (0.05 g, 0.1 mmol) and triphenylphosphine (0.05 g, 0.2 mmol) in toluene (3 cm^3) was heated to reflux for 50h. Addition of light petroleum gave yellow crystals which were identified as trans- $[IrCl(CO)(PPh_3)_2]$ (0.04 g, 57%) by comparison with an authentic sample.¹⁰⁹

(ii) The reaction was repeated as in (i) but in the presence of coumarin

(2.5 mole equivalents). The solution was refluxed for 50h. The solvent was removed in vacuo and the residue chromatographed. Only coumarin was recovered from the reaction and none of the required cycloadduct (120) was detected.

Reaction of (74) with benzaldehyde

A solution of (74) (0.25 g, 1.1 mmol), $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ (0.06 g, 0.07 mmol), and benzaldehyde (0.26 g, 2.5 mmol) in p-dioxane (4 cm³) was refluxed for 16h. The solvent was removed by atmosphere distillation and the residue purified by chromatography (1:50 diethyl ether/light petroleum) to give 4-methylene-2-phenyltetrahydrofuran (133) (0.02 g, 11%). This compound has been previously reported.⁵⁸ R_f 0.45 (1:50 diethyl ether/light petroleum); n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.6 (m, 1H), 2.9 (ddm, 1H, $J=16.0, 6.0$), 4.4 (dm, 1H, $J=12.7$), 4.6 (brd, 1H, $J=12.7$), 4.96 (m, 1H), 5.0 (m, 1H), and 7.4 (m, 5H); $^{13}\text{C}\{-^1\text{H}\}$ (75 MHz), δ 41.2, 71.4, 81.1, 104.3, 125.9, 127.5, and 128.3 p.p.m.



CHAPTER 5

Synthesis of η^3 -Oxodimethylenemethane
Complexes of Platinum, Iridium, and Osmium

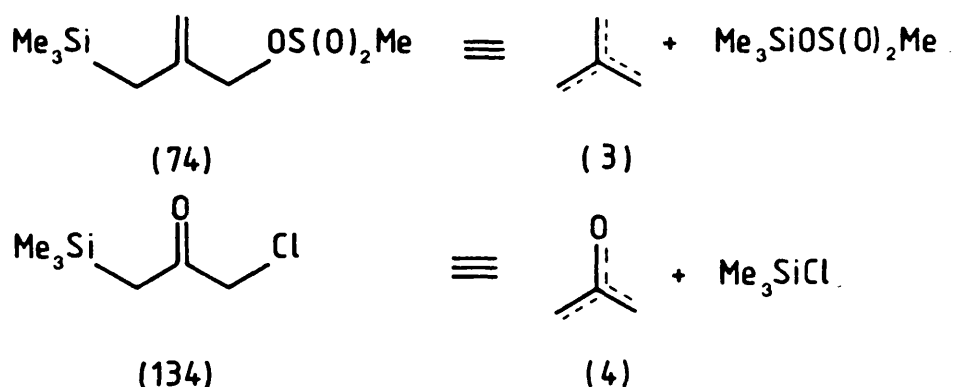
5.1 INTRODUCTION

The utility of the allylic methanesulphonate (74) in the synthesis of stable η^4 -trimethylenemethane metal complexes,¹²⁰ led to an investigation into the reactions of other similarly functionalised silicon compounds with various transition metal complexes to determine the generality of this methodology in generating other, highly reactive, organic species at metal centres.

3-Chloro-1-(trimethylsilyl)propan-2-one (134), readily available from the reaction of trimethylsilylmethylmagnesium chloride with chloroacetic anhydride,^{187,188} can be viewed as a possible precursor to the oxodimethylenemethane fragment (4). Although a number of substituted oxodimethylenemethane complexes of platinum and palladium have been previously synthesised⁶²⁻⁷⁰ the only unsubstituted oxodimethylenemethane complexes isolated to date were obtained from the reaction of $[\text{Ir}(\text{L})_4]\text{Cl}$, ($\text{L} = \text{PMe}_3$ or AsMe_3) with the enolate salt of acetone,⁷¹ see Chapter 1. The major attraction in using 'push-pull' precursors, such as the allylic methanesulphonate (74), in organometallic synthesis results from the importance of an oxidative addition step in generating the organic fragment at the metal centre.¹⁸⁹ There are numerous low-valent metal complexes which undergo oxidative addition reactions⁹⁵ and so a great variety of systems can be investigated. A good analogy is with the large number of allyl complexes which have been synthesised via the oxidative addition of allylic halides and esters to low-valent metal centres.⁹⁵ This Chapter describes the reactions of 3-chloro-1-(trimethylsilyl)propan-2-one (134) with various low-valent metal complexes which afford η^3 -oxodimethylenemethane complexes of platinum, iridium, and osmium.

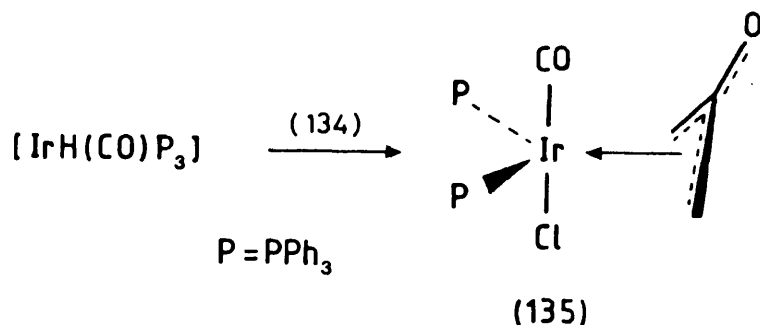
There is some confusion in the literature on the nomenclature used

to describe oxodimethylenemethane complexes and they are also known as oxoallyl, oxyallyl metallacyclobutan-3-one, and η^3 - β -diketonate(2-) complexes.



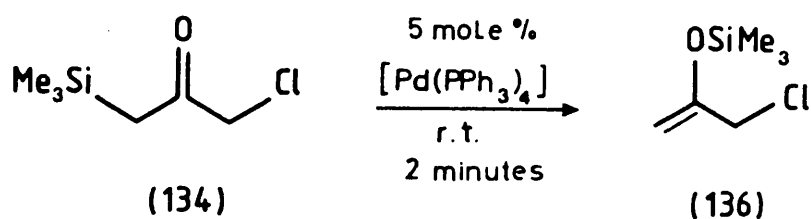
5.2 SYNTHESIS OF η^3 -OXODIMETHYLENEMETHANE METAL COMPLEXES

Treatment of an excess of the ketone (134) with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ in refluxing toluene afforded the η^3 -oxodimethylenemethane complex $[\text{Ir}(\eta^3\text{-CH}_2\text{COCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (135) as an air-stable white solid in almost quantitative yield.¹⁹⁰



Inspection of the organic residue of the reaction showed complete 'Brooke rearrangement'⁹⁰ of the excess ketone (134) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (136). This rearrangement is catalysed by $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ in refluxing toluene and the silylenol ether (136) reacts with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ and $[\text{IrH}(\text{CO})_2(\text{PPh}_3)_2]$ to afford the oxodimethylenemethane complex (135) in high yield. The most effective catalyst for this 'Brooke rearrangement' was either $[\text{Pd}(\text{PPh}_3)_4]$ or

$[\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2]$ which both caused an almost instantaneous isomerisation of the ketone (134) to the silylenol ether (136) at room temperature. The reaction was also catalysed by trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{RhH}(\text{PPh}_3)_4]$ although $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$, which was an effective catalyst for the isomerisation of unsymmetrical trimethylsilyl substituted ketones,¹⁹¹ did not catalyse the rearrangement of (134). The mechanism of this 'Brooke rearrangement' is believed to proceed via oxidative addition of the carbon-chlorine bond of the ketone (134) to the low-valent metal centre since no 'Brooke rearrangement' of the methyl ketone 1-(trimethylsilyl)propan-2-one occurred under analogous conditions. The use of zero-valent palladium or platinum catalysts in the generation of the silylenol ether (136) was used in preference to the published method for this conversion which employs mercury(II) iodide.^{187,192} This latter route was unsuccessful and the ketone (134) was recovered unchanged. The most convenient method for generating the silylenol ether (136) involved treating the ketone (134), or the bromo analogue, with approximately 5 mole % of $[\text{Pd}(\text{PPh}_3)_4]$ in dichloromethane or benzene at room temperature. A simple trap-to-trap distillation was the most effective way of removing the desired product from the metal catalyst and the silylenol ether (136) was isolated in almost quantitative yield. The fact that this is a metal-catalysed reaction was demonstrated by a control experiment using the ketone (134) and triphenylphosphine (10 mole %) in refluxing toluene. After 24h only starting material was isolated.



The ketone (134) also reacted with trans-[IrCl(CO)(PPh₃)₂] in refluxing toluene and afforded the oxodimethylenemethane complex (135). The yellow colour associated with the iridium(I) complex took about 12h to be replaced by the white oxodimethylenemethane complex (135). In contrast the silylenol ether (136) reacted rapidly with trans-[IrCl(CO)-(PPh₃)₂] to give the same product (135) and the reaction was complete within 10 minutes. This suggests that the silylenol ether (136) undergoes oxidative addition to the iridium(I) centre at a faster rate than the ketone (134) and that trans-[IrCl(CO)(PPh₃)₂] is slow at catalysing the 'Brooke rearrangement'. The silylenol ether (136) was expected to be more reactive than the ketone (134) because the allylic carbon-carbon double bond in (136) will be more effective at stabilising positive charge which will form at the carbon attached to the leaving chloride in an S_N2 type transition state of the oxidative addition step,⁸⁷ Figure 19. This stabilisation of positive charge is not available in the ketone (134), Figure 20, and it has also been noted that an electro-positive centre adjacent to the centre undergoing displacement will result in a rate retardation of an S_N2 reaction.¹⁹³

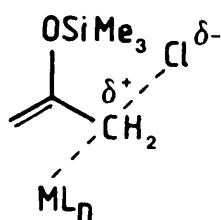


Figure 19

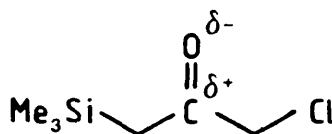
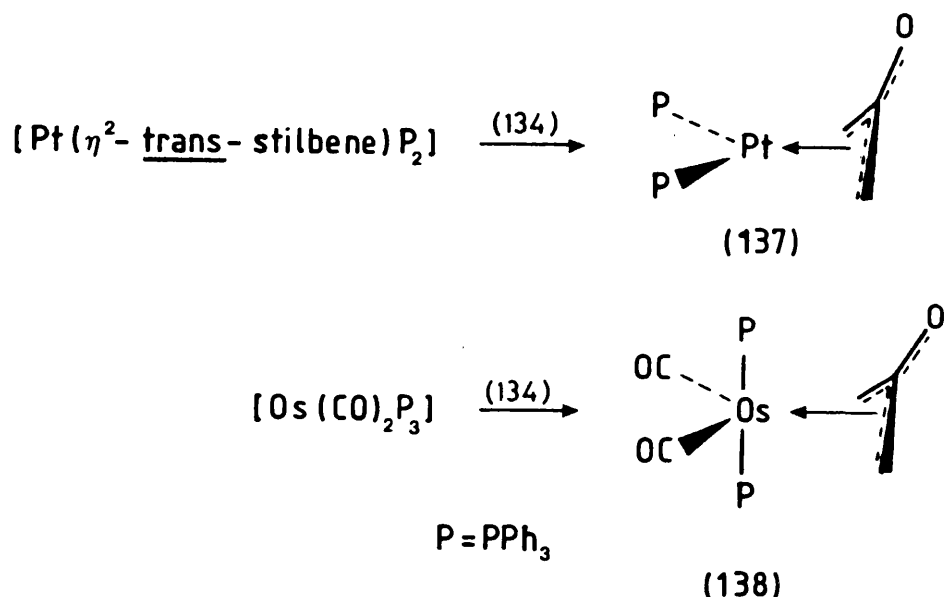


Figure 20

The reactions of the ketone (134) and the silylenol ether (136) with other low-valent metal complexes were also investigated. Thus, a solution of the ketone (134), which would have rapidly rearranged to the silylenol ether (136), reacted at room temperature with [Pt(η^2 -trans-stilbene)(PPh₃)₂] to afford the complex [Pt(η^3 -CH₂COCH₂)(PPh₃)₂] (137).

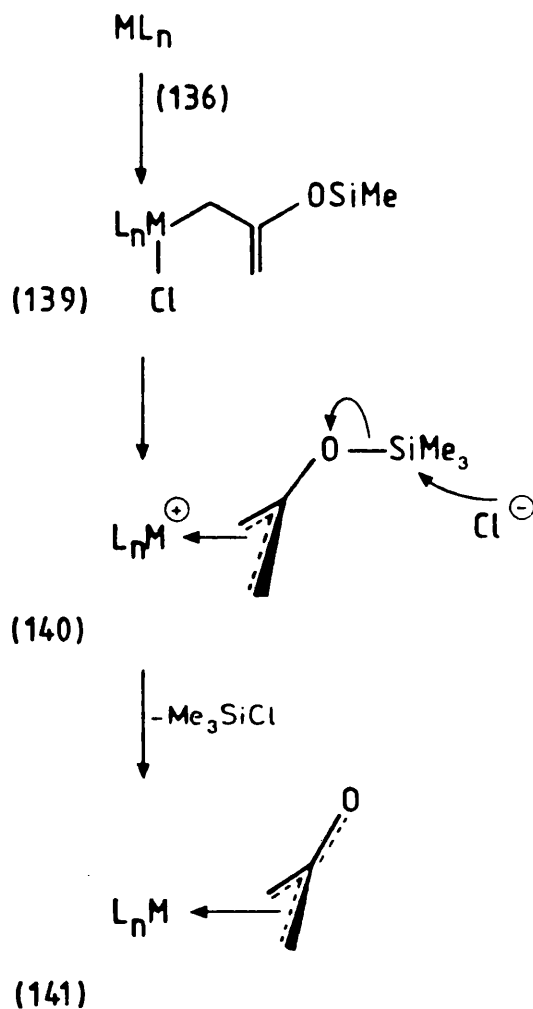
The silylenol ether (136) also reacted with $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ to give the complex $[\text{Os}(\eta^3\text{-CH}_2\text{COCH}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (138) in high yield.



The mechanism for these reactions is uncertain but it is believed to involve oxidative addition of the carbon-chlorine bond of the silylenol ether (136) to the low-valent metal centre forming an η^1 -allyl intermediate (139). Dissociation of chloride ion converts the η^1 -allyl intermediate (139) to an η^3 -allyl complex (140). Attack of chloride ion at the silicon group will effect desilylation of the η^3 -allyl species (140) to afford the oxodimethylenemethane complex (141) and trimethylsilylchloride, Scheme 41. This mechanism is similar to that proposed for the formation of η^4 -trimethylenemethane metal complexes,¹⁸⁹ Chapter 2.

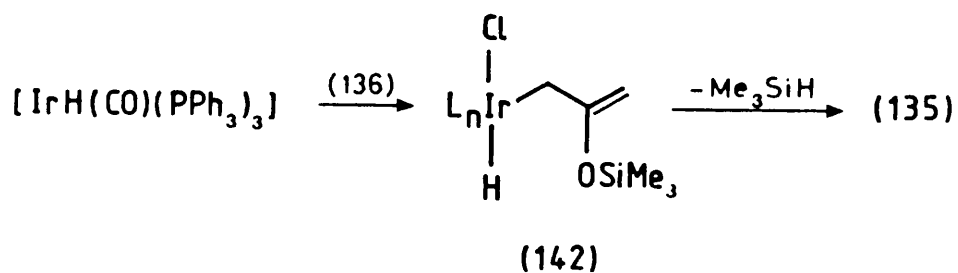
The reaction of the silylenol ether (136) with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ presumably proceeds via an oxidative addition of the allylic carbon-chlorine bond of (136) to the unsaturated metal centre forming an η^1 -allyl intermediate (142). Elimination of trimethylsilane from the intermediate (142) provides an attractive route to the oxodimethylenemethane complex (135).

A rapid reaction between the silylenol ether (136) and trans- $[\text{RhCl}(\text{CO})\text{-}$



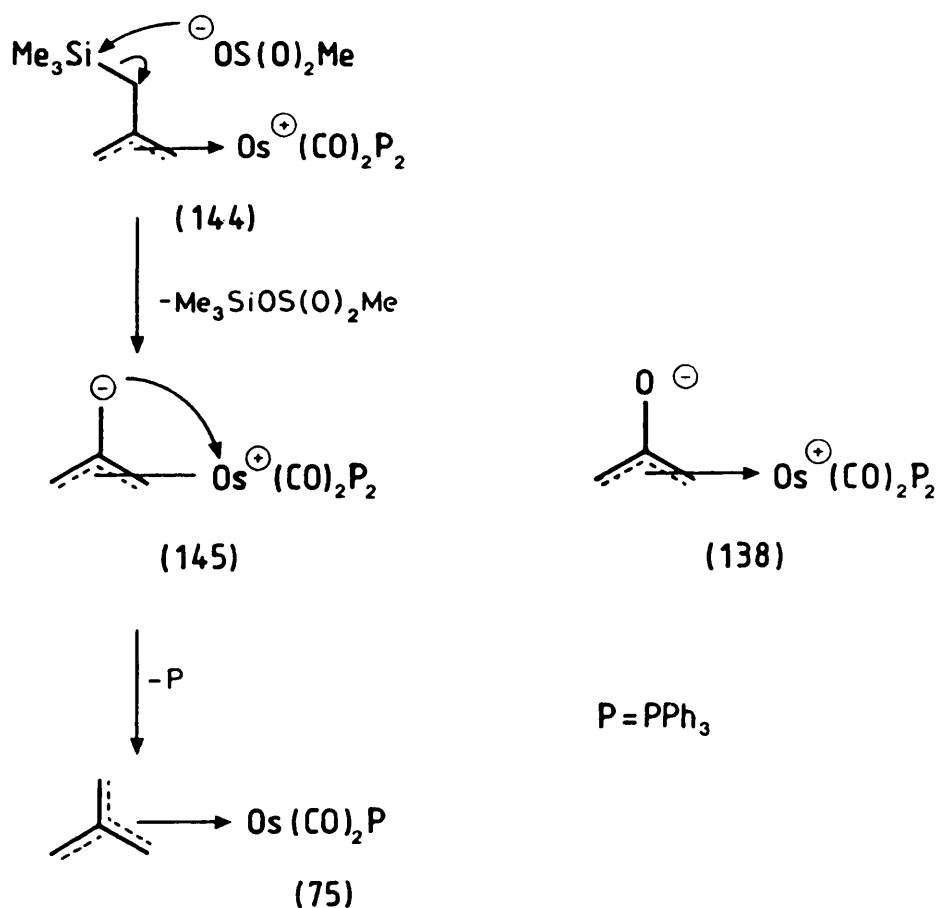
Scheme 41

(PMe₂Ph)₂] in methanol gave the α-rhodaketone complex [Rh(η¹-CH₂COMe)-Cl₂(CO)(PMe₂Ph)₂] (143). Interestingly, there is no reaction between 1-chloropropan-2-one and trans-[RhCl(CO)(PMe₂Ph)₂] under analogous conditions, the rhodium(I) complex being recovered unchanged. This implies that after oxidative addition of the silylenol ether (136) to the rhodium(I) centre a reactive intermediate is abstracting a proton to



give the α -rhodaketone product (143). These reactions also illustrate that the allylic carbon-chlorine bond of the silylenol ether (136) readily oxidatively adds to the rhodium(I) centre whereas the carbon-chlorine bond of 1-chloropropan-2-one does not. Previous studies have shown that 1-chloropropan-2-one and 1,3-dichloropropanone react with more electron-rich platinum(0) complexes to give α -platinaketone complexes.^{63,194}

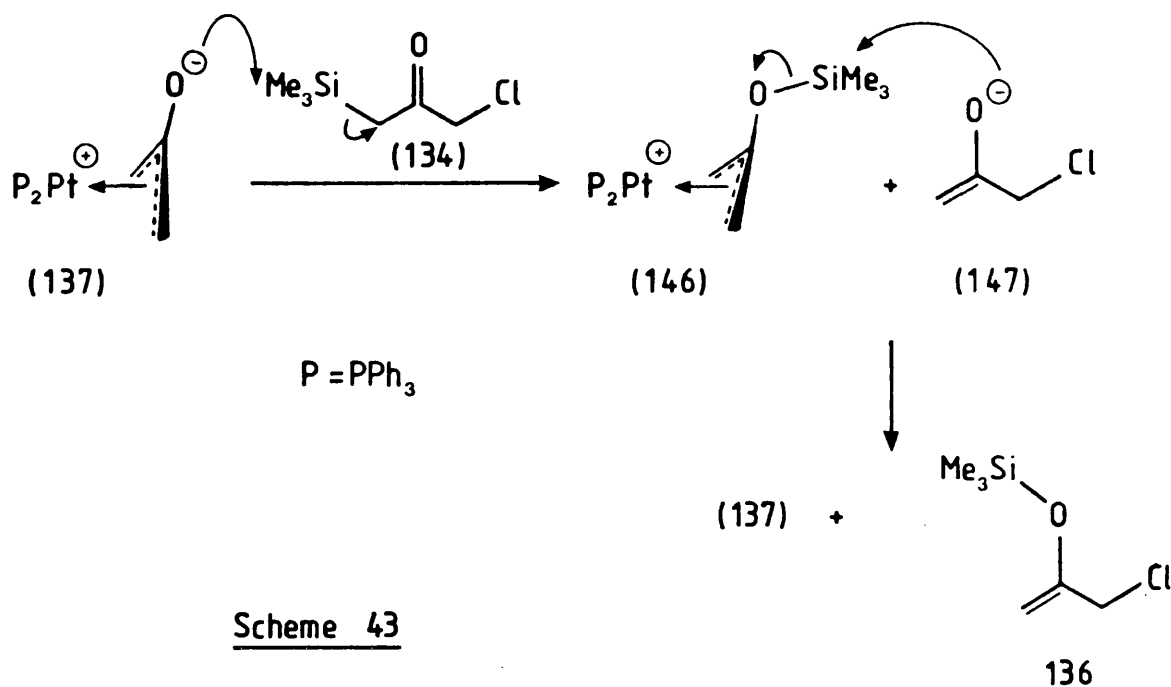
It is interesting to note that the oxodimethylenemethane complexes adopt an η^3 -arrangement and do not rearrange to an η^4 -geometry as is observed for the isoelectronic trimethylenemethane fragment, Chapter 2. Thus, refluxing a toluene solution of the silylenol ether (136) with $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ afforded the η^3 -oxodimethylenemethane complex $[\text{Os}(\eta^3\text{-CH}_2\text{COCH}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (138) whereas, under analogous conditions, the methanesulphonate (74) reacted with $[\text{Os}(\text{CO})_2(\text{PPh}_3)_3]$ to give the η^4 -trimethylenemethane complex $[\text{Os}\{\eta^4\text{-C}(\text{CH}_2)_3\}(\text{CO})_2(\text{PPh}_3)]$ (75). Presumably the reaction of (74) with the osmium complex involves desilylation of the η^3 -2-trimethylsilylmethylallyl intermediate (144) to give initially an η^3 -trimethylenemethane species (145), similar to the η^3 -oxodimethylenemethane complexes synthesised in this Chapter. However, carbon is not as electronegative as oxygen and so the charge on the uncoordinated carbon atom is stabilised by transfer into a metal-ligand bonding orbital and a rearrangement to the observed η^4 -trimethylenemethane product (74) occurs, Scheme 42. In contrast the more electronegative oxygen atom in the η^3 -oxodimethylenemethane complex (138) can accommodate the negative charge rather than rearrange to an η^4 -oxodimethylenemethane geometry, Scheme 42. This stability of the η^3 -oxodimethylenemethane ligand is examined further in the discussion on the structural properties of these complexes.



Scheme 42

Interestingly, the platinum complex (137) is also an effective catalyst for the isomerisation of the ketone (134) to the silylenol ether (136), the reaction proceeding rapidly at room temperature. A consequence of viewing these systems as dipolar η^3 -oxodimethylenemethane complexes, Scheme 42, rather than metallacyclobutan-3-ones⁶⁴⁻⁶⁶ suggests that the carbonyl oxygen will be quite basic. It has previously been noted that the oxygen of the oxodimethylenemethane ligand does have ligand properties.⁶⁹ Thus it is possible that the oxygen is sufficiently nucleophilic to attack the trimethylsilyl-group of the ketone (134), generating a trimethylsiloxyallyl complex (146) and the enolate (147). Attack of the enolate (147) at the silicon group of the trimethylsiloxyallyl species (146) regenerates the oxodimethylenemethane catalyst (137).

and the silylenol ether (136), Scheme 43.



5.3 STRUCTURAL PROPERTIES OF OXODIMETHYLENEMETHANE METAL COMPLEXES

Single-crystal X-ray diffraction studies for the iridium (135) and platinum (137) oxodimethylenemethane complexes have been carried out to establish the nature of bonding of the unsubstituted oxodimethylenemethane fragment. A summary of the important bond lengths and angles are given in Tables 4 and 5 respectively whilst the molecular structures of the complexes (135) and (137) are shown in Figures 21 and 22 along with the crystallographic numbering system.

The co-ordination about the metal atom in the platinum complex (137) is essentially square-planar with the two CH_2 groups occupying two cis positions of the square plane, trans to the mutually cis tertiary phosphine ligands. Thus, the twist between the $P(1)-Pt-P(2)$ and $C(1)-Pt-C(3)$ planes is 5.5° and is similar to the range of 6 to 10° observed in previous studies of palladium and platinum 1,3-disubstituted

TABLE 4^a

Bond Lengths for the complexes (135) and (137)

Bond Length (Å)	Complex	
	(135) M = Ir	(137) M = Pt
M-P (1)	2.432 (2)	2.292 (3)
M-P (2)	2.432 (2)	2.296 (3)
M-C (1)	2.17 (1)	2.14 (1)
M-C (2)	2.56 (1)	2.42 (1)
M-C (3)	2.18 (1)	2.12 (1)
M-C (4)	1.90 (1)	-
M-Cl	2.407 (3)	-
C (1)-C (2)	1.48 (2)	1.47 (2)
C (2)-C (3)	1.50 (1)	1.49 (2)
C (2)-O (1)	1.21 (1)	1.26 (1)

^a See Figures 21 and 22 for crystallographic numbering system.

TABLE 5^a

Bond and plane angles for the complexes (135) and (137)

Angles (°)	Complex	
	(135) M = Ir	(137) M = Pt
P (1)-M-P (2)	109.9 (1)	103.6 (1)
P (1)-M-C (3)	93.0 (3)	94.3 (4)
P (2)-M-C (1)	90.5 (2)	93.6 (4)
C (1)-M-C (3)	66.5 (3)	68.4 (5)
M-C (1)-C (2)	87.1 (6)	81.7 (7)
M-C (3)-C (2)	86.0 (5)	82.2 (8)
C (1)-C (2)-C (3)	106.6 (8)	107.7 (10)
C (1)-C (2)-O (1)	125.0 (9)	124.8 (12)
C (3)-C (2)-O (1)	126.2 (11)	123.8 (14)
Twist ^b	4.4	5.5
Fold ^c	139.0	129.0
C (2)-O (1) incline ^d	13.0	16.9

^a See Figures 21 and 22 for crystallographic numbering system;

^b $\angle P(1)-M-P(2)/C(1)-M-C(3)$;

^c $\angle C(1)-C(2)-C(3)/C(1)-M-C(3)$;

^d $\angle C(1)-C(2)-C(3)/C(2)-O(1)$.

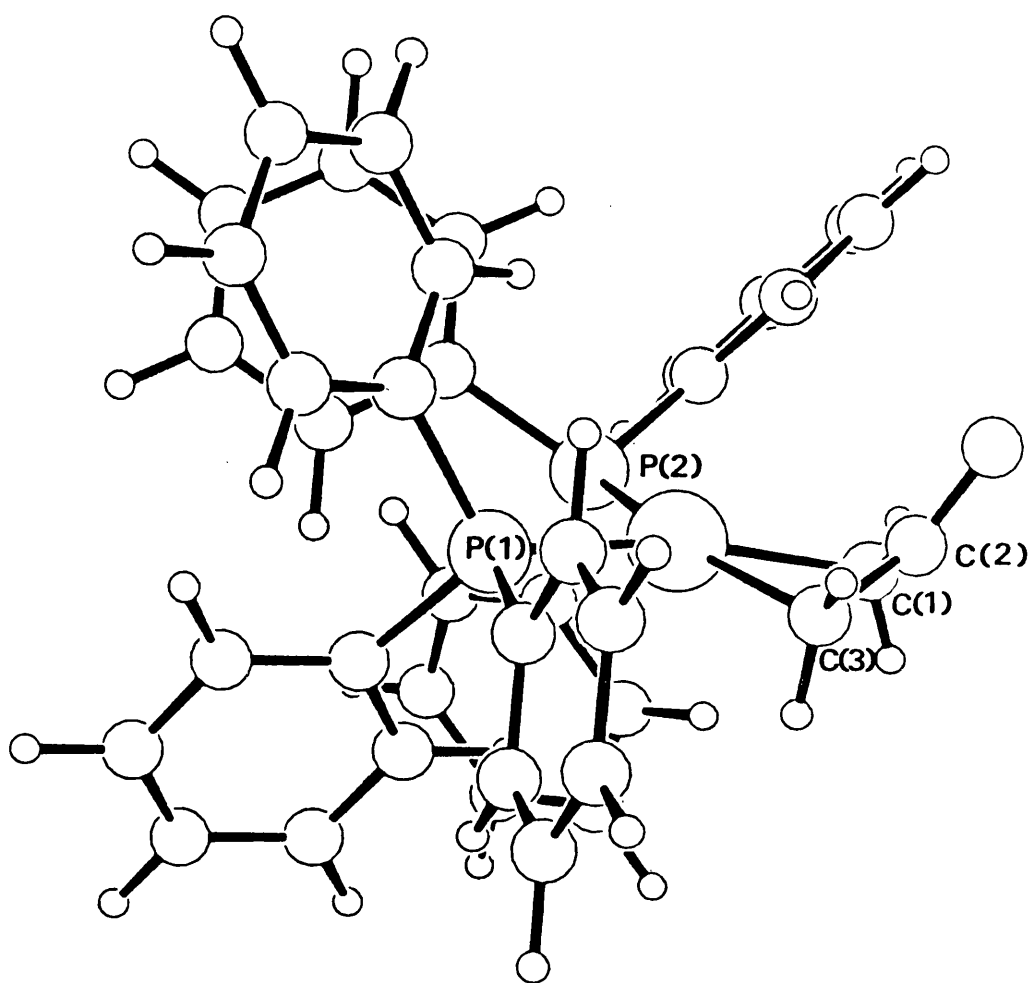
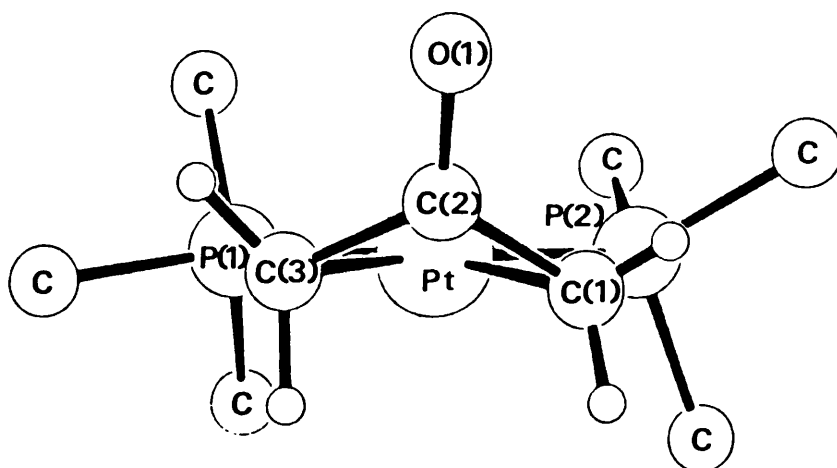


FIGURE 22

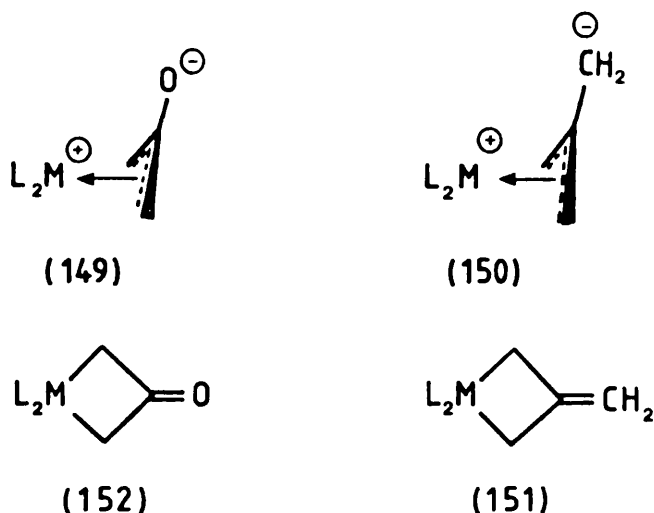
Molecular structure of the complex $[\text{Pt}(\eta^3\text{-CH}_2\text{COCH}_2)(\text{PPh}_3)_2]$ (137). The phenyl rings are omitted from the lower view.



oxodimethylenemethane complexes⁶⁴⁻⁶⁶ which have been described as metallacyclobutan-3-one systems. However, the bonding of the oxodimethylenemethane to the metal centre is significantly different to that found for known structures of platinacyclobutanes.¹⁹⁵⁻²⁰⁰ The Pt-C(1) and Pt-C(3) distances are longer than those in the platinacyclobutane complex $[\text{Pt}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\text{PEt}_3)_2]$ (148),¹⁹⁵ being on average 2.13(1) Å in the oxodimethylenemethane complex (137) versus 2.083(6) Å for (148). More significantly the Pt-C(1)-C(2)-C(3) atoms are not coplanar and this is quantified by the dihedral angle between the planes C(1)-Pt-C(3) and C(1)-C(2)-C(3). This angle is 129° in the platinum complex (137) and is similar to the range of 127-132° observed for 1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium.⁶⁴⁻⁶⁶ The large deviation from planarity is not a feature found for the saturated metallacyclobutanes where the dihedral angles range from 150-180°,¹⁹⁵⁻²⁰⁰ while cyclobutanones are only slightly non-planar, for example in *cis*-1,3-di-*t*-butyl-1,3-dibromocyclobutan-2-one the dihedral angle is 170°.²⁰¹ Another surprising feature of this oxodimethylenemethane complex is that the C(2)-O(1) bond is inclined by 16.9° out of the C(1)-C(2)-C(3) plane towards the platinum. Similar distortions of substituents on the central carbon of η^3 -allyl complexes have been observed, thus in the dimeric η^3 -2-methylallyl palladium chloride complex the methyl group is inclined by 10.9° out of the η^3 -allyl plane towards the metal.²⁰²

The C(1)-C(2) and C(2)-C(3) distances for all of the oxodimethylenemethane platinum complexes are shorter than the corresponding distances found in platinacyclobutanes. Thus in the complex (137) these carbon-carbon distances are 1.47(2) and 1.49(2) Å,¹⁹⁵ while for (148) the distances are 1.53(1) and 1.54(1) Å.¹⁹⁵ In η^3 -allyl complexes the carbon-carbon distances are of the order of 1.40 Å^{202,203} and although the carbon-carbon

distances found in η^3 -oxodimethylenemethane complexes are longer they are still consistent with a contribution to the bonding from an allylic structure (149). A similar description to (149) has been proposed for the trimethylenemethane complex (150).^{50,51} Interestingly, a metallacycle (151)^{44,49} has also been considered and can be regarded as a σ -form related to the η^3 -complex (150). This illustrates the similarity between the oxodimethylenemethane (metallacyclobutan-3-one)- ML_2 and the trimethylenemethane (metallacycle)- ML_2 systems. Theoretical calculations

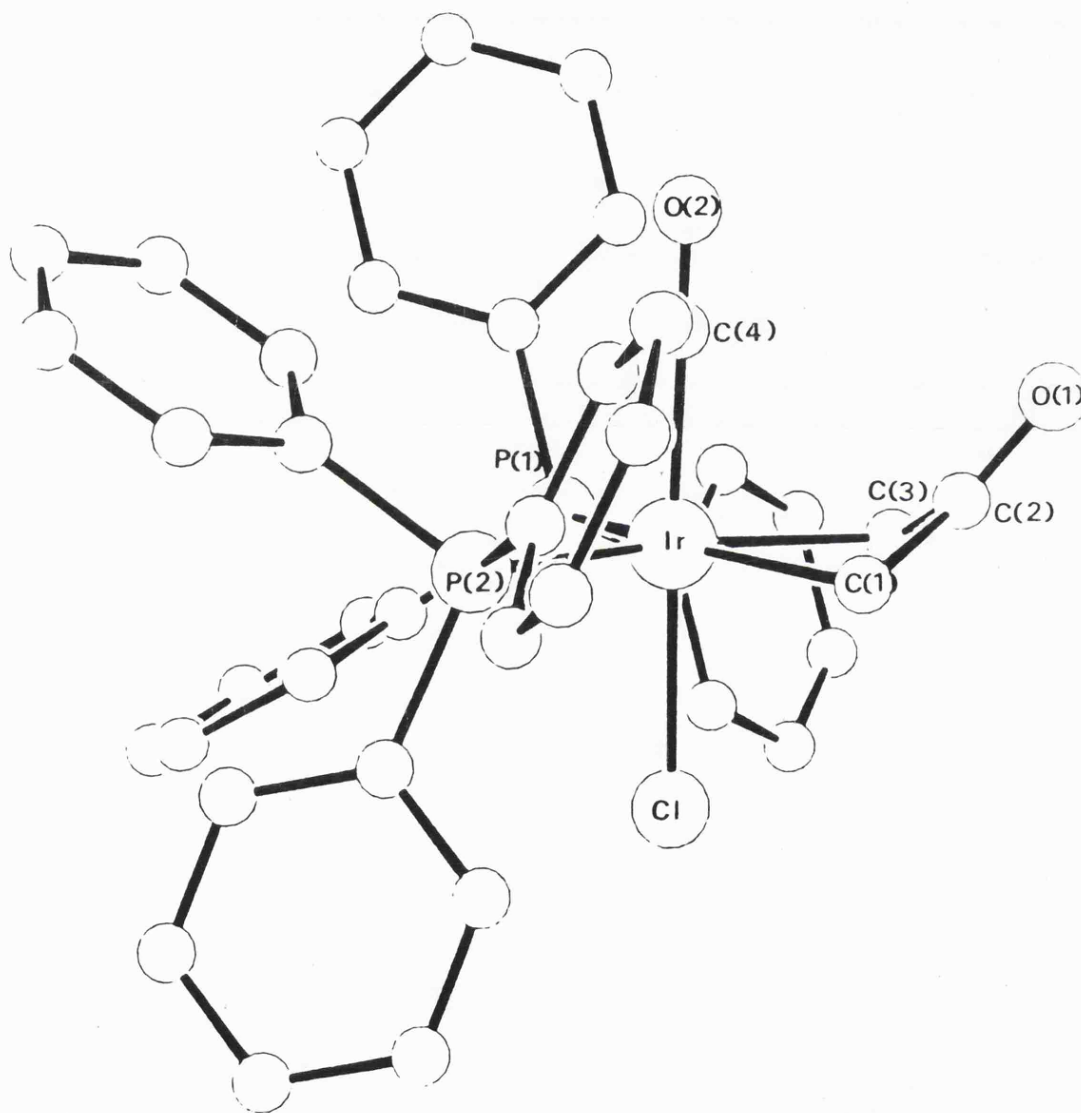


show that a dihedral angle of 96° between the P-Pd-P and trimethylenemethane planes gives the minimum energy conformation in the complex (150) ($M = Pd$, $L = PH_3$).^{51,53}

The d^{10} - ML_2 and d^8 - ML_4 fragments are isolobal and hence both possess frontier molecular orbitals which look approximately the same.¹⁷² Hence similarities between the structures of the platinum complex (137) and the iridium complex (135) would be expected. Figure 21 clearly shows that the oxodimethylenemethane fragment is bonded to the iridium in a similar geometry to that observed for the platinum complex (137), Figure 22. Thus, the two CH_2 groups occupy two cis positions of the octahedron trans to the two tertiary phosphine ligands. The oxodimethylenemethane

FIGURE 21

Molecular structure of the complex $[\text{Ir}(\eta^3\text{-CH}_2\text{COCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (135). The hydrogen atoms are omitted for clarity.

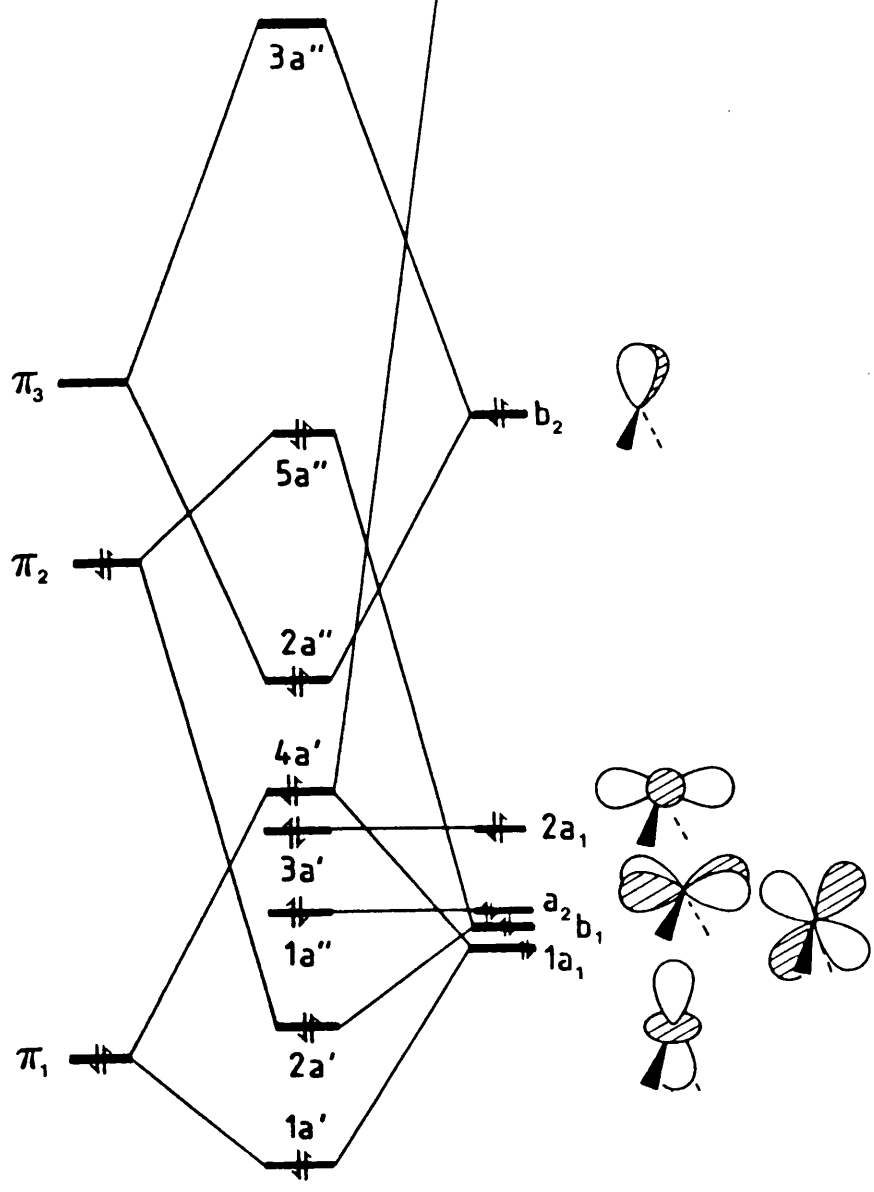
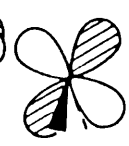
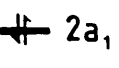
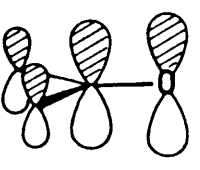
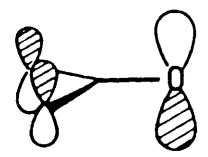
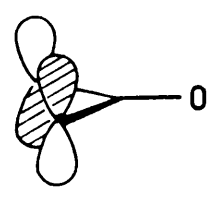
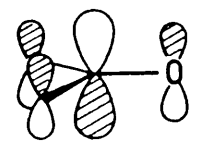
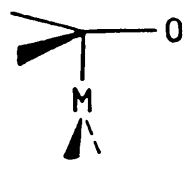
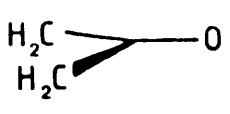


fragment is bonded to the metal in an allylic arrangement such that the dihedral angle between the planes C(1)-Ir-C(3) and C(1)-C(2)-C(3) is 139°. The C(2)-O(1) bond is also inclined by 13.1° out of the C(1)-C(2)-C(3) plane towards the iridium. The tipping of the oxodimethylenemethane fragment towards the iridium carbonyl rather than the chloride ligand is presumably a result of steric effects. The allyl fragment in the complex $[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{PF}_6$ is similarly orientated with the central carbon atom of the allyl tipped towards the carbonyl group,¹⁰⁸ such that the dihedral angle is 120.4°. The dihedral angle of the iridacyclobutane fragment in the complex $[\text{IrH}(\overline{\text{CH}_2\text{CMe}_2\text{CH}_2})(\text{AsMe}_3)_3]$ has not been published but the perspective view of this complex clearly shows that the iridacyclobutane ring is planar.²⁰⁴ In the related octahedral platinacyclobutanes, of the type $[\text{Pt}(\overline{\text{CH}_2\text{CH}_2\text{CH}_2})\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_2]$, the dihedral angle between the C-Pt-C and C-C-C planes range from 152 to 168°.¹⁹⁹ The tipping of the oxodimethylenemethane fragment towards the iridium indicates a contribution to the bonding from a π -allylic type structure in the complex (135). This is again reflected in a shortening of the carbon-carbon bond distances of the oxodimethylenemethane ligand in the iridium complex (135) [1.48(2) and 1.50(1) Å] relative to those found in the platinacyclobutane complex $[\text{Pt}(\overline{\text{CH}_2\text{CH}_2\text{CH}_2})\text{Cl}_2(\text{bipy})]$ [1.63(6) Å].²⁰⁰ However, the carbon-carbon distances found for the oxodimethylenemethane ligand of the complex (135) are not as short as those observed for the η^3 -allyl complex $[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{PF}_6$ [1.38(3) and 1.40(3) Å].¹⁰⁸

The bonding of the oxodimethylenemethane fragment to the metal in the complex (137) can be interpreted in a qualitative way by considering the orbital interaction diagram for a $d^{10}\text{-ML}_2$ fragment⁵⁰ with an oxodimethylenemethane ligand,²⁰⁵ using symmetry labels for a C_{2v} ML_2 group, Scheme

44. There are four low energy metal orbitals $1a_1 + a_2 + b_1 + 2a_1$ which are readily identifiable with the $e_g + b_{2g} + a_{1g}$ levels of a D_{4h} square-planar complex. At higher energy is the b_2 orbital which is hybridised towards the oxodimethylenemethane CH_2 groups. The $3a_1$ orbital is the highest energy orbital. The four π -orbitals of the oxodimethylenemethane ligand are on the left of Scheme 44 and are labelled $\pi_1 - \pi_4$. The $1a_1$, $3a_1$ and π_1 orbitals combine to produce three molecular orbitals, the two at lower energy, $1a'$ and $4a'$, are filled. The a_2 and $2a_1$ orbitals are essentially non-bonding but the b_2 orbital is nicely hybridised towards the π_3 -orbital and the strong overlap between these orbitals results in a bonding interaction of the oxodimethylenemethane fragment to the metal. There is a weak interaction between b_1 and π_2 , the resulting orbitals $2a'$ and $5a'$ being filled. However, the overlap between b_1 and π_2 is not as good as that between b_2 and π_3 . The interaction of π_3 with b_2 is at a maximum when the dihedral angle between the L-M-L and oxodimethylenemethane planes is 90° and when the ML_2 fragment is approximately below the two methylene carbons in an η^3 -geometry. The reason why the observed dihedral angle is greater than 90° is due to a contribution to the bonding representation from what can be considered to be a metallacyclobutanone type structure (152). It is also interesting that a dihedral angle of 90° might be predicted in palladium and platinum η^3 -allyl complexes; however, the η^3 -allyl group lies at an angle of between 108° and 119° to the plane containing the metal and the donor atoms of the other ligands.^{202,203}

This bonding picture of the oxodimethylenemethane fragment to a metal centre is similar to that used to predict the mode of bonding of the trimethylenemethane ligand to a d^{10} - ML_2 fragment, Scheme 45.⁵⁰ However, this does not account for the tipping of the C(2)-O(1) bond towards the



Scheme 44

metal. Inspection of Scheme 44 suggests that there will be a repulsive interaction between $1a_1$ and π_1 although this repulsion is moderated slightly by the interaction of $3a_1$. Puckering of the oxodimethylenemethane fragment reorientates π_1 so that the methylene and oxygen orbitals lie in the nodal region of d_z^2 . This bending also mixes s -character into the central carbon of π_1 and results in hybridisation of the π -component on the central carbon C(2) away from the metal, Figure 23. This explanation is similar to that used to account for the puckering of the η^4 -trimethylenemethane ligand in complexes of the type $[M\{\eta^4-C(CH_2)_3\}(L)_3]$, Figure 24.¹⁰¹ An important consequence of this bending action is that it allows mixing of oxodimethylenemethane σ -bonding orbitals with the π_2 and π_3 levels. This mixing is not allowed in the planar oxodimethylenemethane ligand but can occur in the non-planar ligand.¹⁰¹ This results in reorientation of the orbitals in π_3 so that they point more towards the b_2 orbital and so the overlap is more effective. Similar distortions of substituents on the central carbons of η^3 -allyl complexes have been observed.²⁰² This has also been interpreted in terms of a mixing of s -character with π -orbitals in the ligand in a way which has been discussed for various cyclic C_nR_n -transition metal π -complexes by Kettle.^{202,206} It should be noted that π_3 of the oxodimethylenemethane and trimethylenemethane fragments is of the same symmetry and energy as the π_2 level of an η^3 -allyl.^{205,207} Hence one might expect similar structural features between allyl, oxodimethylenemethane, and trimethylenemethane metal complexes.

A similar orbital interaction diagram can be used to account for the bonding in the oxodimethylenemethane complex (135), the frontier molecular orbitals of the d^8 - ML_4 fragment being similar to those of the d^{10} - ML_2 fragment.^{172,208}

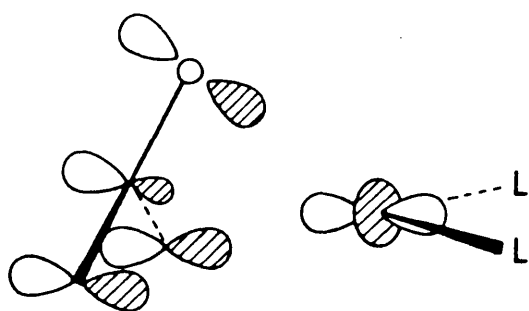


Figure 23

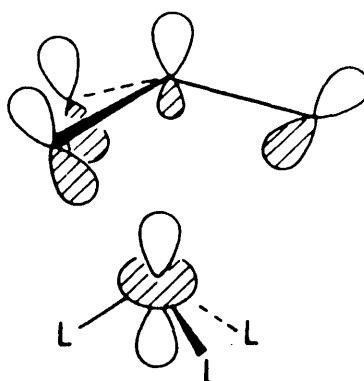
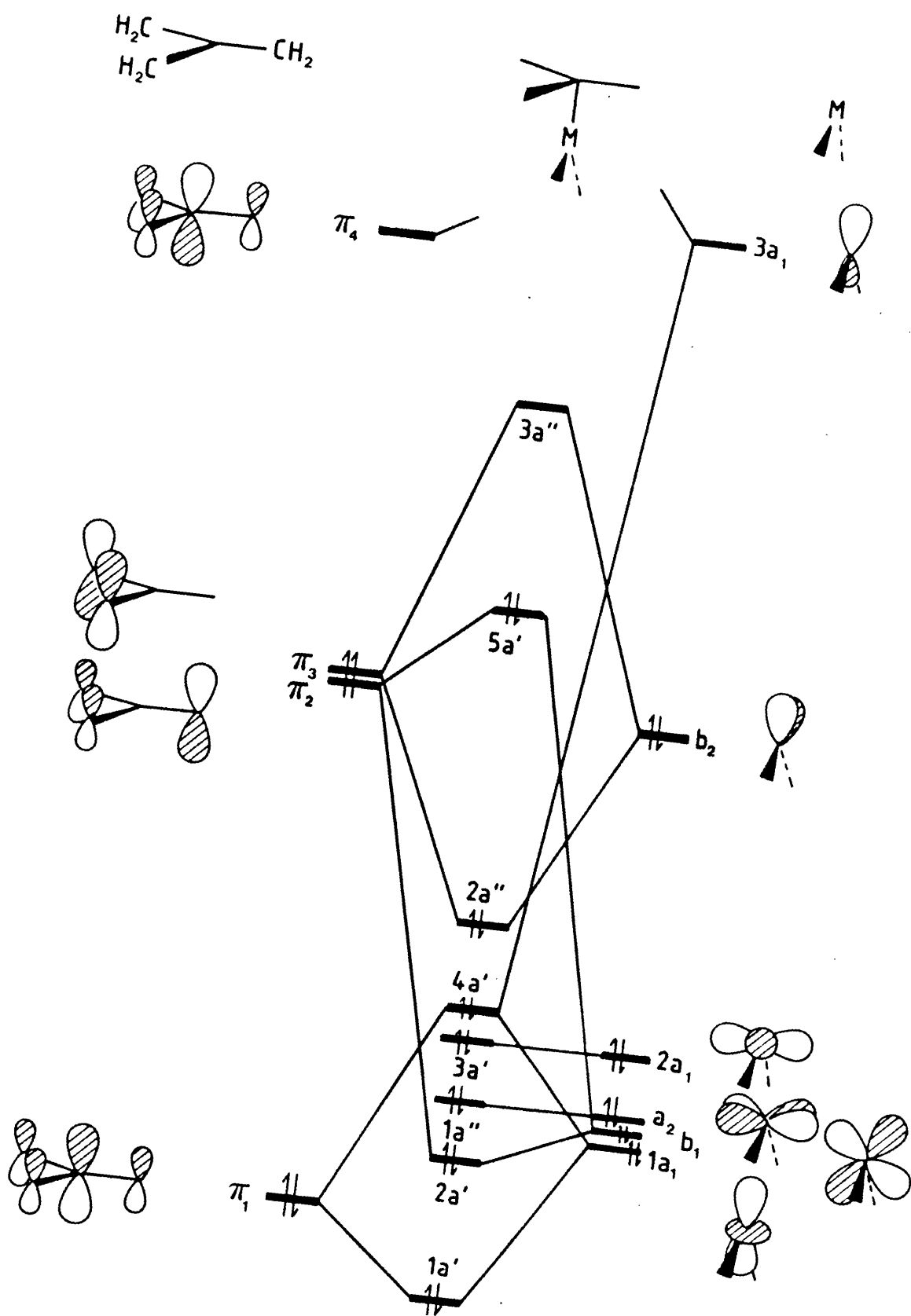


Figure 24

A consequence of considering the oxodimethylenemethane ligand in terms of the allylic structure (149) is that the bond order of the carbon-oxygen bond is less than two. Thus there is a lengthening of the carbon-oxygen bond to 1.26(1) Å in the platinum complex (137) compared to 1.21 Å in cis-1,3-di-*t*-butyl-1,3-dibromocyclobutan-2-one. The weakening of the carbon-oxygen bond is also detected in the i.r. spectra of these oxodimethylenemethane complexes and this is discussed in the next section.

The fact that the platinum complex (137) is more stable than the isoelectronic trimethylenemethane complexes $[M(\eta^3\text{-C}(\text{CH}_2)_3)(\text{L})_2]$ ($M = \text{Pd}, \text{Pt}$) which have not been isolated (see Chapter 4), is due to the substitution of a much more electronegative oxygen atom for a methylene unit. If one considers the orbital interaction diagram for a trimethylenemethane fragment with a $d^{10}\text{-ML}_2$ fragment, Scheme 45, and compares this with the oxodimethylenemethane- $d^{10}\text{-ML}_2$ system, Scheme 44, one can see that the principle difference is that the two highest π -levels in the trimethylenemethane fragment, π_2 and π_3 , are degenerate. However, substitution of a methylene group with an oxygen atom lowers the energy of π_2 but π_3 remains unaffected. π_3 is the principal source of bonding to the ML_2 fragment so one wants this orbital to be at



Scheme 45

relatively high energy to interact well with b_2 . The π_2 level is essentially non-bonding to the ML_2 fragment, that is the HOMO $5a'$ in Scheme 44 has mainly π_2 -character. Thus the lower π_2 lies energetically, the more stable it will be, in a kinetic sense, with respect to reaction with electrophiles. The π_2 level in the η^3 -trimethylenemethane analogue lies at relatively higher energy, Scheme 45, and hence the intermediates $[M\{\eta^3-C(CH_2)_3\}(L)_2]$ ($M=Ni, Pd, Pt$) readily react with electrophiles, see Chapter 4. The stability of the π_2 level in the oxodimethylenemethane fragment relative to π_2 level in trimethylenemethane also accounts for the formation of η^3 -oxodimethylenemethane- d^8 - ML_4 complexes rather than η^4 -oxodimethylenemethane- d^8 - ML_3 complexes. Thus, the low energy of the π_2 level in the oxodimethylenemethane ligand decreases the tendency of the oxygen atom to co-ordinate to the metal to form an η^4 -complex. The π_2 level in the trimethylenemethane ligand in the intermediate (145) lies at a relatively higher energy and stabilisation is achieved by co-ordination to the metal in an η^4 -geometry, Scheme 42.

Clearly a quantitative analysis of the bonding in oxodimethylenemethane metal complexes would account for the observed structures. In such a study of nickel, palladium, and platinum η^3 -allyl complexes the predicted dihedral angles increase in the order nickel < palladium < platinum.²⁰⁷ It has previously been noted that the palladium 1,3-disubstituted oxodimethylenemethane complexes have a smaller dihedral angle than the platinum analogues^{64,65} and a quantitative analysis may account for this trend.

Surprisingly, theoretical studies on the η^3 -trimethylenemethane- ML_2 system have been restricted to a planar trimethylenemethane fragment.^{50,51} Following the observation that in the complex (137) the carbon-oxygen bond of the oxodimethylenemethane fragment is inclined by 16.9° out of

the C-C-C plane towards the metal one might predict that a similar distortion of the trimethylenemethane ligand would be expected in the intermediates $[M\{\eta^3-C(CH_2)_3\}(L)_2]$, (M=Ni, Pd, or Pt; L = tertiary phosphine). Fenske-Hall calculations on $[Pd\{\eta^3-C(CH_2)_3\}(PH_3)_2]$ ⁵³ gave the lowest energy geometry when the PdL_2 unit was situated very near the axis formed by the two methylene carbons.⁵⁰ Thus, the structure observed for the oxodimethylenemethane platinum complex (137) may be very similar to the structure of the reactive intermediates $[M\{\eta^3-C(CH_2)_3\}(L)_2]$.^{48,49}

Recently an η^4 -oxodimethylenemethane complex has been isolated. An X-ray diffraction study shows that the oxodimethylenemethane ligand is bridging two ruthenium centres with three atoms bonded to one ruthenium and one methylene carbon bonded to the other ruthenium.²⁰⁹ As would be expected in an η^4 -oxodimethylenemethane complex the carbon-oxygen bond is longer than that observed in the η^3 -derivatives. Thus, in the η^4 -complex the carbon-oxygen distance is 1.317(7) Å while for the η^3 -complex (137) the distance is 1.26(1) Å. The carbon-carbon distances in the η^4 -geometry are shorter than the corresponding distances found in the η^3 -arrangement. Thus, in the η^4 -complex the distances are 1.436(8) and 1.447(8) Å compared with 1.47(2) and 1.49(2) Å in the η^3 -complex (137). This binuclear complex illustrates that the oxodimethylenemethane ligand can co-ordinate to metals in a π -type geometry and the η^4 -structure observed²⁰⁹ is reminiscent of the η^4 -trimethylenemethane ligand, see Chapter 2.

5.4 THE I.R. SPECTRA OF OXODIMETHYLENEMETHANE METAL COMPLEXES

The i.r. spectra of the complexes (135), (137), and (138) exhibit a strong band attributed to the carbonyl of the oxodimethylenemethane

ligand in the region 1635 to 1550 cm^{-1} . The frequency observed for the platinum complex (137) at 1550 cm^{-1} is lower than that found for the complexes $[M(\eta^3\text{-CHR}\text{COCHR})(\text{L})_2]$ ($M = \text{Pd, Pt}$; $R = \text{CO}_2\text{Me, CO}_2\text{Et}$),⁶⁴⁻⁶⁶ $[M(\eta^3\text{-CHR}\text{COCH}_2)(\text{L})_2]$ ($M = \text{Pd, Pt}$; $R = \text{COMe, CO}_2\text{Me}$),⁶⁷⁻⁷⁰ which exhibit bands in the region 1635 to 1592 cm^{-1} and 1575 to 1545 cm^{-1} respectively. Thus, the number of functional groups on the oxodimethylenemethane ligand have an effect on the carbonyl stretching frequency. The substitution of electron-withdrawing groups at the carbon atoms should make delocalisation of electron density into the carbonyl group of the oxodimethylenemethane fragment less important.¹¹³ This will result in a stronger carbon-oxygen bond in the substituted oxodimethylenemethane complexes relative to the unsubstituted derivatives.

The complexes $[\text{Ir}(\eta^3\text{-CH}_2\text{COCH}_2)\text{H}(\text{L})_3]$ ($\text{L} = \text{PMe}_3, \text{AsMe}_3$) exhibit bands at 1560 and 1572 cm^{-1} respectively.⁷¹ These low carbon-oxygen stretching frequencies suggest that the oxodimethylenemethane ligand co-ordinates to the iridium atom in a similar arrangement to that observed for the iridium (135) and platinum (137) η^3 -oxodimethylenemethane complexes.

The carbon-oxygen stretching frequencies of the carbonyl of the oxodimethylenemethane ligand are notably lower than those found for cyclobutanone compounds ($1780\text{-}1760\text{ cm}^{-1}$)¹¹³ and the α -rhodaketone complex (143) (1670 cm^{-1}). This lowering of the carbonyl stretching frequency is due to a contribution to the bonding in these complexes from an allylic-type structure (149) which has the effect of weakening the carbon-oxygen bond. Increasing the allylic contribution to the bonding in these complexes weakens the carbon-oxygen bond and lowers the carbonyl stretching frequency. It has previously been noted that in the 1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium there is an apparent correlation between the dihedral angle

and the carbon-oxygen stretching frequency of the oxodimethylenemethane ligand.⁶³ Thus the values for the platinum derivatives occur at higher frequency than those of the palladium analogues, the latter having a smaller dihedral angle than the platinum complexes.⁶³

The iridium and osmium complexes (135) and (138) exhibit additional strong bands due to the metal carbonyl groups. The two bands observed for the osmium complex (138) are consistent with the presence of two cis carbonyl groups co-ordinated to the metal centre.²¹⁰

5.5 ¹H AND ¹³C-{¹H} N.M.R. STUDY OF OXODIMETHYLENEMETHANE METAL COMPLEXES

The ¹H n.m.r. spectrum of the platinum complex (137) measured at -105°C in [²H₈]-tetrahydrofuran showed the expected features for the illustrated static structure, Figure 22, with two resonances due to the syn and anti protons at δ 2.01 and 2.25 p.p.m. respectively. The assignment of the higher-frequency signal to the anti protons is consistent with the ¹H n.m.r. data for the complexes [M(η³-CH₂COCHR)(L)₂] which show that for the CH₂ group the anti-proton is more deshielded than the syn-proton⁶⁷⁻⁷⁰ with the substituent R occupying an axial position. The magnitude of the proton-proton, proton-phosphorus-31, and proton-platinum-195 coupling constants could not be determined due to the poor resolution at low temperature. Upon warming to room temperature the CH₂ signals in the ¹H-n.m.r. spectrum undergo reversible changes. Thus the CH₂ resonances collapse to a single multiplet, the protons appearing as the A part of an A₄XX' spin system (X = ³¹P) with the expected platinum-195 satellites. This dynamic process was previously observed for the 1,3-disubstituted oxodimethylenemethane complexes⁶⁴⁻⁶⁶ and is consistent with an inversion of the oxodimethylenemethane through a planar transition

state resulting in a conformational transformation in which the two anti-protons become syn-protons and vice versa, Scheme 46. As the temperature increases the rate of inversion of the oxodimethylenemethane also increases and the syn and anti resonances merge. The lifetime of a particular configuration can be determined as a function of temperature and an activation energy for this barrier to inversion can be calculated using the Gutowsky-Holm equation for free energy to activation:¹¹⁵

$$\Delta G_{T_c}^{\ddagger} = -RT_c \ln (\pi \Delta \nu h / 2^{\frac{1}{2}} k T_c)$$

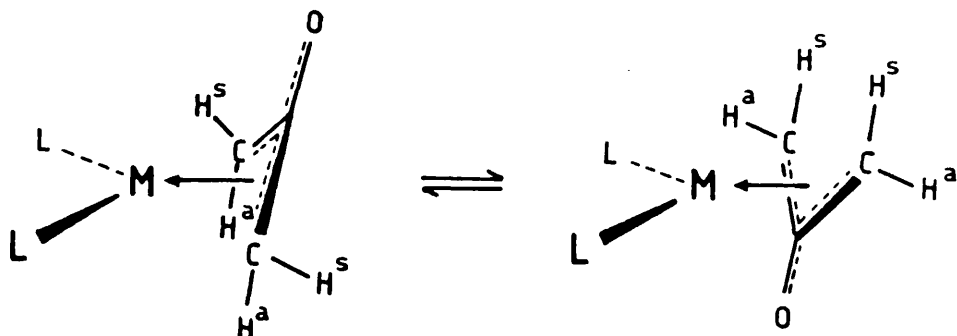
where T_c = coalescence temperature

$\Delta \nu$ = frequency difference between the two signals.

A value of 38.4 kJ mol⁻¹ was calculated from the coalescence temperature (-78°C). This value is slightly greater than the values obtained for the 1,3-disubstituted oxodimethylenemethane platinum complexes which lie in the range 35.3 to 37.3 kJ mol⁻¹,^{64,66} although the value is not as large as the values obtained for 1,3-disubstituted oxodimethylenemethane palladium complexes which were in the range 40.3 to 51.1 kJ mol⁻¹.⁶⁵ The barrier to inversion is presumably a consequence of the π -character of the oxodimethylenemethane fragment. There is delocalisation through a π -system of what can be considered as a C₃H₄O²⁻ ligand in the puckered geometry (149). However, rotation of the two methylene units by 51° to give the planar metallacyclobutan-3-one geometry (152) disrupts this π -delocalisation, although it is important to note that this is compensated by the formation of two strong platinum-carbon σ -bonds at the planar structure. The substitution of electron-withdrawing groups on the oxodimethylenemethane ligand should make delocalisation into the carbonyl group of the oxodimethylenemethane group less important and so the barrier to inversion should decrease. This is consistent with the values obtained for the complex (137) and

$[\text{Pt}(\eta^3\text{-CHRCOCHR})(\text{L})_2]$ ($\text{R} = \text{CO}_2\text{Me}$, COMe ; $\text{L} = \text{donor ligand}$).^{64,66}

Interestingly, the oxodimethylenemethane complexes $[\text{M}(\eta^3\text{-CH}_2\text{COCHR})(\text{L})_2]$ do not exhibit temperature dependent ^1H n.m.r. spectra.^{67,69,70}



Scheme 46

The room temperature ^1H n.m.r. spectrum of the iridium complex (135) exhibited two multiplets due to the oxodimethylenemethane fragment. There is a strong geminal coupling between the methylene protons and an additional coupling to the tertiary phosphine ligand. The spectrum is consistent with either a static or rapidly inverting oxodimethylenemethane ligand since the methylene protons are always inequivalent due to the differing chloride and carbonyl ligands at the metal centre. The ^1H n.m.r. spectrum shows no appreciable change at either low or high temperatures (-90 to $+50^\circ\text{C}$). This suggests that either a lower temperature is required to observe the two static structures or that the complex is non-fluxional. It is difficult to distinguish between these possibilities from the ^1H n.m.r. spectrum.

The room temperature ^1H n.m.r. spectrum of the osmium complex (138) exhibits a triplet resonance associated with the oxodimethylenemethane fragment. This is compatible with either a rapidly-flipping oxodimethylenemethane ligand or a planar structure, the triplet pattern being a result of coupling to two phosphorus-31 nuclei.

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra for these complexes recorded at room

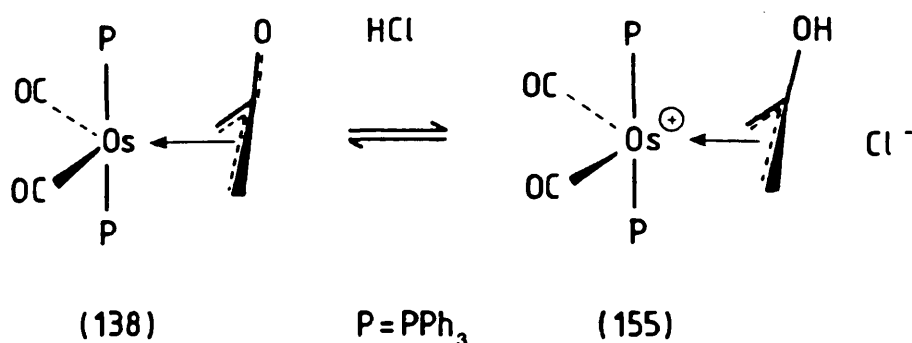
temperature exhibited the expected resonances. Thus the methylene and central carbon atoms have shifts of 27 to 50 p.p.m. and 184 to 197 p.p.m. respectively. The methylene carbons exhibit coupling to phosphorus-31 and the platinum complex (137) shows the expected platinum-195 satellites. Since this platinum complex has phosphine ligands which have chemically equivalent but magnetically inequivalent phosphorus-31 nuclei, the observed methylene carbons appear as the A part of an AXX' spin-system, ($X = {}^{31}\text{P}$).^{211,212} The observed spectrum consists of a doublet of doublets together with the corresponding platinum satellites which appear as the A part of an $AMXX'$ spin-system, ($X = {}^{31}\text{P}$, $M = {}^{195}\text{Pt}$).

5.6 REACTIONS OF OXODIMETHYLENEMETHANE METAL COMPLEXES

An initial study of the reactivity of the complexes (135), (137), and (138) shows that they are susceptible to electrophilic attack. The iridium complex (135) reacts instantaneously with hydrochloric acid and mercury(II) chloride to give the complexes $[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_3)(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2]$ (153) and $[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_2\text{HgCl})(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2]$ (154) respectively.

Interestingly, the osmium complex (138) was recovered unchanged from the reaction with hydrochloric acid. This reaction was monitored by ${}^1\text{H}$, ${}^{13}\text{C}\{-{}^1\text{H}\}$, and ${}^{31}\text{P}\{-{}^1\text{H}\}$ n.m.r. An immediate reaction took place since in the ${}^1\text{H}$ n.m.r. the triplet resonance at δ 1.5 p.p.m. due to the oxodimethylenemethane ligand was replaced by two multiplets at δ 1.7 and 3.4 p.p.m. The ${}^{13}\text{C}\{-{}^1\text{H}\}$ n.m.r. spectrum of the protonated form exhibited resonances at δ 31.4 and 164.9 p.p.m. assigned to the oxodimethylenemethane fragment. These resonances are shifted in position relative to the resonances associated with the osmium complex (138) which had peaks at δ 27.0 and 191.3 p.p.m. These data indicate that the osmium complex (138) has undergone reaction in the highly acidic medium but on neutralisation

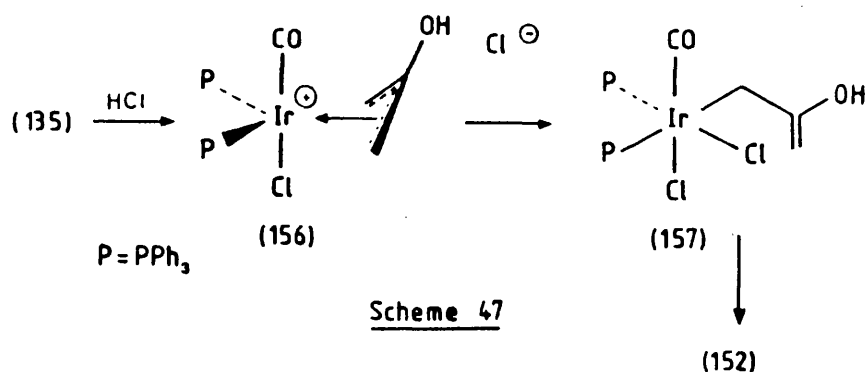
with potassium carbonate the starting material is reformed. The solution i.r. spectrum of the protonated intermediate exhibited two strong bands in the metal carbonyl region but the band associated with the carbonyl of the oxodimethylenemethane fragment was not observed. This implies that protonation at the oxygen of the oxodimethylenemethane ligand has occurred to form an η^3 -hydroxyallyl (155), which deprotonates



on neutralisation. Similar interconversions of η^3 -hydroxyallyl complexes and oxodimethylenemethane complexes have been observed previously, see Chapter 1.⁶⁷ The differing reactivity of the iridium and osmium complexes with hydrochloric acid may be due to the steric effect of two trans triphenylphosphine ligands hindering attack of chloride ion at the osmium. In the iridium complex (135) attack of chloride ion at the metal centre converts the η^3 -hydroxyallyl intermediate (156) to an η^1 -hydroxyallyl complex (157) which tautomerises to the observed keto form (152), Scheme 47.

The platinum complex (137) reacted rapidly with hydrochloric acid to give cis-[PtCl₂(PPh₃)₂], with elimination of the oxodimethylenemethane fragment. Similarly, the osmium complex reacted with chlorine and mercury(II) chloride to form [OsCl₂(CO)₂(PPh₃)₂]. 1,3-Dichloroacetone was detected in the reaction of (138) with chlorine. Under analogous conditions the iridium complex (135) and chlorine gave the complex

$[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_2\text{Cl})(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2] \text{ (158)}.$



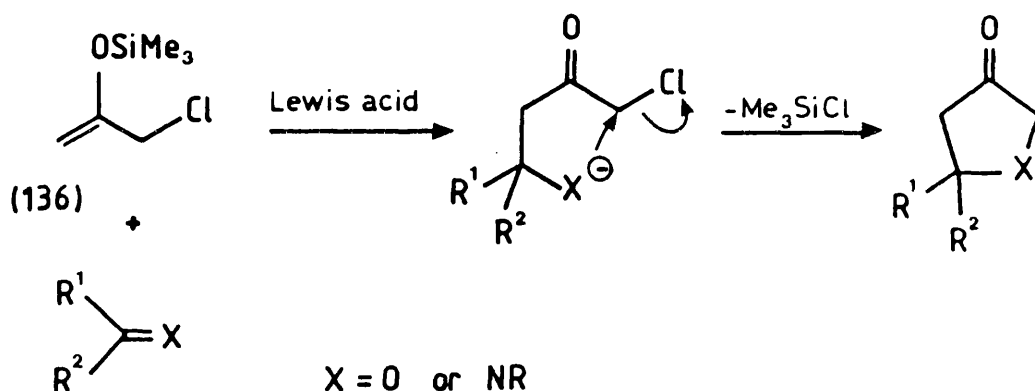
5.7 ATTEMPTED CYCLOADDITION REACTIONS OF THE OXODIMETHYLENEMETHANE FRAGMENT TO ALKENES

Following the success of the trimethylenemethane precursors (47) and (74) in the synthesis of cyclopentanoids^{48,49} the reactions of the oxodimethylenemethane precursors (134) and (136) with various metal catalysts were investigated.

Solutions of the ketone (134) and the silylenol ether (136) were treated with a number of low-valent metal complexes in the presence of both electron-rich and electron-deficient alkenes. No cycloadducts of the oxodimethylenemethane fragment could be isolated. The inability of d^{10} -metal complexes to catalyse the cycloaddition of the oxodimethylenemethane fragment to alkenes contrasts with the ease in which d^{10} -metal complexes catalyse the cycloaddition of trimethylenemethane to alkenes, see Chapter 1.^{48,49} This contrast is believed to be a result of the stability of oxodimethylenemethane complexes. Thus the platinum complex (137) is air stable whereas no platinum trimethylenemethane complexes have been isolated, desilylation of $[\text{Pt}\{\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{SiMe}_3)\text{CH}_2\}(\text{PPh}_3)_2]\text{PF}_6$ (115) giving only the protodesilylated product $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)_2]\text{PF}_6$ (117), Chapter 4. This indicates that the oxodimethylenemethane fragment is not as nucleophilic as the trimethylenemethane ligand. The poorer nucleophilic character of the oxygen of the oxodimethylenemethane fragment

relative to the trimethylenemethane ligand co-ordinated to a d^{10} - ML_2 fragment is due to the 'substitution' of the methylene group of a trimethylenemethane with the more electronegative oxygen atom. This has been discussed in more detail in Section 5.3.

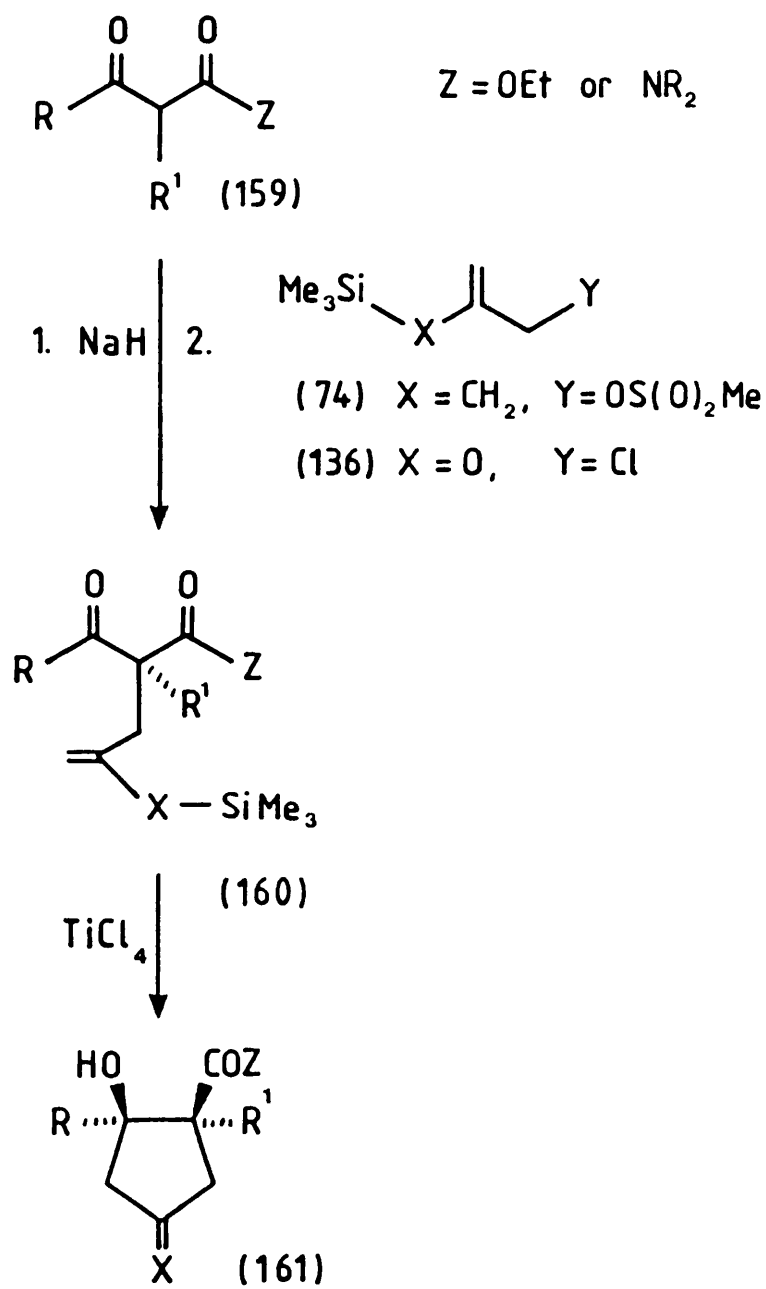
A possible method of cycloadding the oxodimethylenemethane fragment to a ketone or imine may involve the use of a Lewis acid initiated reaction of the silylenol ether (136) similar to that developed by Trost *et al.*, in the cycloaddition of trimethylenemethane to ketones and imines,¹⁵⁷ Scheme 48. Hosomi *et al.*, found that zinc(II) chloride



Scheme 48

initiated the cycloaddition of the oxodimethylenemethane fragment, generated from 3-bromo-3-methyl-2-(trimethylsiloxy)but-1-ene (71, R = Me, X = Br), to 1,3-dienes and alkenes (see Section 1.7) to give [3+4] and [3+2] cycloadducts respectively.^{86,213}

Recently, a Lewis acid mediated chelation controlled cyclisation reaction involving the allylic methanesulphonate (74) has been reported, Scheme 49. The titanium(IV) chloride initiated cyclisation of β -keto-esters and β -ketoamide substituted allylsilanes (160, X = CH₂) provides a single diastereomeric product (161, X = CH₂), Scheme 49.²¹⁴ It may be possible to extend this methodology to the synthesis of cyclopentanones using the silylenol ether (136). Thus the substituted silylenol ether

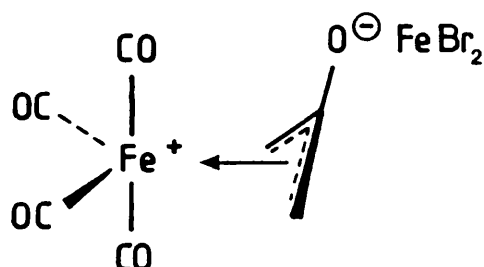


Scheme 49

(160, X=O) would be expected to cyclise in the presence of titanium(IV) chloride to afford cyclopentanones (161, X=O). The coupling of silylenol ethers with ketones is an aldol reaction and it has been previously noted that a stoichiometric amount of titanium(IV) chloride affords the desired aldol products cleanly and in high yields.⁹⁰

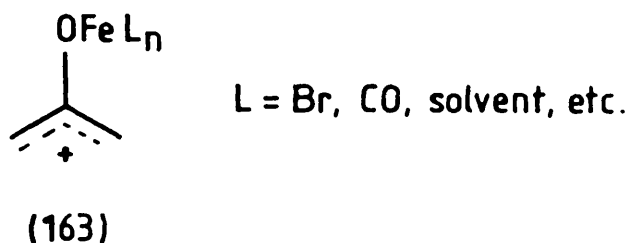
The iron mediated cyclocoupling of α,α' -dibromoketones with alkenes is believed to proceed via an oxodimethylenemethane intermediate,⁷³ Chapter 1. Following the isolation of the isoelectronic η^3 -oxodimethylenemethane complexes of iridium (135) and osmium (138) and noting the similarity between the dehalogenation of α,α' -dibromoketones by $[\text{Fe}_2(\text{CO})_9]$ and the reaction of 3-chloro-2-chloromethylprop-1-ene (8) with $[\text{Fe}_2(\text{CO})_9]$, which gave the η^4 -trimethylenemethane iron complex (7) (Chapter 1), it seems reasonable that the $[\text{Fe}_2(\text{CO})_9]$ mediated cyclocoupling of α,α' -dibromoketones with alkenes proceeds via an η^3 -oxodimethylenemethane intermediate. However, in these reactions the Lewis acid iron(II) bromide is liberated and as the oxygen of the oxodimethylenemethane ligand is predicted to be basic the intermediate involved in these reactions may be of the type (162) in which the oxygen co-ordinates to the iron(II) bromide.

The inability of $[\text{Fe}_2(\text{CO})_9]$ to mediate the cycloaddition of the



(162)

ketone (134) to alkenes or furan may be related to the need for a Lewis acid in these reactions. However, Noyori et al. have previously reported that 1,3-dibromopropanone could not be used as a source of the oxodimethylenemethane fragment in the iron mediated cyclocoupling reactions. This failure was believed to be a result of the instability of unsubstituted oxodimethylenemethane species which Noyori et al. formulated as (163).^{73,83}



5.8 CONCLUSION

3-Chloro-1-(trimethylsilyl)propan-2-one (134) and 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) serve as precursors to the oxodimethylenemethane fragment. Thus the preparation of platinum, iridium, and osmium oxodimethylenemethane complexes can be achieved in high yield. Single-crystal X-ray diffraction studies establish the presence of an η^3 -oxodimethylenemethane ligand which suggests an allylic contribution to the bonding of the ligand to the metal centre. The carbon-oxygen bond of the oxodimethylenemethane fragment is tipped out of the C-C-C plane towards the metal and this is a consequence of the allylic type of bonding in these complexes.

In solution, the platinum complex (137) undergoes rapid equilibration

of the oxodimethylenemethane protons at room temperature. The free energy of activation has been calculated from the coalescence temperature. The low temperature ^1H n.m.r. spectrum of this complex shows the expected features of the static structure. The iridium complex (135) does not exhibit a variable temperature ^1H n.m.r. spectrum.

The oxygen of the η^3 -oxodimethylenemethane ligand is not as nucleophilic as the methylene group of the η^3 -trimethylenemethane ligand and this may explain why the oxodimethylenemethane co-ordinates to a $\underline{d}^8\text{-ML}_4$ fragment in an η^3 -arrangement rather than rearranging to an η^4 -geometry co-ordinated to a $\underline{d}^8\text{-ML}_3$ fragment. The oxodimethylenemethane fragment did not cycloadd to alkenes. However, the relative ease in which the silylenol ether (136) can be generated from the ketone (134), using various low-valent metal catalysts, may result in future developments in the Lewis acid mediated reactions of the silylenol ether (136).

In summary, the allylic methanesulphonate (74) and the silylenol ether (136) act as effective precursors to the trimethylenemethane and oxodimethylenemethane fragments respectively.^{120,190} Thus, elimination of Me_3SiX ($\text{X} = \text{OS}(\text{O})_2\text{Me}$ or Cl) from these bifunctional reagents appears to be a general route to the generation of organic fragments at metal centres. Previously organotin compounds such as allyl trimethyltin, cyclopentadienyl trimethyltin, and indenyl trimethyltin have been reacted with a wide variety of metal carbonyl halides to afford the corresponding π -enyl metal carbonyl derivatives.²¹⁵ The elimination of Me_3SnX from these tin reagents, to generate the π -ligand, is similar to the elimination of Me_3SiX in the synthesis of the trimethylenemethane and oxodi-

methylenemethane metal complexes and would therefore appear to be a general reaction in organometallic chemistry. There is considerable present interest in the use of silicon reagents for organic synthesis^{90,216} and some of these reagents may also find future applications in organometallic synthesis.

5.9 EXPERIMENTAL

Experimental techniques were as described in Chapters 2 and 4. Chloroacetic anhydride (Fluka), bromoacetic anhydride (Lancaster), chloromethyltrimethylsilane, titanium(IV) chloride, dimethylphenylphosphine, tri-n-butylphosphine, furan (Aldrich), mercury(II) chloride (May & Baker), mercury(II) iodide (Fisons), trans-stilbene (Koch-Light), and chlorine (B.O.C.) were used as supplied from commercial sources. Benzaldehyde (Aldrich) was washed with aqueous sodium bicarbonate, dried over anhydrous magnesium sulphate and distilled under nitrogen prior to use. $[\text{IrH}(\text{CO})_2(\text{PPh}_3)_2]$,²¹⁷ $[\text{Ni}(\eta^2\text{-acrylonitrile})_2]$,²¹⁸ $[\text{RhH}(\text{PPh}_3)_4]$,²¹⁹ cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$,²²⁰ $[\text{Fe}_2(\text{CO})_9]$,²²¹ $[\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2]$,²²² trimethylsilylmethylmagnesium chloride,²²³ and 1-(trimethylsilyl)propan-2-one¹⁹² were prepared by the literature procedures.

Preparation of 3-chloro-1-(trimethylsilyl)propan-2-one (134)

A solution of trimethylsilylmethylmagnesium chloride (6 mmol) in diethyl ether (10 cm³) was added dropwise to a solution of chloroacetic anhydride (1.0 g, 6 mmol) in diethyl ether (10 cm³) at -78°C. The solution was stirred at -78°C for 8h and allowed to warm slowly to 0°C. The reaction mixture was recooled to -10°C and 10% aqueous ammonium chloride solution (20 cm³) was added. The organic layer was separated, washed with aqueous sodium bicarbonate solution, and dried over anhydrous potassium carbonate. The solvent was removed in vacuo (15 mmHg) and the

residue purified by vacuum distillation to give a colourless oil (0.69 g, 70%), b.p. 40°C (1 mmHg) which was identified as 3-chloro-1-(trimethylsilyl)propan-2-one (134).¹⁸⁷ I.r. (film) 2960m, 2900w, 1710s, 1405m, 1300w, 1250s, 1190m, 1100s, 1065m, 1040m, 910w, 850vs, 810w, 760w, 695w, 670w and 660w cm^{-1} ; n.m.r. (CDCl_3): ^1H (90 MHz), δ 0.1 (s, 9H, SiMe_3), 2.3 (s, 2H, $\text{CH}_2\text{-SiMe}_3$), and 3.8 p.p.m. (s, 2H, $\text{CH}_2\text{-Cl}$).

The same procedure as above was carried out for the preparation of 3-bromo-1-(trimethylsilyl)propan-2-one using trimethylsilylmethylmagnesium chloride and bromoacetic anhydride. The same work up as above gave a colourless oil which was identified as 3-bromo-1-(trimethylsilyl)propan-2-one (59%).¹⁸⁷ I.r. (film), 2960m, 2900w, 1695s, 1415m, 1305w, 1260s, 1180w, 1095m, 1040m, 855vs, 760w, and 700m cm^{-1} ; n.m.r. (CDCl_3): ^1H (90 MHz), δ 0.2 (s, 9H, SiMe_3), 2.5 (s, 2H, $\text{CH}_2\text{-SiMe}_3$), and 3.9 p.p.m. (s, 2H, $\text{CH}_2\text{-Br}$).

PREPARATION OF OXODIMETHYLENEMETHANE METAL COMPLEXES

$[\text{Ir}(\eta^3\text{-CH}_2\text{COCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (135)

(i) $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ (0.5 g, 0.5 mmol) and 3-chloro-1-(trimethylsilyl)propan-2-one (0.81 g, 4.9 mmol) in toluene (5 cm^3) were heated to reflux for fifteen minutes. A white solid precipitated from the yellow solution. Light petroleum (5 cm^3) was added and the white solid filtered, washed with light petroleum (10 cm^3), and dried in vacuo.

Recrystallisation from dichloromethane/light petroleum gave white crystals of the title complex (0.4 g, 92%), m.p. 210°C (decomp.) (Found: C, 56.1; H, 4.1. $\text{C}_{40}\text{H}_{34}\text{ClIrO}_2\text{P}_2 \cdot 0.25 \text{CH}_2\text{Cl}_2$ requires C, 56.4; H, 4.1%), i.r. $\nu_{\text{C}\equiv\text{O}}$ 2010, $\nu_{\text{C}=\text{O}}$ 1635 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.47 [m, 2H, (CH_2COCH_2), J(HH) 7.9], 2.62 [t, 2H, (CH_2COCH_2), J(HH) 7.9], and 7.4 (m, 30H, PPh_3); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz), δ 37.1 (s, CH_2COCH_2), 164.4

[t, IrCO, J(CP) 4.0], and 197.2 (s, CH₂COCH₂); ³¹P-{¹H} (24 MHz), δ -10.69 p.p.m. (s).

Inspection of the organic residue from the above reaction showed the presence of 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) by comparison of its ¹H n.m.r. spectrum with an authentic sample.^{187,188}

(ii) [IrH(CO)(PPh₃)₃] (0.15 g, 0.15 mmol) and 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) (0.25 g, 1.51 mmol) in toluene (3 cm³) were heated to reflux for ten minutes. Addition of light petroleum (10 cm³) gave a white solid which was filtered, washed with light petroleum, and dried in vacuo to give the title complex (0.12 g, 96%) which was identified by comparison of the ¹H, ³¹P-{¹H}, and i.r. spectra with an authentic sample.

(iii) Under analogous conditions to (ii), [IrH(CO)₂(PPh₃)₂] (0.2 g, 0.26 mmol) and 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) (0.3 g, 1.8 mmol) gave the title complex (0.14 g, 65%) which was identified by comparison of the ¹H, ³¹P-{¹H}, and i.r. spectra with an authentic sample.

(iv) trans-[IrCl(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and 3-chloro-1-(trimethylsilyl)propan-2-one (134) (0.23 g, 1.4 mmol) in toluene (3 cm³) were refluxed for 12h. The white solid was filtered and washed with light petroleum (10 cm³) to give the title complex (0.07 g, 64%).

(v) trans-[IrCl(CO)(PPh₃)₂] (0.07 g, 0.09 mmol) and 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) (0.18 g, 1.1 mmol) in toluene (3 cm³) were refluxed for 10 minutes. The white solid was filtered and washed with light petroleum (10 cm³) to give the title complex (0.06 g, 80%).

[Pt(η^3 -CH₂COCH₂)(PPh₃)₂] (137)

[Pt(η^2 -trans-stilbene)(PPh₃)₂] (0.3 g, 0.3 mmol) and 3-chloro-1-(trimethylsilyl)propan-2-one (134) (0.33 g, 2.0 mmol) in diethyl ether (15 cm³) were stirred for 2h at room temperature. The slightly cloudy solution was filtered and light petroleum (10 cm³) added. A white solid precipitated which was washed with light petroleum and dried in vacuo to give the title complex (0.14 g, 60%), m.p. 190°C (decomp.) (Found: C, 60.0; H, 4.4. C₃₉H₃₄OP₂Pt requires C, 60.4; H, 4.4%); i.r. ν_{CO} 1550 cm⁻¹; n.m.r. (CD₂Cl₂): ¹H (400 MHz), δ 2.25 [br m, 4H, CH₂COCH₂, J(HPt) 48.4], and 7.3 (m, 30H, PPh₃); ¹³C-{¹H} (100 MHz), δ 49.6 [dd, CH₂COCH₂, AXX' system, J = 56.5, 5.0, J(CPt) 251.5], and 183.8 (s, CH₂COCH₂); ³¹P-{¹H} (24 MHz), δ +23.19 p.p.m. [s, J(PPt) 2978]; ¹H (400 MHz), [²H₈]-tetrahydrofuran, -105°C, δ 2.01 (br, 2H), 2.25 (br, 2H), and 7.5 p.p.m. (m, 30H, PPh₃).

[Os(η^3 -CH₂COCH₂)(CO)₂(PPh₃)₂] (138)

[Os(CO)₂(PPh₃)₃] (0.2 g, 0.19 mmol) and 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) (0.3 g, 1.8 mmol) in toluene (5 cm³) were heated to reflux for five minutes. The yellow colour was replaced by a cloudy white solution. The solvent was removed in vacuo, the residue washed with light petroleum, and dried in vacuo. The crude product was purified by chromatography on an alumina column. Elution with dichloromethane and then dichloromethane/methanol (1:2) gave a white solid which was recrystallised from dichloromethane/light petroleum to give white crystals of the title complex (0.11 g, 70%), m.p. 190°C. (Found: C, 58.0; H, 4.2. C₄₁H₃₄O₃OsP₂.0.33 CH₂Cl₂ requires C, 58.0; H, 4.1%); i.r. $\nu_{\text{C}\equiv\text{O}}$ 1990, 1925, $\nu_{\text{C}=\text{O}}$ 1610 cm⁻¹; n.m.r. (CDCl₃): ¹H (300 MHz), δ 1.5 [t, 4H, CH₂COCH₂, J(HP) 8.2], and 7.4 (m, 30H, PPh₃); ¹³C-{¹H} (75 MHz), δ 27.0 [t, CH₂COCH₂, J(CP) 4.1], 184.1 [t, OsCO, J(CP) 10.0],

and 191.3 (s, CH_2COCH_2); $^{31}\text{P}-\{^1\text{H}\}$ (24 MHz), δ +5.24 p.p.m. (s).

$[\text{Rh}(\eta^1\text{-CH}_2\text{COME})\text{Cl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2]$ (143)

trans- $[\text{RhCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ (0.15 g, 0.34 mmol), and 3-chloro-2-(trimethylsilyloxy)prop-1-ene (136) (0.5 g, 3.0 mmol) in methanol (5 cm^3) were stirred at room temperature for five minutes. The solvent was removed in vacuo and the residue crystallised from dichloromethane/light petroleum to give pale yellow crystals of the title complex (0.11 g, 60%), m.p. 132°C (decomp.) (Found: C, 44.9; H, 5.1. $\text{C}_{20}\text{H}_{27}\text{Cl}_2\text{O}_2\text{P}_2\text{Rh}$ requires C, 44.9; H, 5.1%); i.r. $\nu_{\text{C}\equiv\text{O}}$ 2060, $\nu_{\text{C}=\text{O}}$ 1670 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 1.33 (s, 3H, CH_3CO), 2.08 [t, PMe_2Ph , $|^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})|$ 4.3], 2.14 [t, PMe_2Ph , $|^2\text{J}(\text{PH}) + ^4\text{J}(\text{PH})|$ 3.4], 2.35 (m, 2H, CH_2CO), and 7.4 (m, 10H, PMe_2Ph); $^{13}\text{C}-\{^1\text{H}\}$ (75 MHz), δ 11.6 [t, PMe_2Ph , $|^1\text{J}(\text{PH}) + ^3\text{J}(\text{PH})|$ 18.3], 13.0 [t, PMe_2Ph , $|^1\text{J}(\text{PH}) + ^3\text{J}(\text{PH})|$ 17.7], 28.7 (s, CH_3CO), and 37.5 [dt, CH_2CO , $\text{J}(\text{CRh})$ 22.9, $\text{J}(\text{CP})$ 2.8]; RhCO and CH_2CO resonances were not observed; $^{31}\text{P}-\{^1\text{H}\}$ (24 MHz), δ +2.3 p.p.m. [d, $\text{J}(\text{PRh})$ 83.0].

ISOMERISATION REACTIONS OF 3-CHLORO-1-(TRIMETHYLSILYL)PROPAN-2-ONE (134)

(i) HgI_2

To 3-chloro-1-(trimethylsilyl)propan-2-one (134) (0.3 g, 1.8 mmol) was added mercury(II) iodide (0.05 g, 0.1 mmol) and the mixture was stirred for 1h. The ^1H n.m.r. spectrum of a sample indicated that the starting compound was still present and no sign of any reaction was observed. The reaction was stirred for 12h and the ^1H n.m.r. spectrum showed no evidence of any reaction. These conditions isomerise 1-(trimethylsilyl)propan-2-one to 2-(trimethylsiloxy)prop-1-ene.¹⁹²

(ii) Thermal reaction

An n.m.r. sample of (134) in $[\text{D}_8]\text{-toluene}$ was heated to 120°C for

2h. The ^1H n.m.r. spectrum indicated that only starting material (134) was present.

(iii) $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$

To the n.m.r. sample in (ii) was added $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ (0.01 g, 1×10^{-5} mol). There was no initial change in the ^1H n.m.r. spectrum. The solution was heated to 115°C for 2h. The ^1H n.m.r. spectrum showed complete isomerisation of (134) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) which was identified by comparison of the ^1H n.m.r. spectrum with an authentic sample.¹⁸⁷

(iv) $[\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2]$

To a solution of (134) (0.3 g, 1.8 mmol) in $[\text{}^2\text{H}_6]\text{-benzene}$ (1 cm^3) was added $[\text{Pt}(\eta^2\text{-trans-stilbene})(\text{PPh}_3)_2]$ (0.1 g, 0.1 mmol). The ^1H n.m.r. spectrum showed complete isomerisation of the ketone (134) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) after five minutes at room temperature.

(v) $[\text{Pd}(\text{PPh}_3)_4]$

The reaction was repeated as in (iv) using (134) (0.1 g, 0.6 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (0.05 g, 0.04 mmol). The ^1H n.m.r. spectrum showed complete isomerisation to 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) by comparison of the ^1H n.m.r. spectrum with an authentic sample.¹⁸⁷ This reaction can be carried out in dichloromethane. The pure silylenol ether (136) can be isolated by a simple trap-to-trap distillation. The required product is isolated in about 90% yield.

(vi) PPh_3

(134) (0.1 g, 0.6 mmol) and triphenylphosphine (0.016 g, 0.06 mmol) in $[\text{}^2\text{H}_8]\text{-toluene}$ (1 cm^3) were heated to reflux for 24h. The ^1H n.m.r. spectrum showed no sign of any reaction and the starting material

remained unchanged.

(vii) Other Catalysts

The reaction (iii) was repeated with various other metal catalysts to assess their activity. $[\text{RhH}(\text{PPh}_3)_4]$ and trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ also catalyse the isomerisation reaction of 3-chloro-1-(trimethylsilyl)propan-2-one (134) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (136) on refluxing for 12h in toluene. $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ and cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ do not catalyse the 'Brooke rearrangement' under analogous conditions.

The platinum complex (137) caused a rapid isomerisation of the ketone (134) to the silylenol ether (136) at room temperature.

Reaction of 1-(trimethylsilyl)propan-2-one with $[\text{Pt}(\eta^2\text{-trans stilbene})(\text{PPh}_3)_2]$

A solution of 1-(trimethylsilyl)propan-2-one (0.06 g, 0.46 mmol) and $[\text{Pt}(\eta^2\text{-trans stilbene})(\text{PPh}_3)_2]$ (0.03 g, 3.3×10^{-5} mol) in $[\text{}^2\text{H}_2]$ -dichloromethane (0.5 cm³) was stirred for 3h at room temperature. The ¹H n.m.r. spectrum showed no signs of any reaction. The starting compound remained unchanged.

Reactions of 3-bromo-1-(trimethylsilyl)propan-2-one

(i) $[\text{Pt}(\eta^2\text{-trans stilbene})(\text{PPh}_3)_2]$

A solution of 3-bromo-1-(trimethylsilyl)propan-2-one (0.1 g, 0.5 mmol) and $[\text{Pt}(\eta^2\text{-trans stilbene})(\text{PPh}_3)_2]$ (0.03 g, 3.3×10^{-5} mol) in $[\text{}^2\text{H}_8]$ -toluene was stirred for fifteen minutes at room temperature. The ¹H n.m.r. spectrum showed complete isomerisation of the starting compound to 3-bromo-2-(trimethylsiloxy)prop-1-ene by comparison of its ¹H n.m.r. spectrum with an authentic sample.¹⁸⁷

(ii) HgI_2

To 3-bromo-1-(trimethylsilyl)propan-2-one (0.2 g, 0.9 mmol) was added

mercury(II) iodide (0.1 g, 0.2 mmol). The mixture was stirred for 1h. A ^1H n.m.r. spectrum of a sample showed complete isomerisation of the starting compound to 3-bromo-2-(trimethylsiloxy)prop-1-ene by comparison of its ^1H n.m.r. spectrum with an authentic sample. The product was contaminated with 1-bromopropan-2-one.

REACTIONS OF OXODIMETHYLENEMETHANE COMPLEXES

[A] Reactions of $[\text{Ir}(\eta^3\text{-CH}_2\text{COCH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (135)

(i) with hydrochloric acid.

To a solution of (135) (0.15 g, 0.18 mmol) in $[\text{}^2\text{H}_1]$ -chloroform (2 cm^3) was added concentrated hydrochloric acid (1 drop, excess). The ^1H n.m.r. spectrum showed complete reaction of the starting complex. The excess hydrochloric acid was neutralised with sodium bicarbonate and the solution dried over anhydrous potassium carbonate. The solution was filtered and addition of light petroleum gave white crystals of $[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_3)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ (153) (0.15 g, 95%), m.p. 220°C (decomp.) (Found: C, 54.7; H, 3.9. $\text{C}_{40}\text{H}_{35}\text{Cl}_2\text{IrO}_2\text{P}_2$ requires C, 55.0; H, 4.0%); i.r. $\nu_{\text{C}\equiv\text{O}}$ 2045, $\nu_{\text{C}=\text{O}}$ 1690 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 1.25 (s, 3H, $\underline{\text{CH}_3\text{CO}}$), 2.8 [t, 2H, $\underline{\text{CH}_2\text{CO}}$, J(HP) 5.3], and 7.5 (m, 30H, PPh_3); ^{13}C - $\{^1\text{H}\}$ (75 MHz), δ 28.0 (s, $\underline{\text{CH}_3\text{CO}}$), 29.1 [t, $\underline{\text{CH}_2\text{CO}}$, J(CP) 3.2], 160.9 [t, $\text{Ir}\underline{\text{CO}}$, J(CP) 8.0], and 213.0 (s, $\text{CH}_2\underline{\text{CO}}$); ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ -11.49 p.p.m.

(ii) with mercury(II) chloride.

To a solution of (135) (0.05 g, 0.06 mmol) in tetrahydrofuran/acetone (1:1 mixture) (5 cm^3) was added mercury(II) chloride (0.018 g, 0.06 mmol). The solution was stirred for 16h at room temperature. The solvent was removed in vacuo, the residue extracted with dichloromethane, and the solution filtered. The filtrate was concentrated in vacuo and

diethyl ether added. The white solid was filtered and dried in vacuo and identified as $[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_2\text{HgCl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ (154) (0.05 g, 70%), m.p. 195°C (decomp.) (Found: C, 41.3; H, 3.1. $\text{C}_{40}\text{H}_{34}\text{Cl}_3\text{HgIrO}_2\text{P}_2$. CH_2Cl_2 requires C, 41.3; H, 3.0%); i.r. $\nu_{\text{C}\equiv\text{O}}$ 2050, $\nu_{\text{C}=\text{O}}$ 1650 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.0 (s, 2H, CH_2HgCl), 2.85 [t, 2H, CH_2CO , J(HP) 5.4], and 7.5 p.p.m. (m, 30H, PPh_3).

(iii) with chlorine.

Chlorine gas was bubbled through a solution of (135) (0.06 g, 0.07 mmol) in $[\text{}^2\text{H}_1]\text{-chloroform}$ (0.5 cm^3). The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. indicated an immediate reaction. Addition of light petroleum gave a white solid identified as $[\text{Ir}(\eta^1\text{-CH}_2\text{COCH}_2\text{Cl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ (158) (0.05 g, 79%), m.p. 250°C (decomp.) (Found: C, 52.5; H, 3.8. $\text{C}_{40}\text{H}_{34}\text{Cl}_3\text{IrO}_2\text{P}_2$ requires C, 53.0; H, 3.8%); i.r. $\nu_{\text{C}\equiv\text{O}}$ 2030, $\nu_{\text{C}=\text{O}}$ 1700 cm^{-1} ; n.m.r. (CDCl_3): ^1H (300 MHz), δ 2.65 [t, 2H, CH_2CO , J(HP) 5.1], 2.95 (s, 2H, CH_2Cl), and 7.5 (m, 30H, PPh_3); $^{13}\text{C}\{-^1\text{H}\}$ (75 MHz), δ 22.6 (br s, CH_2CO), 46.3 (s, CH_2Cl), and 206.0 (s, CH_2CO); $^{31}\text{P}\{-^1\text{H}\}$ (24 MHz), δ -12.1 p.p.m.

[B] Reactions of $[\text{Os}(\eta^3\text{-CH}_2\text{COCH}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (138)

(i) with hydrochloric acid.

To a solution of (138) (0.15 g, 0.18 mmol) in $[\text{}^2\text{H}_1]\text{-chloroform}$ (1 cm^3) was added concentrated hydrochloric acid (1 drop, excess). The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra showed complete reaction of the starting complex. The excess hydrochloric acid was neutralised with sodium bicarbonate and the solution dried over anhydrous potassium carbonate. The solution was filtered and addition of light petroleum gave a white solid which was identified as the starting complex (138) (0.12 g, 80%) by comparison of its ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. with an authentic sample.

(ii) The reaction was repeated as in (i). The intermediate species, characterised by ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. and i.r. spectroscopic data, is believed to be an η^3 -hydroxyallyl complex $[\text{Os}\{\eta^3\text{-CH}_2\text{C(OH)CH}_2\}(\text{CO})_2(\text{PPh}_3)_2]\text{Cl}$ (155); i.r. (CH_2Cl_2) $\nu_{\text{C}\equiv\text{O}}$ 2025, 1965 cm^{-1} (no $\nu_{\text{C}=\text{O}}$); n.m.r. (CDCl_3): ^1H (300 MHz), δ 1.72 (m, 2H), 2.17 (br s, 2H), and 7.5 (m, 30H, PPh_3); $^{13}\text{C}\{-^1\text{H}\}$ (75 MHz), δ 31.4 [s, $\text{CH}_2\text{C(OH)CH}_2$], 164.9 [s, $\text{CH}_2\text{C(OH)CH}_2$], and 181.1 p.p.m. [t, MCO , $J(\text{CP})$ 9.9].

(iii) with mercury(II) chloride.

To a solution of (138) (0.05 g, 0.06 mmol) in $[\text{}^2\text{H}_1]\text{-chloroform}$ (1 cm^3) was added mercury(II) chloride (0.038 g, 0.12 mmol). The ^1H n.m.r. spectrum indicated that the starting material had all reacted after 3h at room temperature. The solvent was removed in vacuo, the residue washed with diethyl ether and the white solid filtered, washed with diethyl ether and dried in vacuo to give $[\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ (0.04 g, 80%) which was identified by comparison of the i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra with an authentic sample.²²²

(iv) with chlorine.

Chlorine gas was bubbled through a solution of (138) (0.05 g, 0.06 mmol) in $[\text{}^2\text{H}_1]\text{-chloroform}$ (0.5 cm^3) at 0°C. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra indicated an immediate reaction. The ^1H n.m.r. spectrum exhibited a singlet at δ 4.2 p.p.m. which appears at the same shift as 1,3-dichloropropanone.²²⁴ Ethanol was added to the reaction mixture and white crystals were filtered, washed with ethanol, dried in vacuo, and identified as $[\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ (0.045 g, 89%) by comparison of the i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra with an authentic sample.²²²

[C] Reaction of $[\text{Pt}(\eta^3\text{-CH}_2\text{COCH}_2)(\text{PPh}_3)_2]$ (137) with hydrochloric acid

The reaction of (137) with concentrated hydrochloric acid was carried

out as in (i) above in [$^2\text{H}_1$]-chloroform to give cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (80% yield) which was identified by comparison of the i.r. and ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra with an authentic sample.

Attempted catalytic cycloaddition reactions of (134) and (136) with alkenes

A number of reactions were carried out in an attempt to catalyse the cycloaddition of the oxodimethylenemethane fragment, generated from the ketone (134) or the silylenol ether (136), to alkenes. None of the desired cycloadducts were detected and the starting materials were recovered unchanged, apart from the 'Brooke rearrangement' of (134) to (136). The reaction mixtures were analysed by T.L.C. and by ^1H n.m.r. spectra. Table 6 summarises these reactions. Approximately 10 mole % of the metal catalyst was employed in these reactions, and the trap was in excess. A typical run involved the use of 1 mmol of 3-chloro-1-(trimethylsilyl)propan-2-one (134), 2.5 mmol of the trap, and 10 mole % of the metal catalyst in 5 cm^3 of solvent.

TABLE 6

Reagent	Metal Catalyst	Trap	Solvent	Conditions
(134)	$[\text{Pd}(\text{PPh}_3)_4]$	methyl acrylate	benzene	r.t. 24h
"	" + dppe	coumarin	tetrahydrofuran	reflux 24h
"	$[\text{Pd}(\text{PPh}_3)_4]$	"	toluene	" "
"	$[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$	"	"	" "
"	$[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3] + 8 \text{ PMe}_2\text{Ph}$	dimethyl benzylidenemalonate	"	" "
"	$[\text{Ni}(\eta^2\text{-acrylonitrile})_2]$	"	benzene	60°C 24h
"	" + PBu_3	"	"	" "
"	$[\text{Pd}(\text{PPh}_3)_4]$	furan	furan	reflux 24h
"	$[\text{Fe}_2(\text{CO})_9]$ (1 mole equiv.)	"	"	" "
"	"	<u>trans</u> -stilbene	benzene	" 3 days
"	$[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3] + 8 \text{ P}(\text{OEt})_3$	"	toluene	" 24h
"	$[\text{RhH}(\text{PPh}_3)_4] + \text{PPh}_3$	dimethyl benzylidenemalonate	"	" "



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Trimethylenemethane and Oxodimethylenemethane Metal Complexes

Michael David Jones

ABSTRACT

Chapter 1 reviews the literature concerning trimethylenemethane and oxodimethylenemethane metal complexes and their rôle in organic synthesis.

The preparation and characterisation of η^4 -trimethylenemethane metal complexes of iridium, rhodium, osmium and ruthenium are presented in Chapter 2, together with the molecular structure of three of these complexes which establishes the presence of the η^4 -trimethylenemethane ligand. The room temperature ^1H n.m.r. spectra show the expected features for a static structure and no sign of rotation of the trimethylenemethane ligand was observed at higher temperatures.

Preliminary investigation into the reactivity of these trimethylenemethane complexes is detailed in Chapter 3. A series of cationic η^4 -trimethylenemethane complexes are prepared by the reaction of $[\text{Ir}(\eta^4\text{-C}(\text{CH}_2)_3)\text{Cl}(\text{CO})(\text{PPh}_3)]$ with silver hexafluorophosphate in the presence of a donor ligand such as carbon monoxide or ethene. The reactions of these cationic complexes with neutral and anionic nucleophiles are investigated and show that displacement of other donor ligands or attack on co-ordinated carbonyl and ethene ligands occurs, rather than attack at, or displacement of the trimethylenemethane ligand.

Chapter 4 describes the reaction of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene with d^{10} -metal complexes of platinum, palladium and nickel. The isolation of η^3 -2-trimethylsilylmethylallyl palladium and platinum complexes are of interest since they are postulated intermediates implicated in the generation of the catalytic species $[\text{Pd}(\eta^3\text{-trimethylenemethane})(\text{PPh}_3)_2]$. The d^{10} -nickel complex $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$ catalyses the cycloaddition of trimethylenemethane to electron-deficient alkenes and imines, the latter reaction affords a high yield synthesis of 4-methylenepyrrolidines.

The final Chapter describes the reactions of 3-chloro-1-(trimethylsilyl)propan-2-one and 3-chloro-2-(trimethylsiloxy)prop-1-ene with low-valent metal complexes to afford oxodimethylenemethane complexes of platinum, iridium, and osmium. The molecular structure of two of these complexes establishes the presence of an η^3 -oxodimethylenemethane ligand. The silylenol ether, 3-chloro-2-(trimethylsiloxy)prop-1-ene was readily prepared from 3-chloro-1-(trimethylsilyl)propan-2-one, the isomerisation being catalysed by a number of low-valent metal complexes.