SOME CHEMISTRY OF VINYLIDENE, ACETYLIDE AND HYDRIDE COMPLEXES

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by

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B.Sc. (Hons.)

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καὶ αὐτάς ἐστίν πρὸ πάντων, καὶ τὰ πάντα έν αὐτῷ συνέστηκεν

κολοσσαεις *1:17*

And He is before all things and in Him all things hold together.

Colossians 1:17

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SUMMARY

The rapid development of metal vinylidene and acetylide chemistry is a source of new and interesting reactions. Recently a high yield route to some ruthenium vinylidene and acetylide complexes has become available. A study of the chemistry of these and related complexes is described in this thesis. To gain a perspective of previous research in this field of chemistry some literature surveys have been made. The cyclopentadienyl-ruthenium and -osmium phosphine moieties have formed the basis of the chemistry studied; in Chapter One, previous work done with this system is surveyed. A comprehensive review of the chemistry of metal-vinylidene complexes comprises the rest of this Chapter. Often mononuclear vinylidene complexes were reported to be very reactive and so could not be isolated, but were inferred from the products.

In Chapter Two some reactions of stable vinylidene complexes (e.g. $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$) are described. Reactions with alcohols give alkoxy(alkyl)carbene complexes (e.g. $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}$-$PF_6$ with methanol) possessing acidic β-protons, which can be exchanged with D^+ or Me^+, or removed with bases to give vinylether complexes. With oxygen, the vinylidene moiety of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ undergoes an interesting cleavage reaction affording $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and benzaldehyde. The mechanisms of these reactions are discussed briefly.

The electron-rich triple bonds of some metal acetylide complexes undergo 2+2 cycloaddition reactions with electron-deficient olefins such as tetracyanoethylene (tcne). In the reaction of $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ with tcne, a non-isolated paramagnetic complex was detected by e.s.r. spectroscopy, which sequentially yields cyclobutenyl, butadienyl and allylic complexes. A reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne

yields only an allylic complex, $Ru[\eta^3-C(CN)_2C(Ph)C=C(CN)_2](PPh_3)(\eta-C_5H_5)$, formed *via* two radical intermediates. This complex undergoes ligand addition reactions to give butadienyl complexes (e.g. $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(L)(PPh_3)(\eta-C_5H_5)$, $L = CO$ or $CNBu^t$), which, in the former case, reverts to the allylic complex on irradiation. When $Ru(C\equiv CPh)(PPh_3)_2(\eta-C_5H_5)$ reacts with $(NC)_2C=C(CF_3)_2$, however, a dark blue binuclear complex, $\{Ru[\overline{C=C(Ph)C(CF_3)_2C}(CN)_2](PPh_3)(\eta-C_5H_5)\}_2\{\mu-(NC)_2C=C(CF_3)_2\}$, is isolated in high yield. This exhibits a strong temperature dependent e.s.r. signal in the solid state or in solution. In contrast, the reaction of tcne with $Rh(C\equiv CPh)(CO)(PPh_3)_2$ yields only an oxidative addition product, which loses CO in refluxing acetonitrile to give $Rh(C\equiv CPh)(\eta^2-C_2(CN)_4)(NCMe)(PPh_3)_2$. The scope of these reactions has been explored and is reported, with some discussion of possible mechanisms, in Chapter Three.

In order to obtain metal acetylide complexes for study, some convenient, high yield syntheses have been developed. These compounds were readily prepared by deprotonation of vinylidene complexes, or by ligand exchange reactions with acetylide complexes. This chemistry, in addition to a brief survey of the preparative routes to metal acetylide complexes, is reported in Chapter Four.

A convenient route to hydride complexes of ruthenium and osmium has been developed. The halide complexes react readily with sodium methoxide in refluxing methanol to precipitate the metal hydride complexes in high yield. The scope of this reaction has been explored and is reported in Chapter Five.

Much new spectroscopic data have been collected for the cyclopentadienyl ruthenium and osmium systems. Of particular importance is the ^{13}C n.m.r. and mass spectral data. In Chapter Six this data is summarised and interpreted where possible.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of this thesis.

A. Geoffrey Swincer

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ABBREVIATIONS

In General

Å	angstroms
atm.	atmospheres
Bu^t	*tert*-butyl
c.	circa
C_5H_5	cyclopentadienyl
cm	centimetres
cont'.	continued
Cy	cyclohexyl
d	days
dec.	decomposed
dpae	1,2-bis(diphenylarsino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
e.s.r.	electron spin resonance
h	hours
Hz	hertz
i.r.	infrared
kcal mol^{-1}	kilocalories per mole
liq.	liquid
lit.	literature
Me	methyl
MHz	megahertz
min.	minutes
ml	mililitres

ABBREVIATIONS (cont'.)

mm	milimetres
mmol	milimoles
m.p.	melting point
nm	nanometres
n.m.r.	nuclear magnetic resonance
Ph	phenyl
Pr^i	*iso*-propyl
R	alkyl
ref.	reference
sec.	seconds
sp	*ortho*-styryl — diphenylphosphine
thf	tetrahydrofuran
tms	tetramethylsilane
UV	ultraviolet

For Infrared Spectroscopy

br	broad
cm^{-1}	wave numbers (reciprocal centimetres)
m	medium
s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak

For N.M.R. Spectroscopy

ABq	AB quartet
d	doublet

ABBREVIATIONS (cont'.)

dd	doublet of doublets
dq	doublet of quartets
dt	doublet of triplets
dtt	doublet of triplets of triplets
m	multiplet
p.p.m.	parts per million
s	singlet
t	triplet
tt	triplet of triplets

CHAPTER ONE

1.1 INTRODUCTION

A detailed study of some reactions of metal acetylides and their precursors, metal vinylidenes, was made. The initial studies of these reactions always involved the cyclopentadienyl ruthenium bis-triphenylphosphine system, [Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)], followed by subsequent changes in ligands and/or metals.

This chapter contains a comprehensive review of cyclopentadienyl ruthenium and osmium phosphine complexes as well as metal vinylidene chemistry. Some chemistry and preparations of transition-metal acetylides are discussed in Chapters 3 and 4.

1.2 CYCLOPENTADIENYL RUTHENIUM AND OSMIUM CHEMISTRY

The chemistry of cyclopentadienyl ruthenium and osmium systems, excluding metallocenes, is now very extensive and has recently been reviewed.[1] While many similarities can be drawn to the cyclopentadienyl iron work, the larger ionic radius and generally increased stability of these metals, reveals much new chemistry. This is particularly true of the M(PPh$_3$)$_2$(η-C$_5$H$_5$)(M = Ru or Os) systems which have no iron analogues.

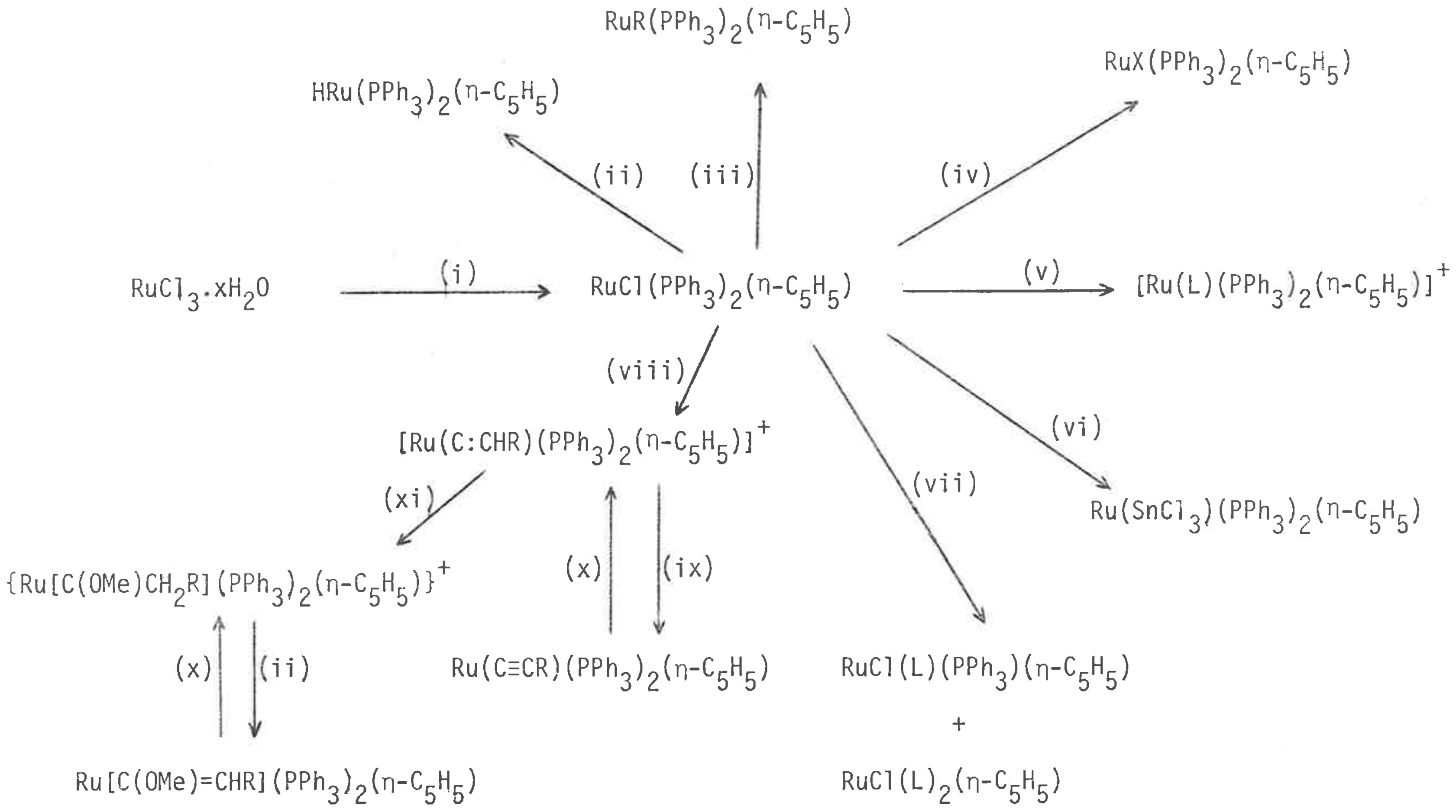
1.2.1 Halides

Halogenation of [Ru(CO)$_2$(η-C$_5$H$_5$)]$_2$ in halogenated solvents gives yellow or orange RuX(CO)$_2$(η-C$_5$H$_5$) (X = Cl, Br or I).[2] The chloride also formed from [RuCl$_2$(CO)$_3$]$_2$ and TlC$_5$H$_5$, or by bubbling air through a solution of [Ru(CO)$_2$(η-C$_5$H$_5$)]$_2$ in CHCl$_3$-EtOH containing HCl.[3] In aromatic solvents, however, in the presence of large anions, the yellow halogen-bridged cations {[Ru(CO)$_2$(η-C$_5$H$_5$)]$_2$X}$^+$ can be isolated.[2] At -80°, these reactions afford green products, thought to be isomeric, which revert to the yellow complexes at room temperature.

It is not possible to replace directly both CO ligands of the $Ru(CO)_2(\eta-C_5H_5)$ group by tertiary phosphines or phosphites. It is thought that the stability of the intermediate monocarbonyl results from a delicate balance of steric and electronic effects.

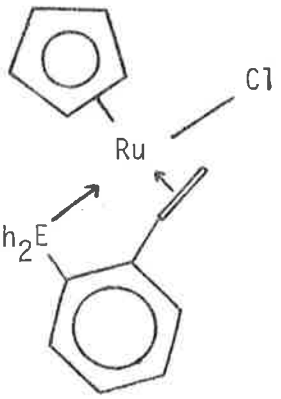
Compounds containing the $Ru(PR_3)_2(\eta-C_5H_5)$ moiety have been made by introducing the cyclopentadienyl group into a suitable tertiary phosphine-ruthenium complex precursor. Thus, the reaction between cyclopentadiene and $RuCl_2(PPh_3)_3$ proceeds in about two days to give the yellow-orange $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1),[4] which has proved to have an interesting chemistry quite distinct from that of the analogous dicarbonyl. This reaction has afforded related compounds containing other tertiary phosphines, and methylcyclopentadiene reacts similarly. With complexes of the type $[Ru_2Cl_3(ER_3)_6]Cl$ (ER_3 = $PMePh_2$, $AsPh_3$), addition of amine or zinc improved the yields. A second route to the PPh_3 derivative is from $RuCl_2(PPh_3)_3$ and thallium(I) cyclopentadienide, but this becomes tedious when large quantities of the chloride are required.[5] Some unpredictability was also found when scaling up the original reaction with cyclopentadiene, probably arising out of the tendency for $RuCl_2(PPh_3)_3$ to form the unreactive dimeric $[RuCl_2(PPh_3)_2]_2$ on standing in benzene solution. The synthetic method of choice is a simple three-component reaction between ruthenium trichloride, cyclopentadiene and triphenylphosphine in refluxing ethanol, from which high yields may be obtained after an hour or so.[6] Most other tertiary phosphine and phosphite derivatives can be obtained from (1) by exchange reactions,[7] the tendency for loss or exchange of one of the PPh_3 ligands being recognised in early studies[5] of the chemistry of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (Scheme 1).

Stepwise displacement of PPh_3 by PMe_3 occurs, with formation of $RuCl(PMe_3)(PPh_3)(\eta-C_5H_5)$ (at 80-100°) and $RuCl(PMe_3)_2(\eta-C_5H_5)$ (at 110°).[8,9]



Scheme 1 Reagents: (i) C_5H_6/PPh_3, EtOH; (ii) NaOMe/MeOH; (iii) LiR; (iv) NaI or KCN (X = I, CN); (v) L [MeOH, RCN, CNR, CO, PR_3, $P(OR)_3$, etc.]/NH_4PF_6; (vi) $SnCl_2$; (vii) L[CO, CNR, PR_3, $P(OR)_3$, etc.]; (viii) HC_2R; (ix) base (H^-, OMe^-); (x) H^+; (xi) MeOH.

Similarly, $RuCl(PMePh_2)(PPh_3)(\eta-C_5H_5)$ was detected spectroscopically in products from the reaction between (1) and $PMePh_2$.[5] Complete exchange of PPh_3 for bidentate dppm or dppe occurs in refluxing benzene[7] or toluene,[8] while the phosphites $P(OR)_3$ (R = Me or Ph) require short heating in decalin to effect complete exchange.[10] Even so, some dehydrochlorination of the $P(OPh)_3$ complex occurs to give the cyclometallated complex (Section 1.2.3.1). 2-Vinylphenyldiphenylphosphine readily displaces two PPh_3 ligands from (1) to give $\overline{RuCl(\eta^2-CH_2=CHC_6H_4PPh_2})-(\eta-C_5H_5)$.[11] The $AsPh_3$ complex has been made from $RuCl_3(AsPh_3)_2(MeOH)$ and cyclopentadiene in the presence of zinc.[5]



E = P or As

Reaction with CO, or with $Fe_2(CO)_9$, readily affords $RuCl(CO)(PPh_3)(\eta-C_5H_5)$, accompanied by $Fe(CO)_4(PPh_3)$ in the latter reaction.[5] Treatment of $RuCl(dppm)(\eta-C_5H_5)$ with CO gives a monocarbonyl, which readily loses CO; it probably contains a monodentate dppm ligand. Isonitriles also displace PPh_3 to give $RuCl(CNR)(PPh_3)(\eta-C_5H_5)$ (R = Bu^t, Cy, $CH_2SO_2C_6H_4Me$-4 or 4-$MeOC_6H_4$).[12] A reaction with excess Bu^tNC at higher temperatures (180°/12 h) gave $RuCl(CNBu^t)_2(\eta-C_5H_5)$.

The osmium complex $OsBr(PPh_3)_2(\eta-C_5H_5)$ can be obtained either from $OsBr_2(PPh_3)_3$ and cyclopentadiene,[5] or from H_2OsBr_6, PPh_3 and cyclopentadiene.[6] Generally similar reactions have been found for this complex where they have been studied, but with the usual reduced reactivity of the third-row element, compared with its second-row congener.[7,13] Thus, both $OsBr(PMe_3)(PPh_3)(\eta-C_5H_5)$ and $OsBr(PMe_3)_2(\eta-C_5H_5)$ have been obtained;[9] with $P(OMe)_3$ or $P(OPh)_3$, short reaction times gave $OsBr(PPh_3)[P(OR)_3](\eta-C_5H_5)$ (R = Me or Ph), while extended heating with excess phosphite was required to give the disubstituted products $OsBr[P(OR)_3]_2(\eta-C_5H_5)$. The bidentate bis-tertiary phosphines dppm and dppe gave the complexes $OsBr(L)(\eta-C_5H_5)$ (L = dppm or dppe) directly.

The halides $RuX(PPh_3)_2(\eta-C_5H_5)$ (X = F, Cl, Br or I) are pale yellow to dark orange in colour, stable in air, and monomeric in solvents such as benzene. The iodide is the major product from reactions between the chloride and MeMgI.[5] Ammonium fluoride reacts with the chloride in the presence of sodium bicarbonate to give $RuF(PPh_3)_2(\eta-C_5H_5)$ as an unstable yellow compound.[10] Preparation of the bromide from $RuH(PPh_3)_2(\eta-C_5H_5)$ and HBr is reported in this thesis (Chapter 5).

Structural studies[14] of $RuCl(L)_2(\eta-C_5H_5)$ (L = PMe_3 and PPh_3) show that the introduction of the bulky PPh_3 ligand (cone angle ∿ 145°) leads to marked steric hindrance, distortion of the tertiary phosphine ligand, and a longer Ru-P vector [2·335(1)Å] compared with the PMe_3 analogue [cone angle 118°, Ru-P, 2·277(6)Å]. The relatively easy displacement of chloride by neutral or anionic reagents is reflected in the long Ru-Cl distance [2·453(2)Å] found in both compounds.

Although both $RuCl(CO)_2(\eta-C_5H_5)$ and $RuCl(PPh_3)_2(\eta-C_5H_5)$ are non-electrolytes in acetone, the phosphine derivative shows ionic behaviour in methanol:

$$RuCl(PPh_3)_2(\eta\text{-}C_5H_5) + MeOH \rightleftarrows [Ru(PPh_3)_2(MeOH)(\eta\text{-}C_5H_5)]^+ + Cl^-$$

The solvento cation can be isolated in low yield by addition of large anions such as tetraphenylborate.[15] The phosphine complex exhibits a tendency to coordinate other donor ligands to give the cationic complexes $[Ru(L)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (see below), and also to lose one or both of the phosphine ligands in reactions affording neutral compounds. The properties and reactions of the two complexes have been compared in detail.[15] Thus, solvento cations are formed with only the more polar solvents and $RuCl(CO)_2(\eta\text{-}C_5H_5)$, and displacement of CO by another ligand is relatively difficult. On the other hand, displacement of PPh_3 from $RuCl(PPh_3)_2$-$(\eta\text{-}C_5H_5)$ occurs readily in non-polar solvents, while the chlorine is readily ionised in polar solvents, being replaced by either solvent or other donor ligands if present. With the more basic ligands, such as PMe_3, chloride is unable to substitute the third PMe_3 ligand in $[Ru(PMe_3)_3(\eta\text{-}C_5H_5)]^+$, which are obtained as stable chloride salts.[14]

1.2.2 Reactions at the Metal-halogen Bond

Sodium borohydride reacts with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ to give $Ru(H_2BH_2)(PPh_3)_2(\eta\text{-}C_5H_5)$, which is thought to contain an $Ru(\mu\text{-}H)_2B$ bridge;[5] the related complex $Ru(B_3H_8)(PPh_3)_2(\eta\text{-}C_5H_5)$ is also known.

Pseudohalide complexes $RuX(PR_3)_2(\eta\text{-}C_5H_5)$ (R = Me, X = Br, I, or SCN;[8] R = Ph, X = CN[15]) are formed by metathetical reactions; the cyanide is also formed readily by decomposition of the cyanoborohydride or cyanotriphenylborate. The former is obtained from the chloride, or better, $[Ru(Me_2CO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, and $NaBH_3CN$; an intermediate $Ru(NCBH_3)(PPh_3)_2(\eta\text{-}C_5H_5)$ can be detected by IR spectroscopy.[15] Protonation of the cyanide affords the hydrogen isocyanide complex $[Ru(CNH)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$,[16] while addition of BPh_3 gives $Ru(CNBPh_3)$-$(PPh_3)_2(\eta\text{-}C_5H_5)$.[15]

The chlorides undergo conventional 'insertion' reactions with $SnCl_2$ to give $Ru(SnCl_3)(PR_3)_2(\eta-C_5H_5)$ (R = Me, Ph); although related reactions have not been described, it is likely that similar derivatives can be obtained with other Group IVB compounds containing the divalent metals.[5,8]

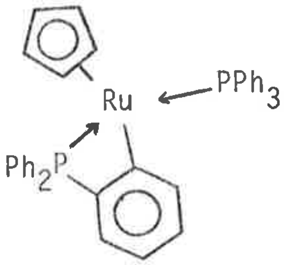
Alkyls are best prepared from the appropriate organolithium derivative and $RuCl(PPh_3)_2(\eta-C_5H_5)$;[5] the benzyl was obtained using $PhCH_2MgBr$.[17] Extrusion of triphenylboron from some tetraphenylborate salts affords $RuPh(PPh_3)_2(\eta-C_5H_5)$;[15] the pentafluorophenyl complex has been prepared from LiC_6F_5 and $RuCl(PPh_3)_2(\eta-C_5H_5)$.[5]

1.2.3 Reactions of $[RuR(PPh_3)_2(\eta-C_5H_5)]$ *(R = H, alkyl)*

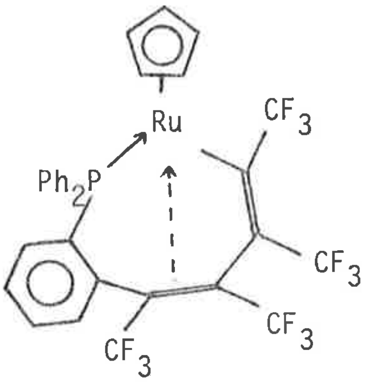
The reactions of hydride and alkyl complexes containing the $Ru(PPh_3)_2(\eta-C_5H_5)$ group have been studied in some detail, and will be described under the headings cyclometallation and reactions with activated olefins and alkynes.

1.2.3.1 Cyclometallation reactions Although the hydride is stable towards the elimination of dihydrogen on heating, the alkyls readily lose alkane with concomitant intramolecular cyclometallation. Thus brief heating of $RuR(PPh_3)_2(\eta-C_5H_5)$ (R = Me or CH_2Ph) in refluxing decalin affords good yields of the cyclometallated complex (2), formed by elimination of methane or toluene, respectively.[10,18] The reaction of hexafluorobut-2-yne with (2) afforded the bis-insertion product (3), the structure of which is analogous to that of $\overline{Rh(CPh{=}CPhCPh{=}CPhC_6H_4PPh_2)}$-$(PPh_3)$, obtained from $\overline{Rh(C_6H_4PPh_2)}(PPh_3)_2$ and C_2Ph_2.[19,20]

Ligand exchange between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and $P(OPh)_3$ in refluxing decalin afforded a mixture of $RuCl[P(OPh)_3]_2(\eta-C_5H_5)$ (4) and $\overline{Ru[C_6H_4OP(OPh)_2]}[P(OPh)_3](\eta-C_5H_5)$ (4a), the latter also being obtained from (2) and $NEtCy_2$, by elimination of HCl.[10] The cyclometallated derivative contains the relatively unreactive five-membered $\overline{\text{RuCCOP}}$ ring and does not react with $C_2(CF_3)_2$ (100°, 1 week).

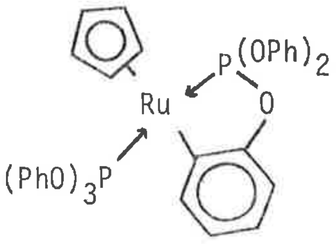


(2)

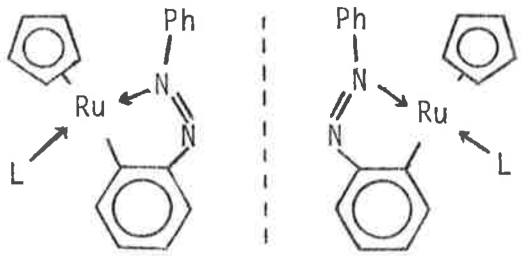


(3)

Dark green chelating 2-(phenylazo)phenyl complexes $\overline{\text{Ru}(C_6H_4N{=}N}\text{Ph})$-(L)($\eta$-$C_5H_5$) (4b, L = CO or PPh_3) have been obtained from reactions between $RuMeL_2(\eta\text{-}C_5H_5)$ and azobenzene,[10,21] or from $[\overline{\text{Ru}(C_6H_4N{=}N}\text{Ph})(CO)_2Cl]_2$ and NaC_5H_5.[22] The carbonyl group is readily displaced by PPh_3.

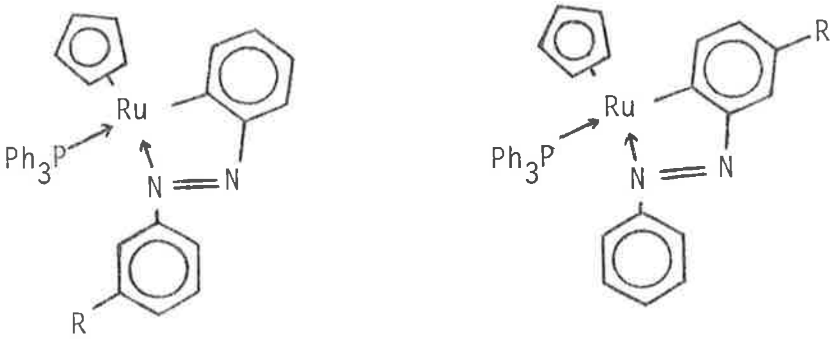


(4a)



(4b) L = CO or PPh_3

Inseparable mixtures of isomeric products (5A and B) were obtained when *meta*-substituted azobenzenes were used in reactions with



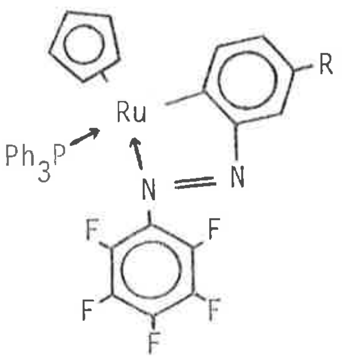
(A) (B)

(5) R = H,Me,OMe,CO_2Et,CF_3

$RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$.[10] Similar products were obtained with $3,5\text{-}(MeO_2C)_2C_6H_3N{:}NPh$, but in this case the isomeric complexes could be separated by chromatography; the major product (43%) was metallated in the Ph group, while the isomer corresponding to (5B) was formed in only 7% yield.

A series of dark green products was obtained from the fluorinated azobenzenes $C_6F_5N{=}NC_6H_4R$, corresponding to the two compounds (6) and (7), and a third containing a phenyl-linked Ph_3P-azobenzene ligand (8).[10] Complex (7) is unusual in being metallated in the fluorinated ring, and was the only product isolated from the reaction with $C_6F_5N{=}NC_6H_3(CO_2Me)_2$.

A single product was also obtained from $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$ and decafluoroazobenzene, the dark green (9). This reaction was one of the first examples of cyclometallation involving elimination of a halide



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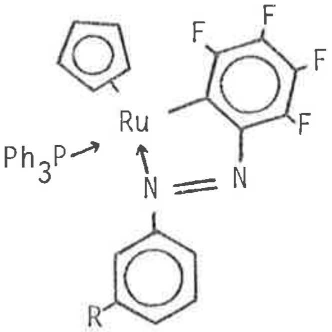
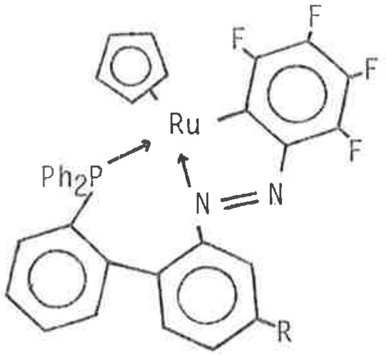


(7)

R = H,Me,CF_3



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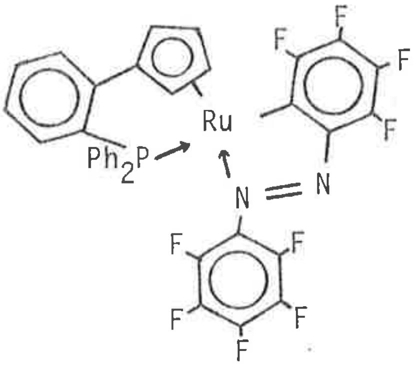


(9)

from the arene ring.[10,23] The unusual structural features in this complex include the metallated polyfluorophenyl ring, and the $Ph_2PC_6H_4C_5H_4$ ligand, presumably formed by phenyl migration to the ring.[24] The azo ligand is non-planar, and reflects the non-bonding interactions that are occurring in the ruthenium coordination sphere.

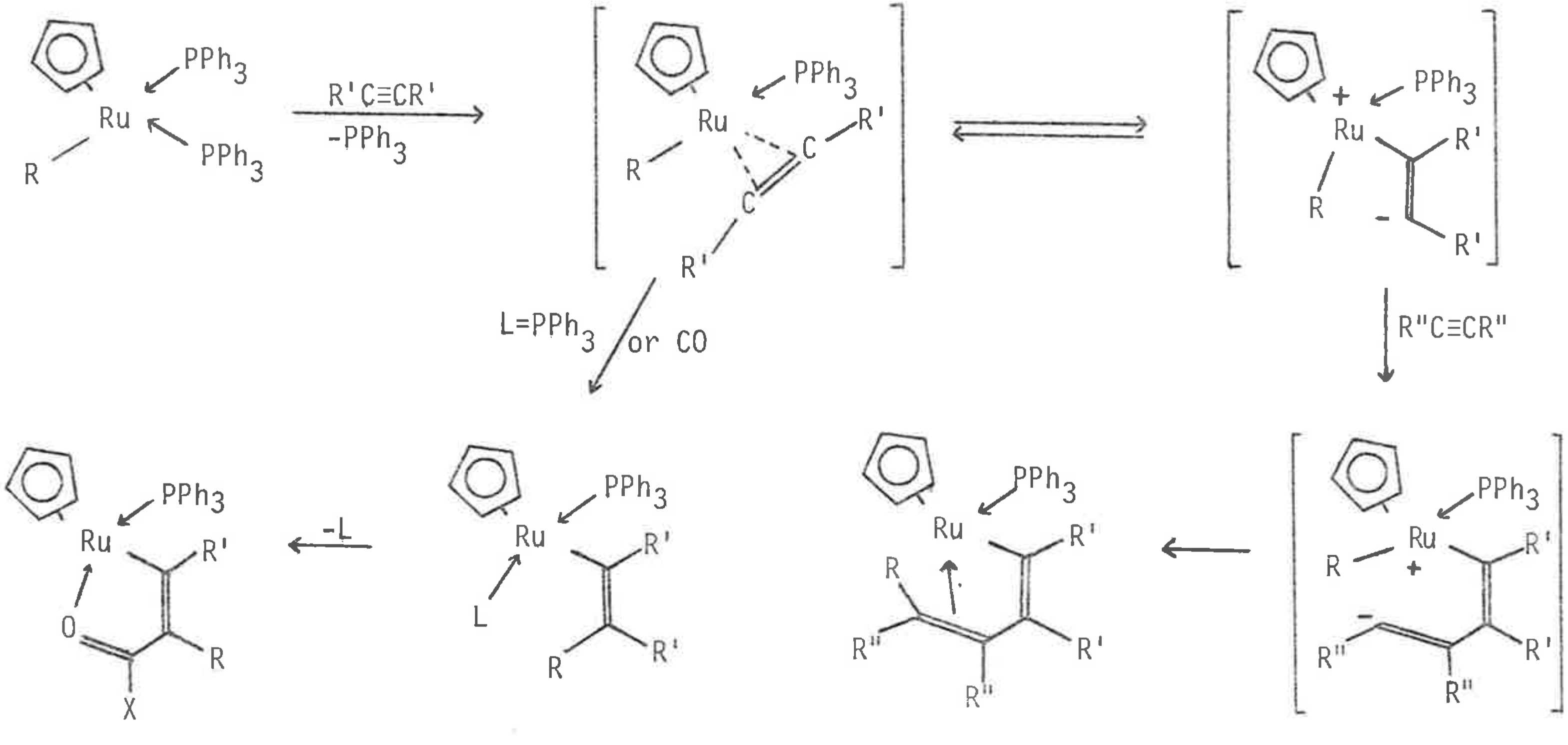
These reactions illustrate a number of possibilities for the formation of metallated complexes.[25] The methyl complex readily metallates phenyl groups by elimination of methane, and the elimination of a variety of alkanes has been studied with $MnR(CO)_5$.[26] The exact mode of elimination of fluorine from the polyfluorophenyl derivatives has not been determined; a possibility is as MeF, the electron-rich $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety readily attacking the C_6F_5 rings by a nucleophilic route. A suggested route to the $C_5H_4C_6H_4$ ligands is mentioned later.

1.2.3.2 Reactions with electron-deficient olefins or alkynes These reactions have been rationalised in terms of dipolar intermediates formed by attack of the electron-rich $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety on the alkynes, which then either undergo an intramolecular reaction, affording vinyl complexes, or further intermolecular attack on a second molecule of alkyne, to give butadienyl derivatives. In some cases, the intermediate oxidative addition of terminal alkynes to give ruthenium(IV) complexes, which undergo reductive coupling of the organic moieties, has been suggested. These ideas are summarised in Schemes 2 - 6.[17,22,27-30]

It is clear that while the products of these reactions may be rationalised by Schemes such as those illustrated, there is not yet sufficient information to predict the nature of such products.

1.2.4 Complexes Containing η^3-allylic Systems

Reactions between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and alkenyl-magnesium or -zinc reagents in toluene/diethyl ether have given 65-80% yields of $Ru(CH_2CR^1{=}CR^2R^3)(PPh_3)_2(\eta\text{-}C_5H_5)$, which on heating are converted to the η^3-allyl complexes $Ru(PPh_3)(\eta^3\text{-}CH_2CR^1CR^2R^3)(\eta\text{-}C_5H_5)$.[31] 2-Methylallyl complexes containing PMe_3, PBu_3 or PCy_3 were also obtained. The *transoid* form of the η^3-allylic complexes is thermodynamically favoured, but after short heating, the *cisoid* form is obtained as the kinetic product. The η^3-$CH_2CHCHMe$ complex was also obtained by heating $Ru(CH_2CH_2CH{:}CH_2)$-$(PPh_3)_2(\eta\text{-}C_5H_5)$. The thermodynamically stable form of the

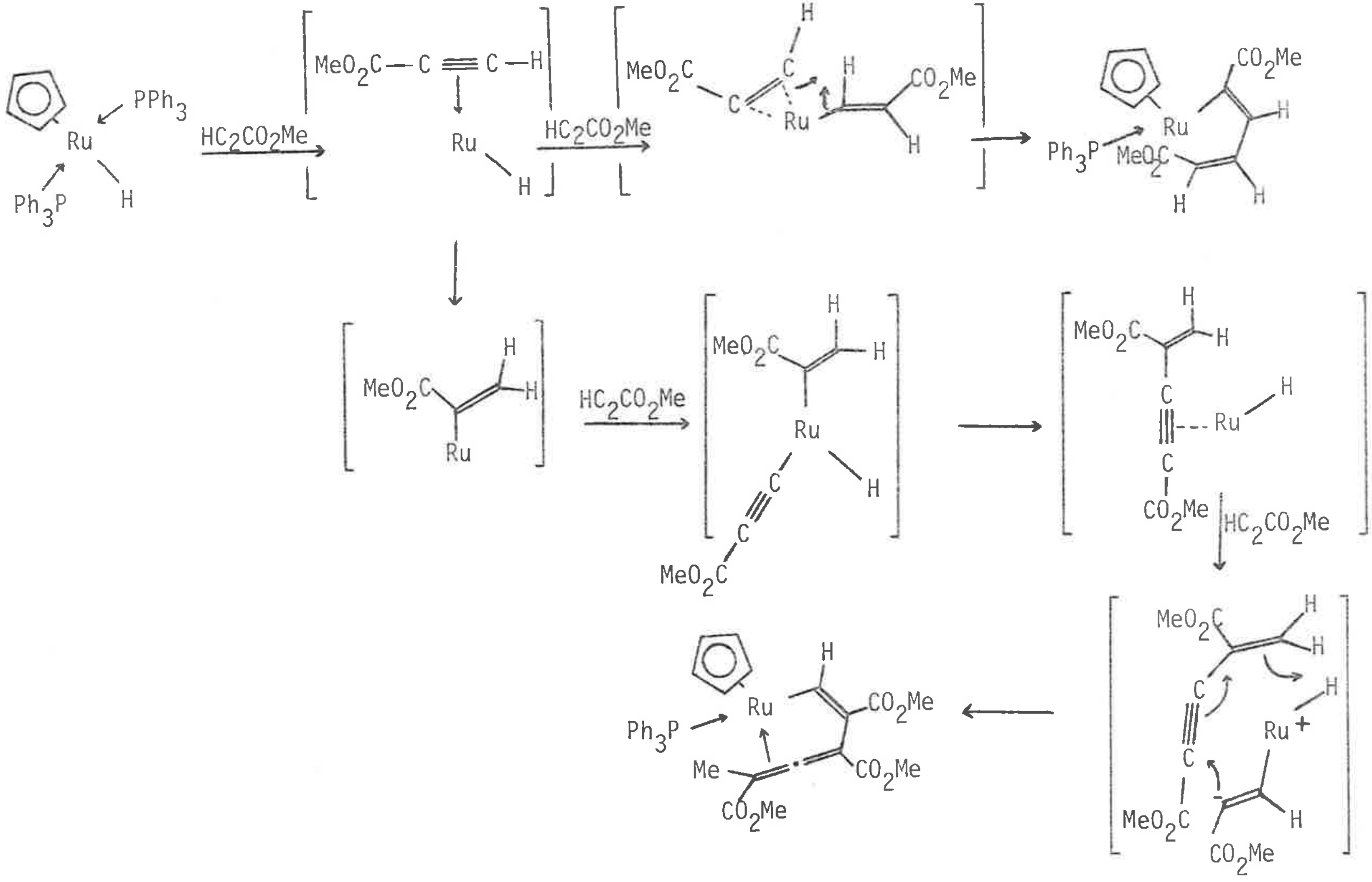


R	R'	X
H	CO_2Me	OMe
Me	CO_2Me	OMe
CH_2Ph	CO_2Me	OMe
Me	Ph	Me

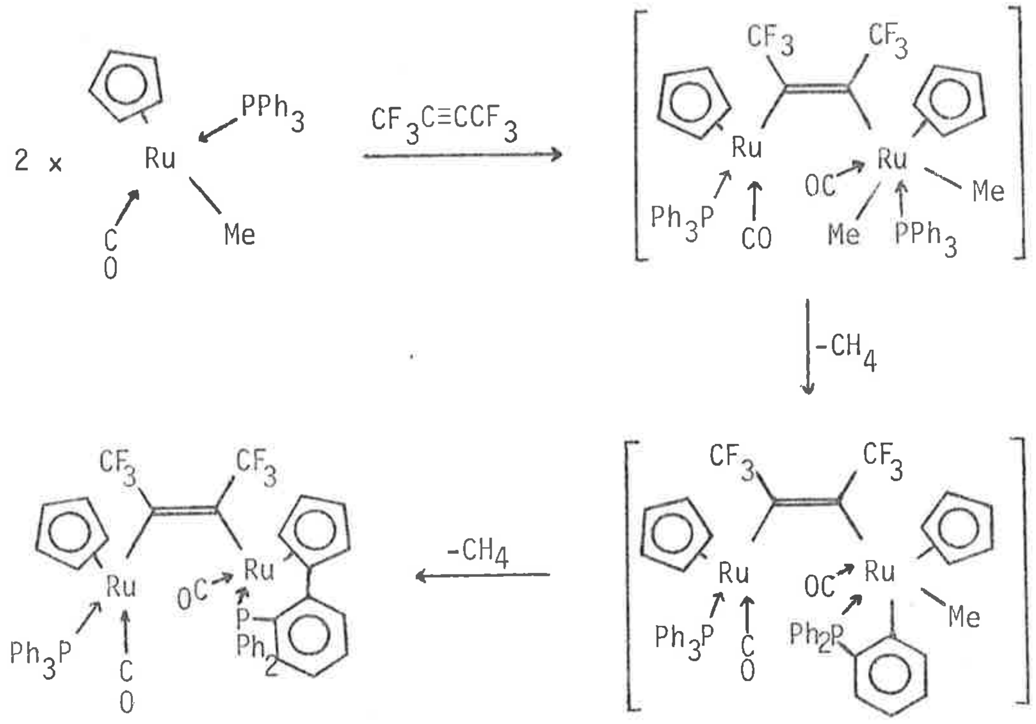
R	R'	L
H	CF_3	PPh_3
H	CO_2Me	PPh_3
H	CF_3	CO
H	CO_2Me	CO
Me	CF_3	CO
CH_2Ph	CO_2Me	PPh_3

R	R'	R"
H	CF_3	CF_3
H	CO_2Me	CF_3
Me	CF_3	CF_3
Me	CO_2Me	CO_2Me

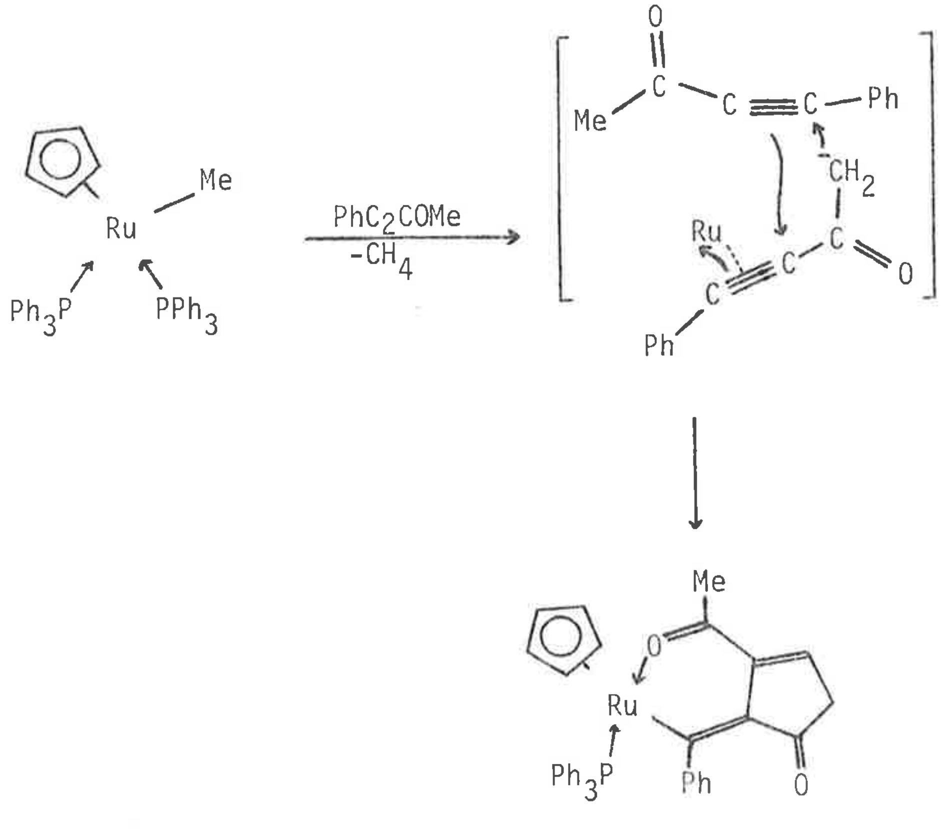
Scheme 2



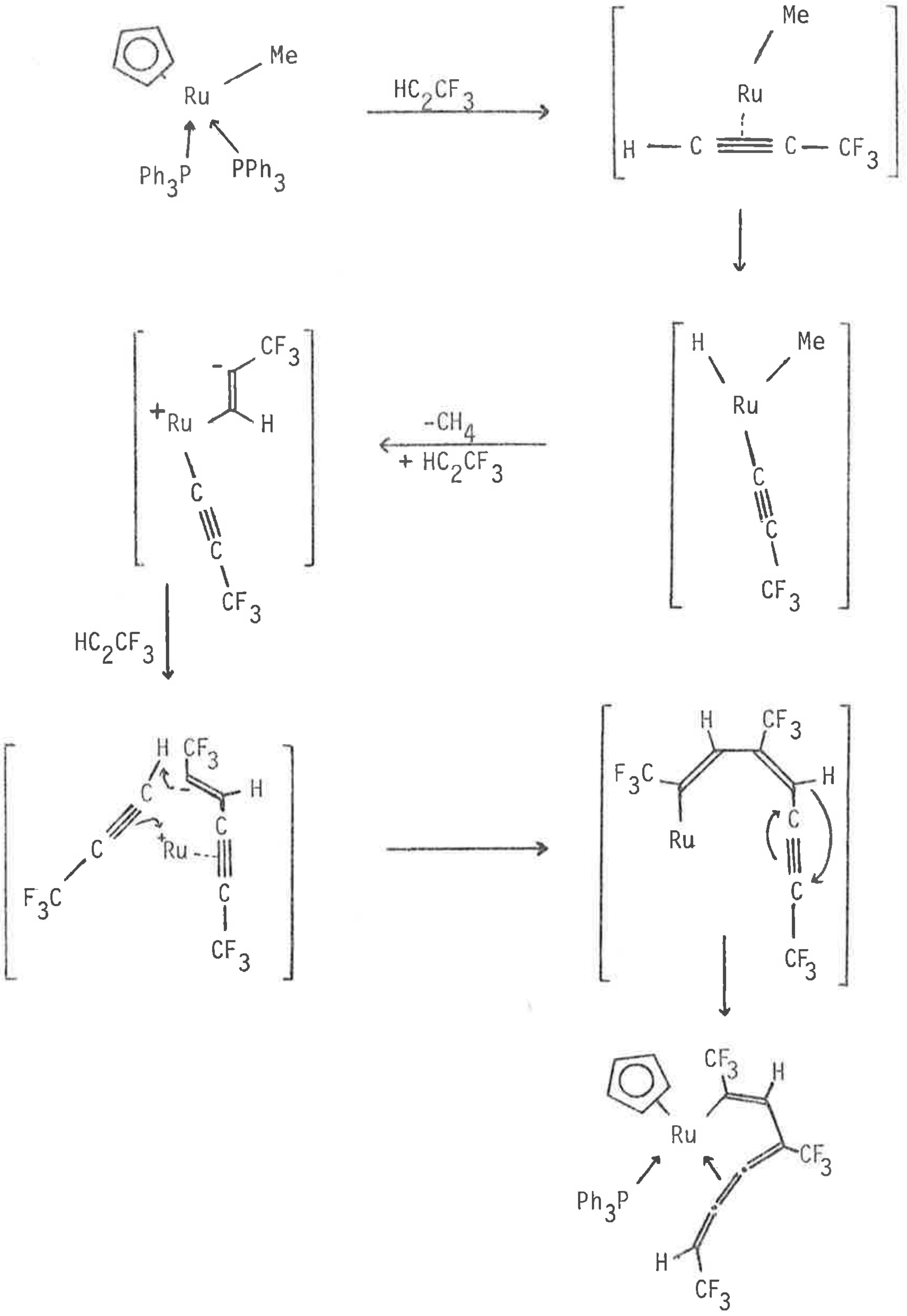
Scheme 3 C_5H_5 and PPh_3 ligands omitted from proposed intermediates



Scheme 4

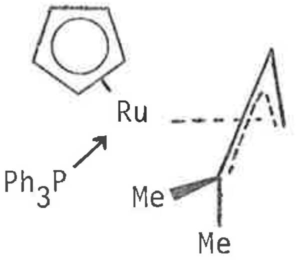


Scheme 5 C_5H_5 and PPh_3 ligands omitted from proposed intermediate



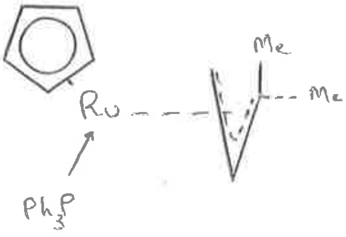
Scheme 6 C_5H_5 and PPh_3 ligands omitted from proposed intermediates.

η^3-crotyl derivative is (10), although two other isomers were detected spectroscopically.



(10)

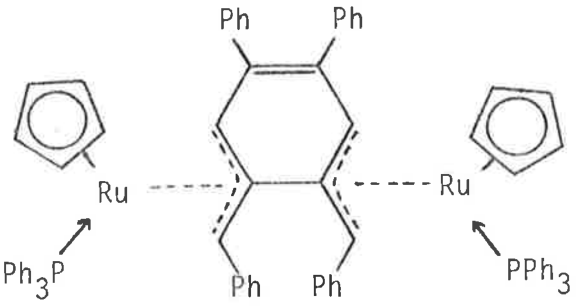
transoid



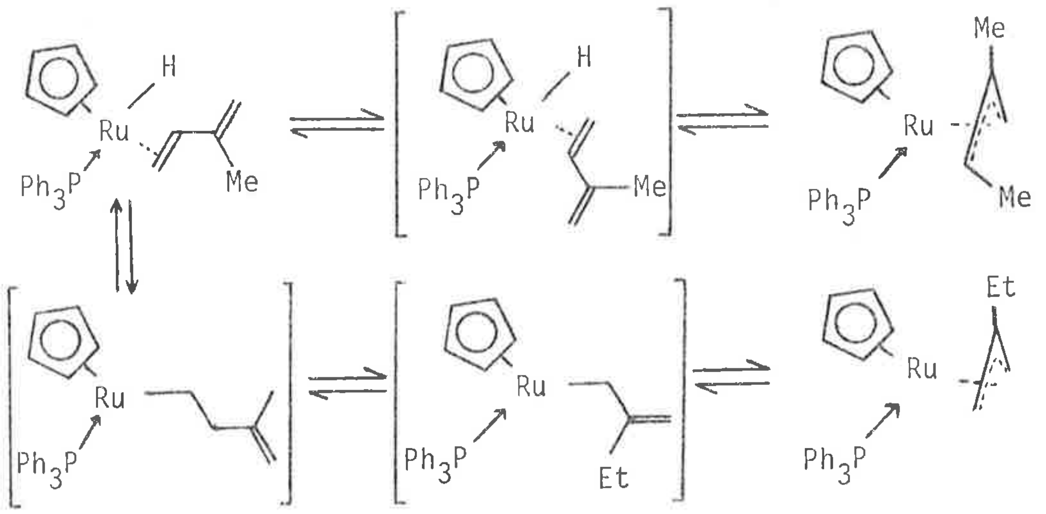
cisoid

Conversion of the η^1-CH_2CHCMe_2 complex to the η^3-complex is accompanied by formation of both η^3-$CH_2CMeCHMe$ and η^3-CH_2CEtCH_2 derivatives, by isomerisation *via* an η^2-pentadiene-hydrido intermediate (Scheme 7).

Another product containing the allylic group is the dark blue binuclear complex (11), obtained from $RuCl(PPh_3)_2(\eta$-$C_5H_5)$ and AgC_2Ph.[32] The formation of the allylic ligand in (11) results from oligomerisation of *four* phenylacetylide units.



(11)



Scheme 7

1.2.5 *Cationic Complexes*

Nucleophilic substitution of chloride in $RuCl(PR_3)_2(\eta\text{-}C_5H_5)$ by neutral donor molecules readily occurs to give cationic complexes, $[Ru(L)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$.[15] The methanol cation has been mentioned above, and the acetone derivative is also known. A solution of the chloride in thf has a deeper colour than the solid, but no cation of the type $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ has been isolated. These cations are best prepared from reactions between the chloride and $AgSbF_6$ carried out in the solvent.

Salts of the acetonitrile cation $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ can be obtained readily from solutions of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in acetonitrile and, for example, $NaBPh_4$,NH_4PF_6, or NH_4BF_4.[33,34]

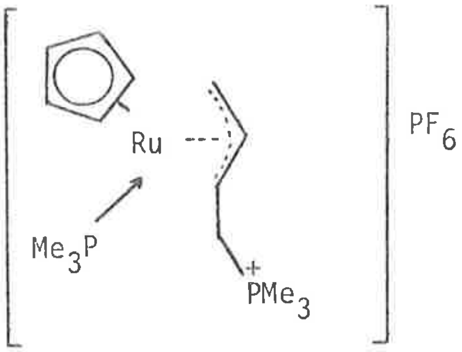
Small phosphines and phosphites displace chloride to give $[Ru(PR_3)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, although it has not yet been possible to coordinate three PPh_3 groups around the metal atom.[7] These complexes are also formed from the acetonitrile cation. Chelating tertiary phosphines react stepwise, as indicated by n.m.r. spectroscopy, to give complexes such as $[Ru(PPh_3)(dppe)(\eta\text{-}C_5H_5)]^+$, $[Ru(triphos)(\eta\text{-}C_5H_5)]^+$

[triphos = $RC(CH_2PPh_2)_3$, R = Me or Et], and $\{Ru[P(OMe)_3]_3(\eta\text{-}C_5H_5)\}^+$. In these examples, displacement of both chloride and PPh_3 occurs. The osmium complex $[Os(PPh_3)(dppe)(\eta\text{-}C_5H_5)]^+$ is formed from $[Os(PPh_3)_2(dppe)(\eta\text{-}C_5H_5)]^+$, which probably contains monodentate dppe.

The reactivity of the chloride in these reactions can be ascribed to both steric and electronic effects. In particular, the size of the tertiary phosphine ligand (and others) as recognised by the 'cone-angle' is of obvious importance.[35] Thus, it is possible to place three small phosphites such as $P(OMe)_3$ (cone-angle 107°) around the central metal atom, but not three PPh_3 groups (cone angle 145°). It is possible to draw up empirical relationships involving total cone angle, etc., but these take no account of the possibility of 'interleaving' the various groups attached to phosphorus.

Cationic olefin complexes have been obtained from precursors which contain tertiary phosphines such as PMe_3[9] or dppe,[36] that is, smaller than PPh_3. Complexes $[Ru(un)(L)_2(\eta\text{-}C_5H_5)]^+$ [un = C_2H_4, C_3H_6, PhCH:CH_2, CH_2:$CHCO_2Me$, CH(CN):CH(CN); L = PMe_3 or ½dppe, but not all combinations] form white or pale yellow crystals; n.m.r. studies show the olefin in $[Ru(C_2H_4)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ is freely rotating. Analogous complexes containing other unsaturated ligands, such as allene, 2,3-dimethylallene, C_2Ph_2, $C_2(CO_2Me)_2$, PhC_2CO_2Et, and CS_2 have been obtained containing the $Ru(PMe_3)_2(\eta\text{-}C_5H_5)$ group.[9]

The reaction between butadiene and $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ is unusual in forming the phosphonium complex (12) via a formal insertion of one end of the diene into the Ru-P bond;[9] with $RuCl(dppe)(\eta\text{-}C_5H_5)$, the conventional $[Ru(\eta^2\text{-}CH_2{:}CHCH{:}CH_2)(dppe)(\eta\text{-}C_5H_5)]^+$ complex is obtained.[36]



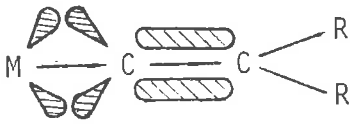
(12)

1.3 *TRANSITION METAL VINYLIDENE AND ALLENYLIDENE CHEMISTRY*

Metal complexes containing unsatured carbene ligands, $:C=CR_2$ and $:C=C=CR_2$, are termed *metal vinylidene* and *metal allenylidene* (*cumulenylidene*) complexes respectively.

Vinylidene ($:C=CH_2$) is an extremely reactive species, with a suspected life-time of 10^{-10} seconds.[37] Metal stabilisation of $C=CR_2$ has led to the isolation of the vinylidene ligand and to a study of its physical properties and reactions.

A dative bond is formed between the ligand and the metal involving a metal-carbon σ-bond, and a π-bond from the metal d orbitals to the π^* orbitals on the α carbon:



Some comparisons can be made between the carbonyl ligand and the unsaturated vinylidene moiety. Particular interest has focussed on the $M=C=C(CN)_2$ systems.[38]

The metal-carbon bond of the vinylidene group can be compared to a $Fe=O$ bond. Formation of iron porphyrin vinylidene complexes has allowed a better understanding of metal oxygen bonding in natural systems.

Cluster complexes containing the $C=CH_2$ ligand have been formed using ethylene and are important models for catalytic reactions. The $C=CH_2$ moiety, a valence tautomer of $HC\equiv CH$, has been detected in the interaction of ethylene and acetylene with various metal surfaces. The vinylidene → acetylene rearrangement has been studied theoretically.[39,46] These results suggest that $C=CH_2$ lies in a very shallow minimum on the C_2H_2 potential energy curve.

The vinylidene ligand has one of the highest π-acceptor capacities known, and phenylvinylidene is only exceeded by SO_2 and CS in electron withdrawing power:[40]

$PPh_3 < CPh_2 < PhC\equiv CPh < PF_3 < CO < AsF_3 < C=CHPh < CS < SO_2$

The extreme electron deficiency of the α-carbon is reflected in low field n.m.r. shifts (*c*. 350ppm) and short metal-carbon bond-lengths.

The vinylidene ligand is extremely versatile and is known to undergo a large range of reactions. Attack can occur at either the α- or the β-carbon, while addition to the olefinic bond or the metal-carbon bond is observed.

Since the first metal vinylidene complex was fully characterised in 1966,[41] a variety of such complexes have been reported in the literature. A brief review has appeared,[42] but recent advances in the isolation and reactions of vinylidene complexes make this up-dated and comprehensive survey desirable.

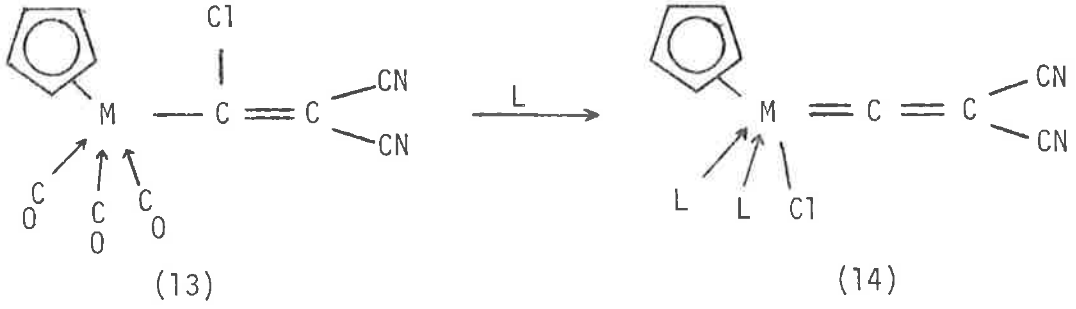
The following discussion has been broadly divided into the preparations of mononuclear, binuclear and cluster complexes, followed by a survey of the reactions of isolated and non-isolated vinylidene complexes. Each metal is treated separately within these sub-divisions. [Some physical data is summarised in Section 1.3.6] The abundance of mononuclear and binuclear complexes has necessitated further division according to preparative methods and reaction types.

1.3.1 *Formation of Mononuclear Vinylidene Complexes*

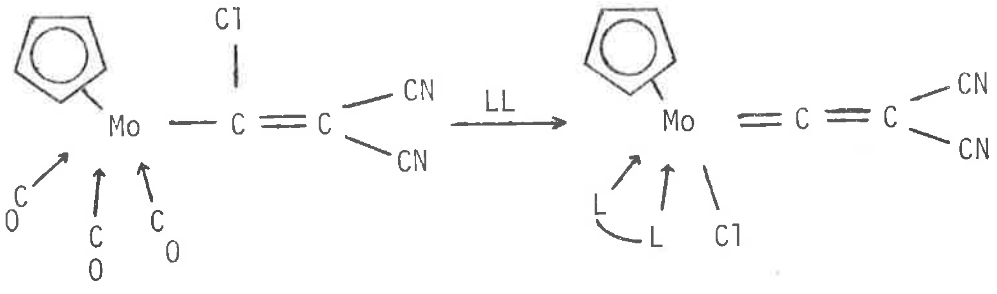
A variety of preparative methods have been used in the formation of vinylidene complexes. These are discussed according to the following preparative routes:

- 1.3 1.1 *By chloride elimination*
- 1.3.1.2 *From terminal acetylenes*
- 1.3.1.3 *From group IVB acetylenes*
- 1.3.1.4 *From metal acetylide complexes*
- 1.3.1.5 *From metal carbyne complexes*
- 1.3.1.6 *From iron acyl complexes*
- 1.3.1.7 *From iron porphyrin complexes*

1.3.1.1 By chloride elimination Migration of chloride from an α-vinyl carbon to the metal leads to formation of vinylidene complexes. This process is best implemented by heating metal carbonyl chloro-vinyl complexes with Group VB ligands in a variety of solvents:[38,43]



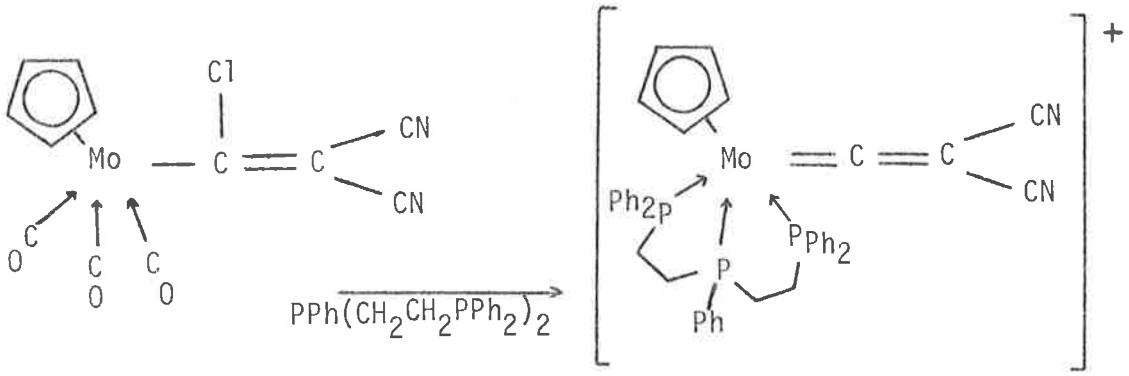
M = Mo or W; L = PPh_3, $AsPh_3$, $SbPh_3$,PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$ $P(OPh)_3$, or $PPh_2(CH_2CH_2PPh_2)$.



(15)

LL = $P(Ph)_2CH_2CH_2PPh_2$ or *cis*-$P(Ph)_2CH{=}CHPPh_2$.

The structure of $Mo[C{=}C(CN)_2](Cl)[P(OMe)_3]_2(\eta\text{-}C_5H_5)$ has been determined.[44,45] A reaction of (13, M = Mo) with $PPh(CH_2CH_2PPh_2)_2$ leads to a cationic complex (16):



(16)

1.3.1.2 From terminal acetylenes A theoretical study of the acetylene-vinylidene rearrangement has been made using the self-consistent electron pairs method.[46] For the non-substituted case the energy gained in isomerising $HC \equiv CH$ to $C = CH_2$ was calculated to be 40 kcal/mol.

Terminal acetylene complexes undergo a 1,2-hydride shift forming vinylidene complexes with a number of metal systems (Table 1).

Table 1 A summary of the products from the reaction:

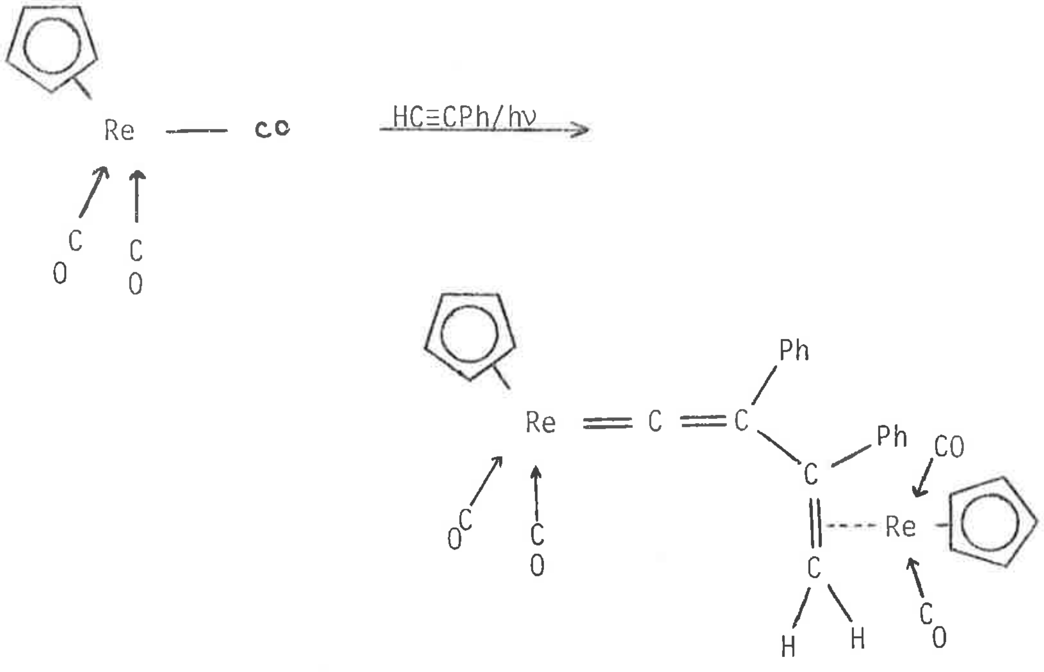
$$[M]X + HC \equiv CR \longrightarrow \{[M] = C = CHR\}^{n+}$$

X = solvent, CO or halide

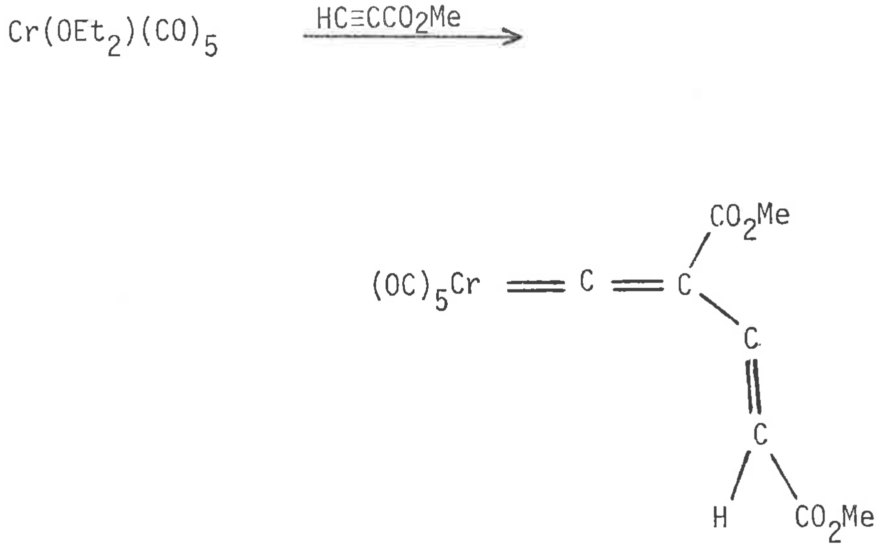
M	R	n	no.	ref.
$Mn(CO)_2(\eta\text{-}C_5H_5)$	Ph	0	17	40, 47-49
$Mn(CO)_2(\eta\text{-}C_5H_4Et)$	Ph	0	18	40
$Re(CO)_2(\eta\text{-}C_5H_5)$	Ph	0	19	50
FeCl(depe)	Ph	1	20	51
$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$	Ph,Me,Pr,	1	21	52
	CO_2Me, C_6H_4F-*p*	1		
	C_6F_5	1		
$Ru(PMe_3)_2(\eta\text{-}C_5H_5)$	H,Me,Ph	1	22	53, 54
$Ru(dppm)(\eta\text{-}C_5H_5)$	Ph	1	23	52
$Ru(dppe)(\eta\text{-}C_5H_5)$	Ph,Bu	1	24	52, 55
$Os(PPh_3)_2(\eta\text{-}C_5H_5)$	Ph	1	25	52

depe = *cis*-$H(PPh_2)C = CH(PPh_2)$.

In some instances a second acetylene unit is incorporated into the vinylidene product:



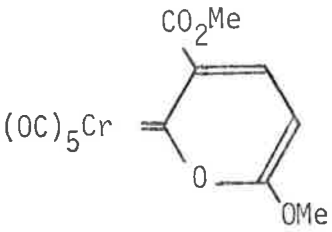
(26, ref. 50)



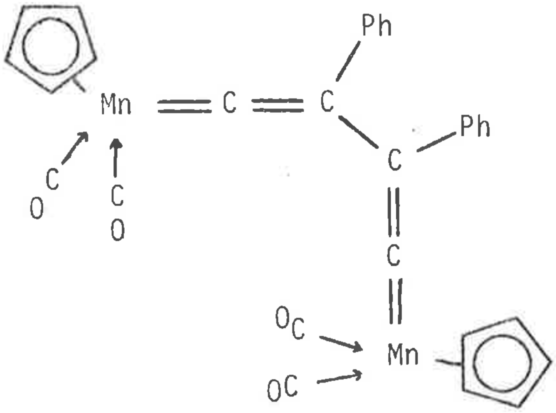
(27, ref. 56)

Compound (27) changes from red to violet in hexane, suggesting the presence of a tautomeric product (28).[56]

A structural study of (17)[48,57] and (26)[50] has been made. A reaction of $Mn(CO)_3(\eta\text{-}C_5H_5)$ or $Mn(CO)_2(thf)(\eta\text{-}C_5H_5)$ with $HC{\equiv}CPh$ yields $Mn_2(C_{16}H_{10})(CO)_4(\eta\text{-}C_5H_5)_2$,[1,9,10] suggesting structure (29) by analogy to (26).

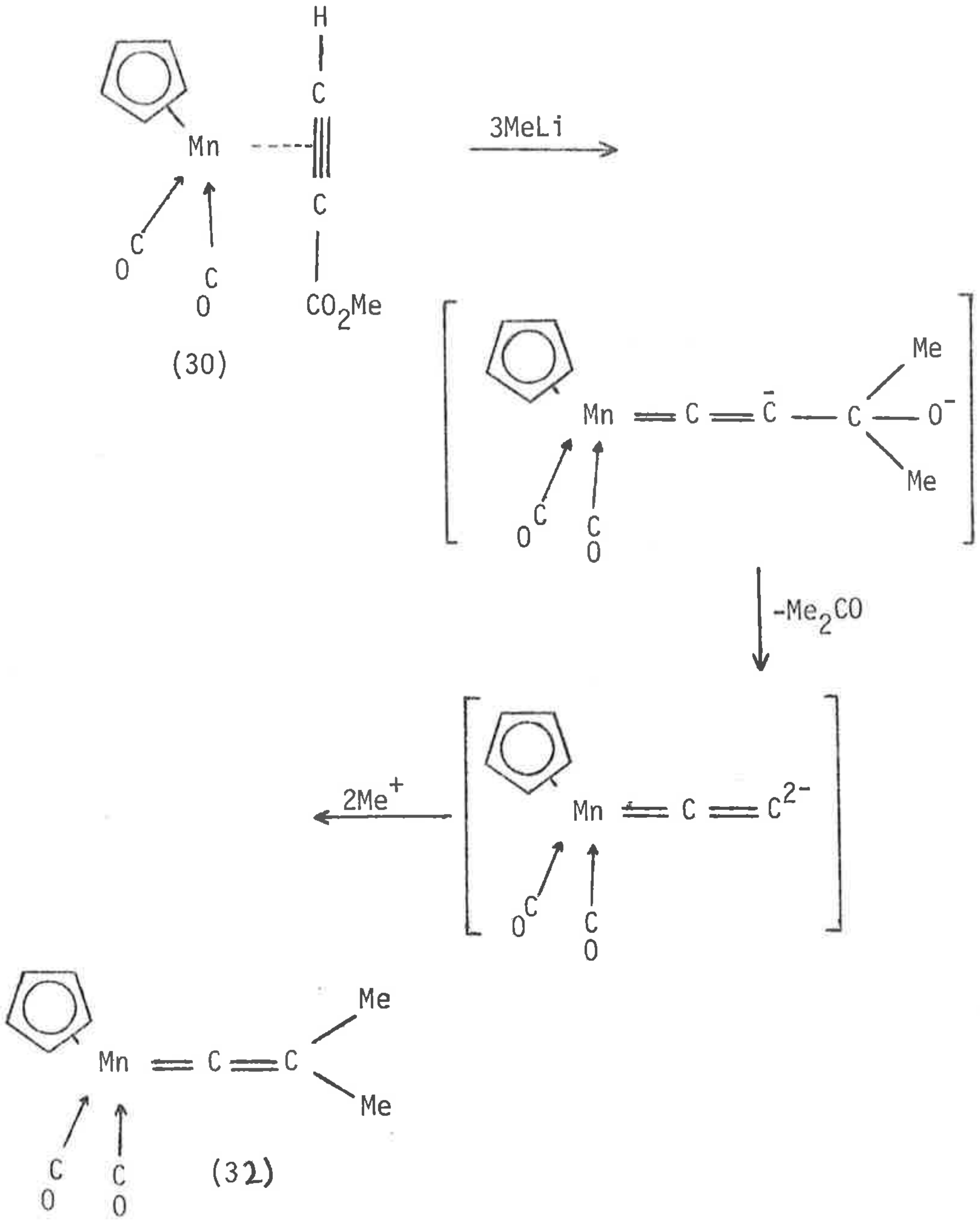


(28)



(29)

These reactions are thought to proceed *via* an η^2-acetylene intermediate, which has been isolated in $Mn(CO)_2(\eta\text{-}C_5H_5)$ reactions while $Re(\eta^2\text{-}HC{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ has been detected spetroscopically. A reaction of $Mn(\eta^2\text{-}HC{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ with aqueous ethanolic KOH gives (29), while rearrangement on alumina gives (17). Treatment of $Mn(\eta^2\text{-}HC{\equiv}CCO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ (30) with an equimolar amount of RLi (-60^0, R = Me, Bu^t, Ph) gave $Mn(C{=}CHCO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ (31).[58,59] A reaction with MeLi followed by $MeOSO_2F$ gave (32), implying the presence of dianionic vinylidene intermediates (Scheme 8).[60]



Scheme 8

1.3.1.3 From Group IVB acetylenes Reactions of some metal complexes with $PhC{\equiv}CEPh_3$ (E = Si, Ge, Sn) also yield vinylidene complexes. The proton required can be extracted from the solvent.

$$[M]X + PhC\equiv CEPh_3 \longrightarrow \{[M]C{=}CHPh\}^{n+}$$

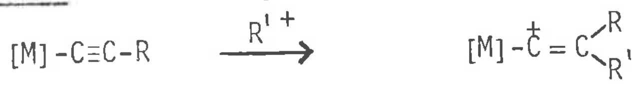
[M]	X	E	n	product (s)	ref.
$Mn(CO)_2(\eta-C_5H_5)$	thf	Si	0	(29)	40, 48
		Ge,Sn	0	(17),(29)	40, 48
$Ru(PMe_3)_2(\eta-C_5H_5)$	Cl	Si	1	(22)	54

The yield of (17) is inversely proportional to the stability of the intermediate π-complex (E = Si>Ge>>Sn).

1.3.1.4 From metal acetylide complexes While vinylidene complexes bearing a proton on the β-carbon can be formed from terminal acetylenes, dialkyl vinylidene complexes are not formed in this manner.

Protonation or alkylation of some metal acetylide complexes, however, leads to a variety of metal vinylidene products (Table 2).

Table 2 A summary of the products from the reaction:



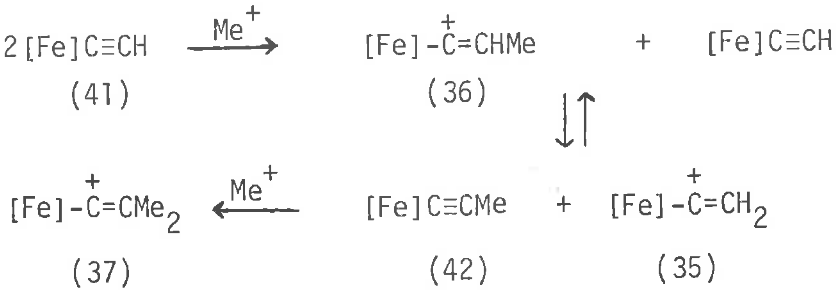
$$[M]-C\equiv C-R \xrightarrow{R'^{+}} [M]-\overset{+}{C}=C\begin{smallmatrix}R\\R'\end{smallmatrix}$$

[M]	R	R'	no.	ref.
$[Mn(CO)_2(\eta-C_5H_5)]^-$	CO_2Me	H, Me	33	61
$Fe(CO)(PPh_3)(\eta-C_5H_5)$	Ph	H	34	62
$Fe(dppe)(\eta-C_5H_5)$	H, Me	H	35,36	63
$Fe(dppe)(\eta-C_5H_5)$	Me	Me	37	63
$Ru(PPh_3)_2(\eta-C_5H_5)$	Ph,Me,Pr,CO_2Me, C_6H_4F-p,C_6F_5	H	38	52
$Ru(PPh_3)_2(\eta-C_5H_5)$	Ph,Me,Pr,C_6F_5	Me	38	52
$Ru(PPh_3)_2(\eta-C_5H_5)$	Ph	Et	39	52
$Ru(PMe_3)_2(\eta-C_5H_5)$	Ph	Me	40	53

Table 2 (continued)

[M]	R	R'	no.	ref.
$Ru(dppm)(\eta-C_5H_5)$	Ph	H	23	52
$Ru(dppe)(\eta-C_5H_5)$	Ph	H	24	52
$Os(PPh_3)_2(\eta-C_5H_5)$	Ph	H	25	52

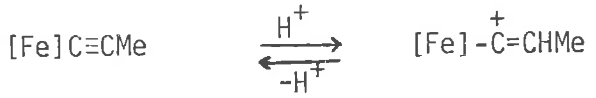
Methylation of $Fe(C_2H)(dppe)(\eta-C_5H_5)$ yields a mixture of (35) and (37) along with a small amount of (36), implying the ethynyl complex (41) to be more basic than the propynyl complex (42).[64]



$$\begin{tikzcd} \underset{(41)}{2[Fe]C\equiv CH} \arrow[r, "Me^+"] & \underset{(36)}{[Fe]-\overset{+}{C}=CHMe} + [Fe]C\equiv CH \arrow[d, shift left] \\ \underset{(37)}{[Fe]-\overset{+}{C}=CMe_2} & \underset{(42)}{[Fe]C\equiv CMe} + \underset{(35)}{[Fe]-\overset{+}{C}=CH_2} \arrow[u, shift left] \arrow[l, "Me^+"'] \end{tikzcd}$$

$[Fe] = Fe(dppe)(\eta-C_5H_5)$

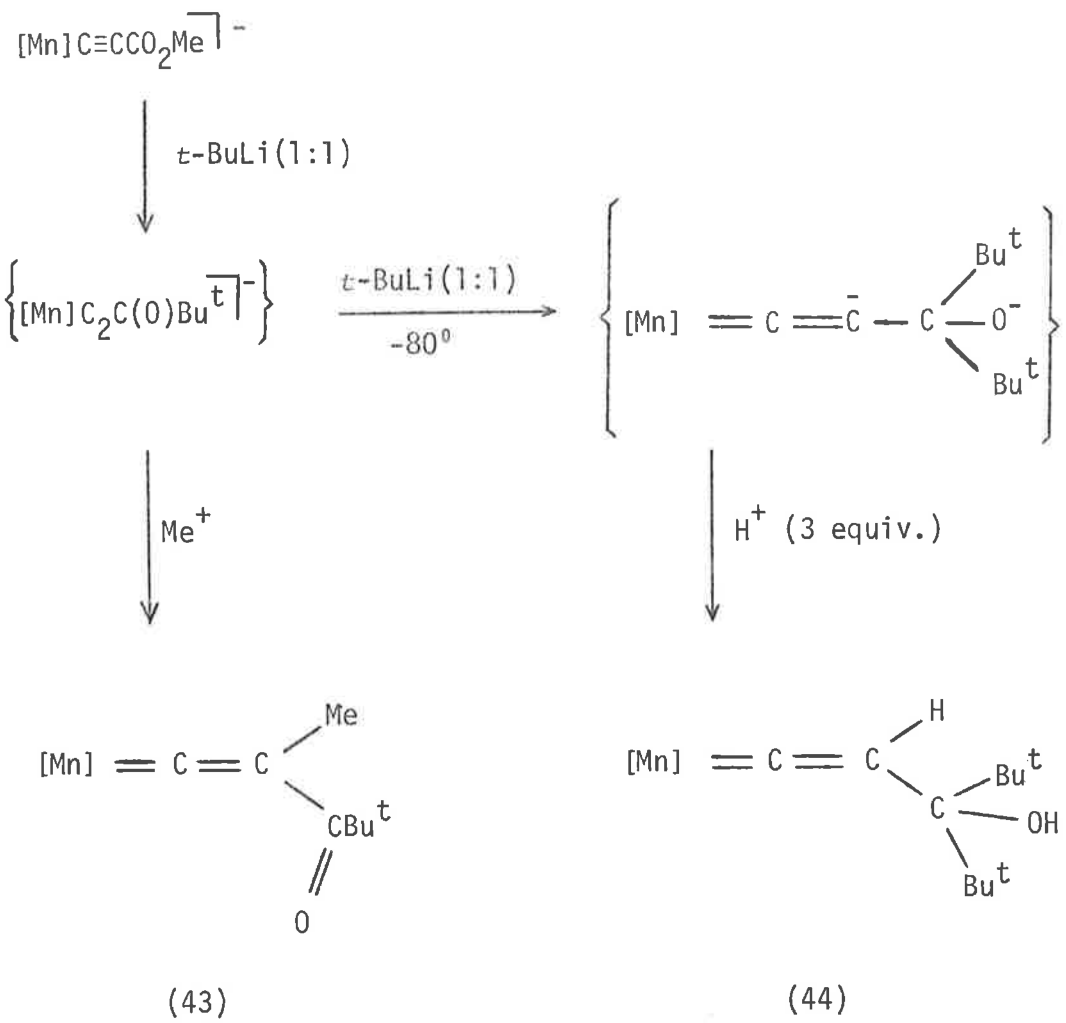
The pKa in the equilibrium



$$[Fe]C\equiv CMe \underset{-H^+}{\overset{H^+}{\rightleftarrows}} [Fe]-\overset{+}{C}=CHMe$$

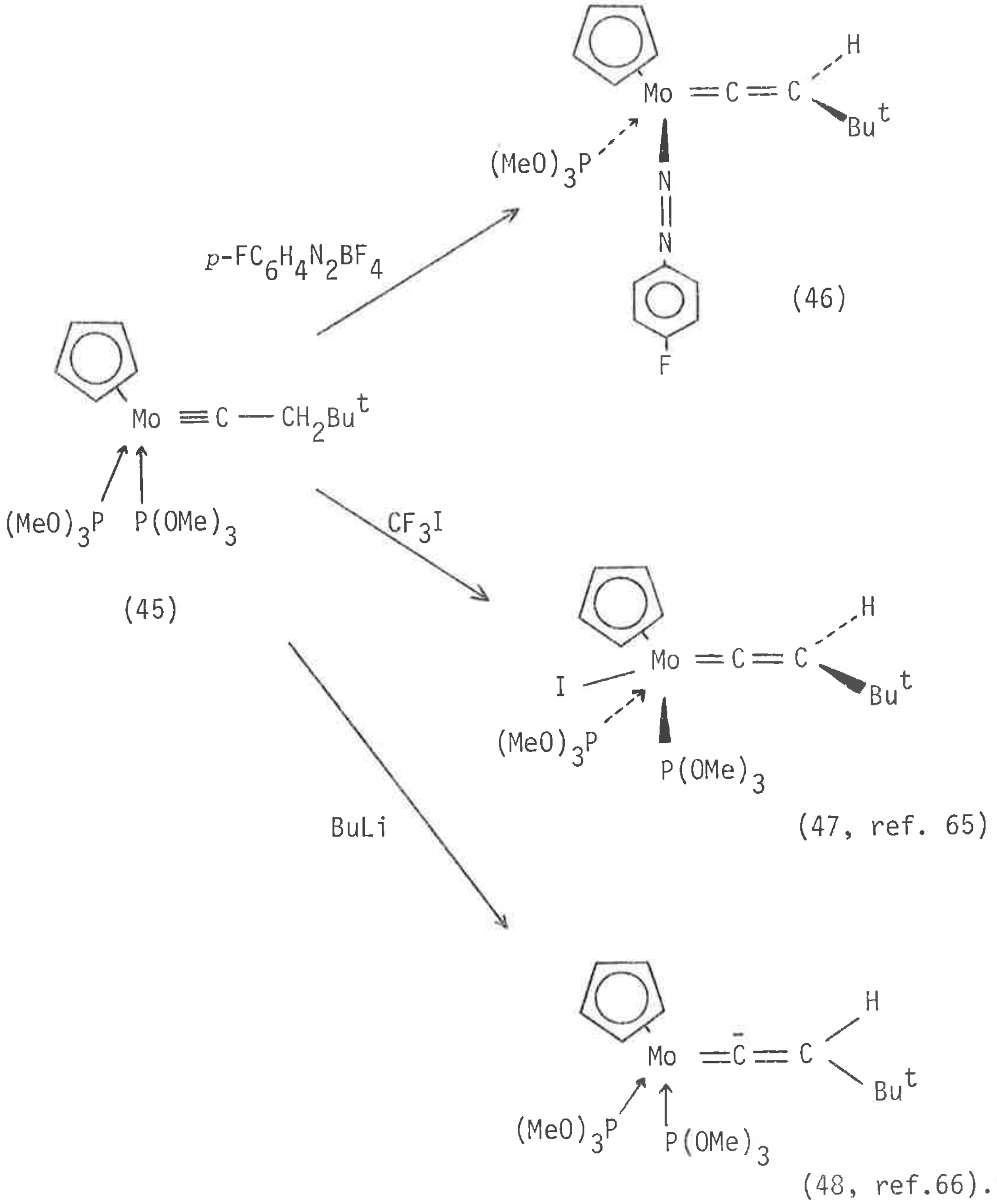
was determined to be 7.74 (2:1 thf-H_2O).[63]

Treatment of $Mn(C_2Ph)(CO)_2(\eta-C_5H_5)$ with BuLi followed by methylation or protonation gave (43) and (44) respectively (Scheme 9).[61]



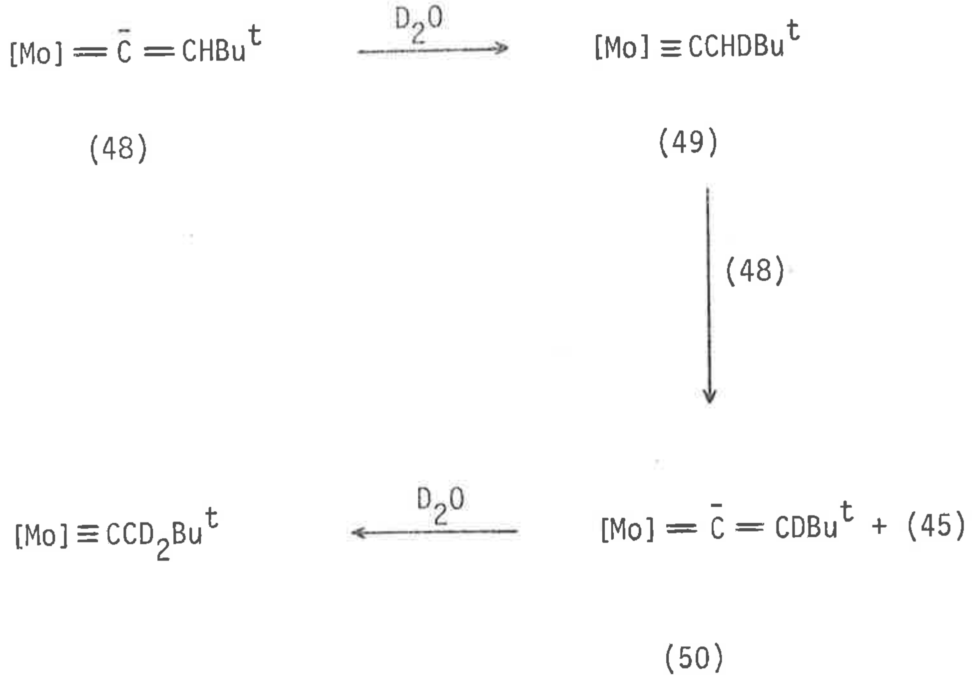
<u>Scheme 9</u> [Mn] = $Mn(CO)_2(\eta\text{-}C_5H_5)$

1.3.1.5 From metal carbyne complexes Deprotonation from the β-carbon of some molybdenum metal carbyne complexes yields metal vinylidene complexes (Scheme 10).



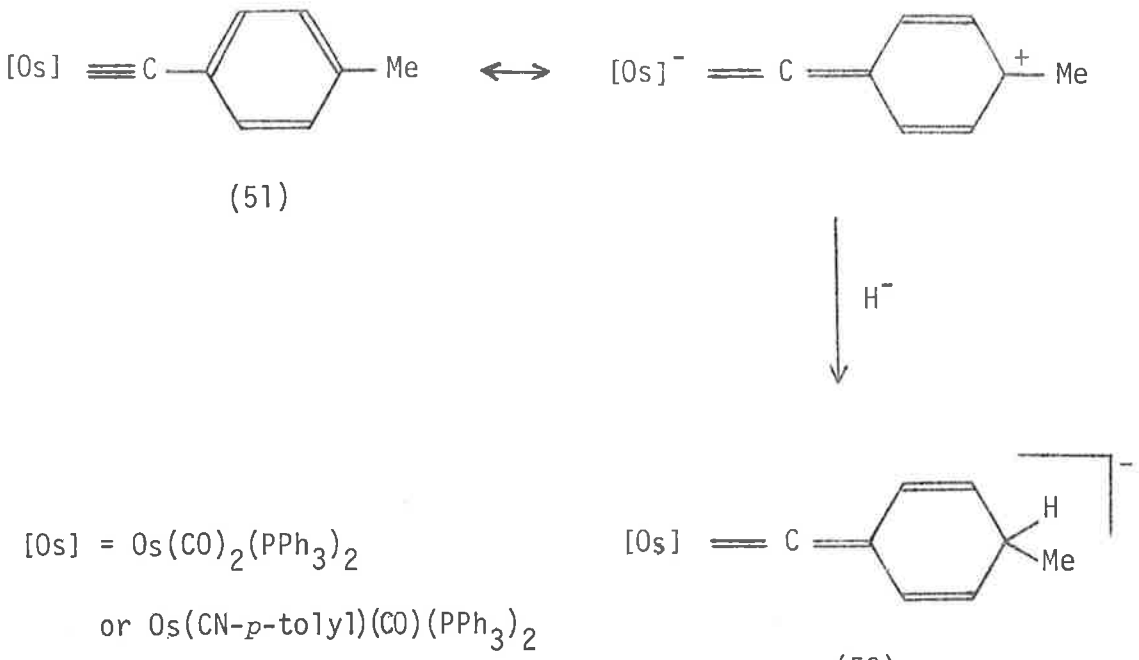
Scheme 10

Deuteration of (48) with D_2O gives a carbyne complex (49) which is selectively deprotonated to give a deuterovinylidene complex (50).[66] This is attributed to the operation of a primary kinetic isotope effect (Scheme 11).



Scheme 11. [Mo] = $Mo(CCH_2Bu^t)[P(OMe)_3]_2(\eta\text{-}C_5H_5)$.

A reaction of $Li(HBEt_3)$ with $[Os(CR)(CO)(L)(PPh_3)_2]^+$ (51; L = CO, CNR; R = *p*-tolyl) gives (52), presumably as a result of H^- attacking a resonance-hybrid of (51).[67]



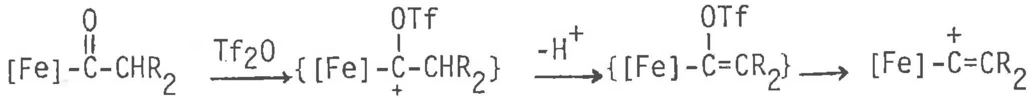
(51)

(52)

[Os] = $Os(CO)_2(PPh_3)_2$

or $Os(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2$

1.3.1.6 From iron acyl complexes Treatment of some iron acyl complexes with $(CF_3SO_2)O$ (Tf_2O) led to the elimination of HO^- and the formation of the vinylidene ligand.[68] Initially the acyl oxygen is thought to attack Tf_2O, followed by deprotonation:



$$[Fe]\text{-}\overset{O}{\overset{\|}{C}}\text{-}CHR_2 \xrightarrow{Tf_2O} \{[Fe]\text{-}\underset{+}{\overset{OTf}{\overset{|}{C}}}\text{-}CHR_2\} \xrightarrow{-H^+} \{[Fe]\text{-}\overset{OTf}{\overset{|}{C}}{=}CR_2\} \longrightarrow [Fe]\text{-}\overset{+}{C}{=}CR_2$$

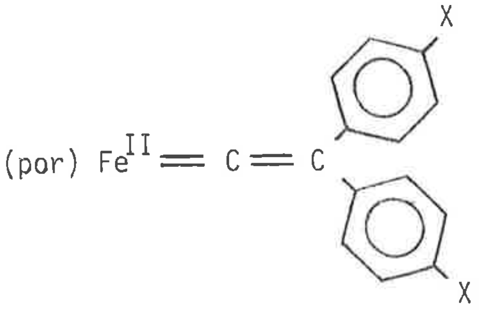
(31)

[Fe]	R
$Fe(CO)(PPh_3)(\eta\text{-}C_5H_5)$	H,Me
$Fe(CO)(PMe_2Ph)(\eta\text{-}C_5H_5)$	H

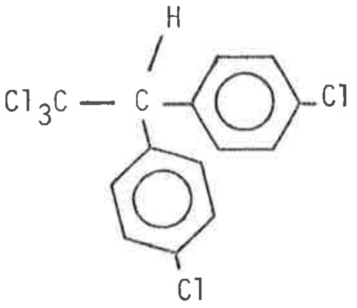
1.3.1.7 From iron porphyrin complexes An understanding of the iron-oxygen bond in natural systems is extremely important.

A number of porphyrin vinylidene complexes (55) have proved to be valuable models of catalase and horseradish peroxidase systems.

These vinylidene complexes have been formed from Fe^{II}(por) [por = *meso*-tetraphenylporphyrin (tpp), octaethylporphyrin (oep), protoporphyrin IX (ppIX), deuteroporphyrin IX dimethylether (dpdme),[69] *meso*-tetra-*p*-tolylporphyrin (ttp),[70] tetraanisylporphyrin (tap)[71]] and ddt (56). Complex (57) has been formed in the same manner.[72] The vinylidene ligand can be formed by removal of two Cl groups to give a Fe=C bond, followed by β-elimination of HCl.



(55) X = Cl
(57) X = H, por = tpp.



(56)

The reversible one-electron oxidation of some of these complexes (with $CuCl_2$ or $FeCl_3$) leads to products having visible spectra similar to those of catalase and horseradish peroxidase.[69,73]

Treatment of (32, por = tpp) with BuSNa (-75°) yielded $\{Fe^{II}[C{=}C(p\text{-}ClC_6H_4)_2](tpp)(BuS)\}^-$, which reverts to starting material on treatment with acetic acid and warming.[74]

1.3.2 Formation of Binuclear Vinylidene Complexes

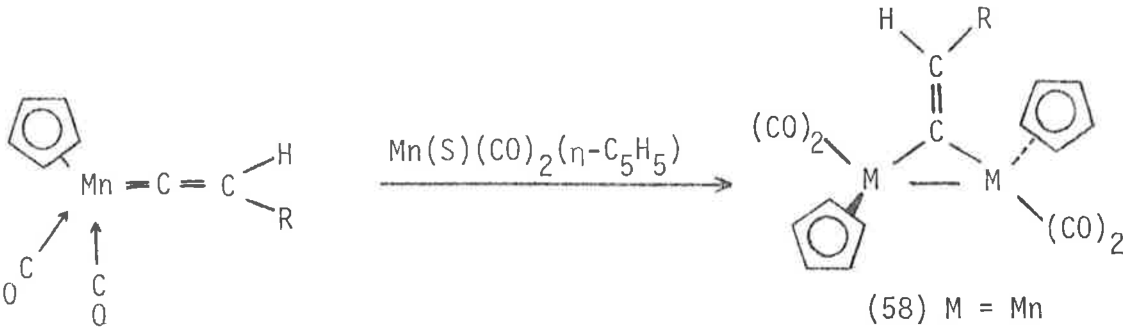
All binuclear vinylidene complexes contain the vinylidene ligand bridging two metal atoms, this reflects the strong π-acceptor capacity of the ligand.

No mixed metal binuclear complexes have been reported.

The formation of binuclear vinylidene complexes is generally different from those of mononuclear vinylidene complexes. These are discussed according to the following preparative routes:

1.3.2.1 From mononuclear vinylidene complexes
1.3.2.2 From terminal acetylenes
1.3.2.3 From diphenyl ketene
1.3.2.4 From 1,1-dichlorovinyls
1.3.2.5 From 1,1-dichlorocyclopropanes
1.2.3.6 By nucleophilic attack on CO
1.3.2.7 By isomerisation

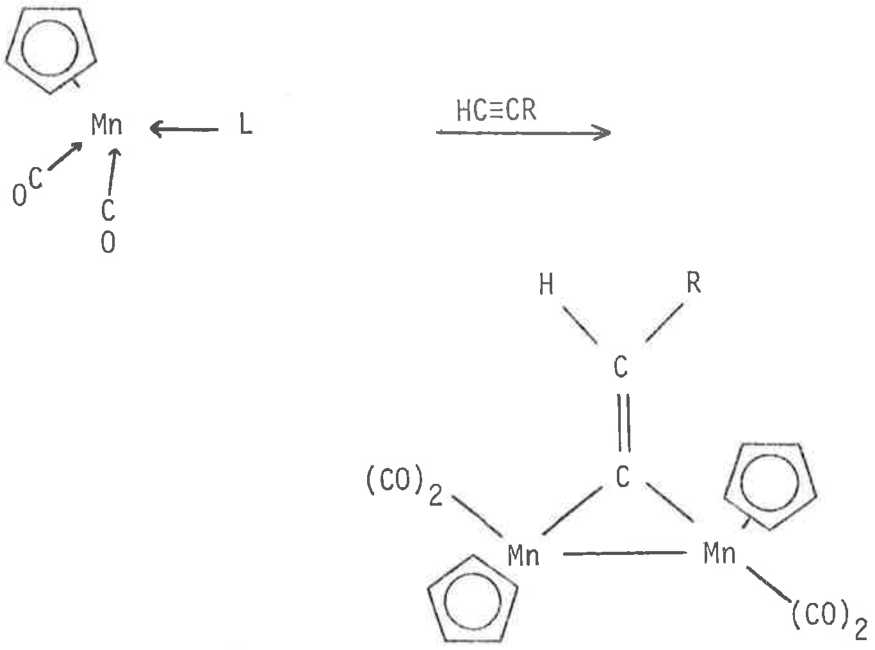
1.3.2.1 From mononuclear vinylidene complexes. A reaction of $Mn[C{=}CHR](CO)_2(\eta\text{-}C_5H_5)$ (R = Ph, 17;[40] R = CO_2Me, 33[61]) with solvento complexes yields *trans* binuclear products (58):



(58) M = Mn
R = Ph, CO_2Me

Complex (58, M = Mn, R = Ph) can also be formed by heating Mn(C=CHPh)$(CO)_2$-(η-C_5H_5), whereas (58, M = Re, R = Ph) is formed upon treating Re(C=CHPh)-$(CO)_2$(η-C_5H_5) with an aqueous ethanolic KOH mixture.

1.3.2.2 From terminal acetylenes A number of binuclear vinylidene complexes have been formed from M$(CO)_2$(L)(η-C_5H_5) (L=CO or thf) and terminal acetylenes:[40,47-49,75-77]

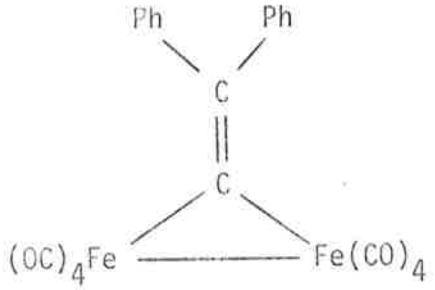


(58)

R = H, Me, CO_2Me, COPh, Ph; L = CO or thf.

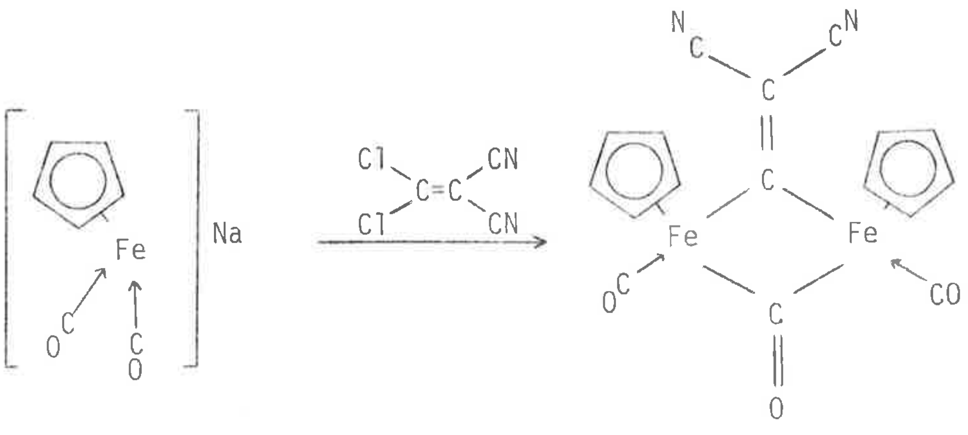
A similar preparation has given $Re_2(\mu^2\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2$.[50] The structure of $Mn_2(\mu^2\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2$ has been determined.[78]

1.3.2.3 From diphenylketene A reaction of $Ph_2C{=}C{=}O$ with either $Fe(CO)_5$ or $Fe_2(CO)_9$ and irradiation gave (59).[41]



(59)

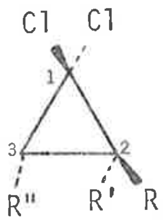
1.3.2.4 From 1,1-dichlorovinyls The binuclear complex $Fe_2[\mu^2\text{-}C{=}C(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (60), formed from $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and $Cl_2C{=}C(CN)_2$, was of particular interest because of its formal resemblance to $[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$.[79] This complex differs from the carbonyl dimer,



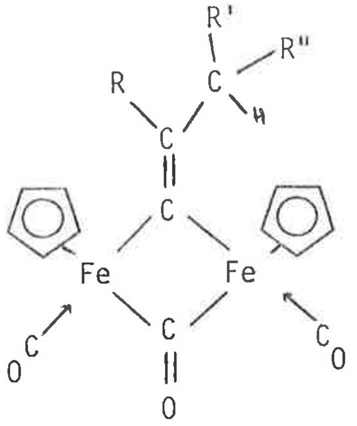
(60)

by being non-fluxional, and not reacting with iodine.[80]

1.3.2.5 From 1,1-dichlorocyclopropanes Reactions of $[Fe_2(CO)_2(\eta\text{-}C_5H_5)]_2$ with substituted cyclopropanes (61) under phase transfer conditions $[NaOH\text{-}H_2O$ (50:50), thf, $(NBu_4)^+HSO_4^-]$ yield a variety of *cis*- and *trans*- alkyl-substituted products (62).[81] The observations that (i) cyclopropenes react to give the same products



(61)

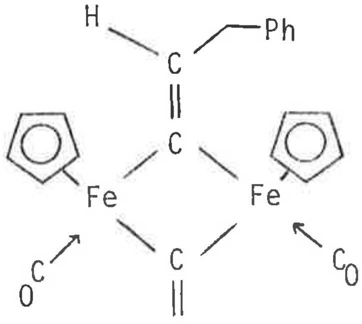


(62)

cis and *trans*

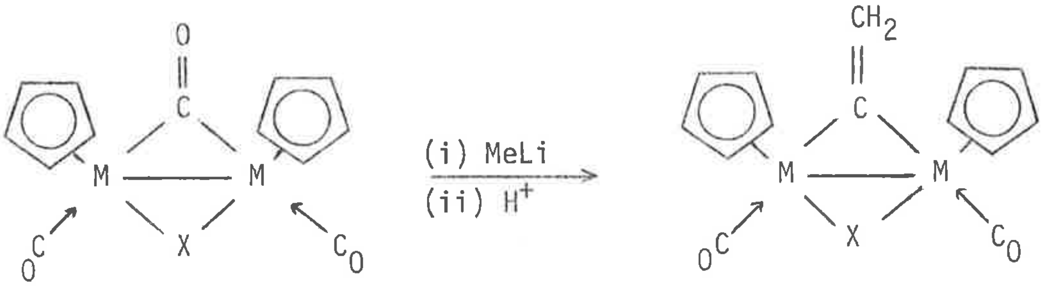
R	R'	R"
Ph	H	Ph
Ph	H	H
Me	H	*p*-tolyl
Me	Me	*p*-tolyl
Me	H	*p*-anisyl
Me	Me	Ph

under phase-transfer conditions, (ii) NaOD-D_2O in the catalyst leads to substitution on C(3), and (iii) reaction of (61, R = Ph, R' = R" = H) gives only (62) and not (63), suggest the formation of an initial cyclopropene intermediate which undergoes C(1)-C(3) ring fission under the phase transfer conditions to give (62).



(63)

1.3.2.6 By nucleophilic attack on CO Reactions of the binuclear complexes (64) and (65) with MeLi followed by acidification yields (66)[82] and (67)[83] respectively. In the reaction of (65) a bridging



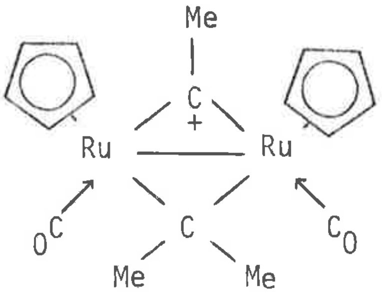
(64) M = Fe, X = CO

(65) M = Ru, X = CMe_2

(66)

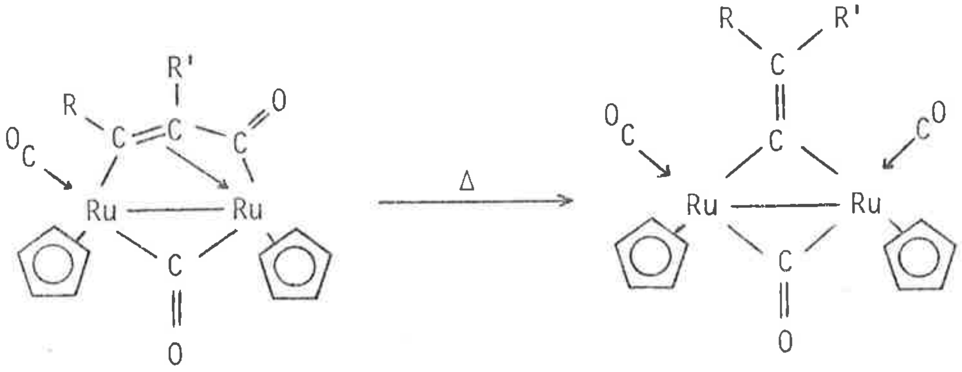
(67)

carbyne intermediate (68) was isolated, which on deprotonation gave (67), implying that these reactions proceed *via* initial attack on a bridging CO ligand.



(68)

1.3.2.7 By isomerisation The α,β-unsaturated bridge linking the two metal atoms in (69) isomerises to a vinylidene ligand on heating.[84] The formation of (70) involves migration of the



(69) (70)

R = H, R' = H or Ph.

α-vinyl-carbon and a 1,2-hydride shift. A deuterated sample of (69, R = D, 88%; R′ = Ph) retained most of the deuterium in the isomerised product (77%), implying a mainly intramolecular process.

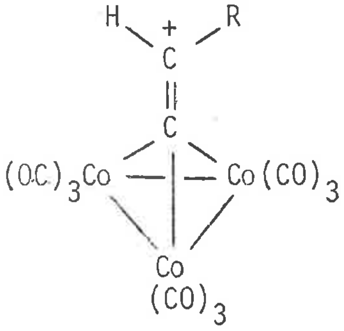
1.3.3 Formation of Metal Cluster Vinylidene Complexes

Metal clusters containing a non-substituted vinylidene ligand have been considered as models in the interaction of an olefin with a metal surface.[85] This species has been detected in the reactions of ethylene and acetylene with Ni(111),[86] Fe(100),[87] and Pt(111)[88,89] surfaces. Theoretical studies of similar manganese systems also raise the possibility of a vinylidene intermediate.[90]

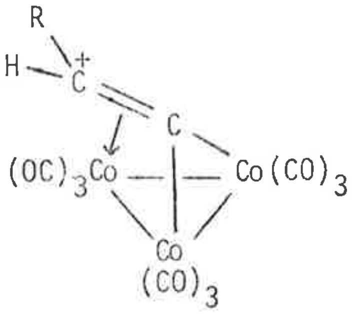
In all cases where structural studies have been reported the vinylidene ligand forms σ bonds to two or three metal atoms and a π bond to the remaining metal atom.

Trinuclear and tetranuclear vinylidene cluster complexes are discussed separately.

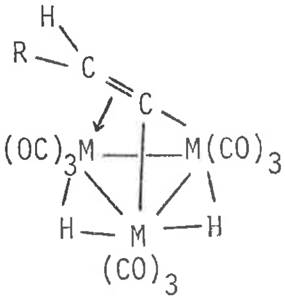
1.3.3.1 μ^3-vinylidene cluster complexes A reaction of $Co_3[\mu^3\text{-CC(OH)HR}](CO)_9$ (R = H, Me, Ph) with propionic anhydride gives $[Co_3(C{=}CHR)(CO)_9]^+$ (71).[91] While a symmetrical complex (72A) might be expected, theoretical calculations indicate that a non-centred structure (72B) is of lower energy.[92] A non-symmetric structure was found for $H_2Os_3(\mu^3\text{-C{=}CHR})(CO)_9$ (73, R = H),[93,94] and its protonated form $[H_3Os_3(\mu^3\text{-C{=}CH}_2)(CO)_9]^+$ (74).[95] Complex (73) was formed from $Os_3(CO)_{12}$ and ethylene; a vinyl complex (75, R = H) is presumably an intermediate in this reaction.[93,94] Upon heating some vinyl complexes (75, R = H, Me, Ph) the corresponding μ^3-vinylidene clusters (73) were formed.[96] In similar reactions $Os_3(CO)_{12}$ and $H_2C{=}CHR$



(72A)

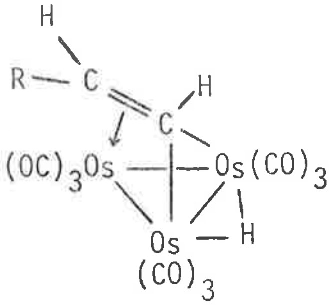


(72B)



(73) M = Os, R = H,Me,Ph.

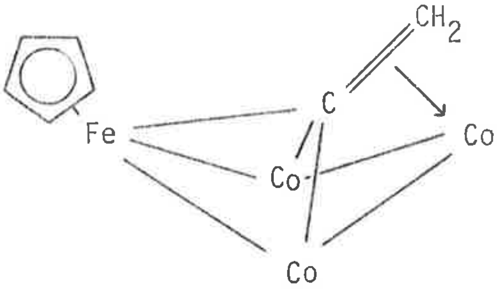
(76) M = Ru, R = H



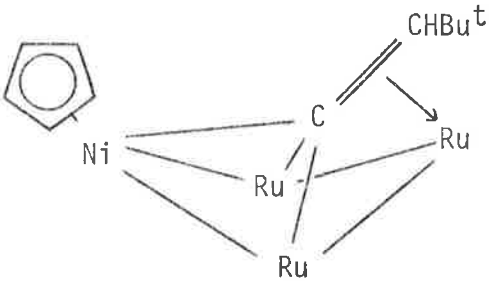
(75) R = H,Me,Ph.

[R = Me, P(*o*-C_6H_4)Ph_2] give μ^3-vinylidene clusters.[97] A reaction of $Ru_3(CO)_{12}$ and ethylene gives $H_2Ru_3(\mu^3\text{-}C{=}CH_2)(CO)_9$ (76) and $H_2Ru_3(\mu^3\text{-}CH{=}CH_2)(CO)_9$ under mild conditions.

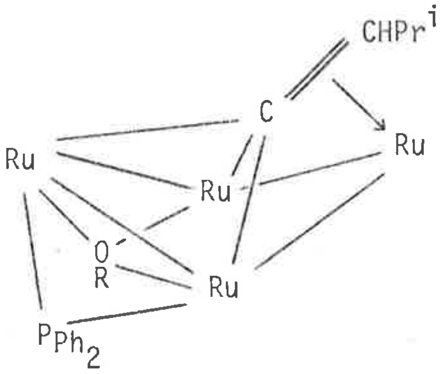
1.3.3.2 μ^4-vinylidene cluster complexes A reaction of $Fe_2(\mu^2\text{-}C{=}CH_2)(\mu^2\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2$ (66) with $Co_2(CO)_8$ yields a mixed-metal vinylidene cluster (77).[98] This is similar to (78), formed in a reaction of $HRu_3(CO)_9(\eta^3\text{-}C{\equiv}CHBu^t)$ and $[Ni(CO)(\eta\text{-}C_5H_5)]_2$.[99] A third 'butterfly' shaped vinylidene cluster (79, R = H, Et) is formed by a cluster-expansion reaction of $Ru_3(\eta^2\text{-}Ph_2PC{\equiv}CPr^i)(CO)_{11}$ in ROH/thf.[100]



(77) $Co_3Fe(\eta^4\text{-}C{=}CH_2)(CO)_{11}\text{-}(\eta\text{-}C_5H_5)$



(78) $NiRu_3(\eta^4\text{-}C{=}CHBu^t)(CO)_9\text{-}(\eta\text{-}C_5H_5)$



(79) $Ru_4(\eta^4\text{-}C{=}CHBu^t)(CO)_{10}\text{-}(OR)(PPh_2);R{=}H,Et.$

(Carbonyl ligands have been omitted for clarity.)

1.3.4 Reactions of Vinylidene Complexes

The vinylidene ligand has a number of possible sites for reaction. The substituents on the β-carbon are open to attack, while addition reactions to the olefin bond are also possible. The electron deficient α-carbon can be a site of electrophilic attack or of insertion reactions into the metal-carbon bond.

The reactions of vinylidene complexes are discussed under the following headings:

1.3.4.1 *Deprotonation to form σ-acetylide complexes*
1.3.4.2 *Addition to the olefinic bond*
1.3.4.3 *Addition to the α-carbon*
1.3.4.4 *Addition to the β-carbon*
1.3.4.5 *Ligand exchange reactions*
1.3.4.6 *Redox reactions of iron porphyrin complexes*
1.3.4.7 *Reactions of* $Fe_2(\mu^2\text{-}C{=}CH_2)(\mu^2\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2$ *(66)*
1.3.4.8 *Reactions of* $H_2Os_3(\mu^3\text{-}C{=}CH_2)(CO)_9$ *(73)*
1.3.4.9 *Other reactions of vinylidene complexes*

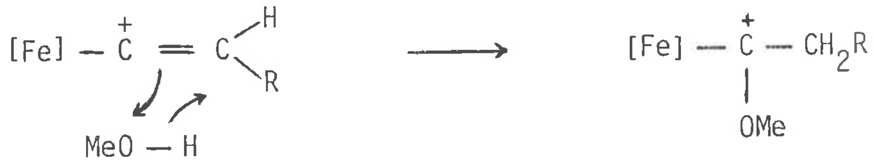
1.3.4.1 *Deprotonation to form σ-acetylide complexes* Cationic vinylidene complexes bearing a β-proton are readily deprotonated to give neutral σ-acetylide complexes (Table 3).

Table 3 A summary of the products from the reaction

$$[M]-\overset{+}{C}=CHR \xrightarrow{\text{base}} [M]-C\equiv CR$$

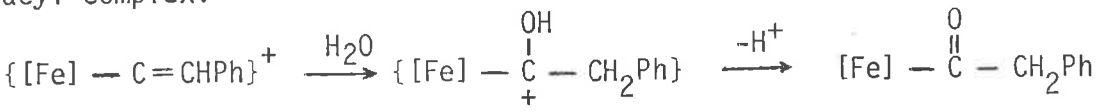
[M]	R	ref.
$Fe(CO)(PPh_3)(\eta\text{-}C_5H_5)$	Ph	62
$Fe(dppe)(\eta\text{-}C_5H_5)$	H, Me	63
$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$	Me, Pr, CO_2Me, Ph, $C_6H_4F\text{-}p$, C_6F_5	52
$Ru(PMe_3)_2(\eta\text{-}C_5H_5)$	Me	53
$Ru(dppm)(\eta\text{-}C_5H_5)$	Ph	52
$Ru(dppe)(\eta\text{-}C_5H_5)$	Ph	52
$Os(PPh_3)_2(\eta\text{-}C_5H_5)$	Ph	52

1.3.4.2 Addition to the olefinic bond A reaction of $[Fe(C=CHR)(CO)(L)(\eta-C_5H_5)]^+$ with methanol yields alkoxy(alkyl)-carbene complexes in an addition reaction:



[Fe]	R	ref.
$Fe(CO)(PPh_3)(\eta-C_5H_5)$	Ph	62
$Fe(CO)(PMe_2Ph)(\eta-C_5H_5)$	H	68

A similar addition reaction is thought to take place when $[Fe(C=CHPh)(CO)(PPh_3)(\eta-C_5H_5)]^+$ (34) reacts with water to give an acyl complex:[62]



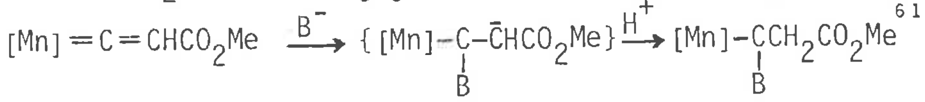
$$\{[Fe]-C=CHPh\}^+ \xrightarrow{H_2O} \{[Fe]-\overset{OH}{\underset{+}{C}}-CH_2Ph\} \xrightarrow{-H^+} [Fe]-\overset{O}{\overset{\|}{C}}-CH_2Ph$$

It is noteworthy that a reverse reaction gives vinylidene complexes from acyl complexes (Section 1.3.1.6).

Further addition reactions of the olefinic bond of vinylidene complexes are described in Chapter 2.

1.3.4.3 Addition to the α-carbon Nucleophilic attack of B^- ($B = H, NH_2, MeO$) results in bonding to the α-carbon of some vinylidene complexes:

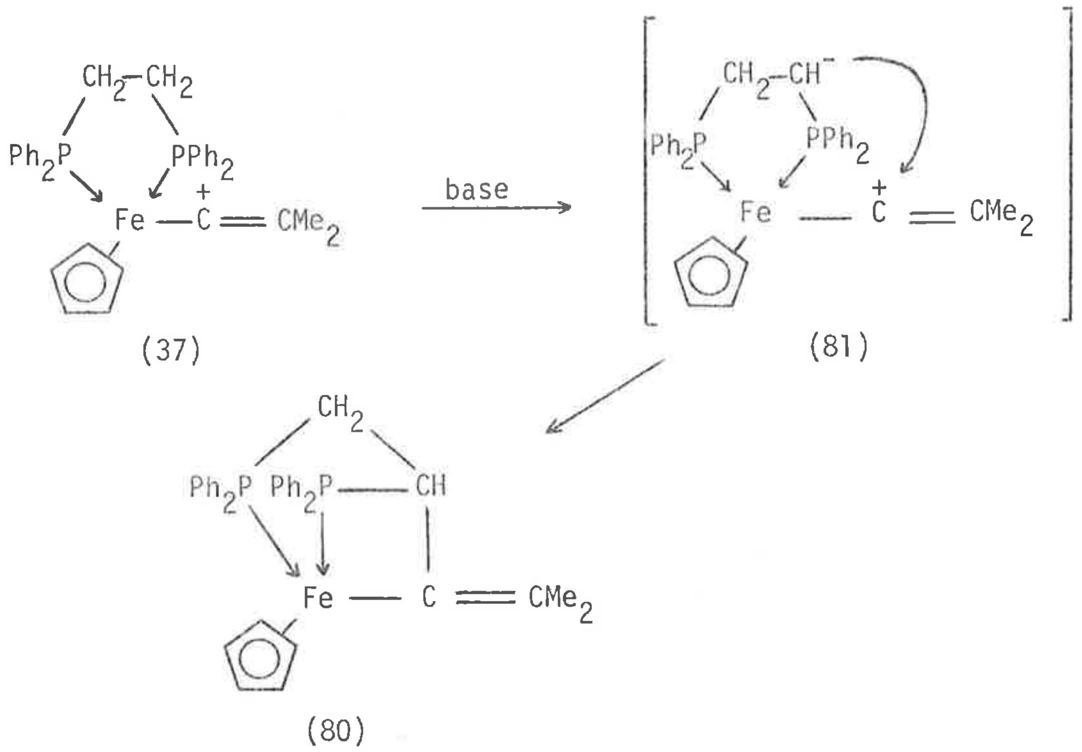
$$[Fe(C=CMe_2)(dppe)(\eta-C_5H_5)]^+ \xrightarrow{H^-} Fe(CH=CMe_2)(dppe)(\eta-C_5H_5)$$ [64]



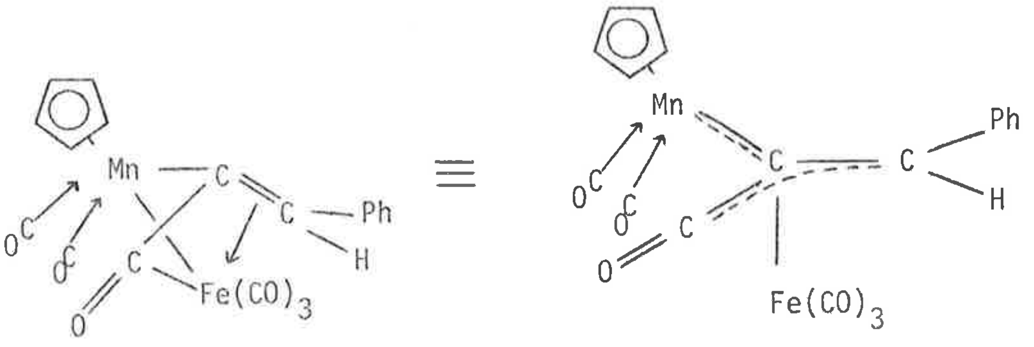
$$[Mn]=C=CHCO_2Me \xrightarrow{B^-} \{[Mn]-\underset{B}{C}-\bar{C}HCO_2Me\} \xrightarrow{H^+} [Mn]-\underset{B}{C}CH_2CO_2Me$$ [61]

$[Mn] = Mn(CO)_2(\eta-C_5H_5)$; $B = NH_2$, MeO.

Treatment of $[Fe(C=CMe_2)(dppe)(\eta-C_5H_5)]^+$ (37) with base gives complex (80).[100a] This suggests the formation of an anionic methylene carbon on the dppe ligand (81), which then can attack the α-carbon:

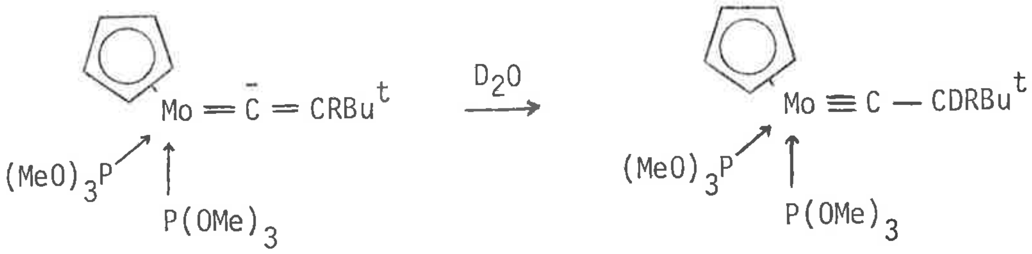


A reaction of $Mn(C{=}CHPh)(CO)_2(\eta\text{-}C_5H_5)$ (17) and $Fe_2(CO)_9$ gave (82), *via* addition of a carbonyl group to the α-carbon of (17).[101] This complex can also be represented as a delocalised system:



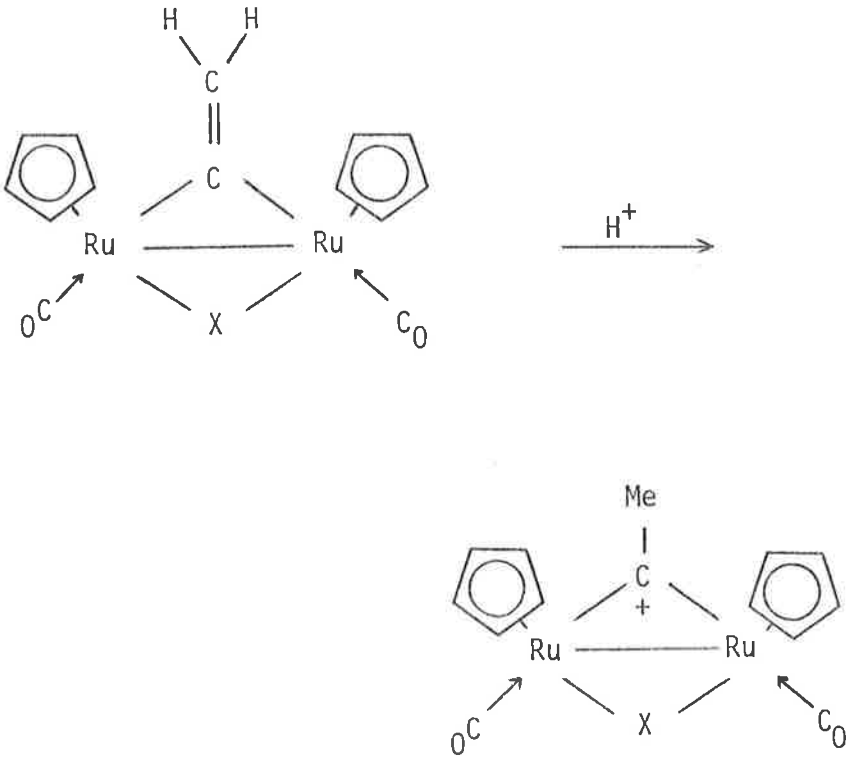
(82)

1.3.4.4 Addition to the β-carbon A reaction of $\{Mo(C{=}CRBu^t)[P(OMe)_3]_2(\eta\text{-}C_5H_5)\}^-$ (48, 50) with D_2O yields carbyne complexes:[66]



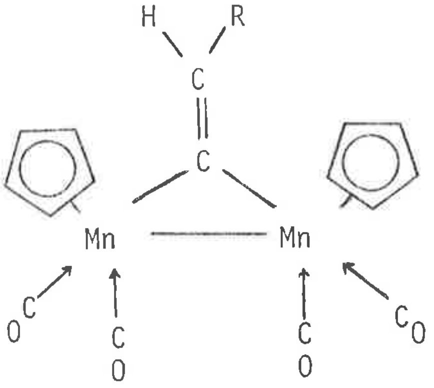
R = H, D.

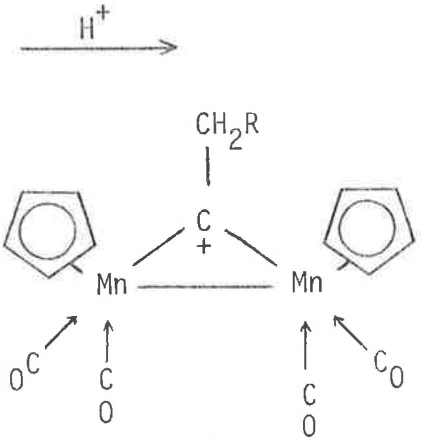
Similarly some binuclear carbyne complexes can be formed by protonation of the vinylidene moiety:



(66) X = CO, ref. 84

(67) X = CMe_2, ref. 83





(58) $R = H, Me, CO_2Me$; ref. 75, 76

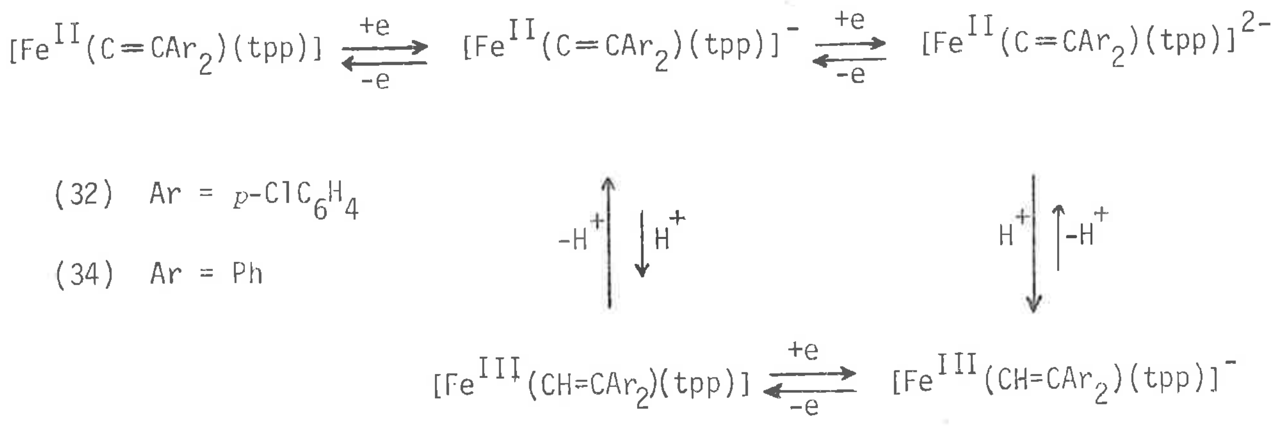
(83)

A mixture of (58, R = H) and (83, R = Me) interconverts to (58, R = Me) and (83, R = H), suggesting a steric influence.[76]

1.3.4.5 Ligand exchange reactions Under mild conditions one carbonyl of $Mn(C{=}CHPh)(CO)_3(\eta\text{-}C_5H_5)$ (17) is substituted by PR_3 (R = Ph, OEt, OPh) to give $Mn(C{=}CHPh)(CO)_2(PR_3)(\eta\text{-}C_5H_5)$ (84).[40, 102] A reaction of $Mn_2(\mu^2\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2$ (58) with PPh_3 also gave (84, R = Ph).

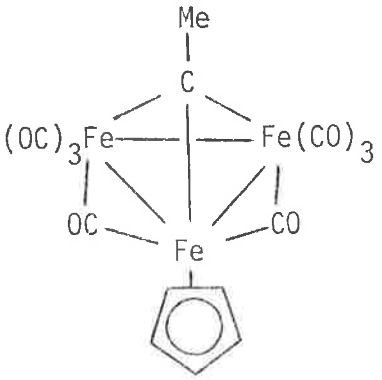
1.3.4.6 Redox reactions of iron-porphyrin complexes Oxidation of $Fe[C{=}C(p\text{-}ClC_6H_4)_2](ttp)$ with $CuCl_2$ inserts the α-carbon into an iron-nitrogen bond.[70] When $Fe[C{=}C(p\text{-}ClC_6H_4)_2](tap)$ is oxidized, the metal is removed completely with the formation of an N — C — N bridge to the porphyrin ring.[71]

Reversible reduction of $Fe(C{=}CAr_2)(tpp)$ is thought to take place by the mechanism shown in Scheme 12.[72]

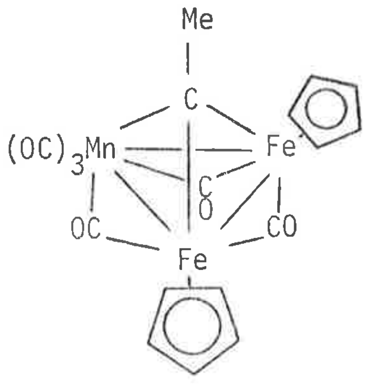


Scheme 12.

1.3.4.7 Reactions of $Fe_2(\mu^2\text{-}C{=}CH_2)(\mu^2\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2$ *(66)* A reaction of (66) with $Co_2(CO)_8$ has been previously described to give (77), where the vinylidene ligand is retained.[98] Other reactions of (66) with $Fe_2(CO)_9$ and $H_3Mn_3(CO)_{12}$ yield the μ^3-carbyne clusters (85) and (86). The formation of complex (86) suggests that an insertion of $C{=}CH_2$ into an Mn-H bond has taken place. Formation of (85) is not well understood, but seems to involve break-up of (66) and hydrogen abstraction.

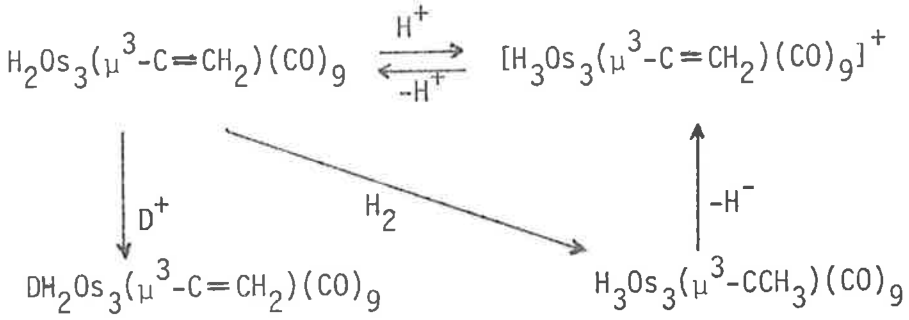


(85)



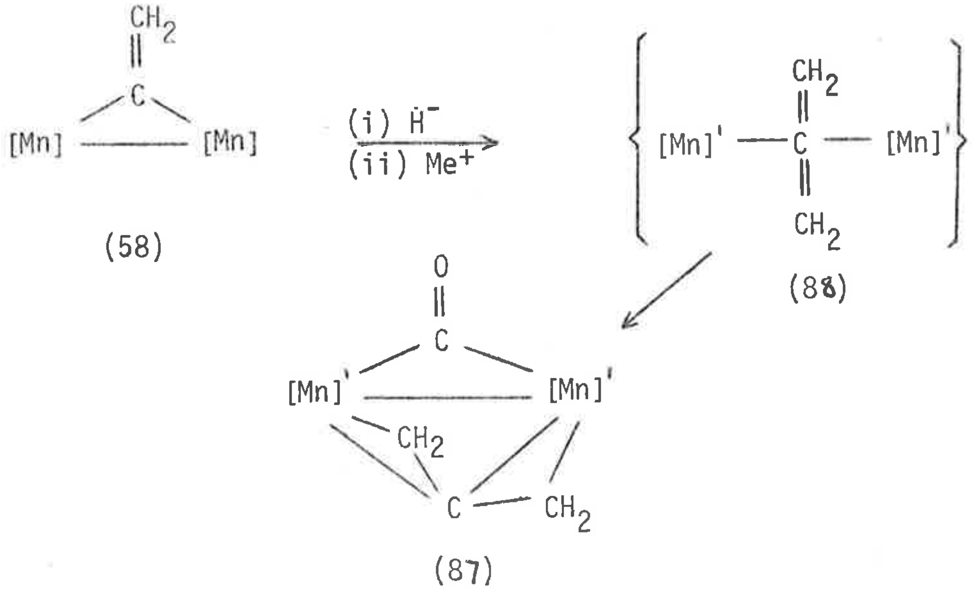
(86)

1.3.4.8 Reactions of $H_2Os_3(\mu^3\text{-}C=CH_2)(CO)_9$ (49) The reactions of $H_2Os_3(\mu^3\text{-}C=CH_2(CO)_9$ are summarised in Scheme 13.[94,95,103] A reaction of (49) with D_2 gives a mixture of $Os_3(C_2H_4D_2)(CO)_9$, $Os_3(C_2H_3D_3)(CO)_9$, and $Os_3(C_2H_2D_4)(CO)_9$.[94] NMR studies indicate that deuterium attack occurs at the organic ligand.



Scheme 13.

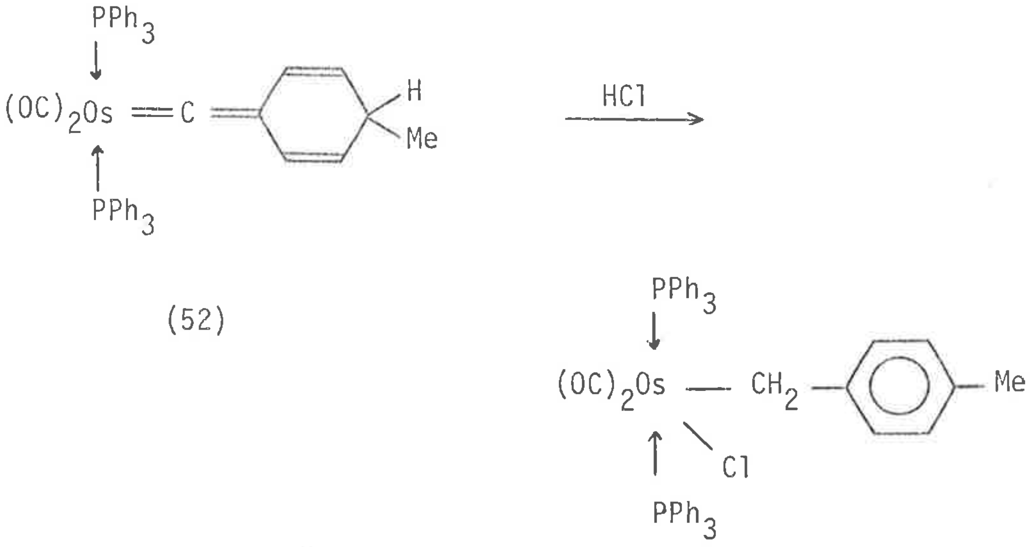
1.3.4.9 Other reactions of vinylidene complexes Treatment of $Mn_2(\mu^2\text{-}C=CH_2)(CO)_4(\eta\text{-}C_5H_5)_2$(58) with $Li(HBEt_3)$ followed by addition of MeI gave (87), suggesting the intermediacy of (88).[76] Complex (87) has an unusual bridging allene ligand.



$[Mn] = Mn(CO)_2(\eta\text{-}C_5H_5)$

$[Mn]' = Mn(CO)(\eta\text{-}C_5H_5)$

A reaction of (52) with HCl gives (82):[67]



(52)

(82)

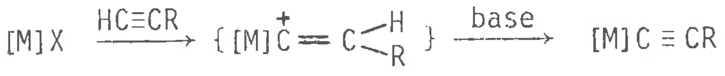
1.3.5 *Non-isolated Vinylidene Intermediates*

In many reactions a vinylidene intermediate is implied but not isolated. These reactions often parallel those described in Section 1.3.4. In many instances the lability of these intermediates can be attributed to a lack of steric hindrance.

These reactions are discussed under the following headings:

- *1.3.5.1 Formation of σ-acetylide complexes*
- *1.3.5.2 Addition to the olefinic bond*
- *1.3.5.3 Addition to the α-carbon*
- *1.3.5.4 1,2-Hydride shifts*
- *1.3.5.5 Displaced vinylidene ligands*
- *1.3.5.6 Cis/trans isomerisation intermediates*

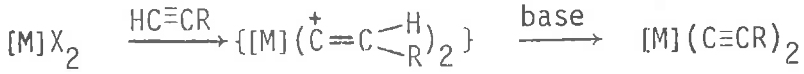
1.3.5.1 Formation of σ-acetylide complexes A 'one-pot' reaction of some metal complexes with terminal acetylenes in the presence of amine bases gives a range of σ-acetylide complexes. It is presumed that a vinylidene intermediate forms and is immediately deprotonated:



$$[M]X \xrightarrow{HC\equiv CR} \{[M]\overset{+}{C}{=}C\genfrac{}{}{0pt}{}{<H}{<R}\} \xrightarrow{base} [M]C\equiv CR$$

$[M] = [Ni(R)(PMe_2Ph)_2]^+$ ($R = C_6Cl_5$, $CCl = CCl_2$, $C_6H_3(OMe)_2$-2,6),[104-106] $Ni(NCS)(PR'_3)_2$(R'=Bu, Ph),[107] $PdX(PEt_3)_2$(X = Cl, Br, I),[108] $PtCl(PMe_2Ph)_2$,[109] $Rh(CO)(PR'_3)_2$(R' = Ph or C_6H_4F-*p*),[110] $[Ir(CO)_2(PPh_3)_2]^+$.[111]

e.g. R = Me, Et, Ph, $C_6H_4C_2H$-*o*.



$$[M]X_2 \xrightarrow{HC\equiv CR} \{[M](\overset{+}{C}{=}C\genfrac{}{}{0pt}{}{<H}{<R})_2\} \xrightarrow{base} [M](C\equiv CR)_2$$

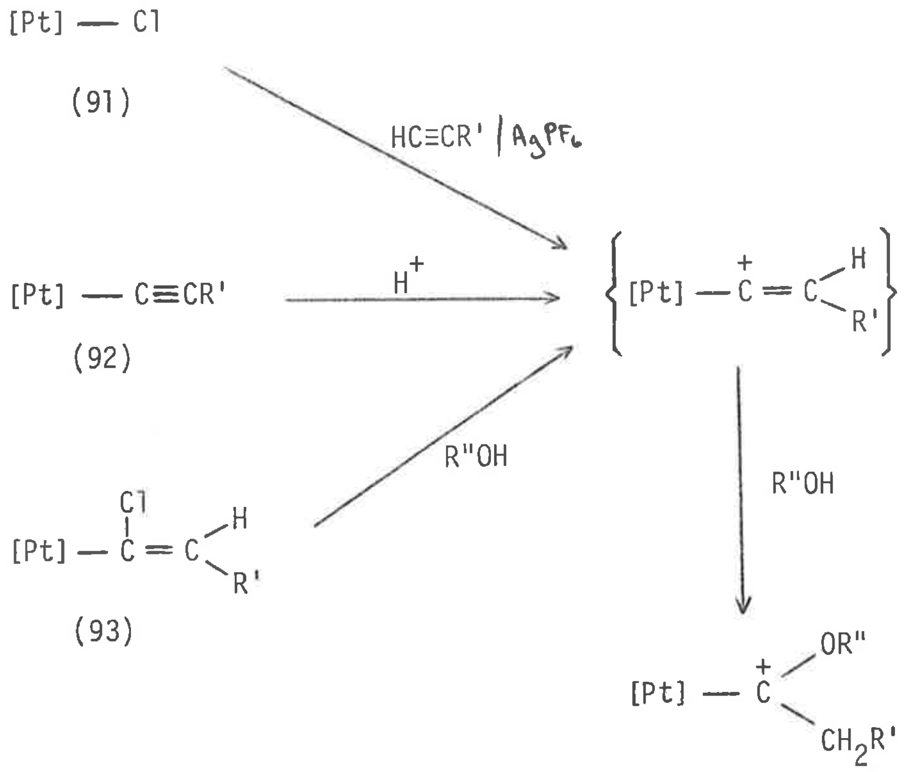
$[M] = Ni(PR'_3)_2$ (R' = Bu, Ph);[107, 112] $Pd(PEt_3)_2$,[113] PtL_2 ($L = PPh_3$, PMe_2Ph, PPr_3).[114-116]

$$[Pd]X_2 \xrightarrow{C_6H_4(C_2H)_2\text{-}p} \{[Pd]_2(\overset{+}{C}{=}C)_2C_6H_4\text{-}p\} \xrightarrow{base} C_6H_4(C\equiv C[Pd])_2\text{-}p$$

$[Pd] = Pd(PEt_3)_2$.[117]

1.3.5.2 Addition to the olefinic bond Treatment of $Fe(C\equiv CR(CO)_2$-(η-C_5H_5)(R = Me,[118] R = Ph[119]) with HCl yields the acyl complex $Fe(COCH_2R)(CO)_2(\eta\text{-}C_5H_5)$ (90). Presumably addition of water to $\{Fe(C{=}CHR)(CO)_2(\eta\text{-}C_5H_5)\}^+$ (89) gives a hydroxy(alkyl)carbene complex which on deprotonation yields (90).

Extensive investigations by Chisholm, Clark and others have led to the isolation of alkoxy(alkyl)carbene complexes of platinum.[120-123] Reactions between metal chlorides (91) and terminal acetylenes, or metal acetylides (92) and acid give highly reactive vinylidene intermediates, which form alkoxycarbene complexes in the presence of alcohols (Scheme 14). Similarly alcoholysis of α-chlorovinyl complexes (93) proceeds to give alkoxycarbene products.[123]



Scheme 14

[Pt] = *trans* - $PtRL_2$

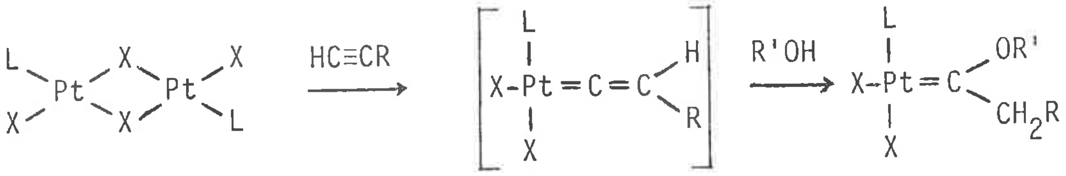
(91) e.g. L = PMe_2Ph, $AsMe_3$; R = Me, Ph, CF_3, $C\equiv CCF_3$; R' = H, alkyl, Ph; R" = Me, Et.

(92) e.g. L = PMe_2Ph, $AsMe_3$; R = Cl, C≡CR'; R' = H, Me, Ph; R" = Me, Et, Pr, Pr^i.

(93) e.g. L = PMe_2Ph; R = Cl, Br; R' = H, Me; R" = Me, Et, Pr, Pr^i.

Strong support for the presence of these intermediates was obtained in isotopic labelling experiments. In such an experiment, H/D exchange of *trans*-$Pt(C\equiv CR)_2(PMe_2Ph)_2$ (92, R = H or D) with MeOD only proceeds in the presence of weak acids. This implies a vinylidene intermediate, because this possesses a more acidic proton than the Pt $-$C$\equiv$CH group.

A range of neutral platinum alkoxy(alkyl)carbene complexes has been formed in reactions of $Pt_2(\mu^2\text{-}X)X_2L_2$, HC$\equiv$CR and R'OH:[124]



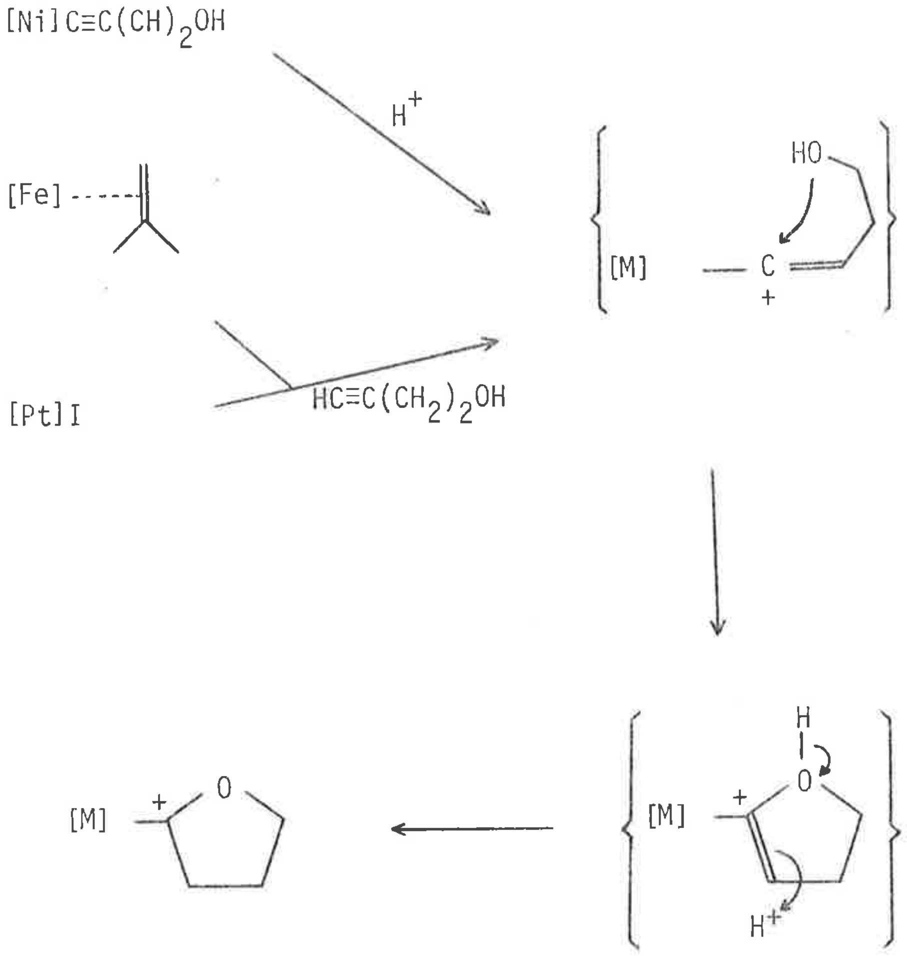
e.g. L=PMe_2Ph, PEt_3; X=Cl, Br, I; R=Me, Et, Ph; R' = Me, Et, Pr.

Reactions of $H_2PtCl_6.6H_2O$ with HC$\equiv$CEMe$_3$ (E = C, Si) in *iso*-propanol gave $Pt_2[C(OPr^i)CH_2CMe_3]_2(\mu^2\text{-}Cl)_2Cl_2$ and $Pt[C(OPr^i)Me]_2Cl_2$ respectively, by the formation of vinylidene intermediates.[125,126]

Similarly complexes of the type *trans*-M[C(OR')CH$_2$R](C$_6$Cl$_5$)(PMe$_2$Ph)$_2$ (M = Ni, R = H, R' = Me, Et, Pr;[127] M = Pd; R = H, Ph; R' = Me[128]) have been isolated from reactions of *trans*-M(C$\equiv$CR)(C$_6$Cl$_5$)(PMe$_2$Ph)$_2$ with HC$\equiv$CR and R'OH.

Some cyclic alkoxycarbene complexes can be formed *via* vinylidene intermediates (Scheme 15).

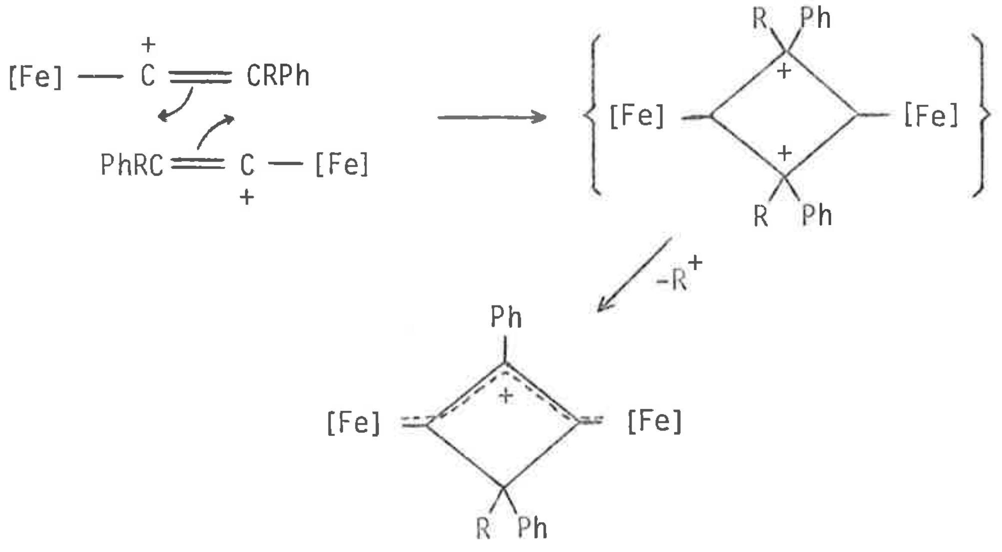
When Fe(C$\equiv$CPh)(CO)$_2$(η-C$_5$H$_5$) is reacted with HPF$_6$, in anhydrous methanol, Fe(COCH$_2$Ph)(CO)$_2$(η-C$_5$H$_5$) (61) was isolated, suggesting vinylidene and alkoxycarbene intermediates.[61] If the protonation was carried out in CH$_2$Cl$_2$[62] or acetic anhydride,[131] however, a binuclear product (93, R = H) is isolated. Similarly a reaction of [Fe(thf)(CO)$_2$(η-C$_5$H$_5$)]$^+$ with HC$\equiv$CPh gave (93, R = H),[62] suggesting cycloaddition of two vinylidene complexes has taken place:



Scheme 15. [M] = $Ni(C_6Cl_5)(PMe_2Ph)_2$; ref. 127

$Fe(CO)_2(\eta\text{-}C_5H_5)$; ref. 129

$PtIMe_2(CF_3)(PMe_2Ph)$; ref. 130

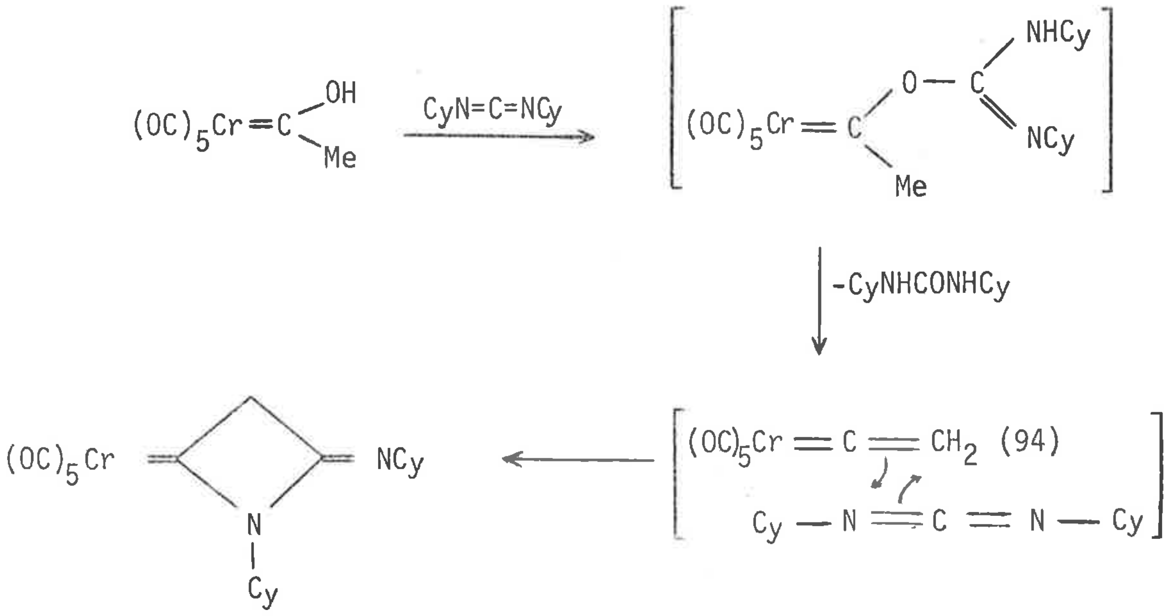


(93)

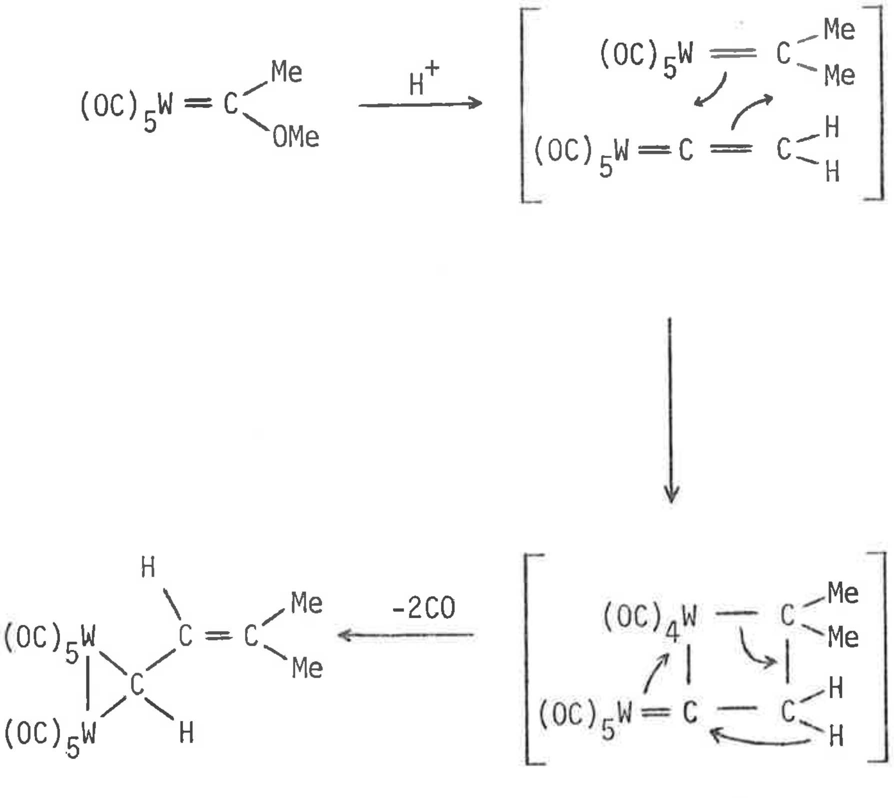
[Fe] = $Fe(CO)_2(\eta\text{-}C_5H_5)$; R = H,Me

Methylation of $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ also gave (93, R = Me).

Cycloaddition of the vinylidene intermediate $[Cr(C{=}CH_2)(CO)_5]$ (94) and CyN=C=NCy(Cy = cyclohexyl) is suggested in the reaction of $Cr[C(OH)Me](CO)_5$ with CyN=C=NCy:[132]



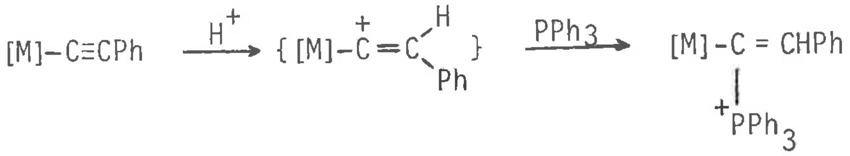
In a reaction proceeding like an olefin metathesis, W[C(Me)OMe](CO)$_5$ reacts with H$^+$ to give (95).[133] Mechanistic studies suggest the intermediacy of (96) (Scheme 16).



Scheme 16.

1.3.5.3 Addition to the α-carbon A reaction of Fe(C≡CMe)(CO)$_2$-(η-C$_5$H$_5$) (97) with anhydrous acetic acid gave Fe[C(OAc)=CHMe](CO)$_2$-(η-C$_5$H$_5$) (98).[118] Initially H$^+$ would attack the β-carbon of (97) forming [Fe(C=CHMe)(CO)$_2$(η-C$_5$H$_5$)]$^+$, giving (98) upon attack of OAc$^-$ at the α-carbon.

Phosphonium complexes (99,[125] 100, 101[134]) have been isolated from protonation reactions of some σ-acetylide complexes in the presence of PPh_3.



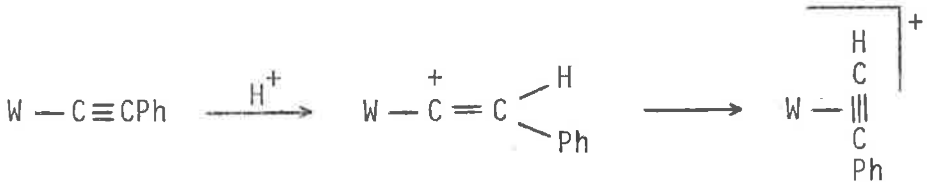
$$[M]\text{-}C{\equiv}CPh \xrightarrow{H^+} \{[M]\text{-}\overset{+}{C}{=}C(H)Ph\} \xrightarrow{PPh_3} [M]\text{-}C(\overset{+}{P}Ph_3){=}CHPh$$

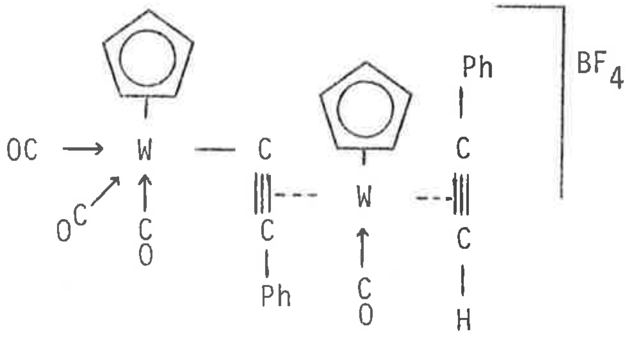
(99) $[M] = Fe(CO)_2(\eta\text{-}C_5H_5)$

(100) $[M] = Mo(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$

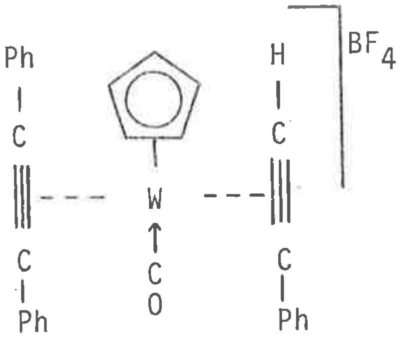
(101) $[M] = W(CO)_3(\eta\text{-}C_5H_5)$

1.3.5.4 1,2-Hydride shifts Protonation of $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ gave (102), while treatment with H^+/C_2Ph_2 gave (103).[135] The η^2-phenylacetylene can be formed *via* a vinylidene intermediate which undergoes a 1,2-hydride shift:



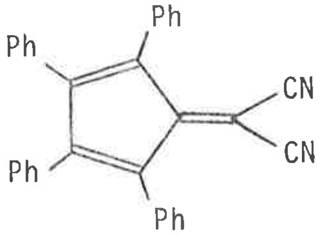


(102)



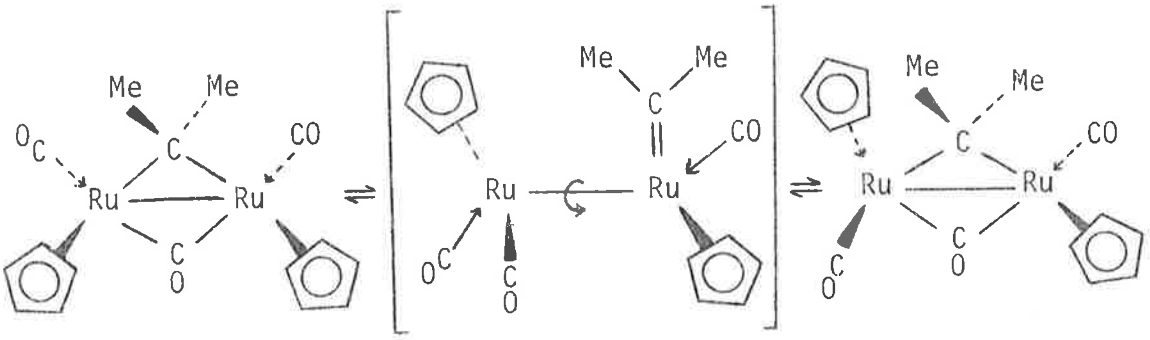
(103)

1.3.5.5 Displaced vinylidene ligands A minor product in the reaction of W[C(Cl)$=$C(CN)$_2$](CO)$_3$(η-C$_5$H$_5$) and PPh$_3$ is WCl(CO)$_2$(PPh$_3$)-(η-C$_5$H$_5$).[43] A vinylidene complex can be formed, from which the C$=$C(CN)$_2$ ligand is then lost. In a reaction of Mo[C(Cl)$=$C(CN)$_2$](CO)$_3$-(η-C$_5$H$_5$) and diphenyl acetylene the displaced vinylidene ligand has been trapped as (104).[38]



(104)

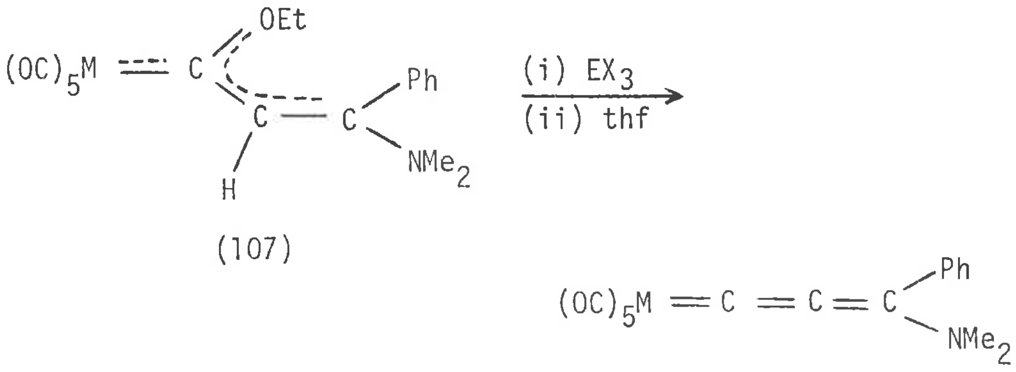
1.3.5.6 Cis/trans isomerisation intermediates Variable temperature n.m.r. studies of the *cis/trans* interconversion of (105) indicate that a pathway exists for carbene mobility. This implies that a terminal vinylidene intermediate (106) is formed[136] in an Adams-Cotton process.[136a]



(105) (106) (105)

1.3.6 *Allenylidene Complexes*

1.3.6.1 Mononuclear allenylidene complexes Upon treating the carbene complexes (107) sequentially with a Lewis acid and a weak base the allenylidene complexes (108) were isolated.[137]



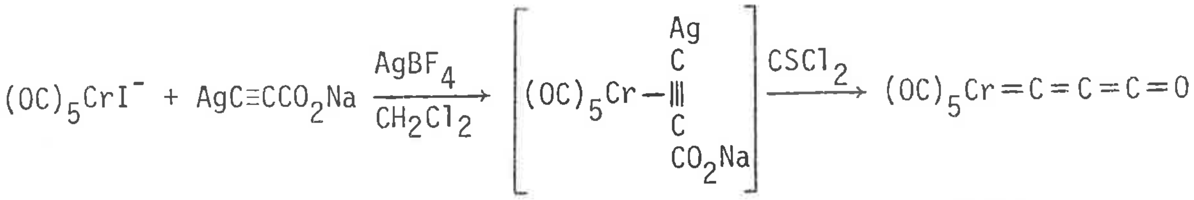
(107)

(108)

M = Cr; $EX_3 = BF_3$

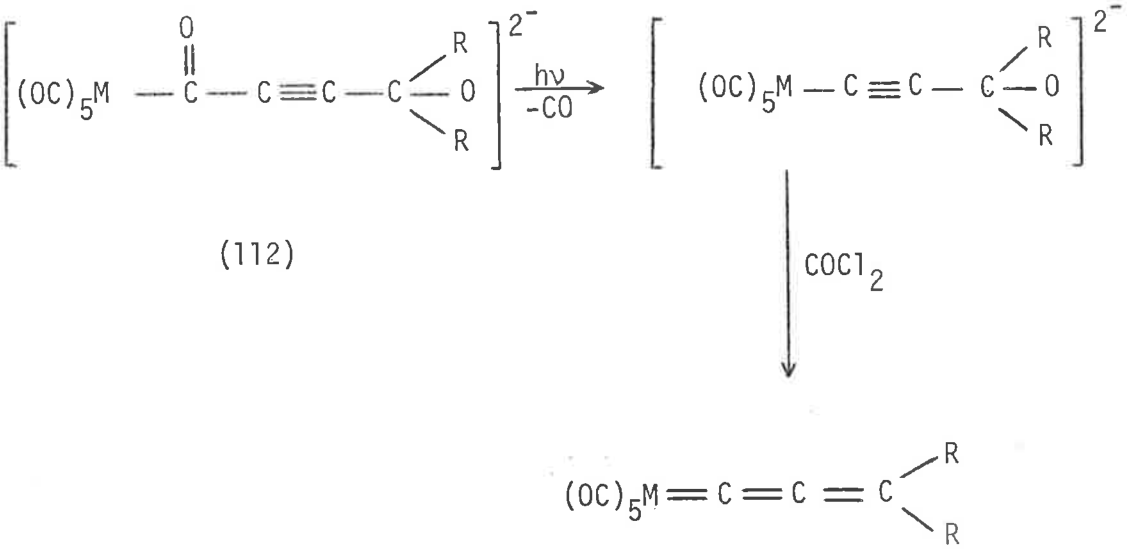
M = W; $EX_3 = AlEt_3$

An allenylidene complex (109), comprising four consecutive unsaturated bonds, has been formed from $[CrI(CO)_5]^-$ and $AgC{\equiv}CCO_2Na$ probably *via* the η^2-bonded alkyne intermediate (110):[138]



(110) (109)

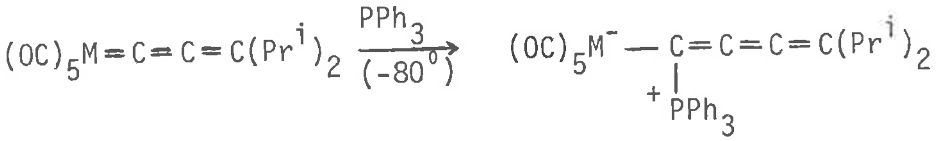
Oxidation of (109), followed by methanolysis, yields $CH_2(CO_2Me)_2$. Dialkylallenylidene complexes of chromium and tungsten (111) have been formed in photochemical reactions of (112):[56]



(112)

M = Cr,W; R = Pr^i,Bu^t. (111)

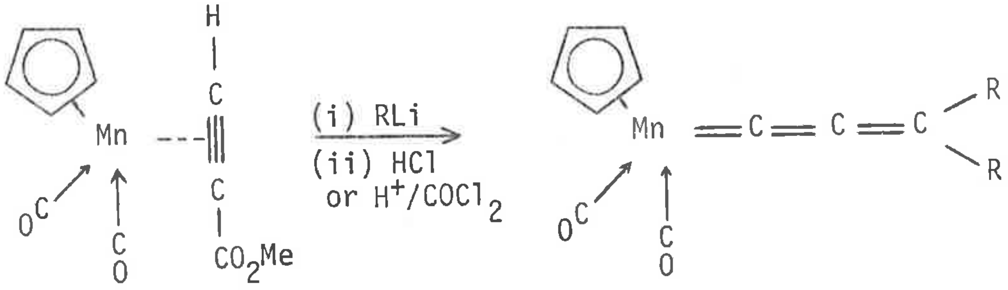
The isopropyl complexes were isolated as triphenyl phosphorane derivatives (113).



$$(OC)_5M{=}C{=}C{=}C(Pr^i)_2 \xrightarrow[(-80^0)]{PPh_3} (OC)_5M^-{-}\underset{{}^+PPh_3}{\underset{|}{C}}{=}C{=}C{=}C(Pr^i)_2$$

(111) M = Cr, W (113)

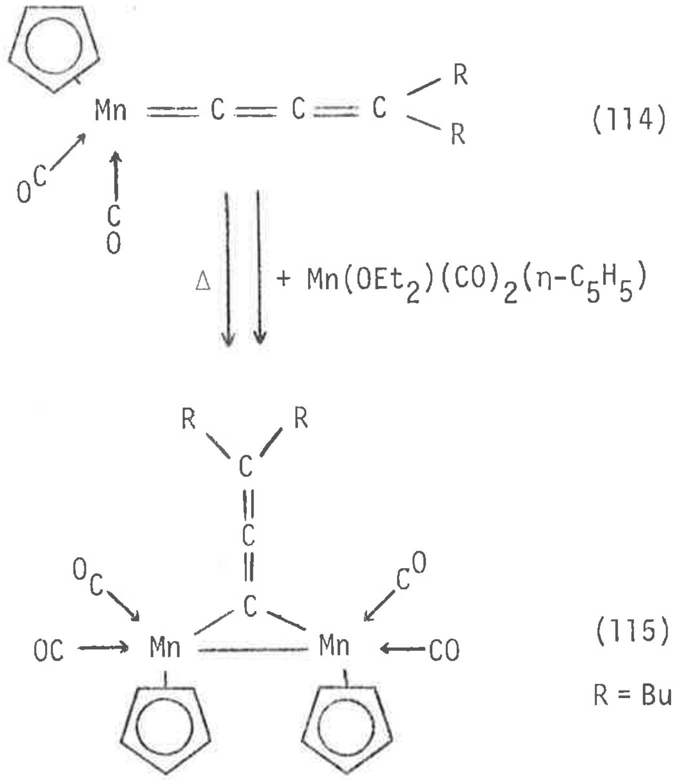
A number of dialkyl and diarylallenylidene complexes (114) have been formed by treating $Mn(\eta^2\text{-}C_2HCO_2Me)(CO)_2(\eta\text{-}C_5H_5)$ (30) with RLi followed by neutralisation:[60,139,142]



(30) (114)

R = Bu^t, Cy, CH_2Ph, Ph.

1.3.6.2 Binuclear allenylidene complexes. Some binuclear manganese complexes have been formed from mononuclear allenylidene complexes by either (i) heating the solids at their melting points under an inert atmosphere,[60,139] or (ii) treating them with $Mn(OEt_2)(CO)_2(\eta\text{-}C_5H_5)$.[141]



(114)

(115)

R = Bu^t, Cy, CH_2Ph, Ph.

1. 3. 7 *Physical Data*

The structural and spectroscopic data available for vinylidene and allenylidene complexes allows characterisation of these systems, and a greater understanding of their properties. The following discussion considers bond lengths and angles (1.3.7.1), infrared and Raman spectra (1.3.7.2) and n.m.r. spectra (1.3.7.3).

1.3.7.1 Bond lengths and angles The C=C bond lengths in mononuclear and binuclear vinylidene complexes range from 1·29 - 1·38 Å. In cluster complexes a general lengthening (1·38 - 1·44 Å) reflects a decreased bond order due to metal-olefin π-bonding. The allenylidene ligand of $Cr[C^1=C^2=C^3(NMe_2)Ph](CO)_5$ (108) has a short C(1)-C(2) length (1·24 Å) and a normal length for C(2)-C(3) (1·37 Å).[137]

The M-C bond lengths in mononuclear and binuclear vinylidene complexes range from 1·8 - 2·0 Å, while those in cluster complexes are sometimes longer (1·8 - 2·2 Å). In $Mn(C=CHPh)(CO)_2(\eta\text{-}C_5H_5)$ (17) a short Mn-C bond-length is observed (1·68 Å). This is also shorter than comparable manganese σ (2·16 Å) and carbene (1·88 Å) bond lengths,[49] presumably as a result of the good π-acceptor characteristics of the vinylidene ligand.

The M=C=C bond angle in mononuclear complexes ranges from linear to 167°. This variation is attributed to electronic rather than steric factors.[44] In some binuclear vinylidene complexes the olefin is observed to twist with respect to the plane of the metals [e.g. 14° in $Fe_2(\mu^2\text{-}C=CPh_2)(CO)_8$ (59)[41] and 11° in $Mn_2(\mu^2\text{-}C=CH_2)(CO)_4(\eta\text{-}C_5H_5)_2$ (58)[75]]. This can be attributed to π-orbital overlap between the α-carbon and the metal.[75]

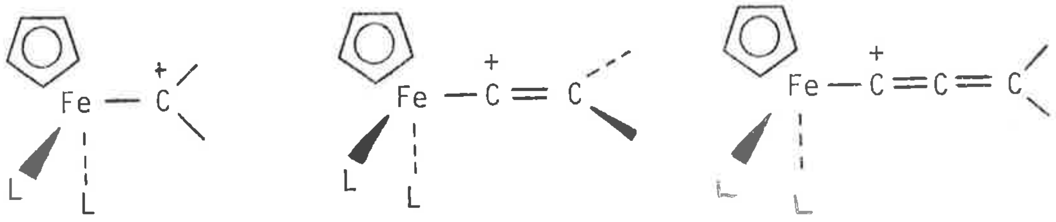
1.3.7.2 Infrared and Raman spectra The infrared absorption for the olefinic bond typically appears between 1590 and 1660 cm^{-1}, with some notable exceptions [e.g. 1749 (22, R = H) and 1480 cm^{-1} (60)[79]]. The allenylidene complexes $Mn(C=C=CR_2)(CO)_2(\eta\text{-}C_5H_5)$ (83, R = Bu^t, Cy, CH_2-Ph, Ph) have ν(C=C=C) absorptions between 1862 and 1887 cm^{-1}.[141]

Raman lines have been recorded for $Mn(C=CHPh)(CO)[P(OPh)_3](\eta\text{-}C_5H_5)$ (84)[40] and $Re(C=CHPh)(CO)_2(\eta\text{-}C_5H_5)$ (19)[50] at 1590 and 1594 cm^{-1} respectively. Exposure of $Mn(C=CHPh)(CO)_2(\eta\text{-}C_5H_5)$ (17) and $Mn_2(\mu^2\text{-}C=CHPh)(CO)_4(\eta\text{-}C_5H_5)_2$ (58) to the laser beam leads to decomposition.[40]

1.3.7.3 NMR spectra In the ^{13}C n.m.r. spectrum of mononuclear vinylidene complexes the α-carbon usually resonates between δ320 and 380 ppm, reflecting the extreme electron deficiency of the system. The β-carbon typically appears between δ118 and 142 p.p.m. The α-carbons of $Ru_2(\mu^2\text{-}C=CH_2)(\mu^2\text{-}X)(CO)_2(\eta\text{-}C_5H_5)$ (67, X = CMe_2),[83] (66, X = CO),[84] and

$Mn_2(\mu^2\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)$ (58)[40] resonate at δ244·5, 249·1 and 329·5 p.p.m respectively. The C(1) and C(3) carbons of $Cr(C^1{=}C^2{=}C^3{=}O)(CO)_5$ (109) are extremely electron deficient and appear at δ440·6 and 389·9 p.p.m. respectively. These values differ markedly from those of C(1), C(2) and C(3) in $Mn(C^1{=}C^2{=}C^3\ Bu^t_2)(CO)_2(\eta\text{-}C_5H_5)$ (81) which resonate at δ331.2, 213·6 and 167·5 p.p.m. respectively.[139]

The ^1H n.m.r. spectra of $[Fe(C{=}CR_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (54, R = H or Me) show singlets due to methylene (R = H, δ5·30) and methyl (R = Me, δ1·66) protons, apart from C_5H_5 and phenyl resonances.[68] This indicates that fast rotation is taking place. Theoretical calculations for iron carbene, vinylidene and allenylidene complexes should have the preferred orientations shown below as a result of M-C π-bonding:[142]



The calculated energy barrier for $[Fe(C{=}CH_2)(CO)_2(\eta\text{-}C_5H_5)]^+$ is only 3·6 kcal mol^{-1}, thus allowing fast rotation. The plane of the CBu^t_2 group in $Mn(C{=}C{=}CBu^t_2)(CO)_2(\eta\text{-}C_5H_5)$ (114) should coincide with the symmetry plane of the molecule, but a singlet at δ1·33 would imply fast rotation[139] (calculated barrier = 3·2 kcal mol^{-1}[142]).

A singlet at δ5·21 in the ^{1}H n.m.r. spectrum of $[Co(\mu^3\text{-}C{=}CH_2)(CO)_9]^+$ (72) indicates that the CH_2 protons are equivalent,[91] implying fast rotation, and thus lending support for a symmetric structure.[92]

Exchange of the vinylidene protons in $H_2M_3(\mu^3\text{-}C{=}CH_2)(CO)_9$ (M = Ru or Os) is observed in n.m.r. experiments, in a process probably involving exchange of the metal bonded hydrogens.[94,143]

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CHAPTER TWO

SOME CHEMISTRY OF VINYLIDENE COMPLEXES

2.1 INTRODUCTION

This chapter describes the reactions of some ruthenium and osmium vinylidene complexes[1] with alcohols, water and dioxygen. Reaction conditions and times were correlated with electronic and steric changes in the complexes.

The α-carbon of the vinylidene moiety is highly electron deficient (as confirmed by ^{13}C n.m.r. spectroscopy, Section 1.3.7.3) and consequently should be very susceptible to nucleophilic attack. Nucleophiles, though, are often bases, preferentially removing the β-proton with consequent formation of σ-acetylide complexes.

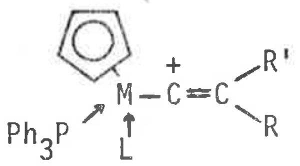
The formation of alkoxy(alkyl)carbene complexes, by the addition of alcohols to the olefinic bond of non-isolated vinylidene intermediates has been extensively explored (Section 1.3.5.2). It has been possible to verify these reactions and to further investigate the reactions of the olefinic bond of some stable vinylidene complexes. As this work progressed similar vinylidene complexes were reported in the literature.[2]

The alkoxy(alkyl)carbene complexes, formed in reactions of vinylidene complexes and alcohols, were deprotonated to alkoxyvinyl complexes. The work involving the oxidation of vinylidene complexes has been explored jointly with Wallis,[3] and that involving cyclic carbene ligands with Thomson and Wallis.[4] Only the author's own work is described in the Experimental section. Much of this work has been reported elsewhere.[5,6]

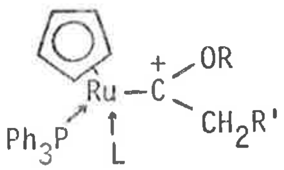
2.2 RESULTS

A series of vinylidene complexes of ruthenium can be prepared and isolated from reactions between appropriate alk-1-ynes, $RuCl(PPh_3)_2(\eta-C_5H_5)$ and NH_4PF_6 in methanol.[1] However these complexes react further with methanol on prolonged heating. Thus, heating a solution of

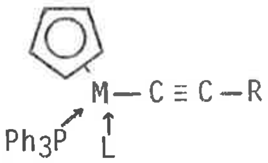
$[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1) in refluxing methanol for 24 h results in a change in colour from the red-purple of the vinylidene complex to yellow. This yellow product may be isolated in high yield in crystalline form, and was characterized as the cationic carbene complex, $\{Ru[C(OMe)\text{-}CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2), formally resulting from addition of methanol across the vinylidene ligand. The complex was formulated on the basis of analytical results (see Experimental section) and its spectroscopic properties. In the infrared, the characteristic band at *c.* 1640 cm^{-1} assigned to the $\nu(CC)$ vibration of the :C=CHPh ligand was absent, while a new band at *c.* 1280 cm^{-1} can be assigned to the $\nu(CO)$ of the C-OMe ligand. The presence of a carbene ligand was further confirmed by the low-field triplet of the metal-bonded carbon, found at δ308.7 in the ^{13}C n.m.r. spectrum.



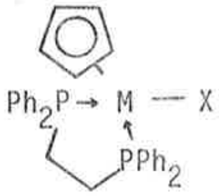
	M	L	R	R'
(1)	Ru	PPh_3	Ph	H
(22)	Ru	PPh_3	Bu^t	H
(23)	Os	PPh_3	Ph	H
(25)	Ru	CO	Ph	H
(14)	Ru	PPh_3	Ph	Me



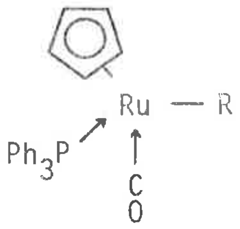
	L	R	R'
(2)	PPh_3	Me	Ph
(15)	CO	Me	Ph
(16)	$CNBu^t$	Me	Ph
(17)	PMe_3	Me	Ph
(18)	$P(OMe)_3$	Me	Ph
(20)	PPh_3	Me	Me
(21)	PPh_3	Me	CO_2Me
(26)	CO	Et	Ph
(27)	CO	Pr^i	Ph



	M	L	R
(3)	Ru	CO	Ph
(4)	Ru	$CNBu^t$	Ph
(5)	Ru	PMe_3	Ph
(6)	Ru	$P(OMe)_3$	Ph
(9)	Ru	PPh_3	Ph
(10)	Os	PPh_3	Ph
(11)	Ru	PPh_3	CO_2Me
(12)	Ru	PPh_3	Me
(13)	Ru	PPh_3	Bu^t
(45)	Ru	PPh_3	COMe



	M	X
(7)	Ru	C ≡ CPh
(8)	Os	C ≡ CPh
(19)	Ru	$^+C(OMe)CH_2Ph$
(24)	Os	$^+C = CHPh$



(28) $R = CH_2Ph$

(29) $R = COCH_2Ph$

Several complexes similar to (2) can be obtained by analogous reactions. A brief examination of the effect of changes in associated ligands, alkyne substituent, and the metal atom, on the reactivity of the vinylidene complexes towards alcohols has been made. These reactions were facilitated by the observation that when the vinylidene complex was formed *in situ* by addition of HPF_6,OEt_2 to an alcoholic solution or suspension of selected σ-acetylides, the reaction times and products were the same as those of the isolated vinylidene complex. This modification was particularly useful when the reaction between the vinylidene complex and the alcohol was fast.

Accordingly several complexes of the types $Ru(C_2Ph)(L)(PPh_3)(\eta-C_5H_5)$ [L = CO (3), $CNBu^t$ (4), PMe_3 (5) or $P(OMe)_3$ (6)] and $M(C_2Ph)(dppe)(\eta-C_5H_5)$ [M = Ru (7) or Os (8)] have been prepared from reactions between $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (9) or $Os(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (10) and the appropriate ligand, have been prepared (Chapter 4). These complexes are obtained in high yield, and are generally more easily handled than the corresponding vinylidene complexes. A study has also been made of some reactions of $Ru(C_2R)$-$(PPh_3)_2(\eta-C_5H_5)$ [R = CO_2Me (11), Me (12), or Bu^t (13)].

The disubstituted vinylidene $[Ru(C_2MePh)(PPh_3)_2(\eta-C_5H_5)]^+$ (14) was also studied.

2.2.1 *Reactions with Methanol*

The σ-acetylides (4)-(7) reacted with HPF_6,OEt_2 in methanol immediately to give red-purple solutions containing the vinylidene complexes. Further reaction with the alcohol proceeded over a time-scale ranging from minutes to days, to give the corresponding methoxy(benzyl)carbene complexes (16)-(19).* These derivatives were isolated and characterized by analytical and spectroscopic methods, most containing ν(CO) bands at *c.* 1260 cm^{-1} for the C-OMe group, together with

* While no intermediate was observed in the reaction of $Ru(C_2Ph)(CO)(PPh_3)$-$(\eta-C_5H_5)$ (3) with HPF_6, OEt_2 in methanol, the isolated product is $\{Ru[C(OMe)CH_2Ph](CO)(PPh_3)(\eta-C_5H_5)\}PF_6$ (15).

appropriate ν(CO) (15), ν(CN) (16) or ν(PO) (18) bands. In some cases, the PF_6 anion was partially hydrolysed, and the isolated salt was found to contain the PO_2F_2 anion, characterized by broad ν(PO) and ν(PF) absorptions at *c.* 1040 and 840 cm^{-1} respectively.[7] In the ^1H n.m.r. spectra, the methoxy protons of the carbene ligand appeared as a sharp singlet in each case. The CH_2 protons of the benzyl group in complexes (15)-(18) appeared as an AB quartet, as the result of the chiral metal atom (pseudo-tetrahedral coordination with four different ligands). The separation of the two doublets increases from 3 Hz (16) to 25 Hz (18). The CH_2 protons resonate as a singlet in complexes (2) and (19). Other resonances in the ^1H n.m.r. spectra were consistent with the other ligands present.

The propyne and methyl propiolate derivatives, $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ [R = Me (12) or CO_2Me (11)], also reacted with methanol in the presence of HPF_6 to give the corresponding carbene complexes (20) and (21) respectively. As expected, the ^1H n.m.r. spectrum of (18) contained a set of ethyl resonances, while the $C(OMe)CH_2CO_2Me$ group in (21) was characterized by the ν(CO) absorption at 1742 cm^{-1}, and OMe resonances at δ3·47 and 3·78.

Methoxycarbene complexes were not obtained in all instances; the methyl phenyl complex, the t-butyl derivative and both osmium complexes being recovered as the corresponding vinylidene complexes (14), (22), (23) and (24), after prolonged (>24 h) heating in refluxing methanol.

2.2.2 *Reactions with Other Alcohols*

Initial studies of the reactions of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ with alcohols showed that, while a slow reaction occurred with methanol, ethanol and higher alcohols did not react with this complex. The higher reactivity found with the monocarbonyl derivative, however, suggested possible reactions between $[Ru(C{=}CHPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ (25) and other alcohols.

The reaction between (25) and ethanol was slower than that with methanol, but after 1 h at room temperature, the ethoxy(benzyl)carbene complex (26) was isolated in moderate yield. The identity of this complex was confirmed by analysis, and appropriate ethyl and benzyl resonances in the ^1H n.m.r. spectrum. In this case, the benzyl CH_2 resonance was also an AB quartet, but overlapped with the CH_2 multiplet from the OEt group. Similarly, the reaction between (25) and isopropyl alcohol at room temperature, afforded a white cationic complex, readily identified as the isopropoxy(benzyl)carbene complex (27).

2.2.3 Reactions with Water

The reaction between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and aqueous HBF_4 afforded a neutral yellow complex (28). The infrared spectrum contained a single $\nu(CO)$ band at 1917 cm^{-1}, and the ^1H n.m.r. spectrum contained resonances assigned to C_5H_5, PPh_3 and CH_2Ph groups; only one PPh_3 ligand was present, however. These data are consistent with the formulation of complex (28) as $Ru(CH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$, and this was confirmed by the mass spectrum.

The product obtained from aqueous HPF_6 and the monocarbonyl complex $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ gave an infrared spectrum containing a strong $\nu(CO)$ band at 1929 cm^{-1}, and a broad band at *c.* 1600 cm^{-1}. The ^1H n.m.r. spectrum contained resonances assigned to C_5H_5, Ph and CH_2Ph groups, while the mass spectrum contained a molecular ion centred on *m/e* 576, and daughter ions formed by loss of CO and/or CH_2Ph groups. The product is thus identified as the phenylacetyl complex $Ru(COCH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (29). The same complex was also isolated from a prolonged reaction between

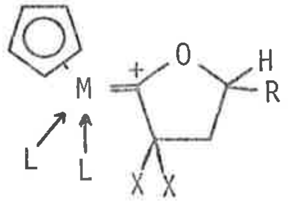
$[Ru(C{=}CHPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ and isopropyl alcohol. Further heating with aqueous acid afforded the known[8] dicarbonyl cation $[Ru(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ (30) [ν(CO) 2078, 2028 cm^{-1}]; the fate of the organic radical was not determined.

2.2.4 *Reactions of ω-Hydroxyalk-1-ynes*

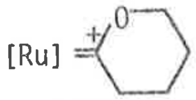
When $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and but-3-yn-1-ol are heated together in the presence of NH_4PF_6, a yellow crystalline material precipitates, and can be isolated in high yield. This compound was characterized as the 2-oxacyclopentylidene complex (31) on the basis of elemental analysis and its spectroscopic properties. In particular, the absence of any ν(OH) and ν(C≡C) bands showed it was not an acetylide, such as $Ru(C_2CH_2CH_2OH)(PPh_3)_2(\eta\text{-}C_5H_5)$, while strong ν(PF) bands confirmed the presence of the hexafluorophosphate anion. The ^1H and ^{13}C n.m.r. spectra contained the usual resonances arising from the C_5H_5 and PPh_3 ligands, together with several signals which can be assigned to the cyclic carbene ligand. In particular, the ^1H n.m.r. spectrum contained well resolved multiplets assigned to a $CH_2CH_2CH_2$ group, while the carbenic nature of the metal-bonded carbon is shown by its very low ^{13}C chemical shift of *c*. 300 ppm. The latter signal is a triplet, by coupling to the two ^{31}P nuclei. The particular assignments of the observed signals are discussed in detail below.

Reactions between $HC_2CH_2CH_2OH$ and $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ or $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ afforded the analogous complexes (32) and (33), while the related ω-hydroxy-alk-1-ynes $HC_2CH_2CHMeOH$ and $HC_2(CH_2)_3OH$ reacted with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ under similar conditions to give complexes (34) and (35), respectively. The ^1H n.m.r. spectra of (32) and (33) were similar to that of complex (31), except that the characteristic PMe_3 resonances replaced those of PPh_3 in complex (32). All these complexes are yellow crystalline solids, stable in air, and soluble in the more polar organic solvents. Complex (34) was prepared to assist with the interpretation of the n.m.r. spectra; complex (35) contains a six-membered cyclic carbene, the 2-oxacyclohexylidene ligand. It was also fully characterized by elemental analysis, and its n.m.r. spectra contained the anticipated extra CH_2 resonance.

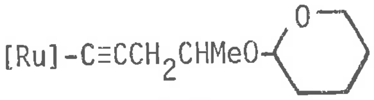
In an attempt to isolate intermediate complexes, the reaction of the tetrahydropyranyl (thp) ether of $HC_2CH_2CHMeOH$ with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ was investigated. In the presence of NH_4PF_6, a methanol solution of the reactants developed a red-purple colour, characteristic of the cationic vinylidene complexes reported earlier.[1] Addition of sodium methoxide resulted in the separation of yellow crystals of the neutral acetylide complex $Ru[C_2CH_2CHMeO(thp)](PPh_3)_2(\eta\text{-}C_5H_5)$ (36), readily identified by elemental analysis and from its mass and n.m.r. spectra (see Experimental).



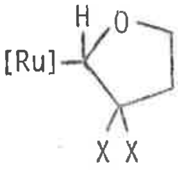
	M	L	X	R
(31)	Ru	PPh_3	H	H
(32)	Ru	PMe_3	H	H
(33)	Os	PPh_3	H	H
(34)	Ru	PPh_3	H	Me
(38)	Ru	PPh_3	D	H
(39)	Ru	PPh_3	D	Me
(40)	Ru	PPh_3	Me	H



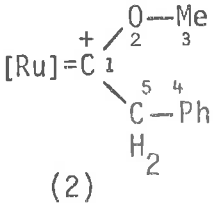
(35)



(36)



(37A) X=H
(37B) X=D



(2)

$[Ru] = Ru(PPh_3)_2(\eta\text{-}C_5H_5)$

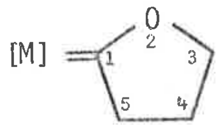
By addition of acid, it was hoped to detect either the vinylidene complex corresponding to (36), or a related intermediate formed by loss of the thp group. In the event, the only product detected or isolated was the cyclic carbene derivative (34).

Reaction of complex (31) with $NaAlH_2(OCH_2CH_2OMe)_2$ afforded a neutral complex shown to be the tetrahydrofuryl derivative (37). This is the product expected to be formed by addition of hydride to the carbene in cation (31); the use of other reducing agents, such as $NaBH_4$ or $LiAlH_4$, did not give any tractable products, probably because of further reaction of the tetrahydrofuryl complex, resulting in cleavage of the organic group from the metal. Complex (37) is very air-sensitive in solution; it shows the higher reactivity expected for a secondary alkyl-metal complex. The spectral parameters are in accord with its formulation, with the appearance of a molecular ion in the mass spectrum. The ^1H n.m.r. spectrum is complex, as expected with a seven-spin system, part of which is also coupled to the ^{31}P nuclei. In the ^{13}C n.m.r. spectrum, the resonance of the metal-bonded carbon is found at 148·7 ppm as the expected triplet [J(CP) 18 Hz].

During attempts to assign the ^1H resonances to specific CH_2 groups in complex (31), the base-catalysed H-D exchange was studied. This occurred readily and specifically on warming a pyridine solution of (31) with D_2O; one of the CH_2 multiplets then disappeared, with concomitant reduction in multiplicity of the other CH_2 resonances, with that at δ1·78 being broadened by the deuterium quadrupole. The ^{13}C n.m.r. spectrum showed that it was the protons attached to C5 which had been exchanged for deuterium to form (38). The site of exchange was finally confirmed by deuteration of the methyl-substituted complex (34), to give (39), in which the CHMe resonances remain unchanged, while the resonances assigned to the methylene group adjacent to the carbene carbon disappear.

The acidity of the two hydrogens attached to C(5) suggested that it should be possible to metallate the carbene ligand in (31); subsequent reaction with, for example, an alkyl halide would enable further examples of these complexes to be obtained. This expectation was realized by treatment of complex (31) with base ($LiBu^n$ or NaOH), followed by iodomethane; the dimethyl complex (40) was then obtained. Characterization of this complex by ^1H and ^{13}C n.m.r. spectroscopy included the observation of resonances at δ1·40 (^1H) and 26·9 ppm (^{13}C) for the equivalent methyl groups, and the reduced multiplicity [compared with (31)] of one of the two remaining CH_2 resonances. The metal-bonded carbene carbon resonated at 310·8 ppm, and again was coupled to the two ^{31}P nuclei.

In complexes (31), (32) and (33), the protons of the carbene ligand (A) give rise to an apparently first-order pattern of two triplets and a quintet. The latter, found in (31) at δ1·77, is readily assigned to the protons attached to C(4), coupled to the two methylene groups at C(3) and C(5). This is confirmed by double irradiation experiments. Assignment of the two triplets, at δ3·74 and 3·93, is ambiguous. The ^{13}C n.m.r. of these complexes show four signals, at δ22·6, 60·8, 81·6 and 300·5. The latter is readily assigned to C(1) on the basis of its large low-field shift, characteristic of an electron-deficient carbene carbon, and the triplet fine structure, arising from coupling to the two equivalent ^{31}P nuclei.



(A)

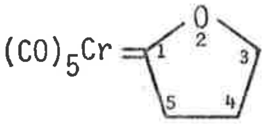
The methyl-substituted complex (34) contains, in addition to the methyl doublet at δ0·85, multiplets at 1·40, 2·06, 3·40 and 4·07. Double irradiation experiments show that the single proton attached to C(3) also resonates at δ4·07. The presence of the methyl group causes the protons of each of the two methylene groups C(4) and C(5) to become inequivalent, giving rise to two pairs of multiplets in a complex ABB'CC' pattern. The ^{13}C resonances for the four ring carbons are found at δ30·1, 61·7, 92·4 and 299·4, the latter again being assigned to C(1). The signal at δ92·4 can be assigned to C(3) on the basis of an off-resonance experiment.

The ^{1}H n.m.r. spectrum of the deuterated complex (38), obtained by H-D exchange with (31), lacks the triplet at δ3·70, while the quintet at 1·89 is replaced by a triplet at 1·78. Of the ^{13}C resonances, that at δ60·8 is broadened and reduced in intensity by interaction with the deuterium quadrupole. With (39), H-D exchange leads to reduction in intensity of the signal at δ4·07, now arising solely from the proton on C(3) and disappearance of the broad multiplet at 3·40; the multiplet at 2·06 changes to a doublet of doublets [one half of an AB quartet coupled to H(3)]. In this case, the ^{13}C resonance at δ61·7 in (34) could not be detected, presumably as a result of broadening by the attached deuterium atoms.

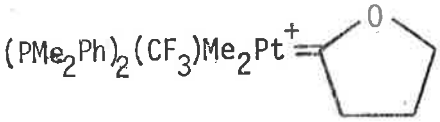
The ^{1}H n.m.r. spectrum of the methylated complex (40) shows the two methyl groups to be equivalent, and the other cyclic carbene protons resonate at δ1·29 and 3·77. The ^{13}C resonance at δ67·0 is readily assigned to the carbon bearing the two methyl groups, and that at 310·8 to C(1); the other carbons resonated at 38·1 and 79·5. In a related complex, $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2), the methyl, benzylic and carbene carbons resonate at δ 62·8, 63·4 and 308·7, respectively.

Table 1. N.m.r. parameters for carbene ligands

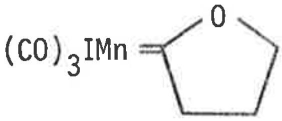
Data for compounds (i)-(iv) from the literature are included for comparison



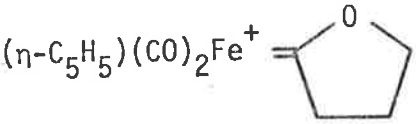
(i)



(ii)



(iii)



(iv)

Complex	Nucleus	C(1)	C(3)	C(4)	C(5)	Me
(31)	^{1}H	-	3·93 t	1·77 q	3·74 t	-
	^{13}C	300·5	81·6	22·6	60·8	-
(34)	^{1}H	-	4·07 m	1:40, 2:06 m	3·40, 4·07 m	0·85 d
	^{13}C	299·4	92·4	30·1	61·7	19·0
(40)	^{1}H	-	3·77 t	1·29 t	-	1·40 s
	^{13}C	310·8	79·5	38·1	67·0	26·9
(2)	^{1}H	-	3·41 s	-	4·95 s	
	^{13}C	308·7	62·8	-	63·4	
(i)^{A}	^{1}H		3:7 t	2·0 q	5·0 t	
(ii)^{B}	^{1}H		4·63 t	0·88 q	2·16 t	
(iii)^{C}	^{1}H		5·11 t	2·00 q	4·20 t	
(iv)^{C}	^{1}H		5·61 t	2·16 q	3·99 t	

A, Ref.9; B, Ref.10; C, Ref.11.

Table 1 summarizes the various assignments which are possible. Assuming that the ring carbon which is methylated in (40) is the same one which undergoes H-D exchange in (31) and (34), that carbon is shown to be C(5) on the basis of the following evidence: (1) complex (34) exchanges *two* hydrogens, and the proton on C(3) does not exchange; (ii) in the D-exchanged complex (39), the protons on C(4) are coupled to one proton, on C(3); (iii) coupling of protons on non-adjacent carbons is not observed.

2.2.5 *Deprotonation of Alkoxy(alkyl)carbene Complexes*

Upon reaction of $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2) with a sodium methoxide solution at room temperature, the methoxyvinyl complex, $Ru[C(OMe){=}CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ (41), precipitated over a few minutes. The yellow powder is stable as a dry solid for only a few days, and decomposes in $CDCl_3$ or CS_2. In the ^1H n.m.r. spectrum a singlet at δ6·03 shows that only one β-proton is present. Other singlets at δ3·37 and 4·52 are assigned to methyl and cyclopentadienyl groups respectively, while a multiplet between 7·0 and 7·5 is assigned to phenyl groups. In the ^{13}C n.m.r. the α-carbon is not observed in the carbene region, but as a triplet at δ193·1. Other singlets at δ59·1, 84·6 and 86·2 are assigned to methyl, β-carbon and cyclopentadienyl groups respectively. The infrared spectrum shows a strong olefinic absorption between 1541 and 1592 cm^{-1}, and a weak CO absorption at 1251 cm^{-1}. The absence of a $\nu(PF_6)$ bond at *c*. 840 cm^{-1} suggests a neutral complex, further confirmed by its high solubility in non-polar solvents. The complex did not give a molecular ion in the mass spectrum, but a peak at *m/e* 793 was observed, corresponding to loss of methoxide from the molecular ion.

Protonation of $Ru[C(OMe){=}CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ (41) with HPF_6,-OEt_2 in an n.m.r. tube produced an immediate change from the spectrum of (41) to the spectrum of $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2).

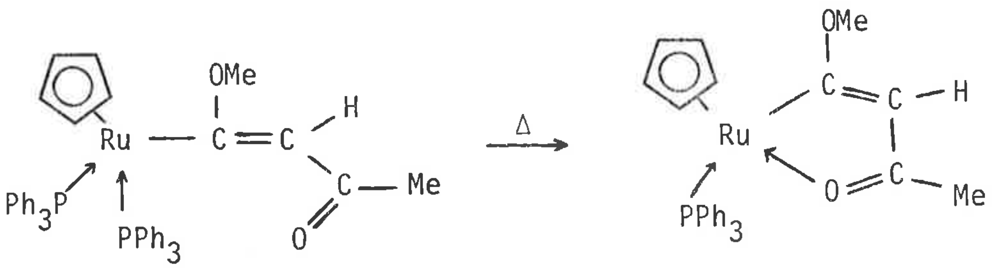
Deprotonation of $\{Ru[C(OMe)Et](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (20) gave a very unstable yellow powder (42). The infrared spectrum of (42) was almost identical to that of $Ru[C(OMe)=CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ (41), indicating that an alkoxyvinyl complex $Ru[C(OMe)=CHMe](PPh_3)_2(\eta\text{-}C_5H_5)$ (42), formed. The complex was too sensitive to be identified by other methods tried.

Deprotonation of $\{Ru[C(OEt)CH_2Ph](CO)(PPh_3)(\eta\text{-}C_5H_5)\}PF_6$ (26), gave a yellow product (43). The mass spectral, infrared and microanalytical data for (43) are consistent with the formation of a vinyl complex $Ru[C(OEt)=CHPh](CO)(PPh_3)(\eta\text{-}C_5H_5)$. In the ^1H n.m.r. spectrum, however, three C_5H_5 resonances appear, implying the presence of three isomers. Chromatographic separation by Humphrey[12] led to transformations on the adsorbent.

A reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with $HC{\equiv}CCOMe$ and NH_4PF_6 in methanol gave an orange solution, which on treatment with NaOMe produced yellow crystals. Chromatographic separation gave the cyclic vinyl complex, $\overline{Ru[C(OMe)=CHCOMe}](PPh_3)_2(\eta\text{-}C_5H_5)$ (44), and the acetylide complex, $Ru(C{\equiv}CCOMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (45). The vinyl complex (44) was best identified by its ^{13}C n.m.r. spectrum which contains singlets at δ23·0, 59·4 78·7 and 112·5 due to methyl, methoxy, and cyclopentadienyl groups and the β-carbon respectively. The α-carbon appears as a doublet at δ271·6, with a phosphorus coupling of 14 Hz. In the ^1H n.m.r. spectrum resonances at δ1·75, 3·60, 4·57, 5·85, and 7·2-7·7 were assigned to methyl, methoxy, cyclopentadienyl, β-carbon and phenyl protons respectively. A molecular ion at *m/e* 528 in the mass spectrum, in addition to microanalytical data, further indicated the formation of (44). The infrared spectrum shows a strong absorption at 1308 cm^{-1}, which is assigned to ν(CO). The bond order appears to be greatly reduced as a result of oxygen bonding to the metal.

The acetylide complex (45) was identified by very strong absorptions at 2048, 2011 and 1602 cm^{-1} in the infrared region, which are assigned to acetylide, carbonyl and acyl groups respectively. The ^1H n.m.r. spectrum shows resonances at δ1·98, 4·39 and 7·4, assigned to methyl, cyclopentadienyl and phenyl groups respectively, while the mass spectrum contains a molecular ion at *m/e* 758.

The mixture from which (44) and (45) were separated was shown by ^1H n.m.r. to contain resonances due to (45) and $Ru[C(OMe){=}CHCOMe](PPh_3)_2(\eta\text{-}C_5H_5)$ (46) (ratio = 5:3). After standing for 48 h at 35° the



(46) (44)

resonances at δ1·95, 3·02, 4·32, 6·06, and 7·4, assigned to the methyl, methoxy, cyclopentadienyl, β-carbon, and phenyl protons of (46), respectively, disappeared with concomitant formation of the peaks of (44). The spectrum of (45) remained unchanged, although a sharp peak appeared at δ7·32 due to free PPh_3.

Attempts to deprotonate $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ (31) with NaOMe or NEt_3 were unsuccessful.

2.2.6 *Reaction with Dioxygen*

A solution of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1) in dichloromethane readily reacts with dioxygen or hydrogen peroxide to give $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (47) and benzaldehyde. Complex (47) was identified by its characteristic[13] infrared [ν(CO) 1987 cm^{-1}, $CHCl_3$] and n.m.r. spectra. The presence of benzaldehyde in petroleum extracts was confirmed by comparative thin layer chromatrography, and the formation of a 2,4-dinitrophenylhydrazone derivative.

2.3 DISCUSSION

2.3.1 *Reactions with Alcohols*

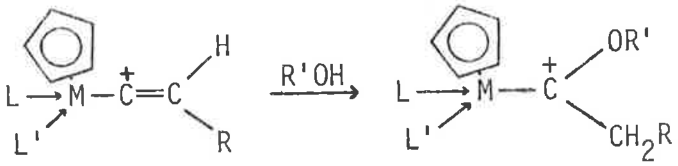
The first part of this Chapter describes the slow reaction of the phenylvinylidene complex $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1) with methanol to give the methoxy(benzyl)carbene complex $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2). This reaction is a formal addition of the alcohol across the vinylidene C=C unit, and the direction of addition follows the polarity expected on the basis of the extreme electron-deficiency of the vinylidene α-carbon, as shown, for example, by its large downfield chemical shift of *c*. 360 ppm (^{13}C n.m.r.). Thus nucleophilic attack of methanol gives a conventional Fischer-type carbene complex; it is interesting that attack of methoxide does not give the related methoxyvinyl complex, but results in deprotonation of the vinylidene to the corresponding σ-acetylide. The methylphenylvinylidene complex (14) does not allow deprotonation to occur, nor is it attacked by methoxide at the α-carbon.

The formation of the methoxycarbene complex from the vinylidene lends support to the proposal of Clark and Chisholm[14] for the intermediacy of the latter (which they preferred to view as a metal-stabilized carbonium ion) in the formation of similar carbene complexes directly from alk-1-ynes.

At the same time, these results raise questions about the conditions necessary to observe the vinylidene complexes directly, and the factors affecting their reactivity. It has proved possible to examine qualitatively the effect of altering the alkyne substituent, associated ligands, metal atom, and reacting alcohol on the reactivity of these complexes. By carrying out the reactions under similar conditions (see Experimental), relative rates of these reactions were obtained, and these data are summarized in Table 2, which also includes some data on iron complexes reported by others.[2] These results suggest that the observed variation in reactivity results from a combination of steric and electronic factors.

Attack of methanol at the α-carbon of the vinylidene ligand will be inhibited by bulky ligands, and facilitated by ligands with smaller steric requirements. A measure of the size of a particular ligand is given by the 'cone angle', and this subject has been extensively discussed by Tolman.[15] In the present series of complexes, the rate of reaction would be expected to be inversely proportional to the cone angle if steric effects predominated, with a series: CO (*c*. 95°) ≃ $CNBu^t$ (*c*. 95°) > $P(OMe)_3$ (107°) > PMe_3 (118°) ≃ PPh_3 (145°). This in fact agrees with the qualitative rate of reaction of methanol with the complexes $[Ru(C{=}CHPh)(L)(PPh_3)(\eta\text{-}C_5H_5)]^+$. Two comments can be made: (i) the cone angle given for Bu^tNC does not take into account the steric effect of the Bu^t group, which would hinder access to the α-carbon relative to CO, and result in a longer reaction time, and (ii) the value for dppe is obtained from a complex containing no PPh_3. There is severe steric interaction between the two PPh_3 ligands in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, such that some distortion of these ligands occurs.[16] An approach which considers changes in only one of the ligands is necessarily approximate.

Table 2. Reactions of vinylidene complexes with alcohols



M	L, L'	R	R'	Reaction conditions^A	Isolated yield (%)
Ru	$(PPh_3)_2$	Ph	Me	reflux; 24 h	82
Os	$(PPh_3)_2$	Ph	Me	reflux; 48 h	no reaction
Ru	dppe	Ph	Me	reflux; 16 h	82
Os	dppe	Ph	Me	reflux, 48 h	no reaction
Ru	$(PPh_3)_2$	Me	Me	reflux; 8 h	60
Ru	CO, PPh_3	Ph	Me	room temp.; 15 min	81
Ru	CO, PPh_3	Ph	Et	room temp.; 1 h	65
Ru	CO, PPh_3	Ph	Pr^i	room temp.; 3 h	60
Ru	$CNBu^t$, PPh_3	Ph	Me	room temp.; 1 h	63
Ru	$P(OMe)_3$, PPh_3	Ph	Me	reflux; 1 h	91
Ru	PMe_3, PPh_3	Ph	Me	reflux; 27 h	82
Ru	$(PPh_3)_2$	CO_2Me	Me	room temp.; 2 h	72
Ru	$(PPh_3)_2$	Bu^t	Me	reflux; 24 h	no reaction
Fe^B	CO, PPh_3	Ph	Me	'highly reactive'	73
Fe^B	dppe	Me	Me	not stated	'unreactive'

A, Time for disappearance of vinylidene complex; B, Ref. 2 .

The influence of electronic factors is more difficult to assess. Ligands such as PMe_3 are good σ donors, but relatively poor π-acceptors; CO on the other hand, and to a lesser extent isocyanides, are better π-acceptors. Thus, with CO in place of a tertiary phosphine, one would expect activation of the vinylidene toward nucleophilic attack by removal of electron density onto the carbonyl ligand. Tolman's electronic factors [obtained by considering the effect of ligands on the A_1 $\nu(CO)$ band in an extensive series of nickel complexes, $Ni(CO)_3(L)$],[15] suggest that the expected rates of reaction should be: $CO > P(OMe)_3 > CNBu^t > PPh_3 > PMe_3$, which also broadly agrees with the qualitative rates of reaction given above.

That both steric and electronic factors influence these reactions is shown in the reactions of $[Ru(C{=}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (R = Me, Ph, CO_2Me), where an increase in the electron-withdrawing nature of R increases the reaction rate. The rate increases in the order $R = CO_2Me > Ph > Me$, as expected if the effect of electron withdrawal from the α-carbon is to increase its susceptibility to nucleophilic attack. From a steric viewpoint, an order of reactivity $R = Me > CO_2Me > Ph$ would be expected. However, in the case of $R = Bu^t$, which is recovered unchanged from refluxing methanol after 24 h, the bulky CMe_3 group also exerts a predominantly steric effect on the reaction rate.

It was not possible to make a detailed comparison of the relative reaction rates down the group Fe-Ru-Os; the only two observations are that neither of the osmium complexes studied react with methanol, and that the iron complex $[Fe(C{=}CHMe)(dppe)(\eta\text{-}C_5H_5)]^+$ is reported by others to be unreactive towards water and alcohols.[2] In the case of the iron complex, this may be a result of steric crowding preventing access of the nucleophile to the α-carbon; with osmium, the explanation is not so clear, although the kinetic inertness of osmium complexes relative to those of ruthenium is well known. The reaction of $[Fe(C{=}CHPh)(CO)(PPh_3)\text{-}(\eta\text{-}C_5H_5)]^+$ with methanol is fast, to give the iron analogue of (15).

Although most of the complexes react with methanol, ethanol and higher alcohols do not react so readily. The reactions of ethanol and isopropyl alcohol with $[Ru(C{=}CHPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ have been studied, with isolation of the ethoxy- and isopropoxy-(benzyl)carbene complexes. In this series, the order of reactivity was found to be $MeOH > EtOH > Pr^iOH$, that is, a decrease in reaction rate as the size of the alkyl group increases.

It is noteworthy that the methylplatinum(II)-vinylidene intermediates proposed by Chisholm and Clark[14] are four-coordinate square-planar derivatives, and there is essentially no hindrance to attack by the alcohol solvent from above or below the square-plane. In these reactions, only alkoxy(alkyl)carbene complexes were ever isolated.

2.3.2 *Reactions with Water*

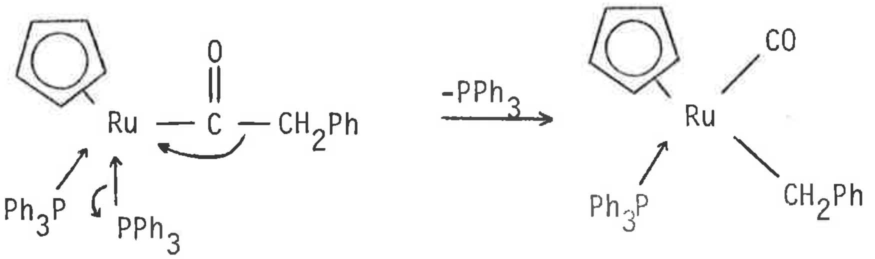
The reaction of water with the phenylvinylidene complexes $[Ru(C{=}CHPh)(L)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (L = CO and PPh_3) has also been examined. The major product isolated from the reaction of the monocarbonyl derivative was the phenylacetyl complex $Ru(COCH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (29). This reaction is similar to the apparent hydrolysis of the iron complex $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ in the presence of aqueous acid,[17] and both reactions may be considered to proceed <u>via</u> an intermediate hydroxycarbene complex, which forms the acyl complex by loss of a proton [equation (1)]:

$$[M]{-}C{\equiv}CPh \xrightarrow{H^+} [M]{-}C^+{=}CHPh \xrightarrow{H_2O} [M]{-}C^+(OH)CH_2Ph \xrightarrow{-H^+} [M]{-}COCH_2Ph \qquad (1)$$

where [M] = $Fe(CO)_2(\eta\text{-}C_5H_5)$ or $Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$.

The reaction of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ differs slightly in that the product is the benzyl derivative, $Ru(CH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (28).

In this case it is suggested that a phenylacetyl complex, formed as above, undergoes a spontaneous (under the reaction conditions) intramolecular decarbonylation (or alkyl migration), with concomitant elimination of one triphenylphosphine ligand [equation (2)]:



(2)

The reaction is related to the intermolecular decarbonylations of acyl complexes by, for example, $RhCl(PPh_3)_3$:[18]

$$Fe(COMe)(CO)_2(\eta\text{-}C_5H_5) + RhCl(PPh_3)_3 \xrightarrow{-PPh3} FeMe(CO)_2(\eta\text{-}C_5H_5) + RhCl(CO)(PPh_3)_2$$

Chisholm and coworkers[19] have similarly reported the prolonged reaction of a methylplatinum(II) acetylide with HX (X = Cl or PF_6) in methanol to give the corresponding acyl complex; in this case the intermediate methoxycarbene complex loses MeX:

$$[Pt]\text{-}C{\equiv}CR \xrightarrow[MeOH]{H^+} [Pt]\text{-}C^+(OMe)CH_2R \xrightarrow{X^-} [Pt]\text{-}COCH_2R + MeX \qquad (3)$$

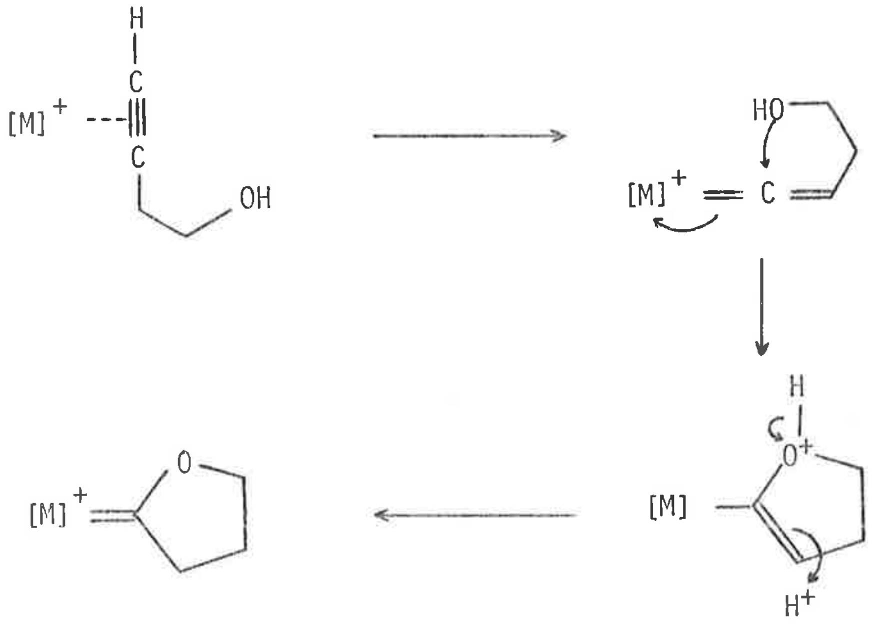
where R = H, Me, Ph.

Further reaction of the phenylacetyl complex (29) with aqueous acid affords the dicarbonyl cation, $[Ru(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$, presumably with elimination of toluene:

$$Ru(COCH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)+H^+ \rightarrow [Ru(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+ + PhCH_3 \quad (4)$$

2.3.3 *Reactions of ω-Hydroxyalk-1-ynes*

In view of the observed intermolecular reactions of the vinylidene group with alcohols, it is feasible that similar intramolecular reactions will take place. Reactions between $HC_2CH_2CH_2OH$ and $RuCl(PR_3)_2(\eta\text{-}C_5H_5)$ (R = Me or Ph) or $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ in the presence of NH_4PF_6 have given cationic complexes containing the 2-oxacyclopentylidene ligand. Reactions with $HC_2CH_2CHMeOH$ or $HC_2(CH_2)_3OH$ gave similar complexes containing the five-membered $\overline{CCH_2CH_2CHMeO}$ and six-membered $\overline{C(CH_2)_4O}$ cyclic carbene ligands, respectively. The formation of these complexes presumably proceeds *via* an intermediate vinylidene complex, which, however, was not detected. A facile intramolecular attack of the hydroxyl function on the vinylidene α-carbon, accompanied by a proton shift, results in formation of the cyclic carbene ligand (Scheme 1).



Scheme 1

Protection of the hydroxyl group by formation of the corresponding tetrahydropyranyl (thp) ether enables the acetylide complex (36) to be isolated; the formation of a red-purple colour in the solution prior to addition of sodium methoxide suggests the initial formation of the analogous vinylidene cation. Addition of acid, which normally cleaves thp ethers to regenerate the alcohol, results in immediate cyclization to form complex (31); no intermediates could be detected either visually or by ^1H n.m.r.

The related reaction between $HC_2CH_2CH_2OH$ and $[Fe(\eta^2\text{-}CH_2{=}CMe_2)(CO)_2(\eta\text{-}C_5H_5)]^+$ also gives the η^2-2,3-dihydrofuran complex, formed by a competing nucleophilic attack on the η^2-alkyne-iron complex before rearrangement to the η^1-vinylidene isomer.[20] In the studies reported here, no evidence was found for the formation of any η^2-vinyl ether complexes; it may be significant that I have not been able to deprotonate the cyclic carbene complexes to the derived η^1-dihydrofuryl complex, although addition of hydride to the carbene carbon affords the η^1-tetrahydrofuryl complex (37). In this respect the reactivity of the complexes also differs markedly from that of *trans*-$\{Ni(C_6Cl_5)[\overline{C(CH_2)_3O}](PMe_2Ph)_2\}^+$, which is readily deprotonated by NEt_3.[21]

Complexes (31) and (34) undergo facile base-catalysed H-D exchange, e.g. by addition of D_2O to a solution of (31) in pyridine. Analysis of the ^1H and ^{13}C n.m.r. spectra show that it is the two protons attached to C5 which exchange. Similar observations have been made with cyclic carbene complexes of manganese.[11,22]

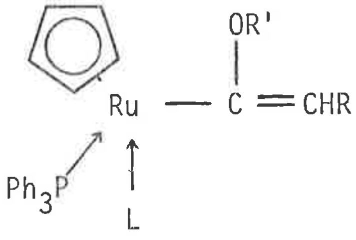
Consideration of these results suggested that the carbene ligand might be metallated readily, and indeed reaction of (31) with $LiBu^n$, or NaOH, followed by treatment with iodomethane, afforded the dimethylated complex (40). Even with a deficiency of $LiBu^n$, (40) is the only new complex produced; the monomethyl derivative was not detected. Apart from the obvious synthetic implications of this reaction, interest centres in the remarkably facile metallation which occurs in preference to attack of the nucleophile at the highly electron-deficient carbene carbon; the latter reaction may be sterically too demanding.

2.3.4 Deprotonation of Alkoxy(alkyl)carbene Complexes

The β-protons of $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2) undergo H-D exchange to give $\{Ru[C(OMe)CD_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$.[23] The acidity of these protons is further demonstrated in a reaction of (2) with NaOMe yielding the vinylether complex $Ru[(OMe)=CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ (41). Vinylethers are unstable compounds and readily isomerise to aldehydes or ketones. This is not observed for the vinylether metal complexes described here. Similar products have been isolated upon deprotonation of some nickel[21] and platinum[19] alkoxycarbene complexes.

The stability of the vinyl complexes in the solid state is increased by acidic ligands and electron withdrawing substituents (Table 3).

Table 3. A range of alkoxyvinyl complexes and their relative stabilities in the solid state.

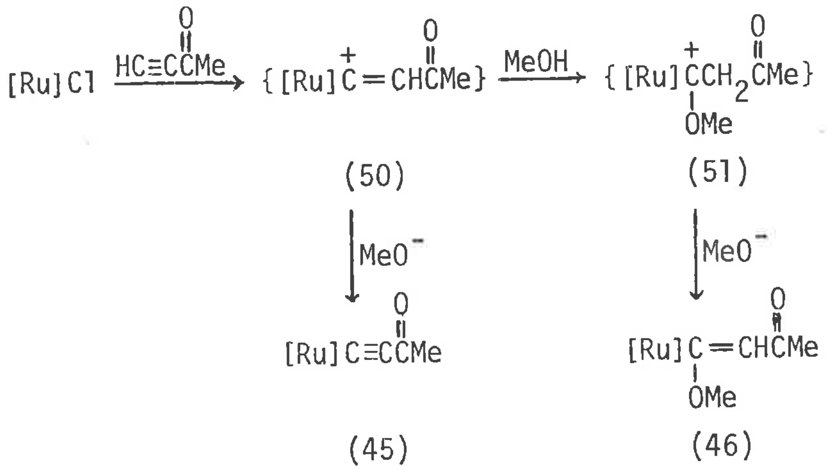


R	R'	L	no.	
Me	Me	PPh_3	(42)	very unstable
Ph	Me	PPh_3	(41)	unstable
CO_2Me	Me	PPh_3	(48)[A]	stable
Ph	Me	CO	(49)[A]	stable
Ph	Et	CO	(43)	stable

A, Ref. 12.

Changing only the β-substituent leads to a marked increase in stability ($CO_2Me > Ph > Me$) as the electron-withdrawing power increases. Replacement of PPh_3 with the less basic CO ligand also leads to a more stable complex. This result is expected for the vinyl moiety as it is electron-rich and stabilised by electron-withdrawing groups. An opposite trend is observed for alkoxycarbene complexes where electron-withdrawing substituents destabilise the system by increasing the electron deficiency of the carbene carbon.

The formation of products (45) and (46) in the reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with 3-butyn-2-one suggests the formation of the intermediates (50) and (51). Deprotonation of a mixture of (50) and (51) yields (45) and (46) respectively:



$$[Ru]Cl \xrightarrow{HC\equiv C\overset{O}{\overset{\Vert}{C}}Me} \{[Ru]\overset{+}{C}{=}CH\overset{O}{\overset{\Vert}{C}}Me\} \xrightarrow{MeOH} \{[Ru]\underset{OMe}{\overset{+}{C}}CH_2\overset{O}{\overset{\Vert}{C}}Me\}$$

(50) (51)

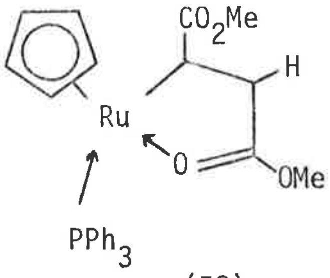
$$\downarrow MeO^- \qquad \downarrow MeO^-$$

$$[Ru]C\equiv C\overset{O}{\overset{\Vert}{C}}Me \qquad [Ru]\underset{OMe}{C}{=}CH\overset{O}{\overset{\Vert}{C}}Me$$

(45) (46)

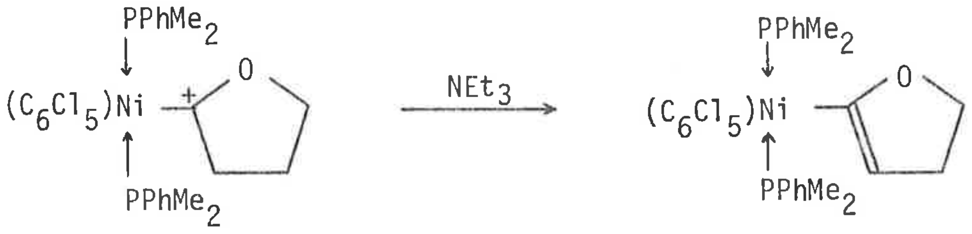
$[Ru] = Ru(PPh_3)_2(\eta\text{-}C_5H_5)$

The loss of PPh_3 from (46) to give $\overline{\mathrm{Ru[C(OMe)=CHCO}}\mathrm{Me]}(PPh_3)(\eta\text{-}C_5H_5)$ (44) has been described (Section 1.2.3.2). The metallated carbonyl group of (44) has an unusually low infrared absorption band at 1308 cm^{-1}. While this is attributed to a reduction in bond order due to bonding with the metal, a related metallated vinyl complex (52) exhibits an absorption at 1586 cm^{-1}.[25] The reason for this difference is not well understood at this stage.



(52)

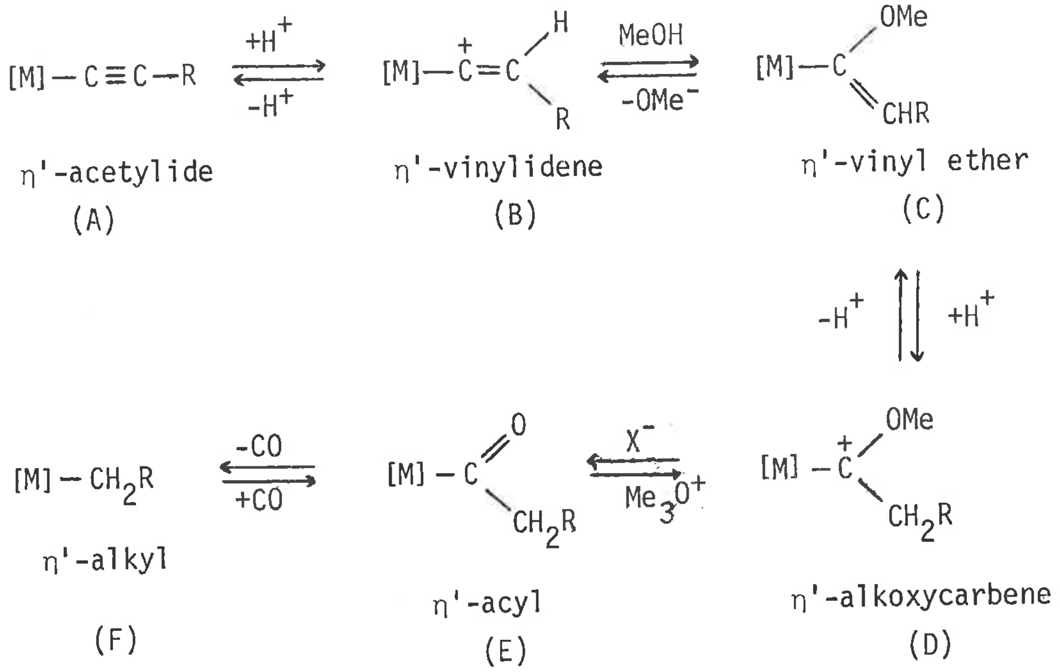
Surprisingly the cyclic carbene complex (31) could not be deprotonated to a vinyl ether, despite the known acidity of the β-protons. This contrasts with the nickel system (53), which is deprotonated by NEt_3 under mild conditions:[21]



(53)

The reason for this difference is not obvious at present.

In summary it is useful to recall the interrelationships between η^1-carbon ligands which are summarised in Scheme 2. The reactions described in this Chapter link the η^1-acetylide complex with the η^1-alkyl complex and have shown the isolation of all intermediates,

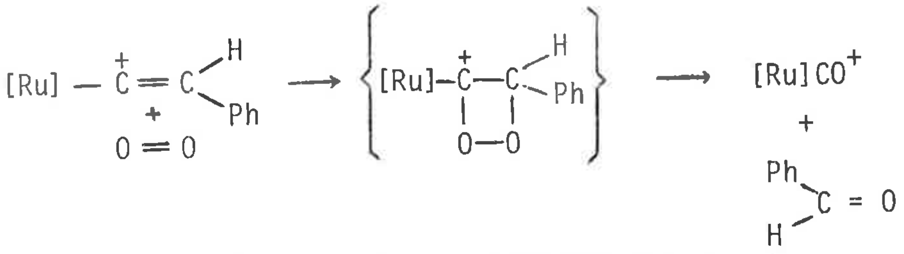


Scheme 2.

that is, steps (A) → (B), (B) → (D), (C) ⇄ (D), (B) → (E), and (E) → (F). The carbonylation/decarbonylation process is well documented,[26] while most of the other processes have been described in Chapter One.

2.3.5 *Reactions with Dioxygen*

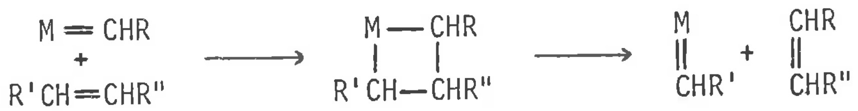
The reaction of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ with dioxygen was reported to give $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and benzoic acid.[3] It has now been shown that benzaldehyde is the sole organic product detected in this reaction. Benzoic acid is only formed when an aqueous base extraction is used in the work up. The formation of benzaldehyde suggests a 2 + 2 cycloaddition reaction, followed by ring cleavage:



$[Ru] = Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ or $Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$

There is no evidence for the formation of an intermediate cyclic peroxide complex. However, some organic molecules involving five membered peroxide rings are known.[27]

The reaction of the vinylidene complexes with dioxygen may be compared to the olefin metathesis reaction:[28]



Note however, that the olefin adds to the M-C(1) bond, while dioxygen adds to the C(1)-C(2) bond. Addition reactions of the C(1)-C(2) bond in vinylidene complexes are described in Section 1.3.5.2.

The oxidation of the vinylidene complexes is not well understood and requires further investigation.

2.4 *EXPERIMENTAL*

General Conditions

All reactions were carried out in a nitrogen atmosphere and, where necessary, these conditions were used for work-up of the reaction products. Solvents were dried with (i) sodium (tetrahydrofuran, diethylether, petroleum fractions, benzene, toluene), (ii) magnesium (methanol, ethanol), (iii) calcium chloride (dichloromethane, chloroform), or (iv) Linde 4 Å molecular sieves (*d*-chloroform, d^6-acetone, d^6-benzene). Light petroleum refers to a fraction of b.p. 40-60°, while hexane refers to the fraction of b.p. 60-80°.

Chromatography was routinely carried out on columns of alumina (BDH, Fluka or Ajax) initially packed in light petroleum. Thin layer chromatography was carried out on plates coated with silica (Merck or

Camag).

Elemental microanalyses were determined by the Canadian Microanalytical Service (Vancouver), or the Australian Microanalytical Service (Melbourne).

Mass spectra were recorded on an AEI-GEC MS 3074 spectrometer (70 eV ionizing energy). The mass values were calculated using the most abundant isotopes (i.e. ^{56}Fe, ^{102}Ru, ^{192}Os, ^{184}W).

Infrared spectra were recorded (using sodium chloride plates or solution cells) on Perkin Elmer 457 or 683 double beam infrared spectrometers over the range 4000 - 600 cm^{-1} and were calibrated with polystyrene (1583·1, 906·7 cm^{-1}) or CO gas (2147·1 cm^{-1}).

NMR spectra were recorded on Varian T60 (^{1}H, 60 MHz), Bruker WP-80DS (^{1}H, 80 MHz; ^{13}C, 20·1 MHz), or Bruker HX-90E (^{31}P, 36·43 MHz) spectrometers. Deuterated solvents were always used in 2,5 or 10 mm tubes, with tms (^{1}H or ^{13}C) or PPh$_3$ (^{31}P) as internal references. Carbon and phosphorus spectra were generally broad-band decoupled, except when off-resonance decoupling was required.

ESR spectra were recorded on a Varian E-9 spectrometer operating at X-band frequences.

Starting Materials

The σ-acetylide complexes $RuC_2R(PPh_3)_2(\eta\text{-}C_5H_5)$ and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, and the vinylidene complexes $[Ru(C{=}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (R = Me, Ph, and CO_2Me) were prepared by literature methods.[1] The preparations of $RuC_2Bu^t(PPh_3)_2(\eta\text{-}C_5H_5)$, $Ru(C_2Ph)(L)(PPh_3)(\eta\text{-}C_5H_5)$ (L=CO or $CNBu^t$), and $Os(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ are described in Chapter 4, while that for $[Ru(C{=}CHBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ is given at the end of this section. Literature methods were used in the preparation of $Ru(C_2Ph)[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$[5] and the halides $RuCl(PR_3)_2(\eta\text{-}C_5H_5)$(R=Ph,Me)[29,30] and $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$.[31]

Reactions of Substituted Vinylidene Complexes with Methanol

$[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (1)

Addition of HPF_6,OEt_2 (5 drops, excess) to a suspension of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0·13 mmol) in methanol (25 ml) afforded a red solution of the vinylidene complex. After heating at reflux point for 24 h the colour of the solution had changed to yellow. Evaporation to about half-volume and cooling resulted in the deposition of yellow *crystals* of $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2), which were collected and recrystallized (dichloromethane/methanol) (70 mg, 56%), m.p. 182-185° (Found: C, 61·8; H, 4·5%. $C_{50}H_{45}F_6OP_3Ru$ requires C, 61·9; H, 4·6%). Infrared (Nujol): ν(CO) 1265s, ν(PF) 840vs(br); other bands at 1625w, 1605w, 1590w, 1438s, 1303w(br), 1190w, 1163w, 1122m, 1090m, 1076m, 1060w, 1004w, 948w, 759m, 748m, 695s, 559w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 3·49, s, 3H, OMe; 4·84, s, 5H, C_5H_5; 5·06, s, 2H, $C\underline{H}_2Ph$; 7·31, m, 35H, Ph. ^{13}C n.m.r.: δ($CDCl_3$)62·8, s, OMe; 63·4, s, CH_2; 92·0, s, C_5H_5; 122·3-136·0, m, C_6H_5; 308·7, t, *J*(CP) 12 Hz, RuC.

The same methoxy(benzyl)carbene complex was obtained by heating $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$(230 mg, 0·24 mmol) in refluxing MeOH (50 ml) for 24 h. The yellow crystals (190 mg, 82%) were shown to be identical with the complex prepared from the σ-acetylide (i.r., n.m.r.).

All other reactions were similar to that described above, differing only in reaction times. The following reactions of σ-acetylide complexes with methanol in the presence of HPF_6,OEt_2 were carried out:

(A) *$Ru(C_2Ph)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$*[30] (90 mg, 0·15 mmol), after 27 h, gave white *crystals* (from CH_2Cl_2/Et_2O) of $\{Ru[C(OMe)CH_2Ph](PMe_3)(PPh_3)(\eta\text{-}C_5H_5)\}PO_2F_2$ (17) (90 mg, 82%), m.p. 90° (dec.) (Found: C, 55·9; H, 4·7%. $C_{34}H_{39}F_2O_3P_3Ru$ requires C, 56·8; H, 5·3%). Infrared (Nujol): ν(CO) 1247m, ν(PO) 1052vs(br), ν(PF) 842m(br), other bands at 1602w, 1313w, 1280w, 1000w, 954s, 753m(br), 725m(br), 696s, 664w, 553w cm^{-1}.

^{1}H n.m.r.: δ($CDCl_3$) 1·30, d, *J*(PH) 10 Hz, 9H, PMe_3; 3·52, s, 3H, OMe; 4·68, ABq, *J*(AB) 16 Hz, 2H, CH_2; 4·98, s, 5H, C_5H_5; 7·54, m, 20H, Ph.

(B) $Ru(C_2Ph)[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$ (110 mg, 0·17 mmol), after 1 h, afforded yellow *crystals* (from light petroleum/diethyl ether) of $\{Ru[C(OMe)CH_2Ph][P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)\}PO_2F_2$ (18) (120 mg, 91%), m.p. 160-163° (Found: C, 52·5; H, 4·9%. $C_{35}H_{39}F_2O_6P_3Ru$ requires C, 53·3; H, 5·0%). Infrared (Nujol): ν(CO) 1260s, ν(PO) 1030vs(br), ν(PF) 845m, other bands at 1301w, 1195sh, 1187sh, 1183m, 1122m, 1113sh, 1080s, 949m, 879m, 861m, 833sh, 805sh, 790m, 772m, 752m, 738m, 715m, 692m, 680w, 663w, 559w, 530w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 3·51, s, 3H, OMe; 3·53, d, *J*(PH) 11 Hz, 9H, POMe; 4·74, ABq, *J*(AB) 16 Hz, 2H, CH_2; 5·02, d, *J*(PH) 1 Hz, 5H, C_5H_5; 7·48, m, 20H, Ph.

(C) $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (150 mg, 0·28 mmol), for 2 h, gave pale yellow *crystals* (from CH_2Cl_2/Et_2O) of $\{Ru[C(OMe)CH_2Ph](CO)(PPh_3)\text{-}(\eta\text{-}C_5H_5)\}PF_6$ (15) (170mg, 81%), m.p. 140° (dec.) (Found: C, 54·0; H, 3·6%. $C_{33}H_{30}F_6O_2P_2Ru$ requires C, 53·8; H, 4·1%). Infrared: ν(CO) 2000vs, ν(C-OMe) 1269s, ν(PF) 840vs(br); other bands at 1440w, 1323s, 1190w, 1175w, 1170w, 1096m, 1034w, 1013m, 1002m, 986w, 922w, 912w, 883s, 764sh, 760m, 752m, 695s, 559w, 550w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 3·88, s, 3H, OMe; 4·38, ABq, *J*(AB) 16 Hz, 2H, CH_2; 5·30, s, 5H, C_5H_5; 7·61, m, 20H, Ph.

(D) $Ru(C_2Ph)(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$ (50 mg, 0·08 mmol), for 1 h, gave light yellow *crystals* (from light petroleum/CH_2Cl_2) of $\{Ru[C(OMe)CH_2Ph]\text{-}(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)\}PF_6$ (16) (40mg, 63%), m.p. 164-168° (Found: C, 56·1; H, 5·0; N, 1·7%. $C_{37}H_{39}F_6NOP_2Ru$ requires C, 56·1; H, 4·9; N, 1·8%). Infrared: ν(CN) 2160s; ν(CO) 1287s; ν(PF) 840vs(br); other bands at 1606w, 1601w, 1590w, 1252w, 1236w, 1210m, 1200sh, 1191sh, 1176w, 1163w, 1136m, 1095m, 1085m, 1071m, 1062w, 1003w, 759m, 750w, 735m, 696s, 663w, 556w cm^{-1}.

^{1}H n.m.r.: $\delta(CDCl_3)$ 1·28, s, 9H, CMe_3; 3·93, s, 3H, OMe; 4·25, ABq, *J*(AB) 2 Hz, 2H, CH_2; 5·01, s, 5H, C_5H_5; 7·47, m, 20H, Ph.

(E) Ru(C_2Ph)(dppe)(η-C_5H_5) (40 mg, 0·06 mmol), for 16 h, gave a yellow *powder* (from light petroleum/dichloromethane) of {Ru[C(OMe)CH_2Ph]-(dppe)(η-C_5H_5)}PO_2F_2 (19) (40 mg, 82%), m.p. 240° (Found: C, 60·6; H, 4·8%. $C_{41}H_{37}F_2O_3P_3Ru$ requires C, 60·7; H, 4·6%). Infrared: ν(CO) 1258s, ν(PO) 1051s(br); ν(PF) 824s; other bands at 1272m, 1203w, 1164w, 1128m, 1105sh, 1097sh, 1079s, 1040m, 1025w, 1002w, 954w, 888w, 841w(br), 751s, 719w, 705sh, 700m, 692m, 663w, 537w cm^{-1}. ^{1}H n.m.r.: $\delta(CDCl_3)$ 2·93, s, 3H, OMe; 4·05, s, 2H, CH_2; 5·10, s, 5H, C_5H_5; 7·40, m, 25H, Ph.

(F) Ru(C_2Me)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0·27 mmol), for 8 h, gave yellow *crystals* of {Ru[C(OMe)Et](PPh_3)$_2$(η-C_5H_5)}PF_6 (20) (150 mg, 60%), m.p. 210-211° (Found C, 59·7; H, 4·3%. $C_{45}H_{43}F_6OP_3Ru$ requires C, 59·5; H, 4·7%). Infrared: ν(CO) 1284s; ν(PF) 840s(br); other bands at 1588vw, 1577vw, 1440m, 1435m, 1304m, 1226m, 1177m, 1159sh, 1114w, 1094m, 1085m, 1074sh, 1049m, 1022sh, 1014m, 1004sh, 976w, 943w, 928sh, 881w, 758m, 743m, 693s, 679sh, 664w, 556w cm^{-1}. ^{1}H n.m.r.: $\delta[(CD_3)_2CO]$ 1·27 t, *J*(HH) 7·5 Hz, 3H, $CH_2\underline{Me}$; 3·48, s, 3H, OMe; 3·65, q, *J*(HH) 7·5 Hz, 2H, CH_2; 5·05, s, 5H, C_5H_5; 7·48, m, 35H, Ph.

(G) Ru(C_2CO_2Me)(PPh_3)$_2$(η-C_5H_5) (100 mg. 0·13 mmol), for 2 h at room temperature, gave yellow *crystals* [from light petroleum (b.p. 60-80°)/CH_2Cl_2] of {Ru[C(OMe)CH_2CO_2Me](PPh_3)$_2$(η-C_5H_5)}PF_6 (21) (90mg, 72%), m.p. 164-166° (Found: C, 58·5; H, 4·3%. $C_{50}H_{45}F_6O_3P_3Ru$ requires C, 58·1; H, 4·6%). Infrared: ν(ester CO) 1742s, ν(CO) 1285m; ν(PF) 835vs(br); other bands at 1592w, 1312w, 1293w, 1255m, 1188w, 1135w, 1092sh, 1078sh, 1040vs(br), 1002sh, 990sh, 943w(br), 735m, 725m, 690m, 665w, 560w cm^{-1}. ^{1}H n.m.r.: $\delta(CDCl_3)$ 3·47, s, 3H, CO_2Me; 3·78, s, 3H, OMe; 4·55, s, 2H,

CH_2; 4·88, s, 5H, C_5H_5; 7·42, m, 30H, Ph.

(H) The vinylidene complex $[Ru(C{=}CHBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (120 mg, 0·14 mmol) was heated in refluxing methanol (25 ml) for 24 h with no apparent change in colour of the solution. Evaporation and filtration of a dichloromethane extract (2 ml) into diethyl ether (50 ml) afforded a fine orange-pink precipitate, identified (i.r.) as recovered vinylidene complex (22) (110 mg, 92%).

(I) Similarly, the complexes $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (10) and $Os(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (8) afforded only the corresponding vinylidene derivatives [in 75% (22) and 93% (23) yields, respectively] after addition of HPF_6,OEt_2 and heating in refluxing methanol for 48 h. The σ-acetylide (8) was recovered (91%) by deprotonating the vinylidene complex with sodium in methanol.

Reactions of $[Ru(C_2HPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ with Other Alcohols

(A) With ethanol A suspension of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (140 mg, 0·27 mmol) in ethanol (15 ml) was treated with HPF_6,OEt_2 (10 drops, excess) at room temperature. After stirring for 1 h, the resulting precipitate was collected, washed with Et_2O and dried, to give $\{Ru[C(OEt)CH_2Ph](CO)(PPh_3)(\eta\text{-}C_5H_5)\}PF_6$ (26) as a white *powder* (130 mg, 65%), m.p. 134-136° (Found: C, 54·5; H, 4·2%. $C_{34}H_{32}F_6O_2P_2Ru$ requires C, 54·4; H, 4·3%). Infrared: ν(CO) 1991vs, ν(C-O) 1259s, ν(PF) 841vs(br); other bands at 1606w, 1578w, 1441m, 1335w, 1318s, 1298m, 1194w, 1169w, 1150sh, 1120w, 1097s, 1077w, 1066w, 1034w, 1013m, 997m, 924w, 753m, 745w, 713w, 703s, 694s, 664w, 548w cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·18; t, *J*(HH) 7 Hz, 3H, Me; 4·3, m, 4H, $C\underline{H}_2Me+C\underline{H}_2Ph$; 5·27, s, 5H, C_5H_5; 7·57, m, 20H, Ph.

(B) With isopropyl alcohol A suspension of Ru(C_2Ph)(CO)(PPh_3)-(η-C_5H_5) (200 mg, 0·38 mmol) in isopropyl alcohol (10 ml) was treated with HPF_6,OEt_2 (5 drops) at 20°. The product began to separate after 30 min, and was filtered off after 3 h and washed with Et_2O to give pure {Ru[C(OPr^i) CH_2Ph](CO)(PPh_3)(η-C_5H_5)}PF_6 (27) as a white *powder* (170 mg, 60%), m.p. 98-100° (Found: C, 54·4; H, 4·1%. $C_{35}H_{34}F_6O_2P_2Ru$ requires C, 55·0; H, 4·5%). Infrared ν(CO) 1989vs; ν(C-O) 1298m; ν(PF) 841s; other bands at 1198w, 1183vw, 1155m(br), 1098s, 1089sh, 1073m, 1051m, 1028vw, 1001w, 918w, 760w, 749m, 739w, 712w, 701s, 690s, 660m, 557w cm^{-1}. ^{1}H n.m.r.: δ[$(CD_3)_2CO$] 1·28, d, *J*(HH) 6 Hz, 6H, Me; 4.35, ABq, *J*(AB) 2 Hz, 2H, CH_2; 5·47, s, 5H, C_5H_5; 7·60, m, 20H, Ph. The C$\underline{H}Me_2$ resonance was obscured by the H_2O signal in the solvent at δ *c*. 2·5.

Reaction Between [Ru(C_2HPh)(PPh_3)$_2$(η-C_5H_5)]BF_4 and Water

The vinylidene complex was prepared *in situ* from Ru(C_2Ph)(PPh_3)$_2$-(η-C_5H_5) (350 mg, 0·44 mmol) in tetrahydrofuran (30 ml) and HBF_4,OEt_2 (8 drops, excess). Water (1·5 ml) was added, and the solution was stirred at room temperature (2 h) and refluxed (2 h). Evaporation of solvent left a yellow *solid*, which was washed with methanol (2 x 5 ml), and recrystallized (dichloromethane/methanol) to give pure Ru(CH_2Ph)(CO)-(PPh_3)(η-C_5H_5) (28) (80 mg, 33%), m.p. 140-141° (Found: C, 67·6; H, 4·7%; *M*, 548. $C_{31}H_{27}OPRu$ requires C, 68·0; H, 5·0%; *M*, 548). Infrared ($CHCl_3$): ν(CO) 1917s cm^{-1}; other bands (Nujol): 1595m, 1575w, 1314w, 1210w, 1188sh, 1182w, 1162w, 1121vw, 1110vw, 1095sh, 1091m, 1071w, 1049w, 1028w, 1000m, 908m, 860vw, 850vw, 808m, 758m, 748s, 736m, 731m, 698s, 649w, 580w, 561w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 2·24, m, 1H, CH_2; 2·86, m, 1H, CH_2; 4·62, s, 5H, C_5H_5; 7·03, m, 5H, Ph; 7·39, m, 15H, PPh_3.

Reaction Between $[Ru(C_2HPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ *and Water*

A suspension of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (170 mg, 0.32 mmol) in aqueous isopropyl alcohol (25 ml) was treated with HPF_6,OEt_2 (10 drops) at room temperature (45 min) and then at reflux (1·5 h). Evaporation to *c.* 10 ml afforded a product on cooling, which was recrystallized (dichloromethane/light petroleum) to give pure $Ru(COCH_2Ph)(CO)(PPh_3)$-$(\eta\text{-}C_5H_5)$ (29) as yellow *needles* (100 mg, 54%), m.p. 182-183° (Found: C, 67·2; H, 4·7%; *M*(mass spectrometry), 576. $C_{32}H_{27}O_2PRu$ requires C, 66·7; H, 4·7%; *M*, 576). Infrared ($CHCl_3$): ν(CO) 1927vs, ν(acyl CO) 1606vs; other bands (Nujol) at 1435m, 1310vw, 1232w, 1162w, 1145w, 1097s, 1082w, 1072w, 1029w,1007w, 988s, 911w, 899w, 850vw, 838vw, 805m, 754s, 749sh, 743m, 723w, 691s, 663m, 620w, 595w, 573vw, 552vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 3·72, ABq, *J*(AB) 14 Hz, 2H, CH_2; 4·85, s, 5H, C_5H_5; 7·43, m, 20H, Ph.

In an analogous experiment, HPF_6,OEt_2 (10 drops, excess) in CH_2Cl_2 (10 ml) was added slowly to a solution of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (100 mg, 0·19 mmol) in CH_2Cl_2 (20 ml) and water (1 ml). After 1·5 h at room temperature the infrared spectrum of the reaction mixture showed that the only carbonyl-containing complex present was complex (29). After heating (24 h), the infrared spectrum showed the disappearance of complex (29) with concomitant formation of the known[8] complex $[Ru(CO)_2$-$(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ (30) identified by its infrared spectrum, and by comparison with the product from the reaction described below.

The isopropoxycarbene complex (27) was heated in wet ether (60°/7h; autoclave); the cooled reaction mixture was evaporated and the residue recrystallized [hexane/acetone] to give light yellow crystals of $[Ru(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ (30) (40 mg, 71%), m.p. 205-208° (Found: C, 47·3; H, 3·0%. Calc. for $C_{25}H_{20}F_6O_2P_2Ru$: C, 47·6; H, 3·2%). Infrared

($CHCl_3$): ν(CO) 2078vs, 2028vs [lit.[14] 2069, 2022 (CH_2Cl_2)]; (Nujol) ν(PF) 840vs; other bands at 1098s, 1025vw, 1000w, 974w, 925vw, 745s, 705m, 685s, 664w cm^{-1}. ^{1}H n.m.r.: δ[$(CD_3)_2CO$] 5·97, s, 5H, C_5H_5; 7·73, m, 15H, Ph.

Preparation of Cyclic Carbene Complexes of Ruthenium and Osmium

(A) $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ *(31)*. A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (2·56g, 3·53 mmol), but-3-yn-1-ol (240 mg, 3·52 mmol) and NH_4PF_6 (0·7g, 4·2 mmol) was heated in refluxing methanol (40 ml). After 15 min, pure $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (31) precipitated as yellow *microcrystals* (2·91 g, 91%), m.p. 260° (dec.) (Found: C, 59·7; H, 4·7; F, 12·4%. $C_{45}H_{41}F_6OPRu$ requires C, 59·7; H, 4·6; F, 12·6%). Infrared (Nujol): ν(CO) 1185s, 1095m; ν(PF) 848vs; other bands at 1587vw, 1574vw, 1316w, 1285w, 1125w, 1078w, 1059m; 1035vw, 1006w, 995w, 950vw, 937sh, 786vw, 756s, 731w, 705s, 692sh, 568s, 547m, 535s, 526sh, 510w, 475w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 1·77, q, *J*(HH) 8 Hz, 2H, C(4)H_2; 3·74, t, *J*(HH) 8 Hz, 2H, C(5)H_2; 3·93, t, *J*(HH) 8 Hz, 2H, C(3)H_2; 4·82, s, 5H, C_5H_5; 6·97, 7·33, 7·40, m, 30H, PPh_3. ^{13}C n.m.r.: δ($CDCl_3$) 22·6, s, C(4); 60·8, s, C(5); 81·6, s, C(3); 91·2, s, C_5H_5; 128·3-135·9, m, PPh_3; 300·5, t, *J*(CP) 14Hz, RuC.

(B) $\{Ru[\overline{C(CH_2)_3O}](PMe_3)_2(\eta\text{-}C_5H_5)\}PF_6$ *(32)*. A mixture of $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ (110 mg, 0·31 mmol), but-3-yn-1-ol (100 mg, 1·5 mmol) and NH_4PF_6 (100 mg, 0·6 mmol) was heated in refluxing methanol (50 ml) for 1 h, forming a nearly colourless solution. Evaporation and recrystallization of the residue (dichloromethane/cyclohexane) afforded pure $\{Ru[\overline{C(CH_2)_3O}](PMe_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (32) as white *microcrystals* (110 mg, 66%), m.p. > 280° (dec.) (Found: C, 33·9; H, 5·4%. $C_{15}H_{29}F_6OP_3Ru$ requires C, 33·8; H, 5·5%). Infrared (Nujol): ν(CO) 1295m, 1285sh, 1147s;

ν(PF) 841vs; other bands at 1311vw, 1224vw, 1200vw, 1076m, 1058vw, 998vw, 955s, 725m, 672w, 662vw, 560w cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 1·45, $X_9X'_9$ part of $X_9AA'X'_9$ spin system, separation of outer lines 9·6 Hz, 18H, PMe_3; 1·97, q, *J*(HH) 7 Hz, 2H, $C(4)H_2$; 3·8, t, *J*(HH) 8 Hz, 2H, $C(5)H_2$; 4·64, t, *J*(HH) 7 Hz, 2H, $C(3)H_2$; 5·16, s, 5H, C_5H_5. ^{13}C n.m.r.: δ($CDCl_3$) 22·7, m, C(3)+PMe_3; 59·4, s, C(2); 80·5, s, C(4); 88·7, s, C_5H_5; 296·9, t, *J*(CP) 14 Hz, RuC.

(C) $\{Os[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ *(33).* A mixture of $OsBr(PPh_3)_2$-(η-C_5H_5) (210 mg, 0·23 mmol), but-3-yn-1-ol (130 mg, 1·94 mmol) and NH_4PF_6 (140 mg, 0·8 mmol) was heated in refluxing methanol (40 ml). After 30 min the pale yellow solution was reduced in volume yielding yellow *microcrystals*. These were recrystallized from dichloromethane/cyclohexane to give pure $\{Os[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (33) (0·18 g, 74%), m.p. 257-259° (Found: C, 54·1; H, 4·1%. $C_{45}H_{41}F_6OOsP$ requires C, 54·3; H, 4·2%). Infrared (Nujol): ν(CO) 1177s, 1089s, 1078m; ν(PF) 839vs; other bands at 1310vw, 1284w, 1060w, 1057w, 1027vw, 999m, 946vw, 777vw, 757sh, 751s, 744m, 697s, 684m, 666w, 560w, 540vw cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 1·83, q, *J*(HH) 7·4 Hz, 2H, $C(4)H_2$; 3·14, t, *J*(HH) 7·5 Hz, 2H, $C(5)H_2$; 3·78, t, *J*(HH) 7·3 Hz, 2H, $C(3)H_2$; 4·97, s, 5H, C_5H_5; 7·2, m, 30H, PPh_3. ^{13}C n.m.r.: δ($CDCl_3$) 23·6, s, C(4); 62·0, s, C(5); 80·8, s, C(3); 88·4, s, C_5H_5; 128·2-137·8, m, PPh_3; 263·4, t, *J*(CP) 10 Hz, OsC.

(D) $\{Ru[\overline{C(CH_2)_4O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ *(35).* A mixture of $RuCl(PPh_3)_2$-(η-C_5H_5) (200 mg, 0·28 mmol), NH_4PF_6 (50 mg, 0·3 mmol) and pent-4-yn-1-ol (40 mg, 0·48 mmol) was heated in refluxing methanol (50 ml) for 30 min. The solution was cooled, filtered and reduced in volume until yellow

crystals separated. Two recrystallizations (dichloromethane/methanol) gave pure $\{Ru[\overline{C(CH_2)_4O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (35) as fine, light yellow *crystals* (140 mg, 55%), m.p. 232-234° (Found: C, 59·6; H, 4·6%. $C_{46}H_{43}F_6$-OP_3Ru requires C, 60·1; H, 4·7%). Infrared (Nujol): ν(CO) 1248sh, 1238s, 1085m, 1072sh; ν(PF) 839vs; other bands at 1044m, 1016vw, 995vw, 917vw, 748m, 739m, 719w, 695s, 678w, 555vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·26, 1·57, m, 2 x 2H, $C(4)H_2$+$C(5)H_2$; 3·52, m, 4H, $C(3)H_2$+$C(6)H_2$; 4·76, s, 5H, C_5H_5; 7·09, 7·30, 7·38, m, 30H, C_6H_5. ^{13}C n.m.r.: $\delta(CDCl_3)$ 16·4, s, 20·3, s, C(4)+C(5); 55·3, s, C(6); 73·0, s, C(3); 91·4, s, C_5H_5; 128·1-137·2, m, PPh_3.

Reduction of Complex (1): Preparation of the Tetrahydrofuryl Complex (37)

Addition of $NaAlH_2(OCH_2CH_2OMe)_2$ (1 ml of a 70% solution in toluene; Vitride) to $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (500 mg, 0·55 mmol) in dry tetrahydrofuran (25 ml) resulted in slight effervescence, and a rapid change in colour of the solution to golden yellow. After stirring at ambient temperature for 3.5 h, ethyl acetate (1 ml) was added to destroy excess complex hydride, and the mixture was evaporated. Chromatography (alumina) of a dichloromethane extract of the residue gave a yellow fraction, eluted with diethyl ether; evaporation and recrystallization from the same solvent gave yellow *granules* of $Ru[\overline{CH(CH_2)_3O}](PPh_3)_2$-$(\eta\text{-}C_5H_5)$ (37A) (300 mg, 72%), m.p. 137-140° (dec.) [Found: C, 70·6; H, 5·7%; *M*(mass spectrometry), 762. $C_{45}H_{42}OP_2Ru$ requires C, 71·0; H, 5·6%; *M*, 762]. Infrared (Nujol): ν(CO) 1095s, 1091sh; other bands at 1588w, 1438s, 1328vw, 1316vw, 1242vw, 1191w, 1185vw, 1166vw, 1077vw, 1055w, 1035vw, 1001w, 988sh, 962sh, 938vw, 888vw, 872vw, 861vw, 838w, 809m, 801w, 771m, 766w, 757m, 747m, 715m, 708s, 704sh, 690w, 628vw, 600vw, 549s, 537s, 526s, 508s, 480w, 473sh, 456vw, 446w, 435m cm^{-1}.

^{1}H n.m.r.: δ($CDCl_3$) 1·32, t, J 5·6 Hz, 1H; 2·23, q, J 6 Hz, 2H; 3·41, q, J 5·6 Hz, 2H; 5·64, dtt, J 1, 6, 16 Hz, 1H (these signals are assigned collectively to the protons of the tetrahydrofuryl group; no individual assignments could be confirmed); 4·21, s, 5H, C_5H_5; 7·18, m, 30H, PPh_3. ^{13}C n.m.r.: δ(C_6D_6) 44·4, s, C(3); 52·4, s, C(2); 62·9, s, C(4); 86·6, s, C_5H_5; 127·8-140·5, m, PPh_3; 148·7, t, J(CP) 18 Hz, RuC.

A similar reaction with the deuterated complex (38) afforded golden-yellow *crystals* of the 5,5-dideutero complex (37B) (300 mg, 72%), m.p. 150-151° (dec.) (Found: C, 70·5; H, 5·4%. $C_{45}H_{40}D_2OP_2Ru$ requires C, 70·8; H, 5·8%). ^{1}H n.m.r.: δ($CDCl_3$) 1·36, t, J 6 Hz, 1H, CH; 2·27, t(br), J 5 Hz, 2H, CH_2; 3·39, t, J 5 Hz, 2H, CH_2; 4·21, s, C_5H_5; 7·14, m, PPh_3. The signal at δ 5·64 found in the spectrum of complex (37A) is not present in the spectrum of (37B).

H-D Exchange Experiment

Deuterium oxide (1 ml) was added to $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2·0 g, 2·21 mmol) dissolved in dry pyridine. The solution was stirred for 1¼ h under nitrogen while warming on a water bath (70-80°). After this time, examination of the ^{1}H n.m.r. spectrum showed that the CH_2 triplet at δ 3·70 had reduced intensity, with a concomitant change of the upfield quintet to a triplet. After cooling to room temperature, dry diethyl ether (40-50 ml) was added, and trituration of the resulting oil caused it to solidify. Filtration, washing with diethyl ether until pyridine was completely removed, and drying (0·01 mm) afforded the deuterated complex $[Ru(\overline{CCD_2CH_2CH_2O})(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (38) (1·75 g, 88%), m.p. 220-225° (dec.) (Found: C, 60·0; H, 4·6%. $C_{45}H_{39}D_2F_6OP_3Ru$ requires C, 59·6; H, 4·8%). Infrared (Nujol): ν(CO) 1217s, 1096s; ν(PF) 849vs; other bands at 1589w, 1556w, 1438s, 1316w, 1275vw, 1196m, 1171m, 1118vw, 1102m, 1063vw, 1035 vw, 1010w, 975m, 891m, 788vw, 760s, 754m, 710sh, 706s, 696m, 607w, 570s, 547s, 536s, 527m, 518m, 506m, 471m, 465m, 454vw, 429m cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 1·78, t (br), *J*(HH) 7·5, 2H, CH_2; 3·90, t, *J*(HH) 7·5, 2H, CH_2; 4·82, s, 5H, C_5H_5; 6·97, 7·33, 7·40, m, 30H, PPh_3. ^{13}C n.m.r.: δ($CDCl_3$) 22·6, s, C(4); 60·8, m, C(5); 81·6, s, C(3); 91·2, s, C_5H_5; 128·3-135·9, m, PPh_3; 300·5, t, *J*(CP) 14 Hz, RuC.

Methylation of Complex (31)

Addition of n-butyllithium (0·8 ml of a 2·4 M solution in diethyl ether) to $\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta-C_5H_5)\}PF_6$ (530 mg, 0·59 mmol) in tetrahydrofuran (30 ml) gave a yellow solution. After reaction overnight, iodomethane (1 ml, excess) was added, and the solution was stirred for 4 h. A yellow flocculent precipitate separated. Filtration, and recrystallization of this solid from dichloromethane/light petroleum, afforded yellow *crystals* of $[Ru(\overline{CCMe_2CH_2CH_2O})(PPh_3)_2(\eta-C_5H_5)]PF_6$ (40) (330 mg, 60%), m.p. 197-198° (Found: C, 60·5; H, 4·9%. $C_{47}H_{45}F_6OP_3Ru$ requires C, 60·5; H, 4·9%). Infrared (Nujol): ν(CO) 1181sh, 1167m, 1159m, 1096m; ν(PF) 851vs; other bands at 1317w, 1096m, 1023w, 1008vw, 973m, 756s, 708s 570m, 547m, 536s, 527sh, 510w, 496w, 471w, 428vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 1·29, t, *J*(HH) 6·9 Hz, 2H, C(4)H_2; 1·40, s, 6H, Me; 3·77, t, *J*(HH) 6·9 Hz, 2H, C(3)H_2; 4·97, s, 5H, C_5H_5; 6·98, 7·31, 7·40, m, 30H, PPh_3. ^{13}C n.m.r.: δ($CDCl_3$) 26·9, s, Me; 38·1, s, C(4); 67·0, s, C(5); 79·5, s, C(3); 89·0, s, C_5H_5; 128·5-135·7, m, PPh_3; 310·8, t, *J*(CP) 12 Hz, RuC.

Deprotonation of Alkoxycarbene Complexes

(A) $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta-C_5H_5)\}PF_6$ *(2).* Upon adding a sodium methoxide solution (sodium, 50 mg, 0·002 g atom, in methanol, 15 ml), to a stirred suspension of (2)(300 mg, 0·31 mmol) in methanol (30 ml), a fine yellow *powder* was precipitated. After 2 h this was collected and identified as $Ru[C(OMe)=CHPh](PPh_3)_2(\eta-C_5H_5)$ (41) (225 mg, 88%) m.p. 137-139° (Found C, 72·1; H, 5·0%. $C_{50}H_{44}OP_2Ru$ requires C, 72·9; H, 5·4%). Infrared (Nujol): ν(C=C) 1592m, 1588sh, 1570w, 1541s; ν(CO) 1251w cm^{-1}; other bands at 1433s, 1310w, 1197w, 1187w, 1183sh, 1156w, 1119vw, 1108vw, 1088s, 1070w, 1041s, 1030sh, 1000w, 919w, 893w, 841vw, 830w, 796m, 770w, 750m, 738m, 722vw, 696vs, 618vw cm^{-1}. ^1H n.m.r.: $\delta(C_6D_6)$ 3·37, s, 3H, CH_3; 4·52, s, 5H, C_5H_5; 6·03, s, 1H, =CH; 7·0-7·5, m, 35H, Ph. ^{13}C n.m.r.: $\delta(C_6D_6)$ 59·1, s, CH_3; 84·6, s, =CH; 86·2, s, C_5H_5; 123·0-143·2, m, Ph; 193·1, t, *J*(PH) 7·5 Hz, RuC.

In a 'one-pot' synthesis of (41), $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1·0 g, 1·38 mmol), phenylacetylene (200 mg, 2·0 mmol) and NH_4PF_6 (250 mg, 1·53 mmol) in methanol (50 ml) were heated at reflux point for 22 h. Upon cooling, sodium (200 mg) was added and the solution refluxed briefly to give $Ru[C(OMe)=CHPh](PPh_3)_2(\eta-C_5H_5)$ (41) (970 mg, 85%) as a yellow powder.

(B) $\{Ru[C(OMe)Et](PPh_3)_2(\eta-C_5H_5)\}PF_6$ *(20).* A mixture of (20) (100 mg, 0·11 mmol) and sodium (50 mg, 0·002 g atom, in methanol 15 ml) was heated at reflux point for 1 h. After cooling and filtering under anaerobic conditions, the solution was further cooled (-10°) to precipitate $Ru[C(OMe)=CHMe](PPh_3)_2(\eta-C_5H_5)$ (42) (74 mg, 88%) as a yellow *powder*, m.p. 130° (dec). Infrared (Nujol): ν(C=C) 1580s, 1563s; ν(CO) 1188m cm^{-1}; other bands at 1432s, 1318m, 1160sh, 1152w, 1106m, 1091sh, 1088s, 1070w, 1053s, 1040sh, 1028w, 1009w, 1002sh, 1000w, 988vw,

977vw, 877m, 860sh, 830w, 798m, 750m, 740s, 721vw, 698vs, 681m cm^{-1}. The infrared spectrum was virtually identical to that of (41). The complex proved highly unstable preventing further characterization.

(C) $\{Ru[C(OEt)CH_2Ph](CO)(PPh_3)(\eta\text{-}C_5H_5)\}PF_6$ *(26).* Upon mixing a suspension of (26) (130 mg, 0·17 mmol) in methanol (50 ml) with a sodium methoxide solution (sodium, 50 mg, 0·002 g atom, in methanol, 15 ml) a yellow *powder* precipitated. After 30 min this was collected and identified as $Ru[C(OEt)=CHPh](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (43) (90 mg, 86%) m.p. 226-228° (Found: C, 67·9; H, 5·1%, *M*, (mass spectrometry), 604. $C_{34}H_{31}O_2PRu$ requires C, 67·7; H, 5·2%, *M*, 604). Infrared ($CHCl_3$): ν(CO) 1938vs; ν(C=C) (Nujol) 1593w, 1572m, 1551s; ν(C-O) 1263m cm^{-1}; other bands at 1633s, 1340w(br), 1198w, 1182w, 1157w, 1109w, 1088s, 1059s, 1025w, 1007sh, 997s, 990m, 907w, 892w, 841sh, 832m, 797s, 753sh, 746s, 730w, 692sh, 688s, 659w cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 0·4-1·5, m, 3H, CH_3; 3·5-4·2, m, 2H, CH_2; 4·92, 4·98, 5·03, 3 x s, 5H, C_5H_5; 5·92, s, br, 1H, CH; 7·0-7·5, m, 30H, Ph.

Protonation of $Ru[C(OMe)=CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ *(41).*

A solution of (41) in $CDCl_3$ within an n.m.r. tube showed resonances at δ3·15 (CH_3), 4·33 (C_5H_5), and 5·66 (=CH), which disappeared on addition of HPF_6,OEt_2 with concomitant formation of peaks at δ3·49 (CH_3), 4·84 (C_5H_5), and 5·06 (CH_2) due to $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2).

Reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ *with 3-butyn-2-one*

A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (300 mg, 0·41 mmol), NH_4PF_6 (75 mg, 0·46 mmol), and 3-butyn-2-one (50 mg, 0·74 mmol) in methanol (90 ml) was heated at reflux point until an orange solution formed. On cooling, a sodium methoxide solution (sodium, 50 mg, 0·002 g atom, in methanol, 10 ml) was added and the mixture taken to dryness, washed with water (3 x 30 ml), and the residue extracted with chloroform (50 ml). After warming for 4 d (35-40°), preparative t.l.c. (7:10 diethyl ether/cyclohexane) yielded two major products:

(i) $\overleftarrow{\mathrm{Ru[C(OMe){=}CHCOMe]}}(\mathrm{PPh_3})(\eta\text{-}\mathrm{C_5H_5})$ (44, R_f = 0·9) was isolated from dichloromethane/hexane under anaerobic conditions as a yellow *powder* (32 mg, 15%) m.p. 134-138° (Found: C, 63·7; H, 5·4%, *M*(mass spectrometry), 528. $C_{28}H_{27}O_2PRu$ requires C, 63·8; H, 5·2%, *M*, 528) Infrared (Nujol): ν(CO) 1308s cm^{-1}; other bands at 1720m, br, 1583w, 1572w, 1212w, 1190m, 1180m, 1167m, 1149w, 1133m, 1100w, 1090m, 1070w, 1028w, 998w, 977m, 929w, 829vw, 798sh, 781m, 757m, 747w, 739m, 721w, 696s, 692s, 681w, 664vw, 642w cm^{-1}. ^{1}H n.m.r.: $\delta(C_6D_6)$ 1·75, d, J(PH) 1·5 Hz, 3H, CH_3; 3·60, s, 3H, OCH_3; 4·57, s, 5H, C_5H_5; 5·85, s, 1H, =CH; 7·2-7·7, m, 15H, Ph. ^{13}C n.m.r.: $\delta(C_6D_6)$ 23·0, s, CH_3; 59·4, s, OCH_3; 78·7, s, C_5H_5; 112·5, s, =CH; 127·3-138·0, m, Ph; 201·8, s, CO; 271·6, d, J(CP) 14 Hz, RuC.

(ii) $\mathrm{Ru(C{\equiv}CCOMe)(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})$ (45, R_f = 0·3), was isolated as yellow *microcrystals* from dichloromethane/methanol (46 mg, 15%) m.p. 213-216° (Found: C, 70·6; H, 5·2%, *M*(mass spectrometry), 758. $C_{45}H_{38}OP_2Ru$ requires C, 71·3; H, 5·1%, *M*, 758). Infrared (CH_2Cl_2): $\nu(C\equiv C)$ 2048vs; $\nu(C\equiv O)$ 2011vs; $\nu(C{=}O)$ 1602vs cm^{-1}; other bands at (Nujol) 1437s, 1346w, 1311vw, 1266vw, 1218m, 1206sh, 1192sh, 1184w, 1151w, 1104vw, 1097s, 1089s, 1071w, 1061vw, 1029w, 1009w, 1001w, 978w, 912vw, 862w, 833m, 811m, 757m, 742s, 696vs cm^{-1}. ^{1}H n.m.r.: $\delta(CDCl_3)$ 1·98, s, 3H, Me; 4·39, s, 5H, C_5H_5; 7·4, m, 30H, Ph.

Similarly $\mathrm{RuCl(PPh_3)_2}(\eta\text{-}\mathrm{C_5H_5})$ (150 mg, 0·21 mmol), and 3-butyn-2-one (200 mg, 2·9 mmol) were reacted in methanol (30 ml, 30-35°) for 1·25 h.

The mixture was filtered into a sodium methoxide solution (sodium, 50 mg, 0·002 g atom, in methanol, 10 ml) which led to the precipitation of yellow *crystals*(90 mg). These were identified by ^{1}H n.m.r. spectroscopy as a 3:5 mixture of $Ru(C{\equiv}CCOMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (45) (*c.* 22%, ^{1}H n.m.r. as described above) and $Ru[C(OMe){=}CHCOMe](PPh_3)_2(\eta\text{-}C_5H_5)$ (46) [*c.* 34%, ^{1}H n.m.r.: $\delta(CDCl_3)$ 1·95, s, 3H, Me; 3·02, s, 3H, OMe; 4·32, s, 5H, C_5H_5; 6·06, t, *J*(PH) *c.* 1 Hz, 1H, =CH; 7·4, m, Ph]. Upon standing in $CDCl_3$ (48 h, 35°) the spectrum of (45) remains unchanged, while (46) loses PPh_3 to give $\overline{Ru[C(OMe){=}CHCO}Me](PPh_3)(\eta\text{-}C_5H_5)$ (44) [^{1}H n.m.r.: $\delta(CDCl_3)$ 1·65, d, J(PH) 1·5 Hz, 3H, Me; 3·73, s, 3H, OMe, 4·49, s, 5H, C_5H_5; 5·62, d, J(PH) 1·5 Hz, 1H, =CH; 7·3, m, Ph]. A sharp singlet appeared at δ7·32 and is assigned to free PPh_3.

Reaction of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ *with Dioxygen.*

(A) After stirring a solution of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (200 mg, 0·21 mmol) in dichloromethane (20 ml) for 20 h under an oxygen atmosphere, hexane was added until all the organometallic salt had precipitated. Benzaldehyde was shown to be the only organic product in the supernatant by t.l.c. (1:9 diethyl ether/light petroleum) and by formation of the 2,4-dinitrophenylhydrazone, m.p. 234° (lit 237°). Extraction of the residue into dichloromethane (2 x 5 ml) and dropwise filtration into stirred diethyl ether (50 ml) gave $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$-$PF_6$ (134 mg, 73%) as a fine white *powder*; this was confirmed by i.r. and n.m.r. comparison with literature values.[13]

(B) Stirring a mixture of $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (300 mg, 0·32 mmol) and H_2O_2 (30%, 5 ml) in dichloromethane (30 ml) for 1 h, and using the work-up procedure described above, gave $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$

(170 mg, 62%) and benzaldehyde (2,4-dinitrophenyl hydrazone derivative, m.p. 234°, lit. 237°).

Preparation of $[Ru(C{=}CHBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ *(22).*

3,3-Dimethylbutyne (15 drops, excess) was added to a suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (280 mg, 0.39 mmol) and ammonium hexafluorophosphate (70 mg, 4·3 mmol) in methanol (50 ml). The mixture was heated at reflux for 15 min, to give a red solution which was evaporated to dryness. Extraction of the solid residue with dichloromethane (3 ml) and filtration into stirred diethyl ether (50 ml) gave a fine orange-pink precipitate, which was collected, reprecipitated from a dichloromethane/diethyl ether mixture, and finally filtered off, washed with light petroleum/diethyl ether, and dried to give pure $[Ru(C{=}CHBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (22) (270 mg, 76%) as a reddish-purple *powder*, m.p. 170-173° (Found: C, 61·4; H, 4·6%. $C_{47}H_{45}F_6P_3Ru$ requires C, 61·5; H, 4·9%). Infrared (Nujol): ν(CC) 1672m, 1646m; ν(PF) 838vs; other bands at 1251w, 1226w, 1092m, 759m, 749w, 743m, 721m, 694s, 663w, 555w cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 1·15, s, 9H, Me; 4·25, t, *J*(PH) 3 Hz, 1H, CH; 5·17, s, 5H, C_5H_5; 7·3, m, 30H, Ph.

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CHAPTER THREE

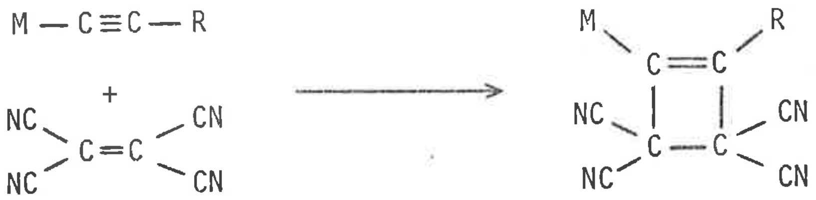
THE REACTIONS OF SOME METAL ACETYLIDE COMPLEXES WITH ELECTRON DEFICIENT OLEFINS.

Page

3.1 *INTRODUCTION*

The electron-rich C≡C triple bond of metal acetylide complexes is attacked by H^+ forming metal vinylidene complexes (Section 1.3.1.4). The possibility of the acetylide bond reacting with other electrophiles was also recognised and led initially to the exploration of reactions between tetracyanoethylene (tcne) and metal acetylide complexes.

Tetracyanoethylene is a well known (2+2)-cycloaddition reagent in reactions with olefinic bonds,[1] and while it seemed possible that a cyclobutenyl product could form by a similar route:



nevertheless such reactions are not known for purely organic alkynes. While an unconfirmed report of such a product did appear,[2] a reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne led to an allylic product, $Ru[\eta^3\text{-}C(CN)_2\text{-}C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$. This unusual result raised a number of questions about the mechanism of the reaction and the chemistry of the products. Hence, a variety of metal acetylide complexes have been treated with tcne and other electron-deficient olefins. The reaction of $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ with tcne has been particularly enlightening, yielding fully characterized cyclobutenyl, butadienyl and allylic complexes. In all cases the initial reaction of the acetylide complex with tcne yields at least one paramagnetic intermediate, detected by its e.s.r. signals.

3.2 RESULTS

3.2.1 Reactions of Tetracyanoethylene (tcne)

3.2.1.1 With W(C≡CPh)(CO)$_3$(η-C$_5$H$_5$) (1) A reaction of W(C≡CPh)(CO)$_3$(η-C$_5$H$_5$) with tcne in benzene led to the immediate formation of a green solution which exhibits a nine-line e.s.r. spectrum (g = 1·997) (This spectrum is discussed in Section 3.2.4.3, Figure 11A). A reaction carried out in diethyl ether, on the other hand, resulted in precipitation of yellow crystals. These were shown to be a cyclobutenyl complex, W[$\overline{\text{C=C(Ph)C(CN)}_2\text{C}}(CN)_2$](CO)$_3$(η-C$_5H_5$) (2), by a crystal structure study (Figure 1). The spectral and microanalytical data are consistent with the structure of this and all other complexes described (see Experimental), except where otherwise noted.

If a solution of complex (2) in CDCl$_3$ was allowed to stand for 24 hours the ^{1}H n.m.r. resonances at δ6·16 (C$_5$H$_5$) and 7·64 (C$_6$H$_5$) disappeared with concomitant formation of new resonances at δ5·91 and 7·8. These resonances are assigned to a butadienyl complex, W{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(CO)$_3$(η-C$_5$H$_5$) (3), which was also formed in a reaction of W(C≡CPh)(CO)$_3$(η-C$_5$H$_5$) and tcne over two days in the dark. This complex was identified by comparing its spectral data with that of similar ruthenium-butadienyl complexes which had been characterized by crystal structure studies (Section 3.2.4 and Experimental).

A minor product in the reaction of W(C≡CPh)(CO)$_3$(η-C$_5$H$_5$) and tcne is W[η^3-C(CN)$_2$C(Ph)C=C(CN)$_2$](CO)$_2$(η-C$_5$H$_5$) (4), also formed by irradiation of complex (3). The structure of complex (4) was determined by X-ray diffraction methods (Figure 2). The particular crystal chosen was obtained directly from the mother liquor and included half a molecule of tcne per unit cell. Spectral properties of similar allylic complexes are discussed in Section 3.2.4.

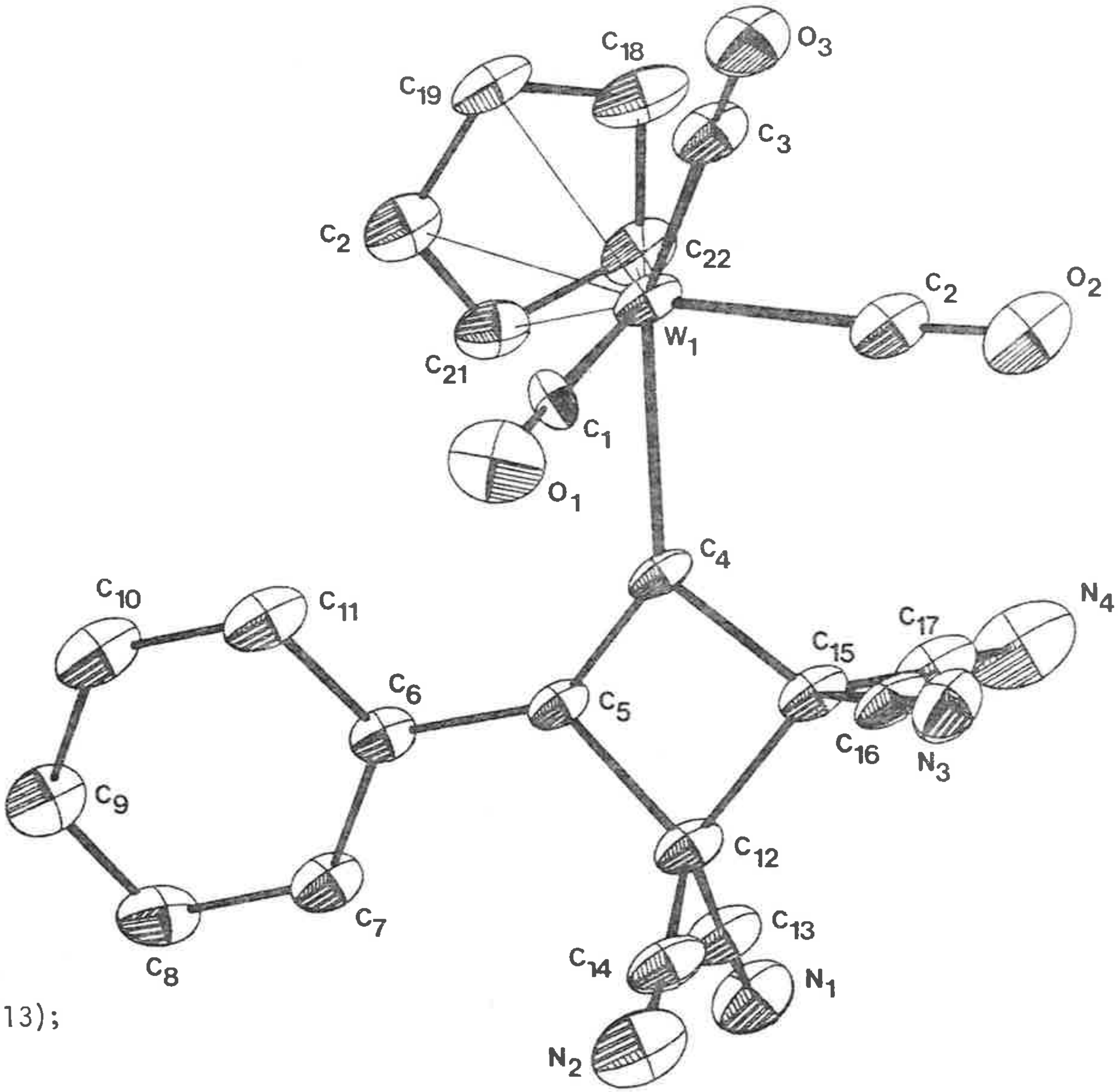


Figure 1. Structure of $W[\overline{C=C(Ph)C(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (2) (by T.W. Hambley, J.R. Rodgers and M.R. Snow). Selected bond lengths: W(1)-C(4), 2·202(9); C(4)-C(5), 1·344(11); C(5)-C(12), 1·524(12); C(12)-C(15), 1·602(13); C(4)-C(15), 1·552(11)Å. R = 3·6%.

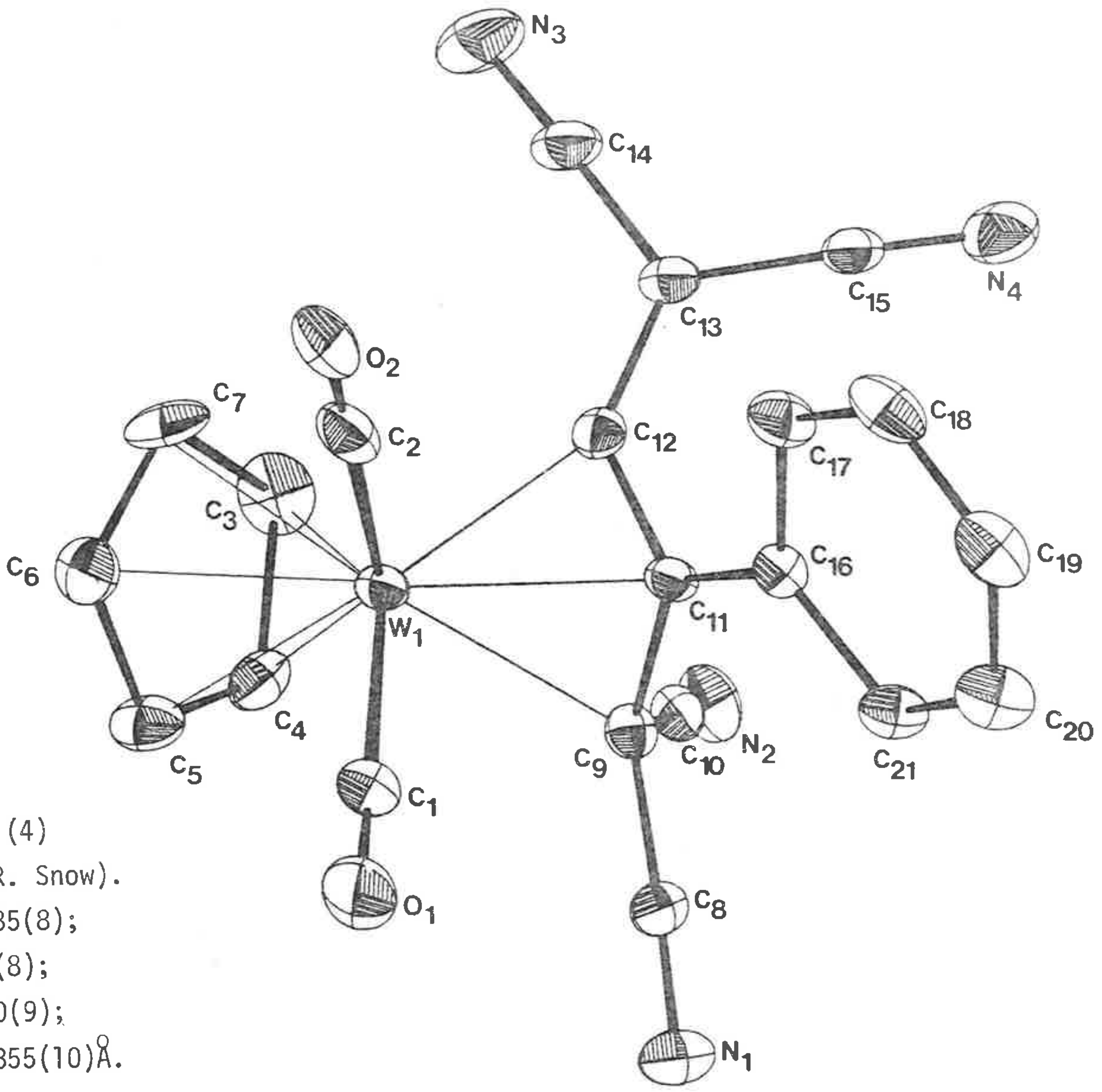
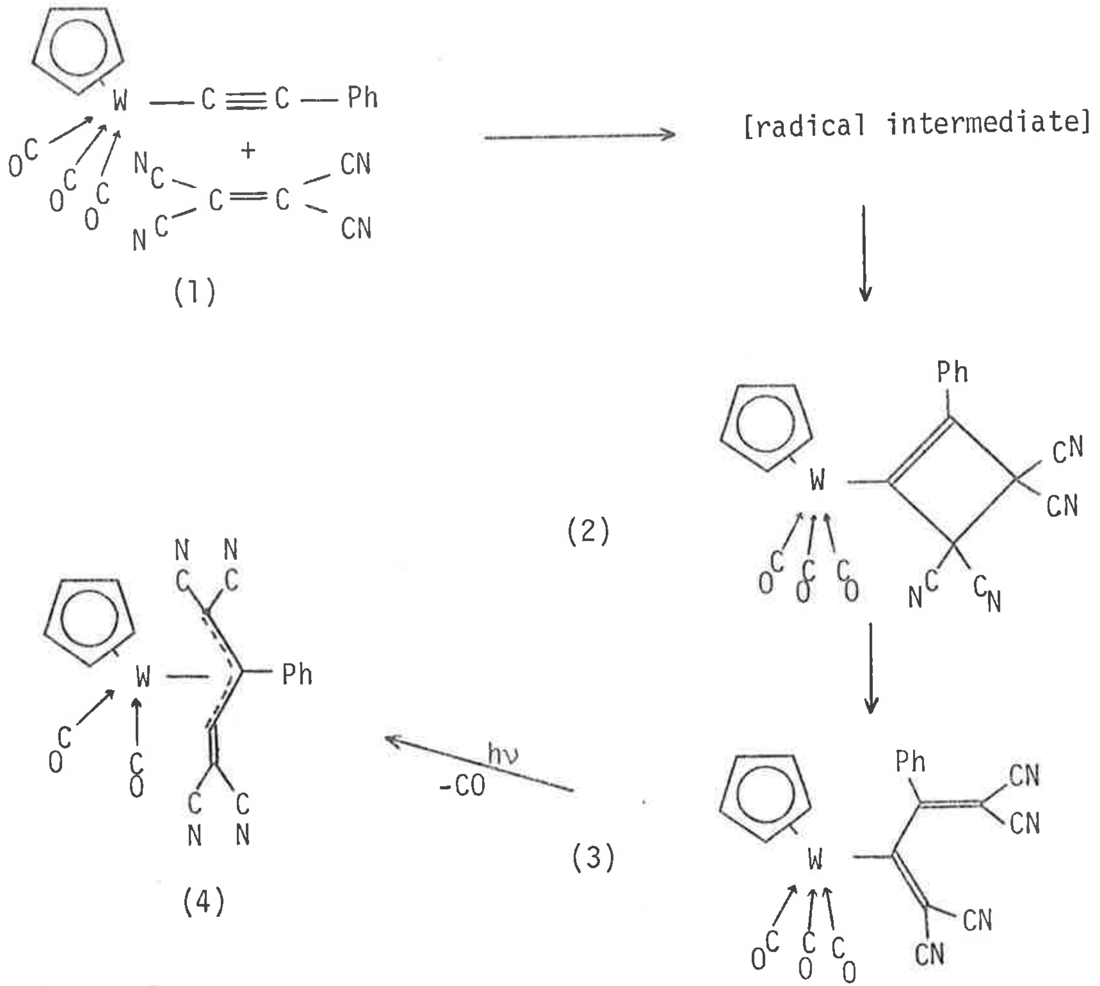


Figure 2. Structure of $W[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (4) (by T.W. Hambley, J.R. Rodgers, and M.R. Snow). Selected bond lengths: W(1)-C(9), 2·285(8); W(1)-C(11), 2·253(7); W(1)-C(12) 2·075(8); C(8)-C(9), 1·429(10); C(9)-C(11), 1·480(9); C(11)-C(12), 1·439(9); C(12)-C(13), 1·355(10)Å. R = 3·9%.

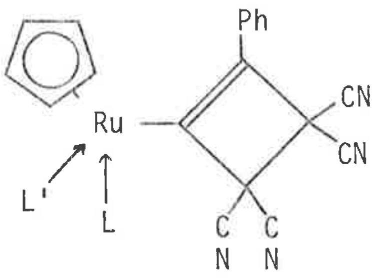
The sequence of steps in the formation of $W[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](CO)_2\text{-}(\eta\text{-}C_5H_5)$ from $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ is summarised in Scheme 1.



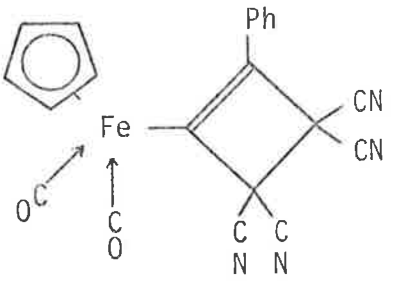
Scheme 1.

3.2.1.2 With cyclopentadienyl iron and ruthenium complexes

3.2.1.2.1 Formation of σ-cyclobutenyl complexes. Upon reacting tcne with $Ru(C{\equiv}CPh)(L)(PPh_3)(\eta\text{-}C_5H_5)$ [L=CO or $P(OMe)_3$] or $Fe(C{\equiv}CPh)(CO)_2\text{-}(\eta\text{-}C_5H_5)$ in diethyl ether, or with $Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$ in benzene, cyclobutenyl complexes (5) - (8) precipitated within minutes. These compounds were identified by comparing their infrared spectra with that of



(5) L = CO, L' = PPh_3
(6) L = $P(OMe)_3$, L' = PPh_3
(8) LL' = dppe



(7)

$W[\overline{C=C(Ph)C(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (Section 3.2.4.2). The mass spectra have molecular ions consistent with a 1:1 tcne/metal acetylide adduct (see Experimental). In solution ring-opening to butadienyl complexes was observed by ^1H n.m.r. spectroscopy, the butadienyl complexes (9) - (12) being subsequently isolated and fully characterized (Section 3.2.1.2.3). Isomerisation of (6) and (7) to the butadienyl complexes was observed in the solid state at room temperature.

3.2.1.2.2 Allylic complexes A reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne in benzene gave a green coloration almost immediately. This solution exhibits a strong e.s.r. signal which comprises a 12-line spectrum ($g = 1{\cdot}999$) and another broad signal of about 14 lines (Figure 13). This spectrum is discussed in Section 3.2.4.3. The colour intensified dramatically over 3 h with a concomitant reduction in the intensity of the e.s.r. signal. Over a longer period orange crystals precipitated. A structural study (Figure 3) showed that an allylic complex, $Ru[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (13), had formed. This complex and the tungsten-allylic complex (4) have characteristic features in their infrared and ^{13}C n.m.r.

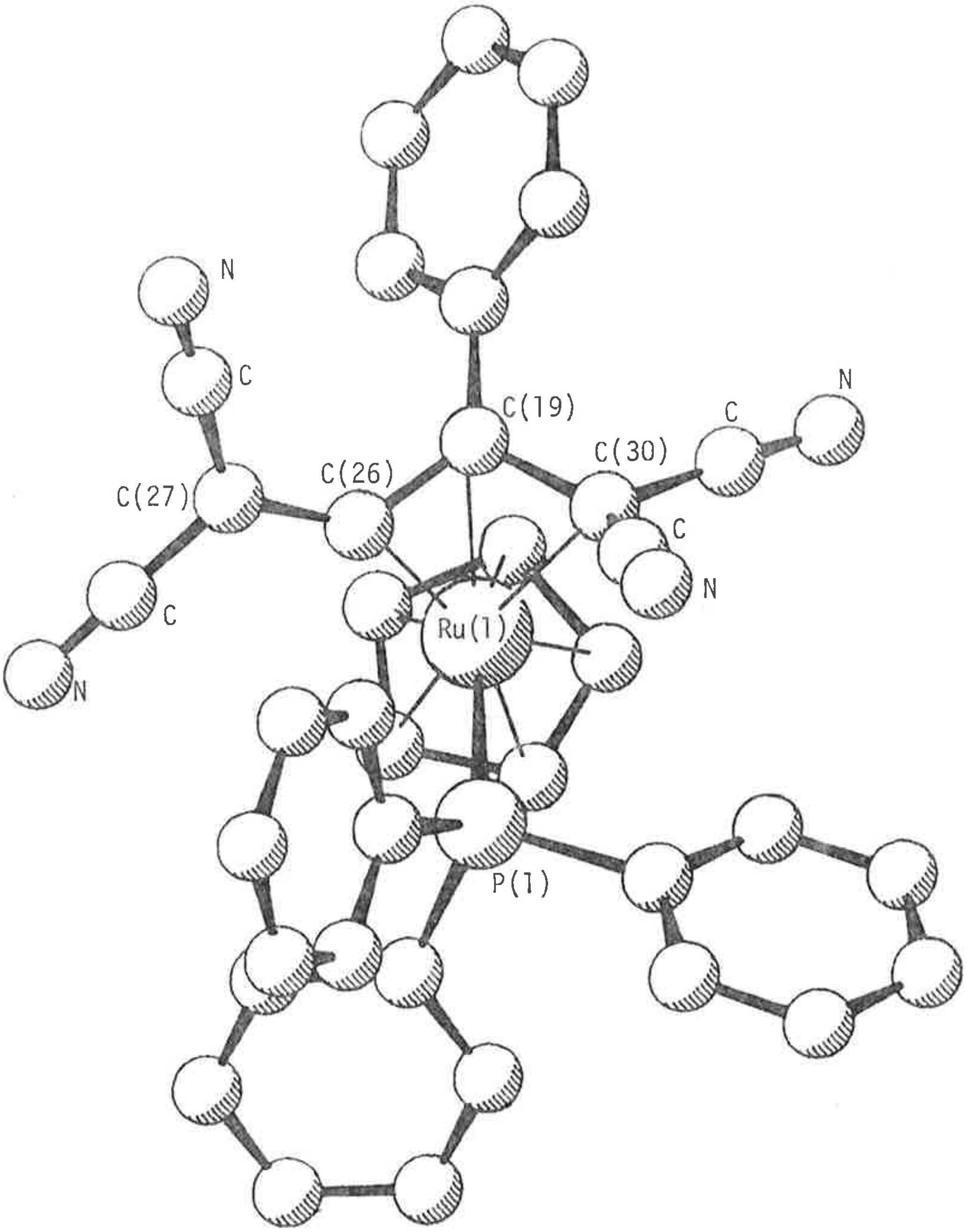
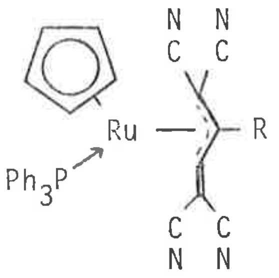


Figure 3. Structure of Ru[η^3-C(CN)$_2$C(Ph)C=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (13) (by J.R. Rodgers and M.R. Snow). Selected bond lengths; Ru(1)-C(19), 2·135(4); Ru(1)-C(26), 1·919(5); Ru(1)-C(30), 2·231(4); C(26)-C(27), 1·383(6); C(19)-C(26), 1·432(7); C(19)-C(30), 1·476(6)Å. R = 4·6%.

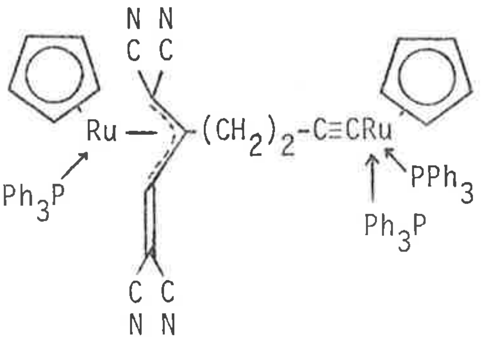
spectra, which are discussed in Section 3.2.4. By comparing these data with that for complexes (14) - (16), the latter have been identified as allylic complexes (Tables 3 and 8). Complex (14) was formed in a reaction



(13) R = Ph

(14) R = Me

of Ru(C≡CMe)$(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne. Complexes (15) and (16) were formed by reacting Ru$(PPh_3)_2(\eta\text{-}C_5H_5)$(C≡CCH$_2CH_2$C≡C)Ru$(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne in equimolar or excess amounts respectively.



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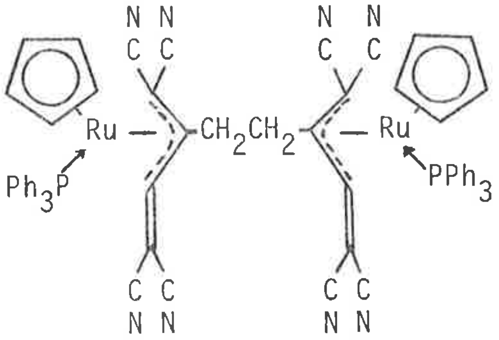


(16)

3.2.1.2.3 Butadienyl complexes If the allylic complex Ru[η^3-C(CN)$_2$-C(Ph)C=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (13) is reacted with CNBu^t at 70° a red butadienyl product, Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(CNBu^t)(PPh$_3$)(η-C$_5$H$_5$) (17), is formed. A similar butadienyl complex, Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(dppe)(η C$_5$H$_5$) (12), was formed in a reaction of Ru(C≡CPh)(dppe)(η-C$_5$H$_5$) with tcne. Both complexes (12) and (17) have been characterized by structural studies (Figures 4 and 5 respectively). These complexes have characteristic features in their ^{13}C n.m.r. and infrared spectra (Section 3.2.4) which

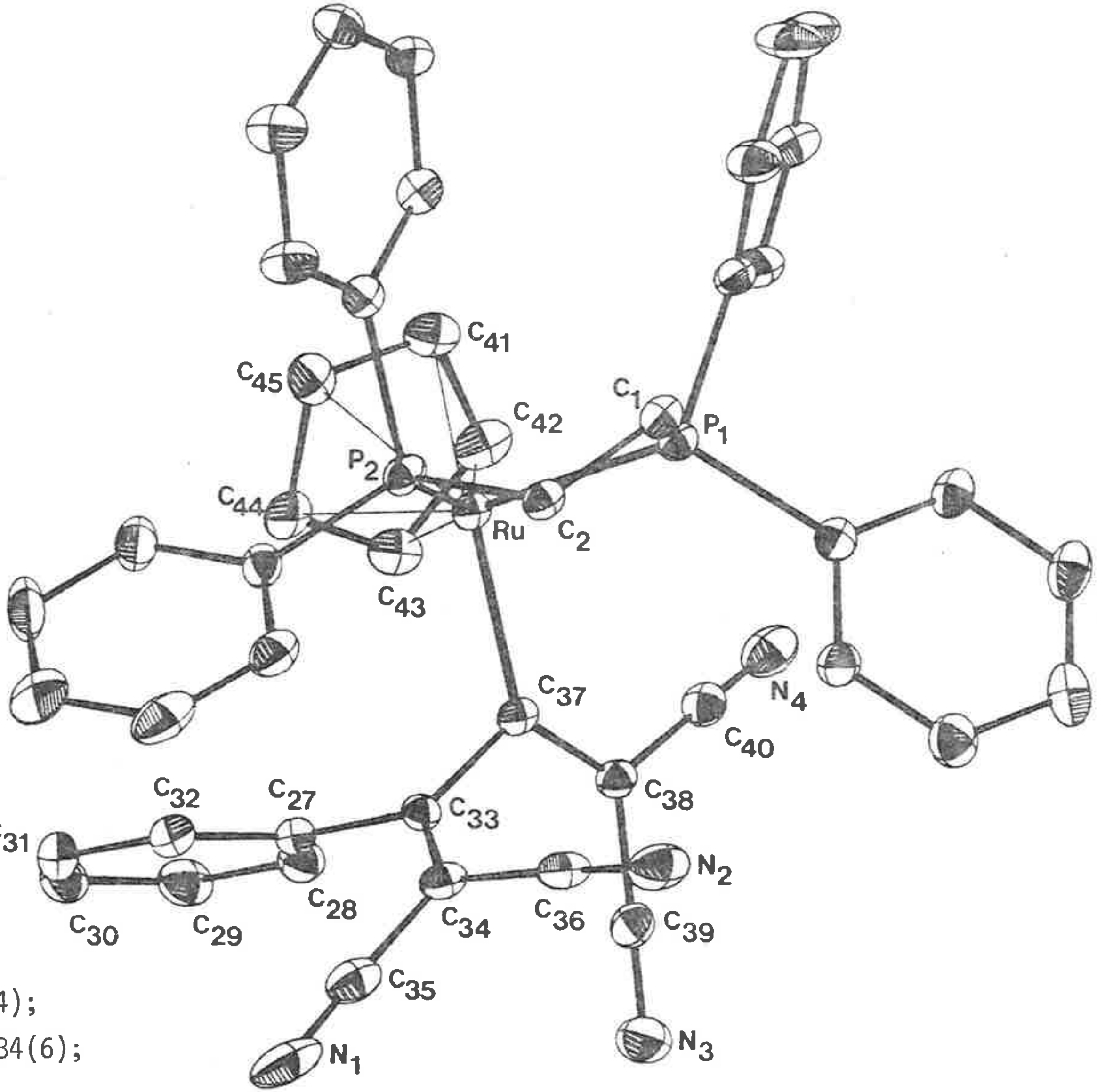


Figure 4. Structure of Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(dppe)-(η-C$_5$H$_5$) (12) (by T.W. Hambley, J.R. Rodgers and M.R. Snow). Selected bond lengths: Ru-C(37), 2·068(4); C(33)-C(34), 1·346(6); C(33)-C(37), 1·484(6); C(37)-C(38), 1·370(6)Å. R = 3·6%.

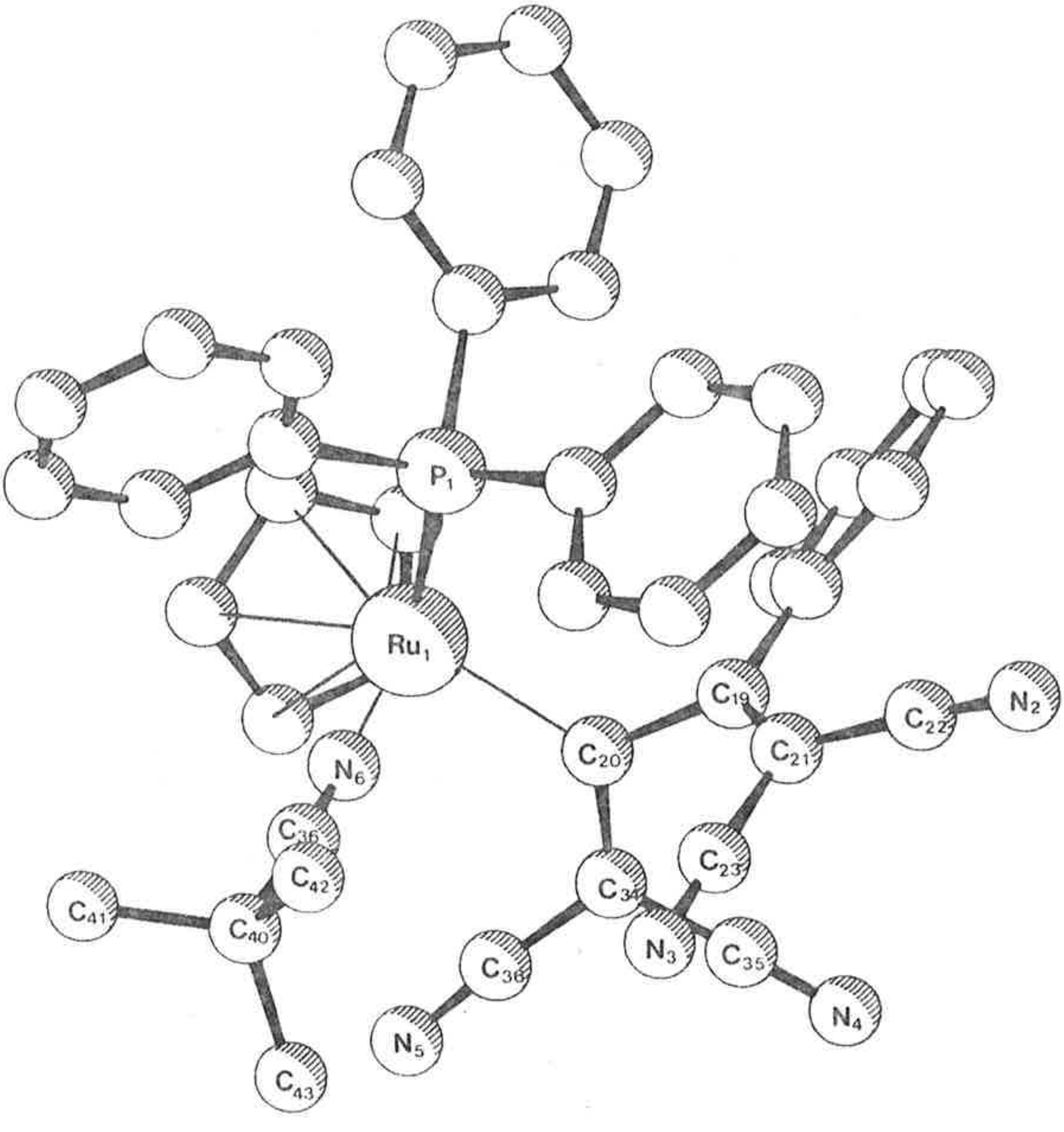
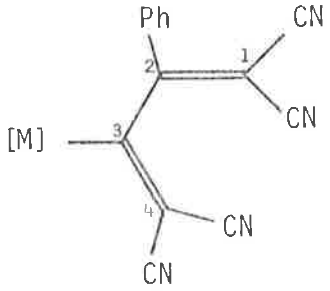


Figure 5. Structure of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$ (17) (by J.R. Rodgers and M.R. Snow). Selected bond lengths: Ru(1)-C(20), 2·074(3); Ru(1)-C(39), 2·003(3); C(19)-C(21), 1·362(4); C(19)-C(20), 1·478(4); C(20)-C(34), 1·382(5)Å. R = 3·7%.



[M]	no.
$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$	9
$Ru[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$	10
$Fe(CO)_2(\eta\text{-}C_5H_5)$	11
$Ru(dppe)(\eta\text{-}C_5H_5)$	12
$Ru(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$	17
$Ru(CNBu^t)_2(\eta\text{-}C_5H_5)$	18

enabled characterization of other butadienyl complexes, (9)-(11) and (18) (Tables 2 and 7). Complexes (9)-(11) were formed in reactions of $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$, $Ru(C{\equiv}CPh)[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$ and $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$, respectively, with tcne. Complex (9) was also formed by carbonylating $Ru[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (13), which reaction was reversed on irradiation. Complex (18) was formed in a reaction of (13) with excess $CNBu^t$ under vigorous conditions (150°). Its ^1H and ^{13}C n.m.r. spectra contained two singlets for each of the methyl and tertiary-carbon resonances suggesting that the two $CNBu^t$ ligands are non-equivalent. The ^1H n.m.r. spectrum of $Ru\{C[{=}C(CN)_2]C(Ph){=}C(CN)_2\}(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$ initially contained resonances due to methyl (δ1·33, s), cyclopentadienyl (4·62, s) and phenyl (7·4, m) protons. Upon warming the n.m.r. tube new methyl and cyclopentadienyl resonances appeared at δ1·26 and 4·54 respectively. An equilibrium dependent on solvent polarity (Table 1) is reached after a few hours. The original isomer, which always predominates, can be

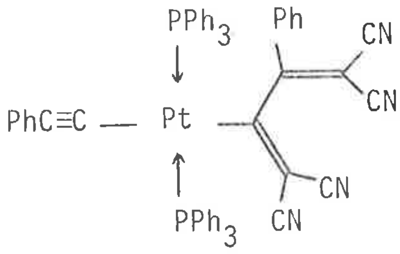
Table 1 The effect of solvent on the ratio of isomers of $Ru\{C[{=}C(CN)_2]\text{-}C(Ph){=}C(CN)_2\}(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$.

Solvent	Dielectric Consant	Isomer Ratio
C_6D_6	2·27	1:2·3
$CDCl_3$	4·81	1:2·3
$(CD_3)_2CO$	20·1	1:2·0
CD_3CN	36·7	1:1·4

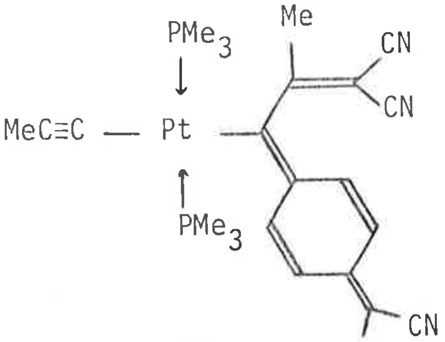
recovered (*c*. 90%) by slow crystallization from light petroleum. In the ^{13}C n.m.r. spectrum only the cyclopentadienyl group reflects the isomerisation with singlets at δ86·7 and 87·0 (major). When Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(CO)(PPh$_3$)(η-C$_5$H$_5$) is dissolved in CDCl$_3$ a similar isomerisation is observed in the ^{1}H n.m.r. spectrum. The two cyclopentadienyl resonances at δ4·86 and 5·16 are in the ratio 2:3. In the ^{13}C n.m.r. spectrum the cyclopentadienyl, carbonyl and diene carbons all reflect the isomerism. The trimethylphosphite complex, Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$), appears to be only one isomer from its ^{1}H n.m.r. spectrum. In changing from Ru[$\overline{\text{C=C(Ph)C(CN)}_2\text{C}}(CN)_2$][P(OMe)$_3$](PPh$_3$)(η-C$_5H_5$) to the butadienyl complex, two non-isolated intermediates are observed from their ^{1}H n.m.r. spectra.

The dppe complex, Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(dppe)(η-C$_5$H$_5$), has two cyclopentadienyl resonances in its ^{1}H (δ4·13, 5·04) and ^{13}C n.m.r. (δ86·3, 86·9) spectra. These do not appear to vary with solvent or time. A number of crystals of the complex have been chosen and their unit cells measured. These are identical to the cell observed for the structural study in Figure 4. Upon dissolving these crystals and observing their n.m.r. spectra the pair of cyclopentadienyl resonances were present in the same ratio as before. These experiments appear to indicate that the complex observed in the structural study gives two cyclopentadienyl resonances. A similar pair of resonances were observed for the cyclobutenyl complex Ru[$\overline{\text{C=C(Ph)C(CN)}_2\text{C}}(CN)_2$](dppe)(η-C$_5H_5$). The nature of the isomerism in these dppe complexes is not understood at this stage.

3.2.1.3 With other complexes A reaction of *trans*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$ with excess tcne gave a butadienyl complex (19). This was identified by its infrared and microanalytical data, and by comparison with a similar complex (20), formed in a reaction of *trans*-Pt(C≡CMe)$_2$(PMe$_3$)$_2$ with



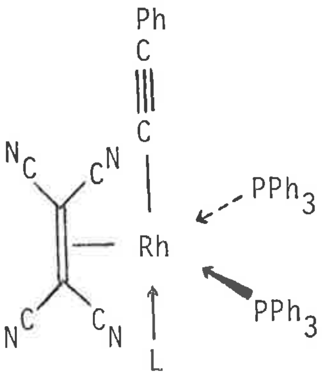
(19)



(20)

7,7,8,8-tetracyanoquinodimethane (tcnq).[3,4]

When *trans*-Rh(C≡CPh)(CO)$(PPh_3)_2$ was treated with tcne, oxidative-addition to the rhodium centre gave $Rh^{III}[\eta^2-C_2(CN)_4](C\equiv CPh)(PPh_3)_2$(co) (21). In the infrared spectrum ν(CO) appears at 2083 cm^{-1}, some 125 cm^{-1} above that observed for Rh(C≡CPh)(CO)$(PPh_3)_2$. Further reaction of (21) with tcne was not observed in tetrahydrofuran even at reflux point. Decomposition occurred if the reaction was carried out in refluxing benzene. In acetonitrile, however, a reaction at elevated temperature led to the displacement of CO by MeCN yielding (22). The identity of (22) was confirmed by a structural study (Figure 6).



(21) L = CO
(22) L = NCMe

Reactions of tcne with Au(C≡CPh)(PPh_3) or Cu(C≡CPh)(PPh_3) were observed but no pure products have yet been isolated.

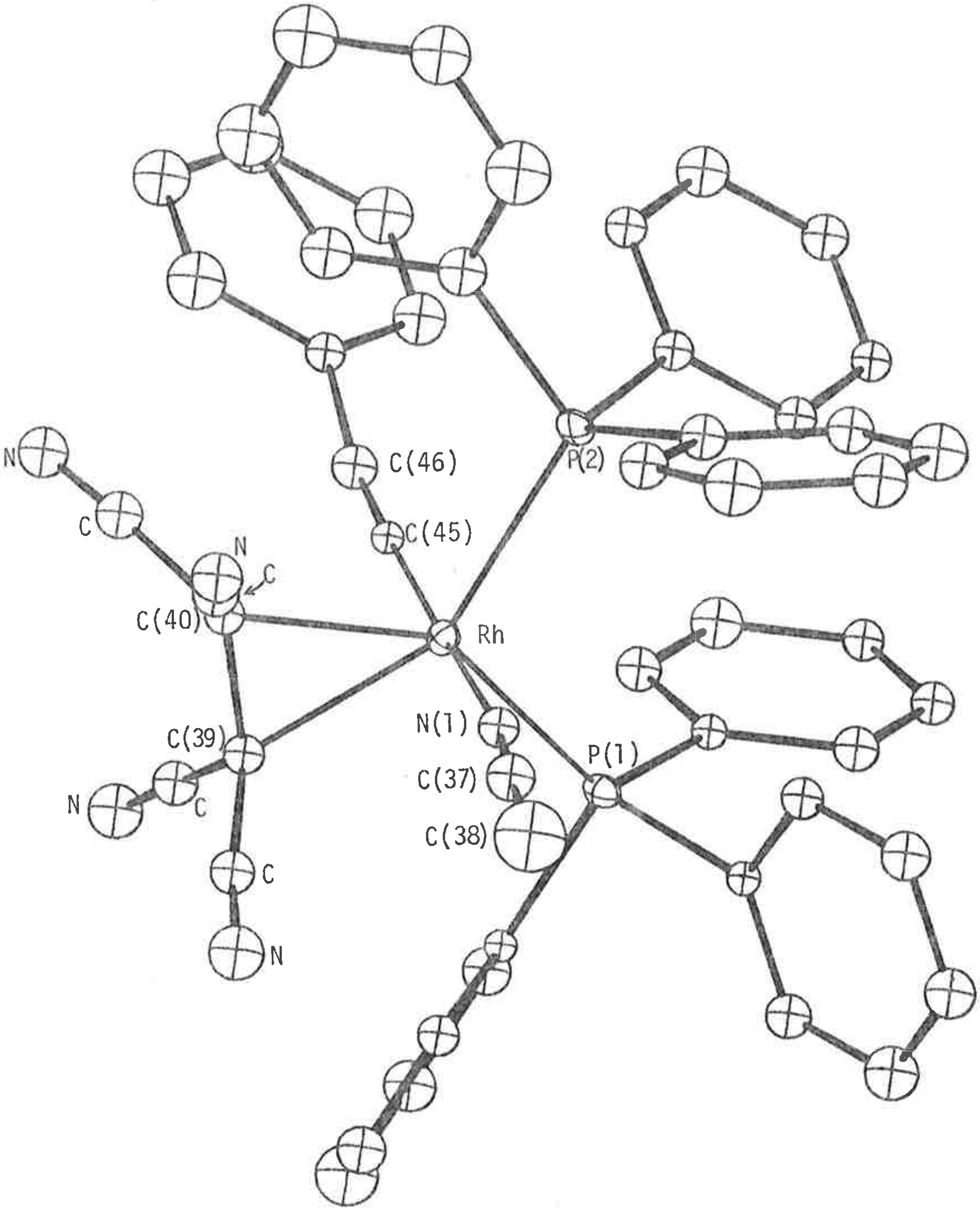
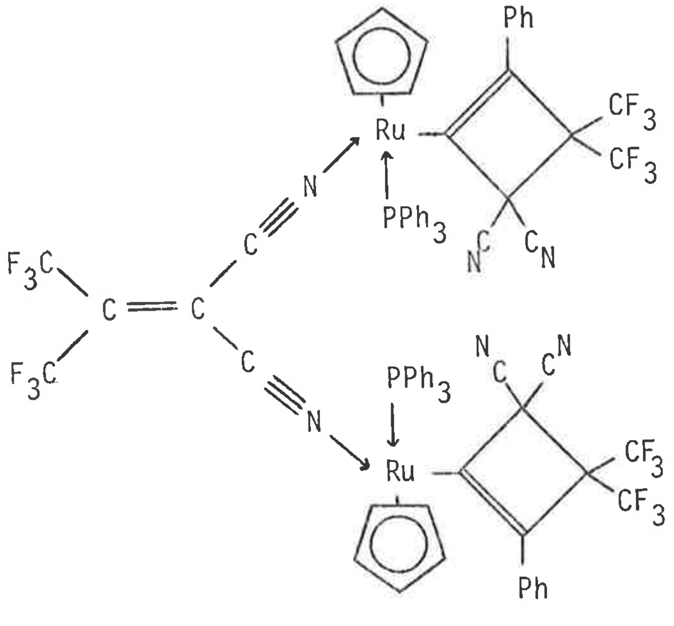


Figure 6. Structure of Rh[η^2-$C_2(CN)_4$](C≡CPh)(NCMe)(PPh_3)$_2$ (22) (by T.W. Hambley and M.R. Snow). Selected bond lengths: Rh-N(1), 2·051(16); Rh-C(39), 2·151(18); Rh-C(40), 2·157(19); Rh-C(45), 1·939(18); C(39)-C(40), 1·453(29); C(45)-C(46), 1·179(28)Å. R = 4·8%.

Tetracyanoethylene deprotonated $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$, yielding the acetylide complex $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$, while no reaction was observed between tcne and $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (100°, 18 h).

3.2.2 *Reactions of* $(NC)_2C{=}C(CF_3)_2$

A reaction of $(NC)_2C{=}C(CF_3)_2$ with $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ in benzene gave an initial green coloured solution which soon changed to an intense aquamarine solution. This exhibited a strong broad e.s.r. signal ($g = 2{\cdot}067$). Crystallization from octane yielded dark blue crystals of (23) which was characterized by a structural study (Figure 7).



(23)

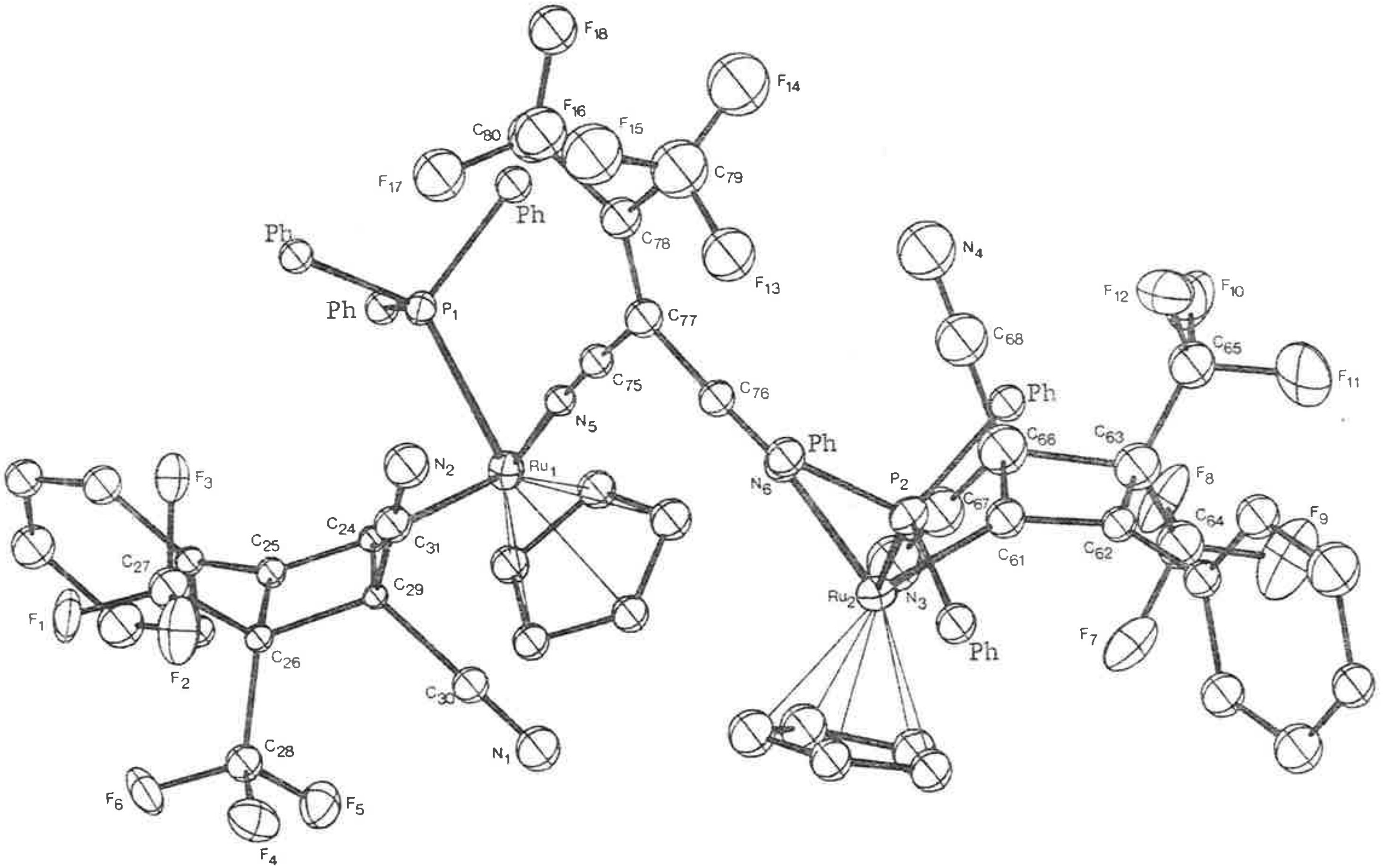


Figure 7. Structure of $\{Ru[\overline{C=C(Ph)C(CF_3)_2C}(CN)_2](PPh_3)(\eta-C_5H_5)\}_2\{\mu-(NC)_2C=C(CF_3)_2\}$ (23) (by T.W. Hambley, J.R. Rodgers and M.R. Snow). Selected bond lengths: Ru(1)-C(24), 2·066(20); Ru(2)-C(61), 2·012(24); Ru(1)-N(5), 1·978(14); Ru(2)-N(6), 1·978(16); N(5)-C(75), 1·167(24); N(6)-C(76), 1·151(28); C(75)-C(77), 1·417(29); C(76)-C(77), 1·408(31); C(77)-C(78), 1·367(34); C(24)-C(25), 1·296(25); C(25)-C(26), 1·528(27); C(26)-C(29), 1·526(25); C(24)-C(29), 1·598(25); C(61)-C(62), 1·385(33); C(62)-C(63), 1·552(36); C(63)-C(66), 1·673(44); C(61)-C(66), 1·667(34)Å. Selected bond angles: Ru(1)-N(5)-C(75), 176·0(18); Ru(2)-N(16)-C(76), 172·3(16); N(5)-C(75)-C(77), 177·2(22); N(6)-C(76)-C(77), 171·3(26); C(75)-C(77)-C(76), 110·3(20)°. R = 4·5%.

If a deficiency of the olefin is used, a mixture of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ and (23) results. This suggests that cycloaddition and ligand displacement occurs simultaneously. The crystals exhibit an e.s.r. signal in solution or in the solid state (g = 2·071, Figure 8). By comparing the area of the curve with that of a one-electron radical (2,2-diphenyl-1-picrylhydrazyl) it was calculated that about 0·04 of an unpaired electron per mole was present (25°). In spite of the small amount of unpaired electron density, n.m.r. spectra could not be observed. The infrared spectrum has bands at 2181s, 2155s, 2118vs, and 2021s, 1613w, 1577w and 1532s, and 1272vs, 1239vs, 1221vs and 1201s cm^{-1} assigned to $\nu(CN)$, $\nu(C{=}C)$ and $\nu(CF_3)$ respectively. In the electronic spectrum two broad absorptions were observed at 553 (ε, 7·2) and 754 nm (ε, 9·1).

The structural study of (23) indicates that $(NC)_2C{=}C(CF_3)_2$ has undergone a (2+2)-cycloaddition reaction with the acetylide group of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ forming a cyclobutenyl system. A unique feature is the dicyanomethylene bridge between the ruthenium atoms. This type of bonding is unprecedented to my knowledge. The e.s.r. signal of this compound decreases in intensity with a lowering of temperature (Figure 9). Below -50° a broadening is apparent, while at -90° the spectrum contains other features which are due to more than anisotropy. This behaviour is consistent with the system having a diamagnetic ground state and a triplet (paramagnetic) excited state which is populated thermally. The features in the frozen solution arise from spin-spin interactions of a triplet species.[5] As the temperature is decreased the population of the excited state decreases, however below -90°, the population increases. This reversal suggests that the energy difference between the ground and excited states decreases at low temperature, possibly due to changes in geometry. Paramagnetism has been observed for $Ti(bipy)(\eta\text{-}C_5H_5)_2$ and at low temperature a spectrum very similar to that for (23) was recorded.[6] It was suggested

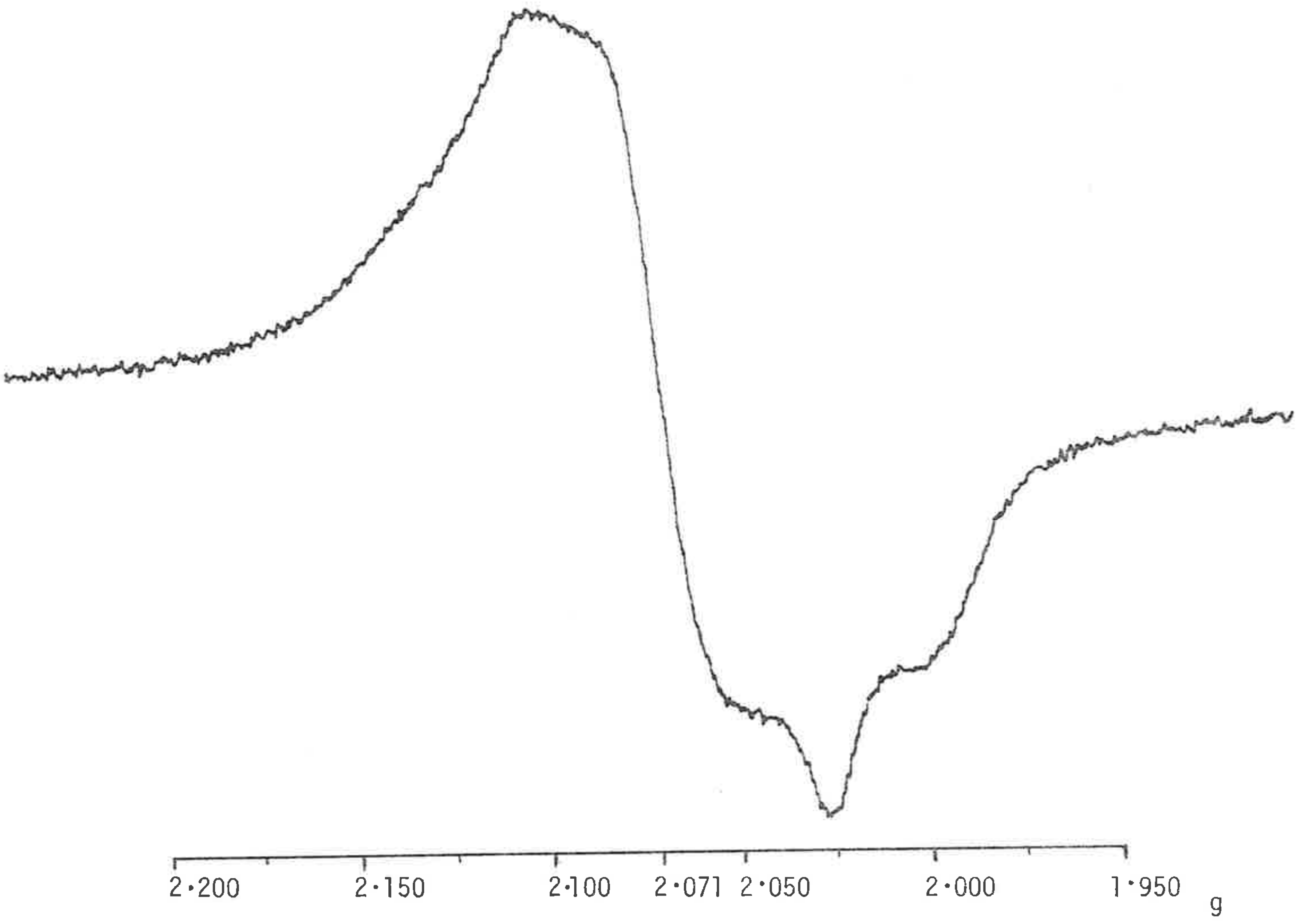


Figure 8. An e.s.r. spectrum of (23) as a solid.

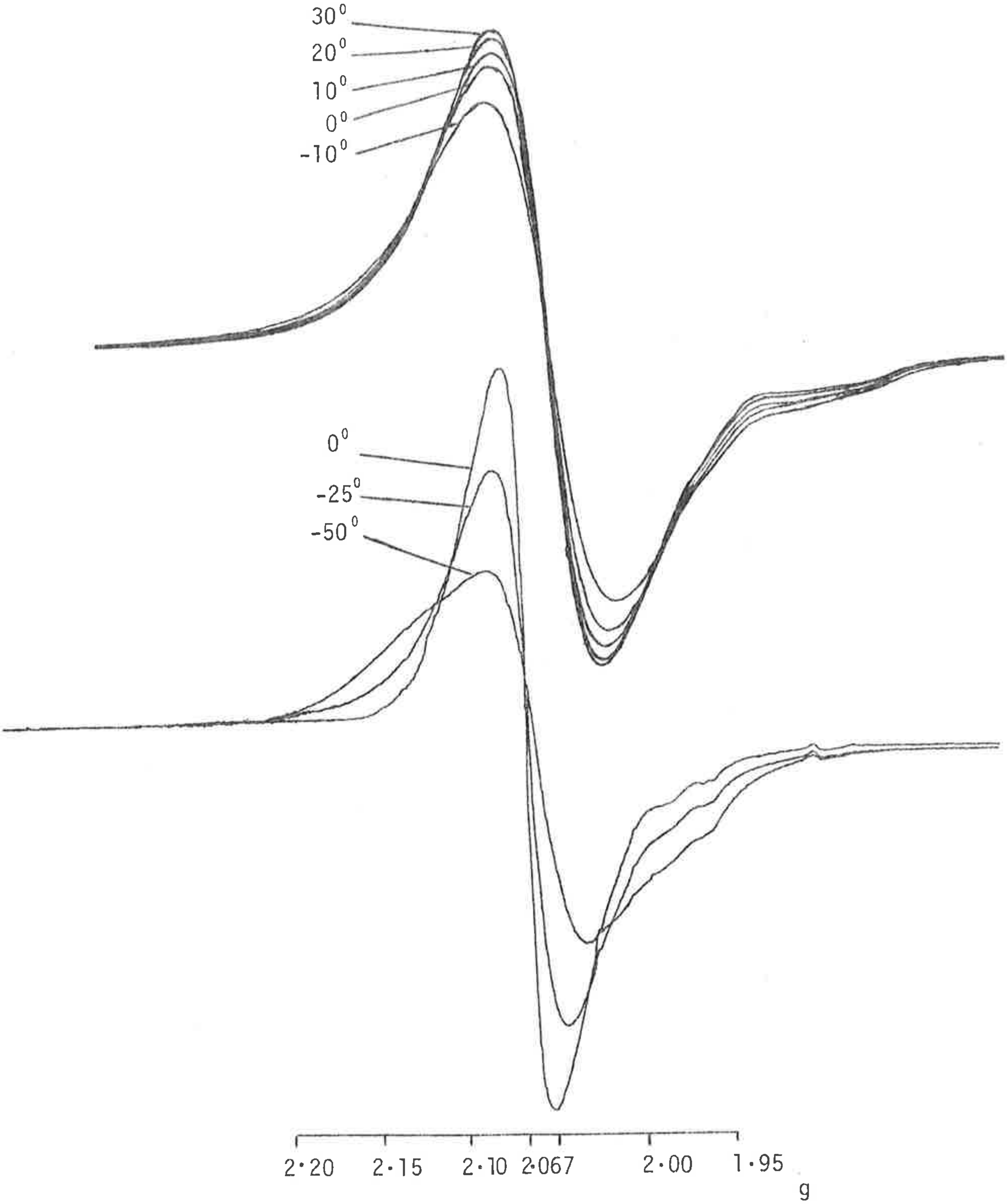


Figure 9. The variation in the e.s.r. signal of (23) with temperature from 30° to -145° in toluene.

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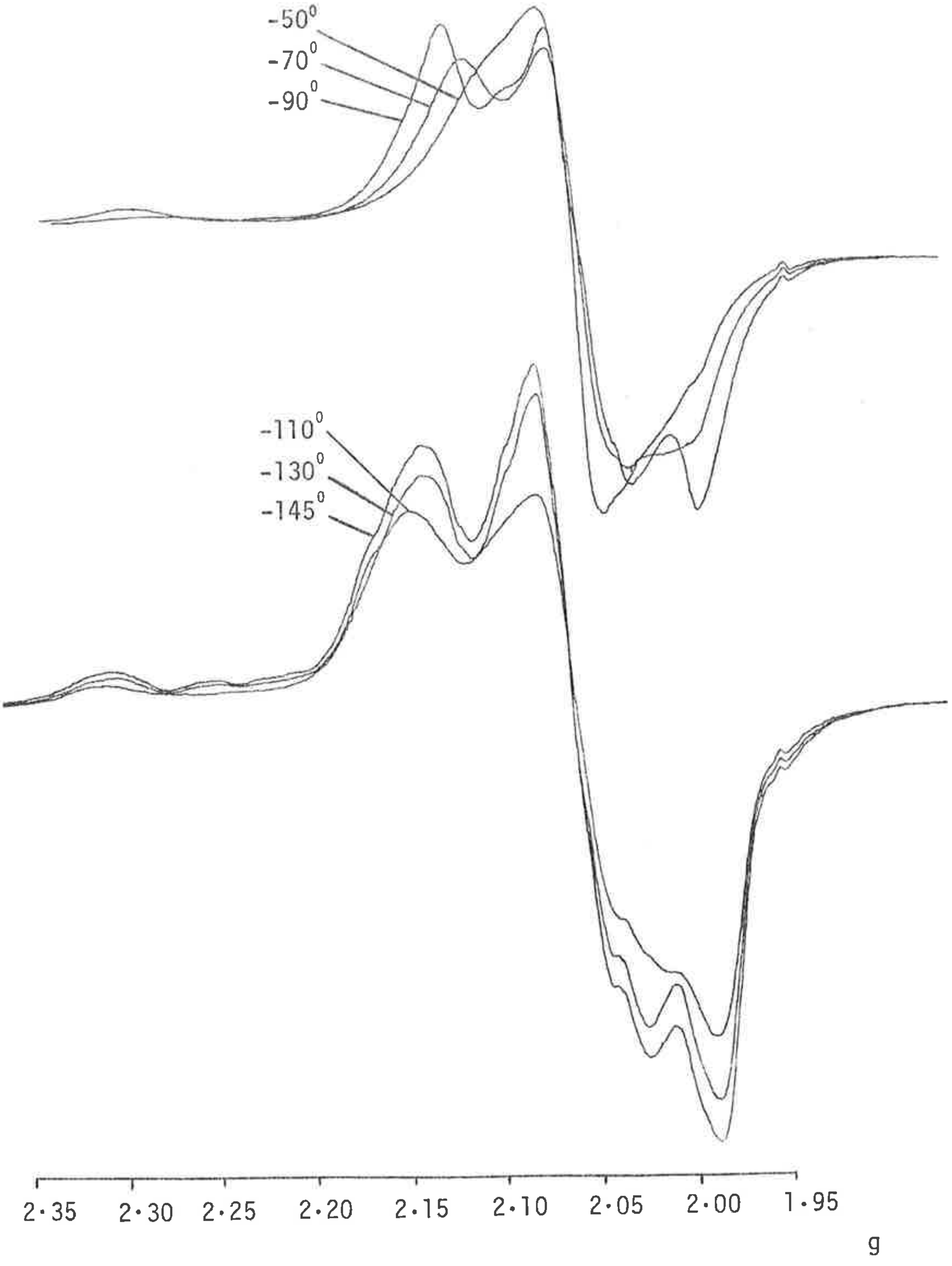
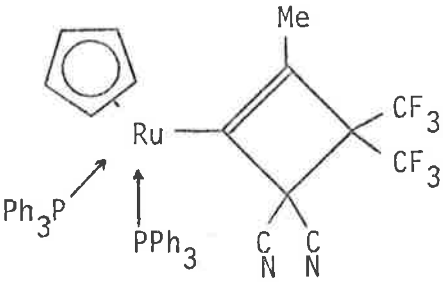


Figure 9 (cont'.)

for Ti(bipy)(η-C_5H_5)$_2$ that one electron was promoted from the metal to the bipyridyl ligand. A similar situation may arise for complex (23) where an electron is excited from the metal onto the bridging dicyanomethylene group.

The intense colour and strong electronic features observed for complex (23) probably arise from transitions between energy levels within the bridging group. It is unlikely that these features arise from the phosphine ligands or cyclobutenyl groups as $\mathrm{Ru[\overline{C{=}C(Me)C(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)}$ (described below) is not intensely coloured.

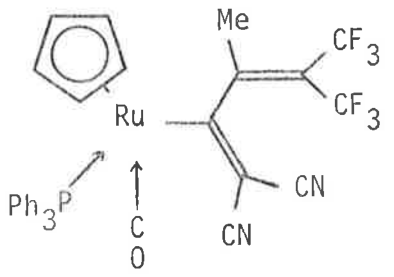
A reaction of $\mathrm{Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)}$ with $\mathrm{(NC)_2C{=}C(CF_3)_2}$ in toluene leads to precipitation of $\mathrm{Ru[\overline{C{=}C(Me)C(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)}$ (24) as yellow microcrystals. A blue tinge in the mother liquor may indicate that an analogue of (23) is a minor product. Complex (24) was shown from ^{1}H n.m.r. and microanalytical data to be a 1:1 adduct of $\mathrm{Ru(C{\equiv}CMe)(PPh_3)_2}$-($\eta$-$C_5H_5$) and $\mathrm{(NC)_2C{=}C(CF_3)_2}$; in the mass spectrum the highest ion appeared



(24)

at *m/e* 682 [$(M\text{-}PPh_3)^+$]. The ^{1}H n.m.r. spectrum has resonances at 0·53 (s), 4·64 (s) and 7·2 (m) assigned to methyl, cyclopentadienyl and phenyl groups respectively. In the ^{13}C n.m.r. spectrum resonances at 16·4 (s), 84·8 (s), 116·4 (s), 127·7 - 140·4 (m) and 149·6 (t, J(CP) = 4 Hz) are assigned to methyl, cyclopentadienyl, cyano, phenyl and Ru-bonded carbons respectively; resonances of other carbons were not observed before the complex decomposed to an unidentified product. In the infrared spectrum an extremely weak band at 2238 cm^{-1} is assigned to $\nu(CN)$ and suggests the formation of a cyclobutenyl group (see Section 3.2.4.2). Other bands at 1572m, and 1270vs, 1220s, 1179vs and 1197sh cm^{-1} are assigned to $\nu(C{=}C)$ and $\nu(CF)$ respectively.

Carbonylation of (24) gives (25) as two separable isomers. The minor isomer has been identified as a butadienyl complex by a structural study (Figure 10). The other isomer has virtually identical infrared, ^{1}H n.m.r. and mass spectra and is also assigned a butadienyl structure. When suitable crystals of this isomer have been obtained, and a structural study undertaken, a better understanding of the isomerism should be possible. In the mass spectrum of both complexes an ion appeared at *m/e* 724, 14 mass units above the molecular ion, presumably due to disproportionation in the mass spectrometer.



(25)

3.2.3 Reactions of Other Olefins

No reaction of $C_2(CO_2Et)_4$ with $Ru(C{\equiv}CPh)(L)(PPh_3)(\eta\text{-}C_5H_5)$ ($L{=}PPh_3$, 150°; $L = CO$, 80°) or $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ (80°) occurred. Similarly when $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $\overline{O(CH_2)_2OC} = C(CN)_2$ or *cis*-$C_2H_2(CO_2Me)_2$ were heated together in refluxing benzene for two and six hours respectively, no reaction was observed.

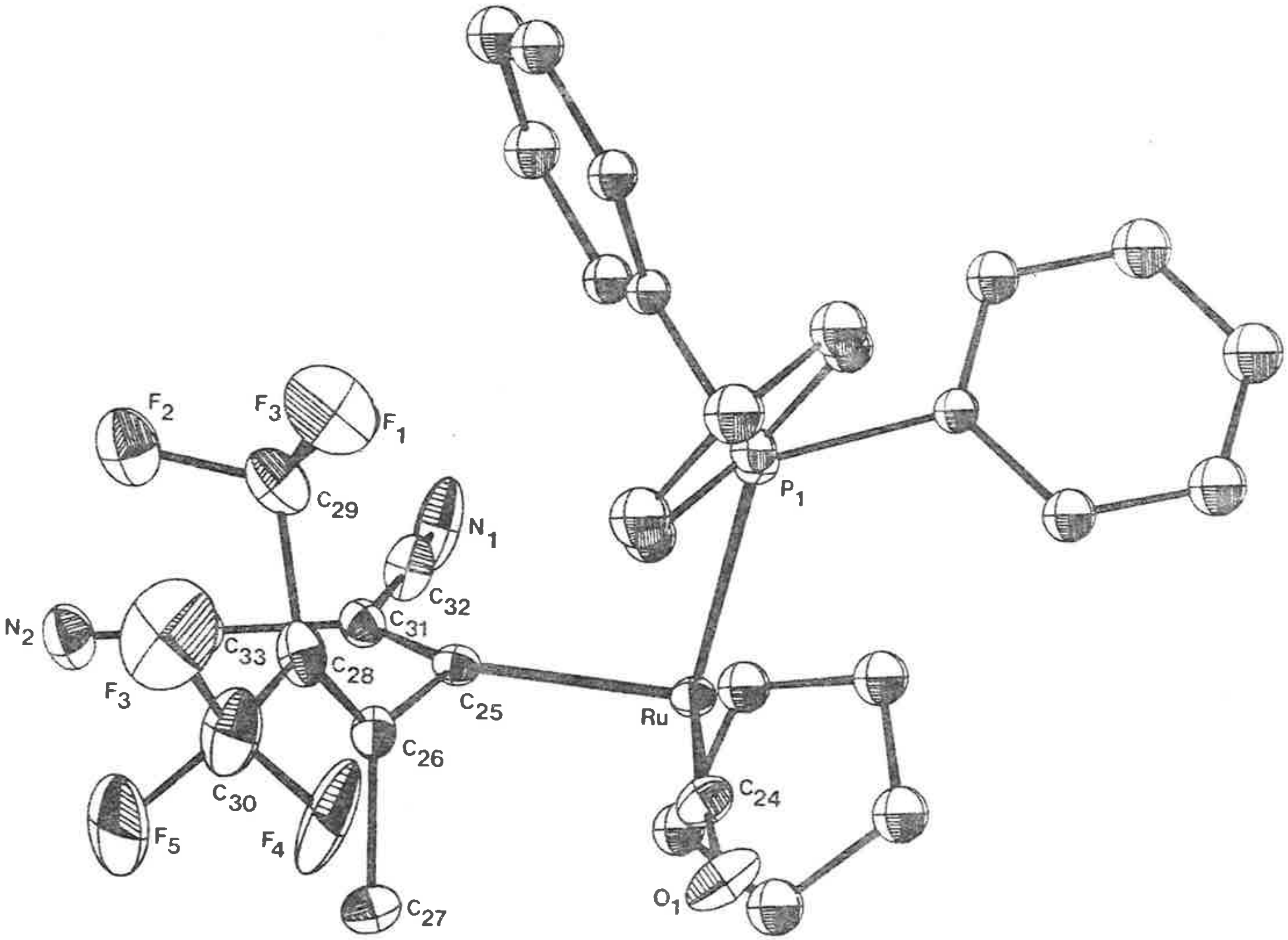


Figure 10. Structure of Ru{C[=C(CN)$_2$]C(Me)=C(CF$_3$)$_2$}(CO)(PPh$_3$)(η-C$_5$H$_5$) (25) (by T.W. Hambley and M.R. Snow). Ru-C(25), 2·106(5); C(25)-C(26), 1·493(8); C(25)-C(31), 1·362(8); C(26)-C(28); 1·328(8)Å. R = 3·9%.

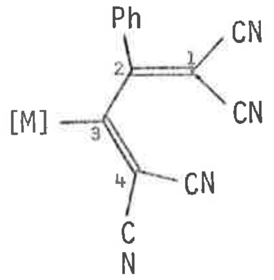
3.2.4 Spectroscopic Data

3.2.4.1 N.M.R. data While the cyclobutenyl complexes isomerised to butadienyl complexes before a ^{13}C n.m.r. spectrum could be recorded, spectra of most of the allylic and butadienyl complexes were recorded. The diene chain was of particular interest and gave characteristic sets of four carbon resonances for the butadienyl (Table 2) or allylic (Table 3) complexes.

The butadienyl complexes have diene resonances at 69·3 - 77·4, 94·0 - 99·8, 177·2 - 184·7, and 213·4 - 226·2 p.p.m. which are assigned to C(1), C(4), C(2) and C(3) respectively. The low field resonances have been assigned to C(3) because the coupling observed [*J*(CP) = 9 Hz for complex (18)] for some phosphine complexes, implying that this carbon is metal bonded. Similar low field resonances have been observed for the metal-bonded carbons of complexes (26) - (29) (Table 4). These carbons have shifts midway between carbene carbons (300 - 360 p.p.m.) and acetylide α-carbons (90 - 116 p.p.m.) suggesting that C(3) is electron deficient. The assignments of C(1) and C(4) have been made using the dicyanomethylene group of complex (27). The β-carbon, which resonates at δ93·9, is similar to C(4) and thus the resonances at *c.* 95 p.p.m. are assigned to C(4). The C(4) resonance of complex (9) is a doublet with fine coupling (*J* = 3 Hz), presumably because of phosphorus coupling through the double bond to C(4). The resonances at *c.* 75 p.p.m. are assigned to C(1); these values are similar to the chemical shifts found for dicyanomethylene carbons of other systems.[10] The remaining resonances at *c.* 180 p.p.m. are assigned to C(2). The unusually low shift of this carbon is not well understood at this stage.

The diene-carbon resonances of the allylic complexes at δ4·7 - 11·0, 63·1 - 66·7, 79·4 - 85·1 and 206·6 - 219·0 are assigned to C(2), C(4), C(1) and C(3) respectively. A consideration of the structure of complex (13)

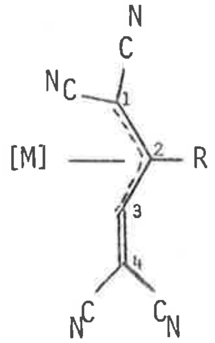
Table 2. ^{13}C n.m.r. data for the diene chain of some butadienyl complexes.



[M]	No.	C(1)	C(2)	C(3)	C(4)
W(CO)$_3$(η-C$_5$H$_5$)	3	77·4, s	182·8, s	221·7, s	99·8, s
Ru(CO)(PPh$_3$)(η-C$_5$H$_5$)	9	75·7, s	181·2, s	215·6, d (12)	94·0, d (3)
		76·2, s	184·7, s	213·4, d (10)	95·0, d (3)
Ru[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$)	10	under CDCl$_3$	177·2, m	223·6, d (15)	97·4, m
Fe(CO)$_2$(η-C$_5$H$_5$)	11	74·9, s	181·2, s	215·1, s	98·0, s
Ru(dppe)(η-C$_5$H$_5$)	12	73·9, m	181·9, m	225·7, m	95·1, m
Ru(CNBu^t)(PPh$_3$)(η-C$_5$H$_5$)	17	73·8, s	178·1, s	224·3, d (9)	95·2, s
Ru(CNBu^t)$_2$(η-C$_5$H$_5$)	18	69·3, s	179·7, s	226·2, s	90·8, s

Coupling constants are placed in parentheses.

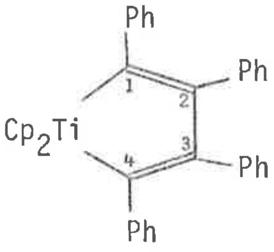
Table 3. ^{13}C n.m.r. data for the diene chain of some allylic complexes.



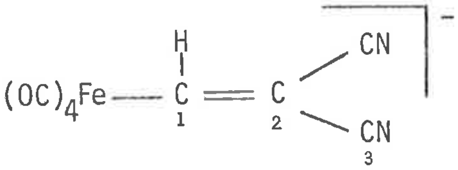
[M]	R	No.	C(1)	C(2)	C(3)	C(4)
$W(CO)_2(\eta-C_5H_5)$	Ph	4	79·4, s	4·7, s	206·6, s	A
$Ru(PPh_3)(\eta-C_5H_5)$	Ph	13	85·1, d(7)	7·3, d(6)	218·8, d(15)	66·7, d(3)
$Ru(PPh_3)(\eta-C_5H_5)$	Me	14	82·9, m	11·0, d(6)	218·3, d(15)	63·1, d(3)
$Ru(PPh_3)(\eta-C_5H_5)$	{Ru}^{B}	15	82·0, d(7)	10·6, d(5)	219·0, d(15)	66·7, d(3)

A, not detected; B, {Ru} = $CH_2CH_2Ru(PPh_3)_2(\eta-C_5H_5)$. Coupling constants in parentheses.

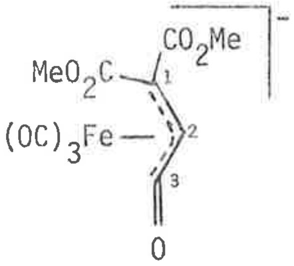
Table 4. The ^{13}C n.m.r. chemical shifts of some metal bonded alkene and allylic complexes



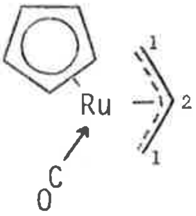
(26)



(27)



(28)



(29)

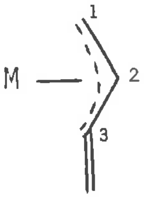
Compound	Carbon	Shift	Ref.
26	1, 4	202·1	7
	2, 3	147·2	
27	1	228·2	8
	2	93·9	
	3, 4	117·1, 121·3	
28	1	49·7	8
	2	24·4	
	3	246·0	
29	1	*32·0/30·9	9
	2	*88·7/67·7	

* *exo/endo*.

reveals that C(3) has a shorter M-C bond distance than does C(1) or C(2) (Table 5). Assuming that a shorter bond would enhance the coupling to phosphorus, C(3) is assigned to the resonance at δ218·8 [J(CP) = 15 Hz]. The resonances at δ7·3 and 85·1 have smaller couplings [J(CP) = 6 and 7 Hz respectively] which allows assignment of C(1) and C(2) to these doublets without differentiating between them. Carbon(1) is a dicyanomethylene carbon and thus the resonance at δ85·1 is assigned to it; while the resonance at δ66·7 is assigned to the other dicyanomethylene carbon [C(4)]. Carbon (4) is coupled to phosphorus [J(CP) = 3 Hz)] *via* the Ru-C(3) = C(4) bond. Similar chemical shifts were found for C(1)-C(3) in complex (28) (Table 4). This is

Table 5. Metal-carbon bond distances in complex (13). Complex (28) is included for comparison. (Distances in Å).

Bond	Complex (13)	 (28)[11]
M-C(1)	2·231	2·093
M-C(2)	2·135	2·023
M-C(3)	1·919	1·897



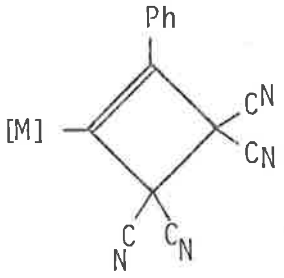
comparable with the allylic complexes (Table 3) as the CO_2Me groups are electron-withdrawing like CN, while the similarities between CO and $C=C(CN)_2$ are well known.[12,13] Carbon(3) of complex (28) has a chemical shift of 246·0 p.p.m. comparable with the low field shifts observed for (4) and (13) - (15), while

C(1) - C(3) have a low-high-low-field shift pattern (49·7, 24·4, 246·6 p.p.m.) also observed for the other allylic complexes (Table 3). The high-field shift of C(2) is unusual and cannot be explained at this point. The complexes differ from normal allylic complexes [e.g. complex (29)] which show a high-low-high chemical shift pattern (Table 4).

Other resonances in the ^{13}C n.m.r. spectra and the ^{1}H n.m.r. spectra confirmed the presence of cyclopentadienyl and phenyl groups, and other functional groups of the complexes (see Experimental).

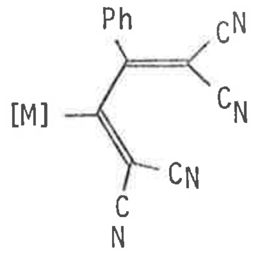
3.2.4.2 Infrared data The infrared spectra of the cyclobutenyl, butadienyl and allylic complexes have distinct absorptions which allow ready differentiation between them (Tables 6 - 8). The cyclobutenyl complexes have an extremely weak cyano absorption at *c*. 2240 cm^{-1}, while in the olefinic region medium-weak bands are observed between 1490 and 1610 cm^{-1}.

Table 6. The infrared ν(CN) and ν(C=C) absorptions of some cyclobutenyl complexes.



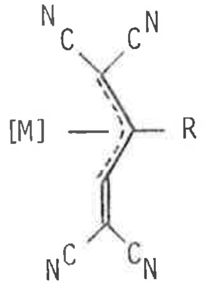
[M]	No.	ν(CN)	ν(C=C)
$W(CO)_3(\eta\text{-}C_5H_5)$	2	2244vw	1489w
$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$	5	2218w	1611vw, 1572vw, 1525w
$Ru[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$	6	2239vw	1609vw, 1587vw, 1568w
$Fe(CO)_2(\eta\text{-}C_5H_5)$	7	2243vw	1601vw, 1583w, 1557w
$Ru(dppe)(\eta\text{-}C_5H_5)$	8	2235vw, 2210vw(br)	1545w

Table 7. The infrared ν(CN) and ν(C=C) absorptions of some butadienyl complexes.



[M]	No.	ν(CN)	ν(C=C)
$W(CO)_3(\eta-C_5H_5)$	3	2222m, 2210m	1522s
$Ru(CO)(PPh_3)(\eta-C_5H_5)$	9	2226m, 2219m, 2212m	1516m
$Ru[P(OMe)_3](PPh_3)(\eta-C_5H_5)$	10	2248vw, 2225w, 2212m, 2202w	1525m
$Fe(CO)_2(\eta-C_5H_5)$	11	2220m, 2207m, 2201m	1533m, 1528sh
$Ru(dppe)(\eta-C_5H_5)$	12	2219w, 2208w, 2199w	1520m
$Ru(CNBu^t)(PPh_3)(\eta-C_5H_5)$	17	2224m, 2216m, 2209m	1510m, 1503sh
$Ru(CNBu^t)_2(\eta-C_5H_5)$	18	2223m, 2216sh	1530m
$Pt(C\equiv CPh)(PPh_3)_2$	19	2218w, 2190w, 2170w, 2120w	1594w, 1588sh, 1573w, 1568sh

Table 8. The infrared ν(CN) and ν(C=C) absorptions of some allylic complexes.



[M]	R	No.	ν(CN)	ν(C=C)
$W(CO)_2(\eta\text{-}C_5H_5)$	Ph	4	2232s, 2222m	1586s
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Ph	13	2215s	1590s
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Me	14	2225s, 2219sh	1615s, 1587m
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	{Ru}[A]	15	2210s	1620s, 1587m
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	CH_2-[B]	16	2220s	1613s

A, {Ru} = $CH_2CH_2Ru(PPh_3)_2(\eta\text{-}C_5H_5)$; B, binuclear allylic complex

The butadienyl complexes have two or three medium-weak absorptions in the cyano region (2120 - 2248 cm^{-1}) and medium olefinic absorptions (1510 - 1594 cm^{-1}). The allylic complexes gave one or two strong ν(CN) bands (2210 - 2232 cm^{-1}) and strong ν(C=C) absorptions (1585 - 1620 cm^{-1}). This trend is exemplified with $W[\overline{C=C(Ph)C(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$, $W\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ and $W[\eta^3\text{-}C(CN)_2C(Ph)C=C(CN)_2](CO)_2\text{-}(\eta\text{-}C_5H_5)$ [ν(CN) 2244vw; 2222m, 2210m; 2232s cm^{-1}, respectively; ν(C=C) 1489w; 1522s; 1586s cm^{-1} respectively].

3.2.4.3 E.S.R. spectra The reactions of tcne with metal acetylide complexes gave a variety of paramagnetic intermediates, which were detected by e.s.r. spectroscopy (Figures 11 - 15). These spectra do not

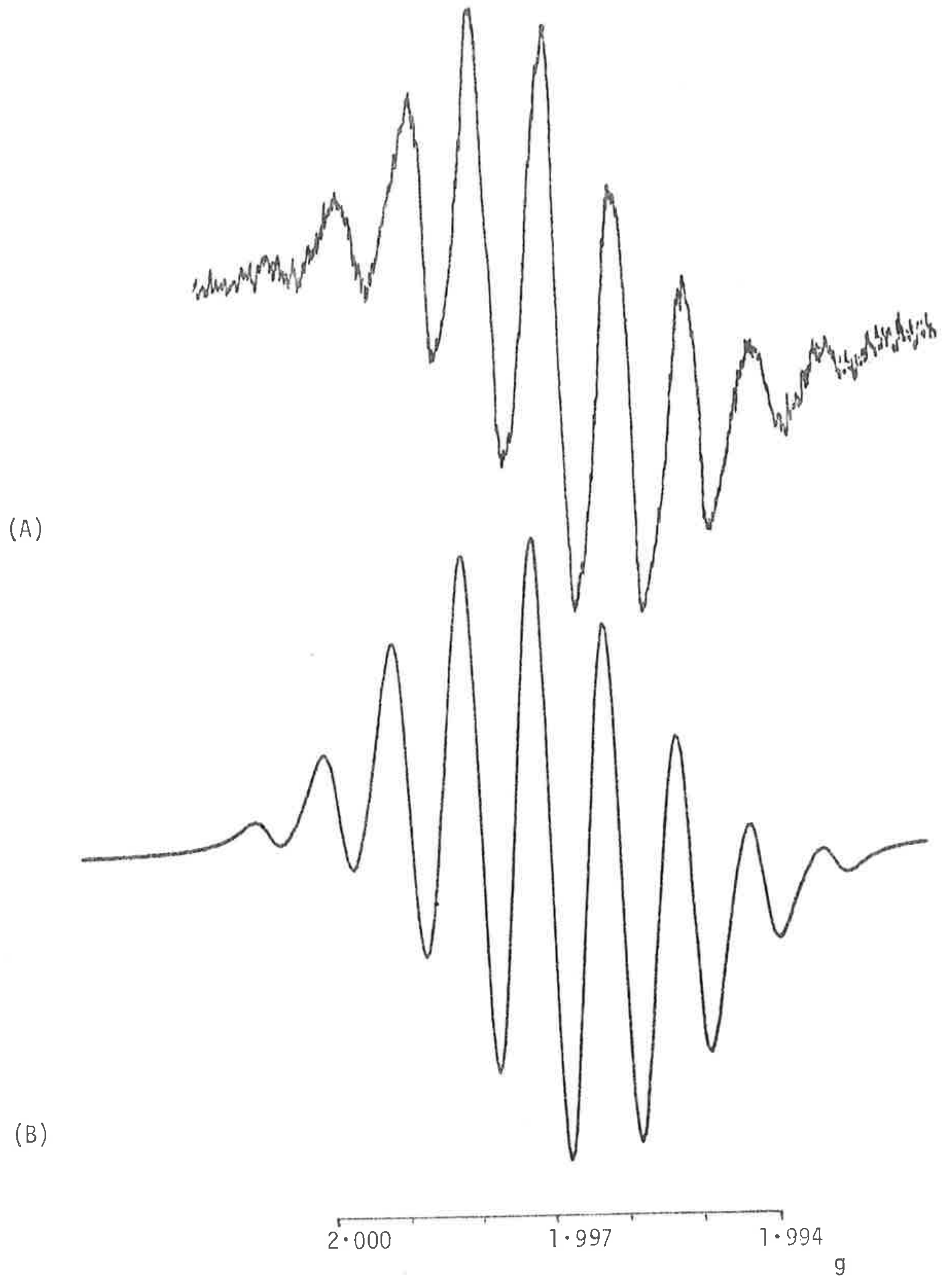


Figure 11. (A) The e.s.r. spectrum observed in the reaction of tcne with $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ in benzene. (B) A simulated spectrum of an electron coupled equally to four nitrogen atoms (a_N = 1·59G).

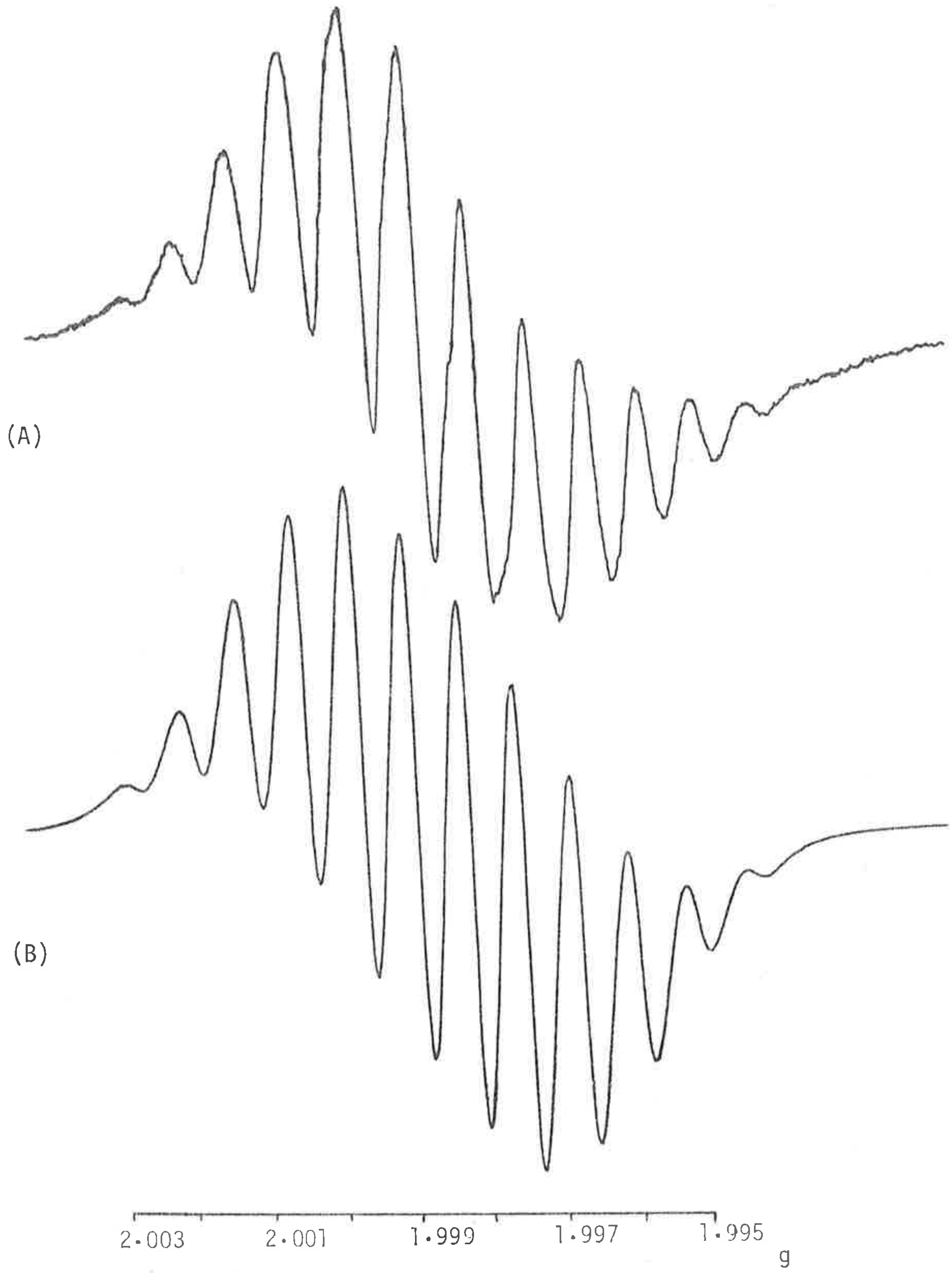


Figure 12. (A) The e.s.r. spectrum observed in the reaction of tcne with $Ru(C\equiv CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ in benzene. (B) A simulated spectrum of one electron coupled to four nitrogen atoms (a_N = 1·57G) and one phosphorus atom (a_P = 4·48G).

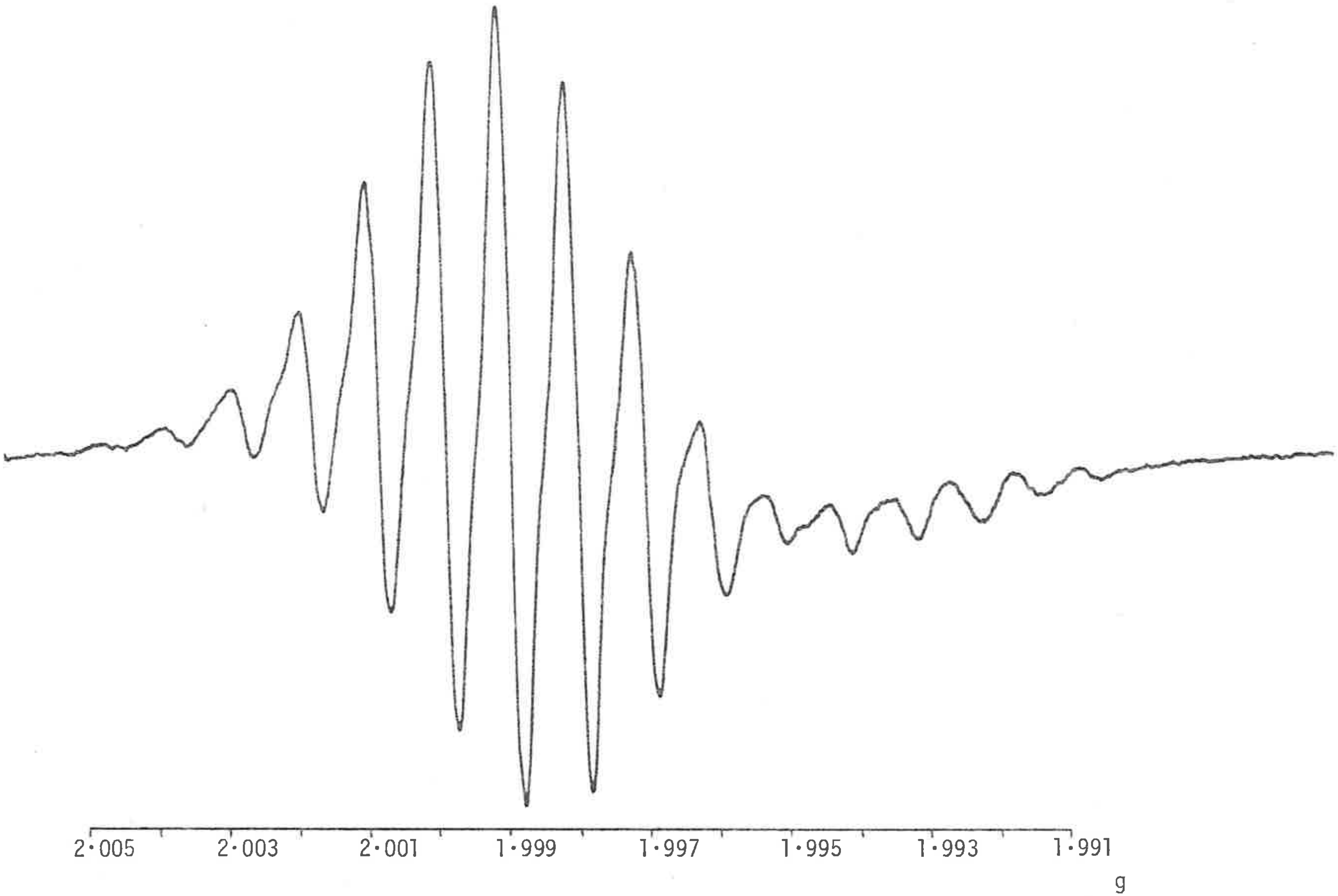


Figure 13. The e.s.r. spectrum observed in the reaction of Ru(C≡CPh)$(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne in benzene.

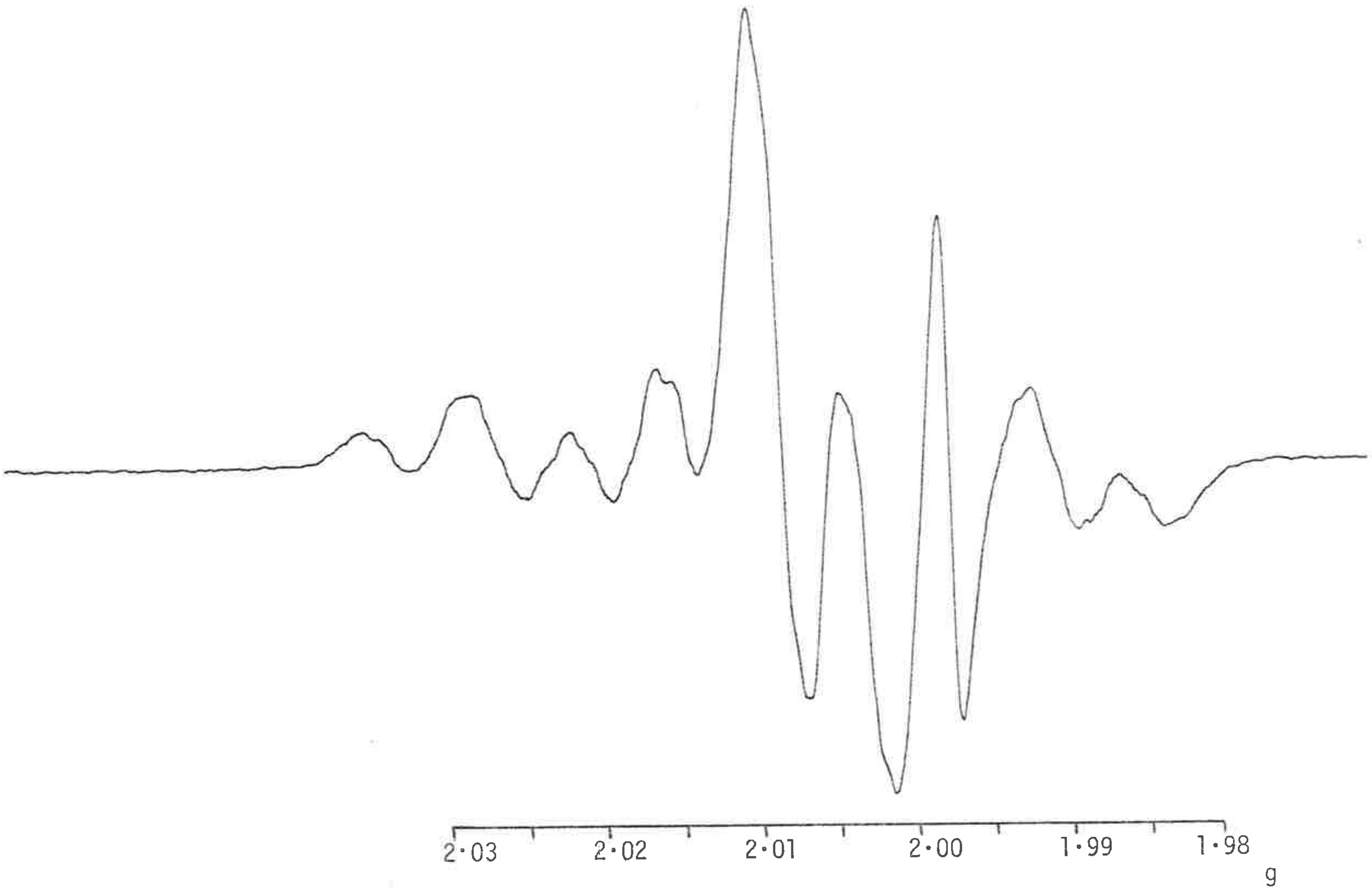


Figure 14. An e.s.r. spectrum observed in the reaction of tcne with *trans*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$ in benzene after 25 min.

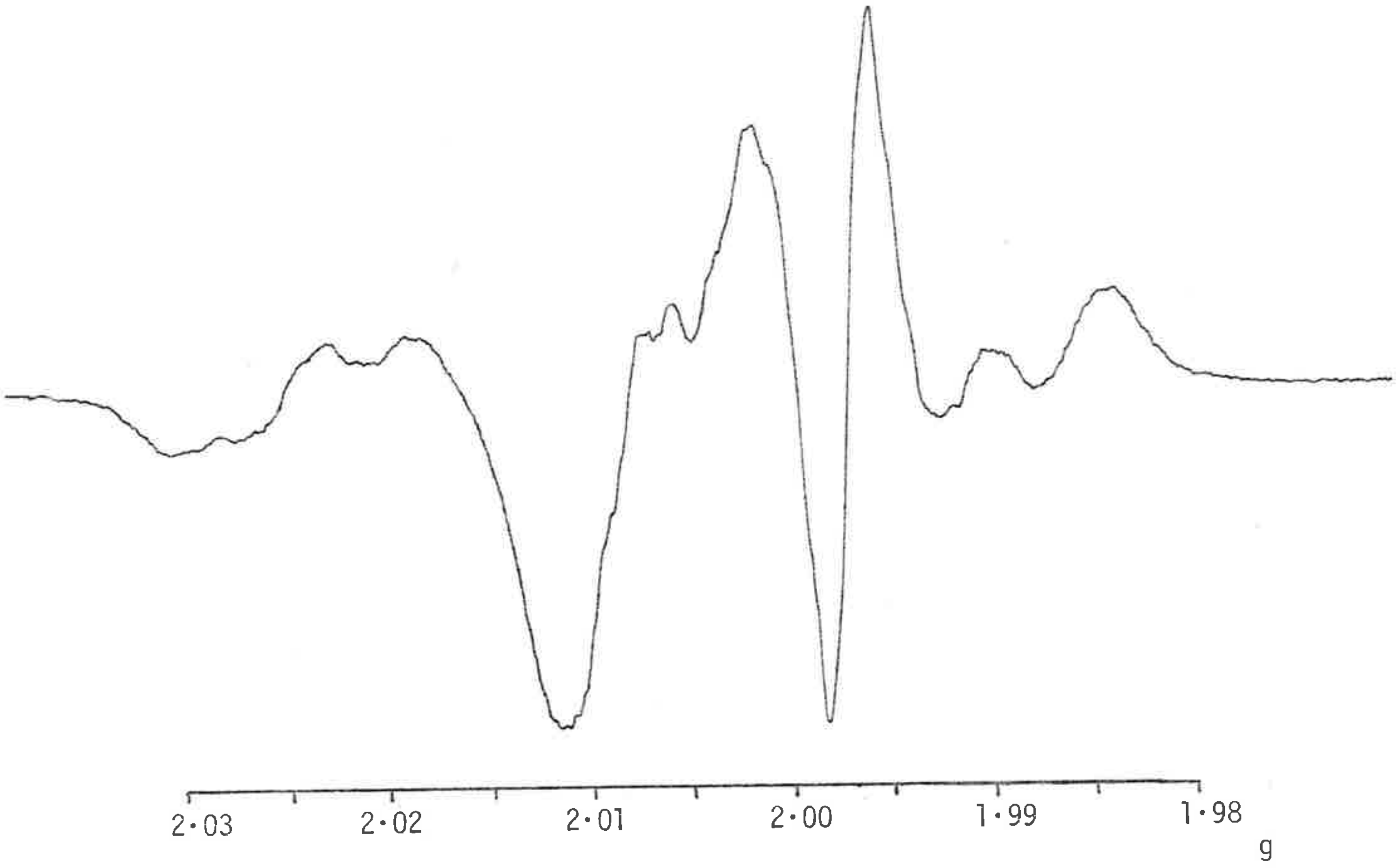
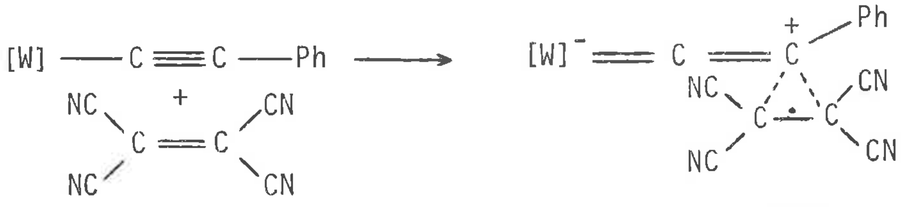


Figure 15. An e.s.r. spectrum observed in the reaction of tcne with Ru(C≡CPh)(dppe)(η-C_5H_5) in benzene after 15 min.

resemble that observed for the tcne radical anion.[14]

The simplest spectrum is observed in the reaction of $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ and tcne (Figure 11A) having nine lines in a regular distribution. A close-fitting simulated spectrum (Figure 11B) is obtained for an electron coupled equally to four nitrogen atoms ($a_N = 1{\cdot}59$ G, line width = 0·73G). The other electron in the pair probably moves onto the metal and is not detected because of signal broadening. A radical species such as (30) can be assigned to this spectrum. The reaction of $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ with tcne gave a spectrum virtually identical to that in Figure 11A.

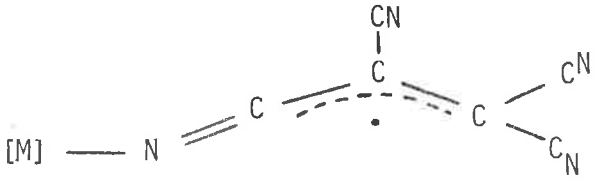


(30)

$[W] = W(CO)_3(\eta\text{-}C_5H_5)$

The spectrum observed in the reaction of $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne (Figure 12A) has 12 lines. A simulated spectrum (Figure 12B) of one electron coupled to four equivalent nitrogens ($a_N = 1{\cdot}57$G) and one phosphorus ($a_P = 4{\cdot}48$G) correlates well with the experimental spectrum. It appears that one PPh_3 is lost upon formation of the paramagnetic species. In the reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with tcne a similar 12-line spectrum is observed, in addition to a broad signal which coincides with the other spectrum (Figure 13). The 12-line signal for the methyl system has a greater line-width, presumably due to coupling with the CH_3 protons. The initial products from the reaction of tcne with $Pt(C{\equiv}CPh)_2(PPh_3)_2$ or $Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$ gave unusual spectra (Figures 14 and 15 respectively) and have not been interpreted.

Radical intermediates have been observed in other reactions of tcne with metal complexes.[15,16] These involve cleavage of M-M or M-C bonds and give spectra consistent with the formation of (31). These spectra are quite different from those shown in Figures 11 - 13.

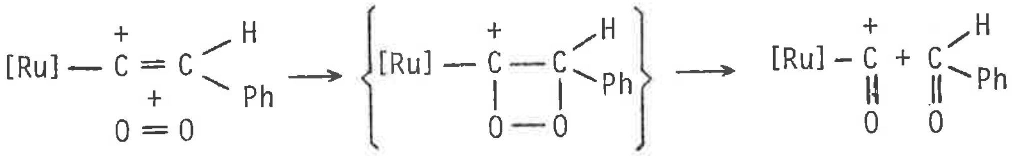


(31)

3.3 DISCUSSION

3.3.1 Reactions Involving Tetracyanoethylene

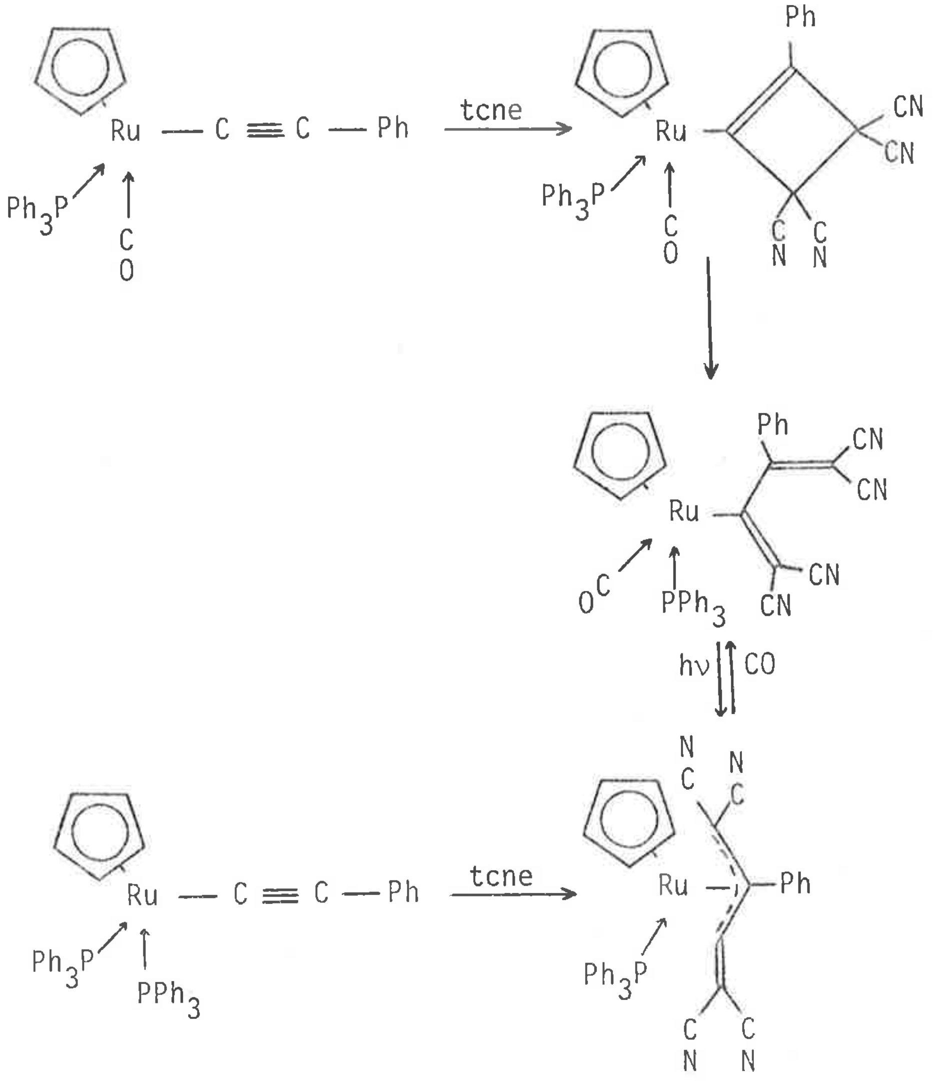
Addition of oxygen to the olefinic bond of $[Ru(C{=}CHPh)(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)]^+$ (32) is thought to proceed *via* an initial (2+2)-cycloaddition reaction followed by ring cleavage (Section 2.3.5):



$[Ru] = Ru(PPh_3)_2(\eta\text{-}C_5H_5)$

A reaction of tetracyanoethylene (tcne) with (32), however, leads to deprotonation and the formation of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$. The basic properties of tcne are well known.[17] No reaction was observed between $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and tcne, even under vigorous conditions. Extension of the reaction to $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$, however, results in an immediate green coloration and the eventual precipitation of an orange product. While only the allylic complex (13) is isolated from this reaction, the reaction of $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ (1) with tcne sequentially gives cyclobutenyl (2), butadienyl (3), and allylic (4) complexes (Scheme 1).

A variety of other cyclobutenyl, butadienyl and allylic complexes have been formed in reactions of metal acetylide complexes with tcne, or by ligand addition to allylic complexes. Examples of these reactions are given in Scheme 2. The initial addition of tcne to the triple bond is



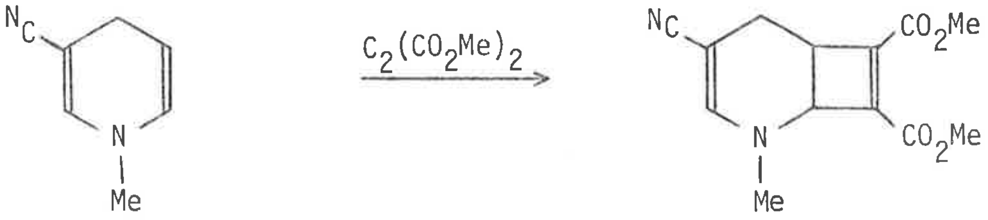
(5)

(9)

(13)

Scheme 2.

unprecedented to my knowledge. Cycloaddition reactions of electron deficient acetylenes with olefins, however, are well known[18]; e.g. $C_2(CO_2Me)_2$ reacts with the heterocycle (33) forming (34) under thermal conditions[19]:

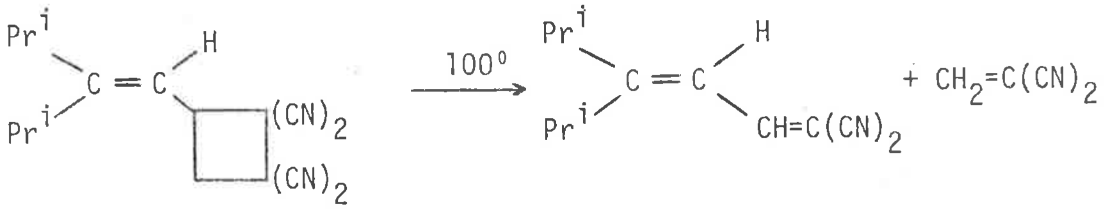


(33) (34)

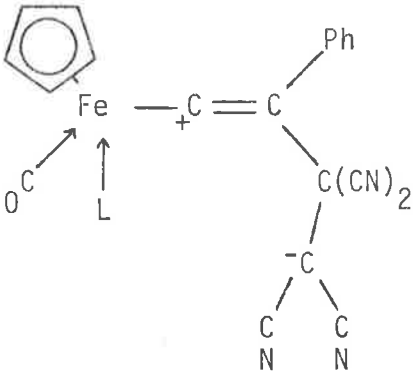
Reactions of tcne with olefins are also well known[1]:

Ring-cleavage of the cyclobutenyl group proceeds under mild conditions, which, in the overall reaction, results in cleavage of the C=C bond of the tcne molecule under mild conditions. Several reports describe the ring-cleavage of cyclobutyl derivatives [(2+2)-cycloadducts of tcne and olefins] under more vigorous conditions (100 - 180°).[20]

e.g.

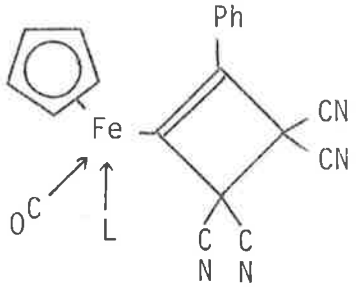


The reaction of $Fe(C{\equiv}CPh)(L)(CO)(\eta\text{-}C_5H_5)$ (L = CO or PPh_3) and tcne was reported to give dipolar (35) and cyclobutenyl (7) products.[2] Upon repeating some of this work (L = CO), and by comparing the spectroscopic data with that of known compounds (Section 3.2.4 and Experimental), it was found that these compounds were the cyclobutenyl (7) and butadienyl (11) complexes, respectively.



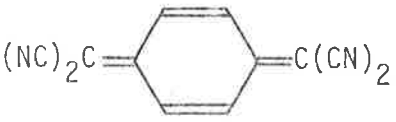
(35)

L = CO,PPh_3

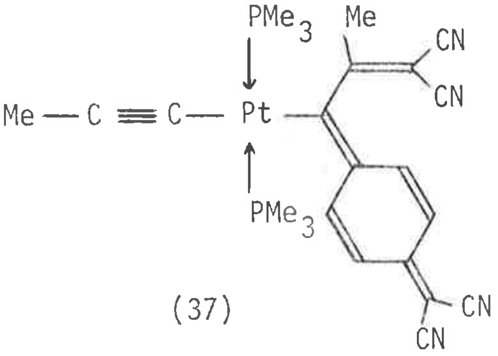


(7)

The reaction of *trans*-$Pt(C{\equiv}CMe)_2(PMe_3)_2$ with tcnq (36) has been described[3], and the butadienyl product subsequently identified by X-ray structural analysis (37).[4] This offers, to my knowledge, the only confirmed reaction product analogous to those described above for tcne.

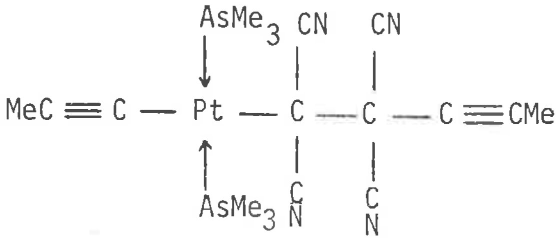


(36)

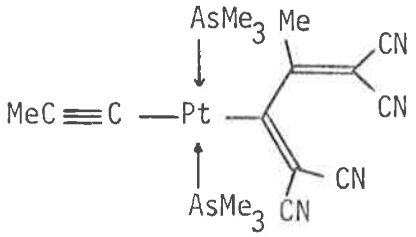


(37)

A reaction of *trans*-Pt(C≡CMe)$_2$(AsMe$_3$)$_2$ with tcne was reported to give an insertion product (38).[21] The infrared data, however, are consistent with the formation of a butadienyl complex (39) [ν(CN) 2225, ν(C=C) 1560 cm^{-1}], but ^{13}C n.m.r. data is required before the nature of the product can be confirmed.



(38)

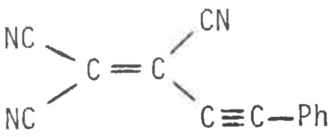


(39)

It is surprising that Rh(C≡CPh)(CO)(PPh$_3$)$_2$ does not undergo cycloaddition reactions with tcne, instead preferring to form the simple oxidative adduct (21). Similar reactions have been described earlier.[22,23] The CO ligand of (21) is readily replaced by the solvent in refluxing acetonitrile, yielding (22). Although not unprecedented[24] substitution of CO by a nitrile is an unexpected result in view of the superior bonding ability of CO.

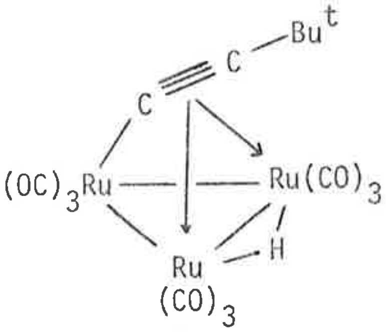
The C≡C triple bond of the acetylide group in (21) does not react with tcne, perhaps because too much electron density has been withdrawn from the bond onto the metal. Another unreactive acetylide bond is encountered in the reaction of tcne with Pt(C≡CPh)$_2$(PPh$_3$)$_2$. After a reaction had taken place with one C≡C bond, the other did not interact with tcne, again maybe due to removal of electron density through the metal to the cyano groups of the newly-formed ligand. A consideration of models did not suggest that steric factors would hinder the approach of tcne.

The reaction of CuC≡CPh with tcne gives an organic product (40),[25] implying that a cycloaddition reaction has not occurred. The acetylide

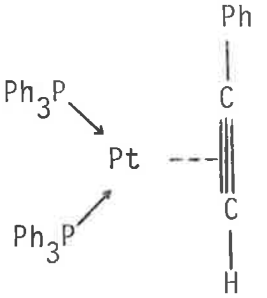


(40)

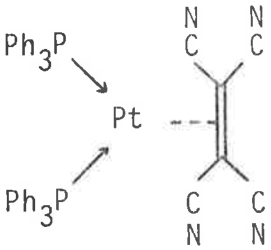
cluster (41), where both π-orbitals are involved in bonding, does not react with tcne.[26] The platinum phenylacetylene complex (42) reacts with tcne to give an η^2-tcne complex (43) by displacement of the phenylacetylene.[27]



(41)



(42)



(43)

These results suggest that a correct balance of electronic conditions is required for cycloaddition of tcne. It seems especially critical that the C≡C bond is electron-rich as π-bonding to the metal or the presence of electron-withdrawing groups on the metal appear to prevent cycloaddition reactions of the triple bond with tcne.

In view of the known reactivity of tcne with olefins[1], it is not understood why a reaction was not observed with the vinyl complexes $Ru[C(OMe)=CHPh](PPh_3)_2(\eta-C_5H_5)$ and $Ru[C(CO_2Me)=CHCO_2Me](PPh_3)_2(\eta-C_5H_5)$.[28]

3.3.2 Reactions Involving Other Olefins

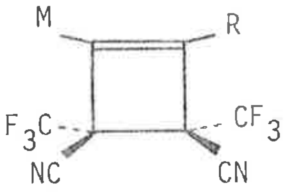
The effect of the olefin on the course of the reaction is dramatically illustrated by some reactions of $(NC)_2C=C(CF_3)_2$. In the reaction with

$Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ an unusual binuclear product (23) is formed. If, however, $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ is reacted with $(NC)_2C{=}C(CF_3)_2$ the cyclobutenyl complex (24) is isolated in high yield. It is noteworthy that the alkyne substituent alters the course of the reaction so significantly.

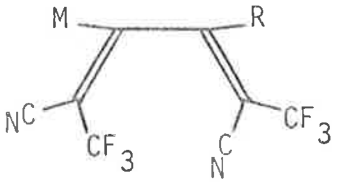
An attempted reaction between $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $C_2(CO_2Et)_4$ gave only starting materials, even at elevated temperatures. Similarly no reaction was observed between $C_2(CO_2Et)_4$ and $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ or $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$. Models show that the latter complexes should present no steric barrier to the approach of the reaction centres, thus suggesting that electronic factors control the course of these reactions.

An attempted reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with the 'push-pull' olefin $(NC)_2C{=}\overline{CO(CH_2)_2O}$ gave only starting materials. This result might be expected considering the electronic differences between this olefin and tcne or $(NC)_2C{=}C(CF_3)_2$. It will be necessary to attempt additions of a wide variety of olefins before the details of this reaction can be understood. By changing the metal acetylide complex and the olefin it should be possible to design organic groups which can be removed to give synthetically useful organic molecules.

The ring opening of cyclobutenes has been extensively studied and reviewed by Woodward and Hoffman.[29] At this stage it cannot be determined whether a conrotatory or disrotatory process occurs in the metal systems described. A study of reactions involving olefins with appropriate substituents should indicate which process takes place. In the thermal reactions of organic molecules cycloadditions and cycloreversions proceed *via* a conrotatory process, thus product (44) might be expected in the ring-opening of (45). It is possible, however, that steric factors will also determine the final configuration of the complex.



(45)



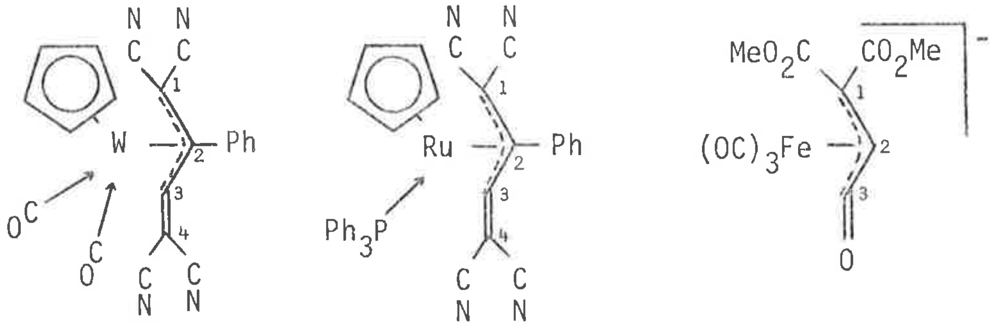
(44)

The ease with which ring-opening occurs can be better understood from a consideration of the structure of $W[\overline{C=C(Ph)C(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (Figure 1). The bond between the dicyanomethylene groups is elongated (1·60 Å), significantly longer than a normal C-C distance (1·53 Å), indicating that the bond is under a fair degree of strain and thus breaks under mild conditions. Some longer C-C bonds are known, however (e.g. 1·64 Å in hexaphenylethane[30]). The same bonds in the cyclobutenyl rings of the binuclear complex (23) have lengths of 1·526 (±0·025) and 1·673 (±0·044) Å. The difference between these is less than three standard deviations and not considered significant. The average bond-length (1·60 Å) is thus the same as that for the tungsten complex above.

3.3.3 Physical Data

The butadienyl complex (17) has a considerable twist in the diene fragment [torsion angle about C(1) - C(2) - C(3) - C(4), 71·8°], which localises the two double bonds [C(1) - C(2), 1·362(4) Å; C(3) - C(4), 1·382(5) Å]. In the allylic complex (13) the C(3) - C(4) bond retains its double bond character [1·362(4) Å], while C(1) - C(2) is lengthened considerably [1·476(6) Å] as a result of its interaction with the metal. The length of C(2) - C(3) is decreased by *c.* 0·046 Å in changing from the butadienyl complex (17, 1·478 Å) to the allylic complex (13, 1·432 Å), suggesting some delocalisation of electron density (Table 9). Complex (4) and the

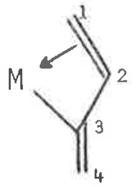
Table 9. Some structural features of selected allylic complexes. Complex (28) is included for comparison. (Distances in Å).



Bond	Complex (4)	 (13)	 (28)[A]
C(1)-C(2)	1·480(9)	1·476(6)	1·440(8)
C(2)-C(3)	1·439(11)	1·432(7)	1·450(7)
C(3)-C(4)	1·383(6)	1·355(10)	-
M-C(1)	2·285 (8)	2·231(4)	2·093(5)
M-C(2)	2·253(7)	2·135(4)	2·023(5)
M-C(3)	2·075(8)	1·919(5)	1·897(5)
∠C(1)C(2)C(3)	104·5(6)°	112·7(4)°	111·0(4)°

A, ref. 11

η^3-acryloyl complex (28)[11] also have a shortened C(2) - C(3) bond. Normally an allylic complex has approximately equal C(1) - C(2) and C(2) - C(3) bonds, with a C(1) - C(2) - C(3) angle of 115 - 124°.[31] In addition the M-C bonds to an allylic group normally have a short-long-short pattern. In complexes (4), (13) and (28) the pattern is short-long-long (Table 9) and suggests that a better interpretation is a σ-bond between M and C3, with a π-bond between M and C(1)=C(2):



In some instances the butadienyl complexes $\mathrm{Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}}$-$\mathrm{(L)(PPh_3)(\eta\text{-}C_5H_5)}$ equilibrate to two isomeric forms. When L = CO (9) or $\mathrm{CNBu^t}$ (17) isomerisation to an equilibrium mixture took place over a few hours at 25°. The equilibrium ratio was shown ($\mathrm{L=CNBu^t}$) to be dependent on solvent polarity (Table 1). The nature of L also affects the equilibrium ratio [L=CO, 1:1·5; $\mathrm{L=CNBu^t}$, 1:2·3; $\mathrm{L=P(OMe)_3}$, 100%; in $\mathrm{CDCl_3}$]. The nature of the isomerism is not well understood and a study of models did not indicate that there were any favoured conformations for the butadienyl ligand. Isomerism is only observed in compounds with four different groups attached to the metal. While metal-centred optical isomers can be formed, other systems of this type exist without detectable isomerism [e.g. $\mathrm{RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)}$ or $\mathrm{Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)}$]. It is suggested that the large cyanodiene group is so arranged that the molecules are now distinguishable even though diastereomers are not formally possible.

The butadienyl complex $\mathrm{Ru\{C[=C(CN)_2]C(Me)=C(CF_3)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}$ (25) is formed as two non-equilibrating and separable isomers. It is hoped that structural studies will yield more information about the nature of these systems.

3.4 *EXPERIMENTAL*

Literature methods were used in the preparation of $Ru(C{\equiv}CR)(PPh_3)_2$-$(\eta$-$C_5H_5)$(R=Me,Ph)[32], $Ru(C{\equiv}CPh)[P(OMe)_3](PPh_3)(\eta$-$C_5H_5)$[33], $Fe(C{\equiv}CPh)(CO)_2$-$(\eta$-$C_5H_5)$[34], $Ru(C{\equiv}CPh)(dppe)(\eta$-$C_5H_5)$[32], $[Ru(C{=}CRPh)(PPh_3)_2(\eta$-$C_5H_5)]PF_6$ (R=H, Me)[32] and *trans*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$.[35] The preparations of $W(C{\equiv}CPh)(CO)_3(\eta$-$C_5H_5)$, $Ru(PPh_3)(\eta$-$C_5H_5)C{\equiv}CCH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta$-$C_5H_5)$, $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta$-$C_5H_5)$ and *trans*-$Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ are described in Chapter Five. Literature methods were used in the preparation of tcne[36], $(NC)_2C{=}C(CF_3)_2$[37], $(NC)_2C{=}C\overline{O(CH_2)_2O}$[38] and *cis*-$C_2H_2(CO_2Me)_2$[39], while $C_2(CO_2Et)_4$ was supplied by Aldrich.

Simulations of the e.s.r. spectra were made using a specially devised programme.[40]

Reactions of Tetracyanoethylene

(A) With $W(C{\equiv}CPh)(CO)_3(\eta$-$C_5H_5)$

(i) For a short period A reaction of $W(C{\equiv}CPh)(CO)_3(\eta$-$C_5H_5)$ (1) (122 mg, 0·28 mmol) and tcne (44 mg, 0·34 mmol) in dichloromethane (15 ml) for 45 min gave a yellow solution which on addition of ethanol yielded yellow *microcrystals* of $W[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2](CO)_3$-$(\eta$-$C_5H_5)$ (2) (120 mg, 76%), m.p. 108 - 114° (dec.) (Found: C, 47·5; H, 1·3; N, 10·0%; *M*(mass spectrometry), 562. $C_{22}H_{10}N_4O_3W$ requires C, 47·0; H, 1·8; N, 10·0%; *M*, 562). Infrared (CH_2Cl_2): ν(CO) 2046s, 1983vs, 1974sh; ν(CN) (Nujol) 2244vw; ν(C=C) 1489w cm^{-1}; other bands at 1445w, 1440m, 1421m, 1363vw, 1352vw, 1338vw, 1313vw, 1291vw, 1247m, 1237m, 1160vw, 1110vw, 1067w, 1061w, 1017m, 1009w, 990vw, 927vw, 918vw, 870vw, 858m, 839s, 831sh, 780w, 770s, 713vw, 695s, 672vw, 663vw cm^{-1}. ^1H n.m.r.: $\delta[(CD_3)_2CO]$ 6·16, s, 5H, C_5H_5; 7·64, s, 5H, Ph. ^{13}C n.m.r.: $\delta[(CD_3)_2CO]$ 94·0, s, C_5H_5; 112·2, 113·2, 2 x s, CN; 127·1, 130·3, 131·4, 131·7, 4 x s, Ph;

216·7, s, CO. Compound (2) converted to (3) before other carbons were detected.

(*Note*: compound (2) must be stored in the dark).

(ii) For an extended period After mixing $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ (400 mg, 0·92 mmol) and tcne (125 mg, 0·98 mmol) in dichloromethane (30 ml) under light free conditions for two days an orange coloured solution developed. This was filtered and crystallized by addition of hexane and evaporation to give orange *microcrystals* of $W\{C[=C(CN)_2]C(Ph)=C(CN)_2\}\text{-}(CO)_3(\eta\text{-}C_5H_5)$ (3) (350 mg, 68%), m.p. >155° (dec.) (Found: C, 46·9; H, 1·4; N, 9·9%; *M*(mass spectrometry), 562. $C_{22}H_{10}N_4O_3W$ requires C, 47·0; H, 1·8; N, 10·0%; *M*, 562) Infrared (CH_2Cl_2): ν(CO) 2046s, 1981vs(br); ν(CN) (Nujol) 2222m, 2210m; ν(C=C) 1522s, cm^{-1}; other bands at 1440m, 1418m, 1258w, 1248w, 1190w, 1181w, 1170w, 1105w, 1062w, 1050m, 1003m, 1000m, 992w, 972vw, 922vw, 882m, 873vw, 868s, 818m, 760s, 736m, 696s, 668vw, 658vw, 647w, 619w cm^{-1}. ^1H n.m.r.: $\delta[(CD_3)_2CO]$ 5·91, s, 5H, C_5H_5; 7·8, m, 5H, Ph. ^{13}C n.m.r.: $\delta[(CD_3)_2CO]$ 77·4, s, C(1); 95·7, s, C_5H_5; 99·8, s, C(4); 113·0, 113·3, 113·5, 116·2, 4 x s, CN; 129·8, 130·7, 130·9, 134·9, 4 x s, Ph; 182·8, s, C(2); 196·9, 216·8, 217·8, 3 x s, CO; 221·7, s, C(3). Further crystallization of the mother liquor yielded orange *crystals* of $W[\eta^3\text{-}C(CN)_2C(Ph)C=C(CN)_2](CO)_2(\eta\text{-}C_5H_5).0{\cdot}5C_2(CN)_4$ (4)(*c*. 20 mg) m.p. 175 - 180° (Found C, 48·2; H, 1·3; N, 14·0%; *M*(mass spectrometry), 534. $C_{21}H_{10}N_4O_2W.0{\cdot}5C_2(CN)_4$ requires C, 48·2; H, 1·7; N, 14·1%; *M*, 534).

(iii) Formation of $W[\eta^3\text{-}C(CN)_2C(Ph)C=C(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ *(4)* A solution of $W\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (3) (120 mg, 0·21 mmol) in d^6-acetone (2 ml) was irradiated (Philips high pressure mercury lamp, 125 w) for 25 h until n.m.r. checks indicated 100% conversion to

$W[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (4). Purification by t.l.c. on silica (1:3 acetone/light petroleum) and crystallization from acetone/ethanol gave orange *crystals* of (4) (70 mg, 62%). Infrared (CH_2Cl_2): ν(CO) 2080vs, 2025vs; ν(CN) (Nujol) 2232s, 2222m; ν(C=C) 1586s cm^{-1}; other bands at 3108m, 1496vw, 1448m, 1420m, 1329w, 1192vw, 1153w, 1107vw, 1078w, 1066w, 1053vw, 1006m, 1003sh, 999sh, 889w, 871s, 833w, 816sh, 812m, 772s, 719vw, 697s cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 5·89, s, 5H, C_5H_5; 7·48, s, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 4·7, s, C(2); 79·4, s, C(1); 94·1, s, C_5H_5; 112·2, 115·2, 116·5, 118·4, 4 x s, CN; 128·7, 129·9, 130·8, 131·5, 4 x s, Ph; 201·1, 203·8, 2 x s, CO; 206·6, s, C(3). [C(4) was not detected].

(B) With $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ A mixture of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1·0 g, 1·26 mmol) and tcne (200 mg, 1·56 mmol) was heated in refluxing benzene (50 ml) for 1·5 h. Chromatography from an alumina column yielded an orange band with dichloromethane, which on crystallization from hexane gave orange *crystals* of $Ru[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (13) (680 mg, 82%), m.p. >210° (dec.) (Found: C, 66·8; H, 3·6; N, 8·3%; *M*(mass spectrometry), 658. $C_{37}H_{25}N_4PRu$ requires C, 67·6; H, 3·8; N, 8·5%, *M*, 658). Infrared (Nujol): ν(CN) 2215s; ν(C=C) 1590s cm^{-1}; other bands at 1405m, 1312vw, 1306vw, 1231vw, 1183vw, 1177vw, 1150vw, 1106vw, 1087w, 1080m, 1077sh, 1068w, 1049vw, 1013w, 993w, 981vw, 883vw, 872vw, 842sh, 839m, 833sh, 829w, 802w, 765m, 753m, 742m, 709vw, 698s, 692s, 689m, 679vw, 660m cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 4·76, s, 5H, C_5H_5; 7·5, m, 20H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 7·3, d, *J*(CP) 6 Hz, C(2); 66·7, d, *J*(CP) 3 Hz, C(4); 85·1, d, *J*(CP) 7 Hz, C(1); 92·3, s, C_5H_5; 111·2, 115·9, 2 x d, *J*(CP) 3 Hz, 118·7, 119·0, 2 x s, CN; 128·5 - 134·9, m, Ph; 218·8, d, *J*(CP) 15 Hz, C(3).

(C) With $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ A mixture of $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0·68 mmol) and tcne (90 mg, 0·70 mmol) in benzene (50 ml)

was stirred (12 h) and then heated at reflux point (1 h). Elution on an alumina column yielded a major orange band (4:1 dichloromethane/light petroleum) and a minor unidentified green band (dichloromethane). Crystallization of the major product from dichloromethane/ethanol yielded orange-red *crystals* of $Ru[\eta^3\text{-}C(CN)_2C(Me)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (14) (178 mg, 44%), m.p. >180° (dec.) (Found: C, 64·0; H, 3·8; N, 9·4%; *M*(mass spectrometry), 596. $C_{32}H_{23}N_4PRu$ requires C, 64·5,; H, 3·8; N, 9·4%; *M*, 596). Infrared (Nujol): ν(CN) 2225s, 2219sh; ν(C=C) 1615s, 1587m cm^{-1}; other bands at 1483m, 1440s, 1411m, 1319w, 1311w, 1297m, 1259m, 1189m, 1160vw, 1134vw, 1109vw, 1093m, 1090s, 1081vw, 1052w, 1028m, 1011w, 999w, 984vw, 959vw, 927vw, 880vw, 861sh, 857m, 842s, 827m, 796s, 759s, 750m, 705sh, 699s, 693w, 640m, 618vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 2·27, s, 3H, Me; 4·79, s, 5H, C_5H_5; 7·5, m, 15H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 11·0, d, *J*(CP) 6 Hz, C(2); 21·1, s, Me; 63·1, d, *J*(CP) 3 Hz, C(4); 82·9, m, C(1); 90·5, s, C_5H_5; 111·6, 115·6, 2 x d, *J*(CP) 3 Hz, 118·0, 118·4, 2 x s, CN; 128·4 - 136·7, m, Ph; 218·3, d, *J*(CP) 15 Hz, C(3).

(D) With $Ru(PPh_3)_2(\eta\text{-}C_5H_5)C{\equiv}CCH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)$ *(17)*

(i) Using an equivalent amount of tcne A reaction of complex (17) (246 mg, 0·17 mmol) and tcne (23 mg, 0·18 mmol) in benzene (35 ml) for 18 h gave a yellow solution. Elution from an alumina column (2:5 dichloromethane/light petroleum) and crystallization from hexane yielded $Ru\{\eta^3\text{-}C(CN)_2C[CH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)]C{=}C(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (15) as a yellow *powder* (141 mg, 63%) m.p. >160° (dec.) (Found: C, 69·1; H, 4·9; N, 4·1%. $C_{76}H_{59}N_4P_3Ru_2$ requires C, 69·0; H, 4·5; N, 4·2%). Infrared (Nujol): ν(CN) 2210s, ν(C≡C) 2100s, ν(C=C) 1620s, 1587m, 1572w cm^{-1}; other bands at 1482s, 1446s, 1327m, 1311sh, 1260vw, 1187m, 1158w, 1090s, 1071w, 1055vw, 1027w, 999m, 920w(br), 843sh, 834m, 819w, 804m, 746s, 696s, 659vw cm^{-1}.

^{1}H n.m.r.: $\delta(CDCl_3)$ 1·5 - 3·2, br, 4H, CH_2; 4·25, s, 5H, C_5H_5 (acetylide); 4·53, s, 5H, C_5H_5 (allyl); 7·2 - 7·5, m, 45H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 10·6, d, *J*(CP) 5 Hz, C(2); 24·6, s, $\equiv C\text{-}\underline{C}H_2$; 39·9, s, C(2)—$\underline{C}H_2$; 66·7, d, *J*(CP) 3 Hz, c(4); 82·0, d, *J*(CP) 7 Hz, C(1); 84·9, s, C_5H_5 (acetylide); 90·1, s, C_5H_5 (allyl); 98·0, t, *J*(CP) 26 Hz, RuC≡; 108·4, s, $\equiv\underline{C}\text{-}CH_2$; 112·6, d, *J*(CP) 3 Hz, 116·1, d, *J*(CP) 3 Hz, 118·6, m, CN; 127·1 - 140·9, m, Ph; 219·0, d, *J*(CP) 15 Hz, C(3).

(ii) Using excess tcne A reaction of (17) (170 mg, 0·12 mmol) and tcne (50 mg, 0·39 mmol) in benzene (30 ml) gave a yellow solution over 18 h. Elution from an alumina column yielded a minor unidentified red band (4:1 dichloromethane/light petroleum) and a major yellow band (dichloromethane) which on crystallization from ethanol gave $\{\overset{*}{C}H_2[\eta^3\text{-}C(CN)_2\text{-}\overset{*}{C}C{=}C(CN)_2]Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2$ (16) as a yellow *powder* (66 mg, 48%) m.p. 107 - 110° (Found: C, 64·3; H, 3·6; N, 9·3%. $C_{64}H_{44}N_8P_2Ru_2$ requires C, 64·6; H, 3·7; N, 9·4%). Infrared (Nujol): ν(CN) 2220s, ν(C=C) 1613s cm^{-1}; other bands at 1438s, 1412w, 1310m, 1259w, 1187w, 1182w, 1158vw, 1089s, 1025vw, 1014vw, 996w, 987sh, 845m, 822w, 755sh, 747s, 701s, 693s, 682sh cm^{-1}. ^{1}H n.m.r.: $\delta(CDCl_3)$ 3·2, m, 4H, CH_2; 4·95, s, 10H, C_5H_5; 7·5, m, 30H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 10·6, d, *J*(CP) 4 Hz, C(2); 38·5, s, CH_2; 63·6, s, C(4); 90·9, s, C_5H_5; 114·0 - 118·6, m, CN; 128·6 - 135·0, m, Ph; C(1) and C(3) were not detected due to low solubility.

(E) With $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$

(i) In diethyl ether A reaction of $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (100 mg, 0·18 mmol) with tcne (100 mg, 0·78 mmol) in diethyl ether (20 ml) over 5 h led to the precipitation of $Ru[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (5) as a yellow *powder* (112 mg, 91%) m.p. 124 - 126°. Infrared (Nujol): ν(CN) 2218w, ν(CO) 1960vs, ν(C=C) 1611vw, 1572vw, 1525w cm^{-1}; other bands at

1713vw, 1312vw, 1241vw, 1235vw, 1184w, 1158vw, 1096m, 1090m, 1072w, 1028vw, 999m, 922vw, 894vw, 838m, 819m, 792vw, 752m, 744m, 697s, 672vw, 662vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 5·10, s, 5H, C_5H_5; 6·9 - 7·5, m, 20H, Ph. The C_5H_5 resonance starts to shrink within minutes with growth of a new peak at δ4·86. After 0·5 h the cyclobutenyl complex (5) all but disappears, while a third peak at δ5·16 becomes clearly visible. After 12 h the peaks at δ4·86 and 5·16, due to the isomers of $\mathrm{Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}$ (9), reach an equilibrium where the low field peak is in slight predominance.

(ii) In benzene A reaction of $\mathrm{Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)}$ (250 mg, 0·45 mmol) and tcne (100 mg, 0·78 mmol) in benzene (25 ml) over 24 h led to the precipitation of a yellow powder. Recrystallization (dichloromethane/cyclohexane) gave yellow *microcrystals* of $\mathrm{Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}$ (9) (280 mg, 91%) m.p. 208 - 209° (Found: C, 66·7; H, 3·9; N, 8·2%; *M*(mass spectrometry), 686. $C_{38}H_{25}N_4OPRu$ requires C, 66·6; H, 3·7; N, 7·9%, *M*, 686). Infrared (CH_2Cl_2): ν(CN) 2226m, 2219m, 2212m; ν(CO) 1949vs cm^{-1}; ν(C=C) (Nujol) 1516m cm^{-1}; other bands at (Nujol): 1303w, 1247vw, 1175vw, 1163w, 1150w, 1108vw, 1082m, 990w, 830m, 816m, 750w, 743w, 732m, 724w, 691sh, 683s, 658w, 640vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 4·86, s, 5H, C_5H_5; 7·46, m, 20H, Ph. After 12 h a new C_5H_5 peak is observed at δ5·16 (*c*. 60%). ^{13}C n.m.r.: δ($CDCl_3$) (the two isomers are separately assigned as A and B; isomer B is more intense) 75·7 (A) (under $CDCl_3$), 76·2 (B), 2 x s, C(1); 90·3 (A), 90·6 (B), 2 x s, C_5H_5; 94·0 (B), d, *J*(CP) 3 Hz, 95·0 (A), d, *J*(CP) 3 Hz, C(4); 112·8, s, 113·6, d, *J*(CP) 4 Hz, 116·9, 117·4, 2 x s, CN; 128·8 - 135·7; m, Ph; 181·2 (B), 184·7 (A), 2 x s, C(2); 204·0 (B), 204·2 (A), 2 x d, *J*(CP) 19 Hz, CO; 213·4, 215·6, 2 x d, *J*(CP) 12 Hz, C(3).

(F) With $\mathrm{Ru(C{\equiv}CPh)[P(OMe)_3]\,(\eta\text{-}C_5H_5)}$

(i) In benzene Upon mixing $\mathrm{Ru(C{\equiv}CPh)[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)}$ (460 mg, 0·70 mmol) and tcne (110 mg, 0·86 mmol) in benzene (25 ml) a white *powder* precipitated. This was identified as $\mathrm{Ru[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2]}$-$\mathrm{[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)}$ (6) (308 mg 56%) m.p. 142 - 145°. Infrared (Nujol): ν(CN) 2239vw; ν(C=C) 1609vw, 1587vw, 1568w; ν(PO) 1059s, 1043s, 1011m $\mathrm{cm^{-1}}$; other bands at 1434m, 1310vw, 1235w, 1183w, 1172w, 1154vw, 1109vw, 1091m, 1001w, 991sh, 861w, 850sh, 837vw, 809m, 792vw, 767m, 754m, 749m, 720m, 707m, 698m, 681m, 659w $\mathrm{cm^{-1}}$. ^{1}H n.m.r.: $\delta(\mathrm{CDCl_3})$ 3·44, d, *J*(PH) 11 Hz, 9H, $\mathrm{CH_3}$; 4·70, d, *J*(PH) 1 Hz, 5H, $\mathrm{C_5H_5}$; 6·3 - 7·4, m, 20H, Ph. On standing two spectra grow over *c.* 15 h: 3·50, d, *J*(PH) 11 Hz, $\mathrm{CH_3}$; 4·70, d, *J*(PH) 1 Hz, $\mathrm{C_5H_5}$; 6·7 - 7·4, m, Ph; and 3·52, d, *J*(PH) 11 Hz, $\mathrm{CH_3}$; 4·84, d, *J*(PH) 1 Hz, $\mathrm{C_5H_5}$; 6·7 - 7·4, m, Ph. After leaving for an extended period (16 h, 100°) the spectrum of (10), described below, is present.

(ii) Formation of $\mathrm{Ru\{C[{=}C(CN)_2]C(Ph){=}C(CN)_2\}[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)}$ *(10)* A solution of $\mathrm{Ru[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2][P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)}$ (6) (270 mg, 0·35 mmol) in chloroform (30 ml) was heated at reflux point for 17 h. Purification by silica t.l.c. (diethyl ether, R_f *c.* 0·4) and recrystallization (dichloromethane/methanol) gave $\mathrm{Ru\{C[{=}C(CN)_2]C(Ph){=}C(CN)_2\}}$-$\mathrm{[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5).0{\cdot}25CH_2Cl_2}$ as red *crystals* (104 mg, 37%) m.p. 170 - 171° (Found: C, 59·8; H, 4·8; N, 6·7%; *M*(mass spectrometry), 782. $\mathrm{C_{40}H_{34}N_4O_3P_2Ru.0{\cdot}25CH_2Cl_2}$ requires C, 60·2; H, 4·3; N, 7·0%; *M*, 782). Infrared (Nujol): ν(CN) 2248vw, 2225w, 2212m, 2202w; ν(C=C) 1525m; ν(PO) 1050s, 1047s, 1042sh $\mathrm{cm^{-1}}$; other bands at 1593vw, 1583vw, 1569vw, 1432s, 1265m, 1188m, 1181m, 1175m, 1160w, 1112vw, 1088m, 1000w, 920w, 912w, 858vw, 838w, 825w, 817m, 780m, 770m, 756sh, 749s, 736m, 722s, 703m, 699m, 682vw, 663vw, 649vw, 623vw $\mathrm{cm^{-1}}$. ^{1}H n.m.r.: $\delta(\mathrm{CDCl_3})$ 3·50, d, *J*(PH) 11 Hz, 9H,

CH_3; 4·69, d, *J*(PH) 1 Hz, 5H, C_5H_5; 5·30, s, 0·5H, CH_2Cl_2; 6·7 - 7·6, m, 20H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 53·6, d, *J*(CP) 12 Hz, CH_3; 86·6, s, C_5H_5; 97·4, m, C(4); 113·9, 114·5, 119·1, 3 x s, CN; 128·2 - 133·8, m, Ph; 177·2, m, C(2); 223·6, d, *J*(CP) 15 Hz, C(3); [C(1) is obscured by $CDCl_3$ peaks].

(G) With $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$

(i) *In diethyl ether* A reaction of $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ (170 mg, 0·64 mmol) and tcne (83 mg, 0·65 mmol) in diethyl ether (15 ml) over 15 min led to the precipitation of $Fe[\overline{C{=}C(Ph)C(CN)_2C}(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (7) as a yellow *powder* (203 mg, 82%) m.p. >69° (dec.). Infrared (Nujol): ν(CN) 2243vw; ν(CO) 2033vs, 1998vs, 1977m (lit. 2040, 1990[2]); ν(C=C) 1601vw, 1583w, 1557w; other bands at 3122w, 1713w(br), 1433vw, 1422w, 1348vw, 1311vw, 1292vw, 1254m, 1187vw, 1160vw, 1119vw, 1107vw, 1094vw, 1063w, 1042vw, 1030vw, 1015m, 1002w, 991w, 972vw, 950vw, 913m, 883w, 860m, 838vw, 780vw, 770s, 720w, 690s, 651vw, 612s, 601m, 590m, 551w, 539vw cm^{-1}. ^1H n.m.r. $\delta(CDCl_3)$ 5·20 (lit. 5·45), s, 5H, C_5H_5; 7·58, s, 5H, Ph. After 20 min this spectrum had all but disappeared with new peaks at 4·93 (lit. 5·13) s, 5H, C_5H_5 and 7·60, s, 5H, Ph due to (11), described below.

N.B. - The solvent used for recording n.m.r. spectra was not given in the literature. This may account for the discrepancy in literature and experimental values.

(ii) *In dichloromethane* After reacting $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ (270 mg, 0·97 mmol) with tcne (135 mg, 1·05 mmol) in dichloromethane (15 ml) for 45 min, filtration and crystallization from hexane yielded orange *crystals* of $Fe\{C[{=}C(CN)_2]C(Ph){=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (11) (290 mg, 74%; lit. 82%[2]), m.p. >360°. Infrared (CH_2Cl_2): ν(CO) 2054s, 2009s (lit. 2050,

2005); ν(CN) (Nujol) 2220m, 2207m, 2201m; ν(C=C) 1533m, 1528sh cm^{-1}; other bands at 1259w, 1171w, 1107vw, 1068w, 1057w, 992w, 960w, 867m, 819w, 764w, 732m, 713w, 688m, 659m, 619w, 593w, 575w cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 4·93, s, 5H, C_5H_5; 7·60, s, 5H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 74·9, s, C(1); 86·9, s, C_5H_5; 98·0, s, C(4); 110·6, 112·5, 115·8, 3 x s, CN; 128·5, 130·1, 133·7, 3 x s, Ph; 181·2, s, C(2) 209·3, 211·0, 2 x s, CO; 215·1, s, C(3).

(H) With Ru(C≡CPh)(dppe)(η-C_5H_5)

(i) In benzene Reaction of a mixture of Ru(C≡CPh)(dppe)-(η-C_5H_5) (600 mg 0·90 mmol) and tcne (136 mg, 1·06 mmol) in benzene (25 ml) for 3 h yielded $\mathrm{Ru}[\overline{\mathrm{C{=}C(Ph)C(CN)_2C}}\mathrm{(CN)_2}]$(dppe)(η-$C_5H_5$) (8) (632 mg, 88%) as a yellow *powder.* Rapid recrystallization (dichloromethane/ethanol) gave $\mathrm{Ru}[\overline{\mathrm{C{=}C(Ph)C(CN)_2C}}\mathrm{(CN)_2}]$(dppe)(η-$C_5H_5$).0·25$CH_2Cl_2$ in a microcrystalline form, m.p. >170° (dec.) (Found: C, 67·2; H, 4·3; N, 7·0%. $C_{45}H_{34}N_4P_2Ru$. 0·25 CH_2Cl_2 requires C, 66·7; H, 4·3; N, 6·9%). Infrared (Nujol): ν(CN) 2235vw, 2210vw (br), ν(C=C) 1545w cm^{-1}; other bands at 1437m, 1311w, 1228sh, 1223w, 1181vw, 1169vw, 1100m, 1071vw, 1025vw, 1000m, 859w, 851w, 845sh, 830vw, 811m, 793vw, 758sh, 749m, 744m, 712m, 701s, 668m, 659w, 645sh, 619vw, 611vw, 591vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 1·5 - 2·6, m, 4H, CH_2; 4·66, 4·99, 2 x s, 5H, C_5H_5; 5·29, s, 0·5H, CH_2Cl_2; 7·0 - 7·9, m, Ph. After 12 h the spectrum of (8) had all but disappeared, while peaks due to (12), described below, had formed. ^{13}C n.m.r.: δ($CDCl_3$) 25, m, CH_2; 85·6, s, C_5H_5; 127·9 - 146·3, m, Ph; other resonances could not be observed before (12) had formed.

(ii) Formation of Ru{C[=C(CN)$_2$]C(Ph)=C(CN)$_2$}(dppe)(η-C_5H_5) (12)

After reacting Ru(C≡CPh)(dppe)(η-C_5H_5) (300 mg, 0·45 mmol) with tcne (60 mg, 0·47 mmol) in benzene (25 ml) for 6 h, the cyclobutenyl product (8) was collected and dissolved in chloroform (25 ml). Upon standing for 7 days, precipitation with ethanol and recrystallization (dichloromethane/methanol) gave red *crystals* of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(dppe)(\eta-C_5H_5).CH_2Cl_2$ (12) (329 mg, 83%) m.p. 212 - 214° (Found: C, 61·9; H, 4·0; N, 6.3%; *M*(mass spectrometry) 794. $C_{45}H_{34}N_4P_2Ru.CH_2Cl_2$ requires C, 62·9; H, 4·1; N, 6.4%; *M*, 794). Infrared (Nujol) ν(CN) 2219w, 2208w, 2199w; ν(C=C) 1520m cm^{-1}; other bands at 1088m, 1058vw, 997vw, 870w, 839vw, 827vw, 813sh, 802m, 763m, 747s, 737m, 718vw, 700s, 692m, 671w, 652sh, 643vw, 620vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1.2 - 2.2, m, 4H, CH_2; 4.13, 5.04, 2 x s, 5H, C_5H_5; 5.29, s, 2H, CH_2Cl_2; 6·2 - 7·8, m, 25H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 24·2 - 27·7, m, CH_2; 53·5, s, CH_2Cl_2; 73·9, m, C(1); 86·3, 86·9, 2 x s, C_5H_5; 95·1, m, C(4); 113·8, 114·6, 118·1, 119.4, 4 x s, CN; 128·6 - 144.8, m, Ph; 181·9, m, C(2); 225·7, m, C(3).

(I) With $Pt(C\equiv CPh)_2(PPh_3)_2$ A reaction of *trans*-$Pt(C\equiv CPh)_2(PPh_3)_2$ (250 mg 0·27 mmol) with tcne (74 mg, 0·58 mmol) in dichloromethane (20 ml) gave a port-red solution after 14 h. After evaporating to dryness, washing with carbon tetrachloride (2 x 50 ml), and extracting with diethyl ether (40 ml), addition of methanol brought out a flocculent white precipitate. This was minor and left unidentified. The solution was filtered and the mother liquor reduced in volume to give a mixture of dark purple/black *powder* and *crystals*. This was identified as $Pt\{C[=C(CN)_2]-C(Ph)=C(CN)_2\}(C\equiv CPh)(PPh_3)_2$ (19) (82 mg, 29%) m.p. >130° (dec.) (Found: C, 66·5; H, 3·6; N, 5·3%. $C_{58}H_{40}N_4P_2Pt$ requires C, 66·4; H, 3·8; N, 5·3%). Infrared (Nujol): ν(CN) 2218w, 2190w, 2170w, 2120w; ν(C=C) 1594w, 1588sh, 1573w, 1568sh cm^{-1}; other bands at 1436m, 1310vw, 1211vw, 1185w, 1157w, 1096m, 1067w, 1026w, 998w, 743m, 706m, 690s cm^{-1}. *Note* when the reagents were mixed in a 1:1 ratio the same product was isolated under the same conditions.

(J) With trans-Rh(C≡CPh)(CO)(PPh$_3$)$_2$ After mixing *trans*-Rh(C≡CPh)(CO)(PPh$_3$)$_2$ (420 mg, 0·56 mmol) and tcne (80 mg, 0·63 mmol) in dichloromethane (20 ml) for 2 h, crystallization from methanol gave yellow *microcrystals* of Rh[η^2-C(CN)$_2$C(CN)$_2$](C≡CPh)(CO)(PPh$_3$)$_2$.0·25CH$_2$Cl$_2$ (21) (470 mg, 94%) m.p. >160° (dec.) (Found: C, 67·9, H, 4·0; N, 6·2%. $C_{51}H_{35}N_4OP_2Rh.0{\cdot}25CH_2Cl_2$ requires C, 67·0; H, 3·9; N, 6·2%). Infrared (CH$_2$Cl$_2$): ν(CN) 2229w, 2223w; ν(CO) 2083s cm^{-1}; other bands at (Nujol) 1432m, 1427m, 1304vw, 1208vw, 1183vw, 1149vw, 1085sh, 1080m, 1014vw, 991vw, 753vw, 743w, 737m, 711vw, 700w, 688m, 680sh, 658w cm^{-1}. ^{1}H. n.m.r.: δ(CDCl$_3$) 7·4, m, 30H, Ph; 5·30, s, 0·5H, CH$_2$Cl$_2$.

(K) With [Ru(C=CHPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$ A reaction of [Ru(C=CHPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$ (500 mg, 0·54 mmol) and tcne (100 mg, 0·78 mmol) in dichloromethane (30 ml) gave a burgundy coloured solution within minutes. After 18 h a spot of the reaction mixture on a t.l.c. plate (silica, 1:1 diethyl ether/light petroleum) indicated that the major products were Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (46) and the product from a reaction of (46) with tcne, Ru[η^3-C(CN)$_2$C(Ph)C=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (13).

(L) With [Ru(C=CMePh)(PPh$_3$)$_2$(η-C$_5$H$_5$)]BF$_4$ A reaction of [Ru(C=CMePh)(PPh$_3$)$_2$(η-C$_5$H$_5$)]BF$_4$ (200 mg, 0·22 mmol) and tcne (50 mg, 0·39 mmol) in dichloromethane (30 ml) did not proceed at room temperature. Heating in an autoclave (50 atm. N$_2$, 18 h, 100°) gave an unchanged red solution which was evaporated to dryness, dissolved in dichloromethane (2 ml) and filtered drop-wise into diethyl ether. A fine pink *powder* was collected and identified by its infrared spectrum as starting material (170 mg, 85%).

Reactions of $(NC)_2C{=}C(CF_3)_2$

(A) With $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ After mixing $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (290 mg, 0·37 mmol) and $(NC)_2C_2(CF_3)_2$ (167 mg, 0·78 mmol) in benzene (30 ml) for 20 h, addition of octane and evaporation gave dark blue *crystals* of $\{Ru[\overline{C{=}C(Ph)C(CF_3)_2C}(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}(NC)_2C{=}C(CF_3)_2\}\cdot 0{\cdot}5C_6H_6$(23) (270 mg, 85%) m.p. 257 - 260° (Found: C, 57·3; H, 3·1; N, 4·8%. $C_{80}H_{50}F_{18}N_6P_2Ru_2\cdot 0{\cdot}5C_6H_6$ requires C, 57·3; H, 3·3; N, 4·7%). Infrared (Nujol): ν(CN) 2181s, 2155s, 2118vs, 2021s, ν(C=C) 1613w, 1577m, 1532s; ν(PF) (major bands) 1272vs, 1239vs, 1221vs, 1201vs cm^{-1}; other bands at 1347s, 1169m, 1161m, 1147vw, 1111m, 1098m, 1095sh, 1074w, 1062vw, 1030vw, 1010vw, 1002vw, 992vw, 974w, 948m, 925vw, 880w, 856vw, 839w, 819m, 772w, 759w, 752w, 747m, 722m, 707s, 699s, 633m, 598w cm^{-1}. UV/visible 553, ε 7·2; 745nm, ε 9·1.

(B) With $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ A solution of $(NC)_2C{=}C(CF_3)_2$ (248 mg, 1·16 mmol) in toluene (4 ml) was added to a solution of $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (700 mg, 0·96 mmol) in toluene (20 ml) under anaerobic conditions. After 30 h $Ru[\overline{C{=}C(Me)C(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (24) had precipitated as a yellow *powder* (743 mg, 82%) m.p. 161 - 163° (Found: C, 62·8; H, 4·0; N, 3·0; F, 12·2%; *M*-PPh_3(mass spectrometry), 682. $C_{50}H_{38}N_2F_6P_2Ru$ requires C, 63·6; H, 4·1; N, 3·0; F, 12·1%; *M*, 944). Infrared (Nujol): ν(CN) 2238vw, ν(C=C) 1572m; ν(CF) (major bands) 1270vs, 1220s, 1197vs, 1191sh cm^{-1}; other bands at 1480m, 1488s, 1311w, 1282m, 1255m, 1236w, 1185s, 1158w, 1150m, 1112vw, 1087s, 1078sh, 1036vw, 1026vw, 1014vw, 1000s, 933m, 873w, 853vw, 848vw, 838m, 825vw, 810m, 752s, 747m, 739m, 713s, 710m, 703m, 700vs, 680m cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 0·53, s, 3H, Me; 4·64, s, 5H, C_5H_5; 7·2, m, 30H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 16·4 s, Me; 84·8, s, C_5H_5; 116·4, s, CN; 127·7 - 140·4, m, Ph; 149·6, t, *J*(CP)

4 Hz, RuC; other resonances not observed.

Reaction of $C_2(CO_2Et)_4$

(A) With $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ A mixture of $Ru(C{\equiv}CPh)(PPh_3)_2$-($\eta$-$C_5H_5$) (200 mg, 0·25 mmol) and $C_2(CO_2Et)_4$ (200 mg, 0·63 mmol) in benzene (20 ml) was stirred for 1·5 h and then heated at reflux point for 10 h. A spot on a t.l.c. plate (silica, 1:2 diethyl ether/light petroleum) indicated that only starting materials were present. This result did not change after the solution was heated in an autoclave (50 atm N_2, 150°; 7 h). The starting materials were recovered without separation (382 mg).

(B) With $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ A mixture of $Ru(C{\equiv}CPh)(CO)$-(PPh_3)(η-C_5H_5) (200 mg, 0·36 mmol) and $C_2(CO_2Et)_4$ (120 mg, 0·38 mmol) in benzene (20 ml) was stirred for 18 h and then heated at reflux point for 4 h. A spot on a t.l.c. plate (silica, 1:1 diethyl ether/light petroleum) indicated that only starting materials were present.

(C) With $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ A mixture of $Fe(C{\equiv}CPh)(CO)_2$-(η-C_5H_5) (50 mg, 0·18 mmol) and $C_2(CO_2Et)_4$ (60 mg, 0·19 mmol) were stirred in benzene (20 ml) for 1 h and then heated at reflux point for 1 h. A spot on a t.l.c. plate (silica, 1:1 diethyl ether/cyclohexane) showed that only starting materials were present.

Reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with $(NC)_2C{=}C\overline{O(CH_2)_2O}$

A mixture of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (40 mg, 0·05 mmol) and $(NC)_2C{=}C\overline{O(CH_2)_2O}$ (7 mg, 0·05 mmol) were stirred in benzene (15 ml) for

18 h without change. After heating at reflux point for 2 h a spot on a t.l.c. plate (silica, 1:2 diethyl ether/light petroleum) showed the presence of only starting materials.

Reaction of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ *with* $cis\text{-}C_2H_2(CO_2Me)_2$

A mixture of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0·13 mmol) and *cis*-$C_2H_2(CO_2Me)_2$ (200 mg, 1·4 mmol) in benzene (25 ml) was stirred for 17 h. A spot on a t.l.c. plate (silica, 1:2 diethyl ether/light petroleum) indicated that only starting materials were present. After heating at refluxing point for 6 h a spot on a t.l.c. plate indicated that a very minor component was present apart from starting materials. The mixture was heated for a further 24 h but a t.l.c. check indicated that a reaction had not taken place.

Reaction of $Ru[\overline{C{=}C(Me)C(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ *(25) with CO.*

A solution of (24) (300 mg, 0·32 mmol) in tetrahydrofuran (20 ml) was carbonylated in an autoclave (50 atm CO, 120°, 20 h). Separation on a silica t.l.c. plate (1:1 diethyl ether/light petroleum) and crystallization (acetone/ethanol) gave two isomers of $Ru\{C[{=}C(CN)_2]C(Ph){=}C(CF_3)_2\}(CO)\text{-}(PPh_3)(\eta\text{-}C_5H_5)$ (26) as yellow *crystals*:

(i) R_f=0·7 (47 mg, 21%) m.p. 229 - 231° (Found: C, 55·9; H, 3·0; N, 4·0; F, 16·0%; *M*(mass spectometry), 710. $C_{33}H_{23}F_6N_2OPRu$ requires C, 55·9; H, 3·3; N, 4·0; F, 16·1%; *M*, 710). Infrared (CH_2Cl_2): ν(CO) 1975vs, ν(CN) (Nujol) 2215w, 2208w, 2202s; ν(C=C) 1620m; ν(CF, major bands) 1345s, 1253s, 1140s cm^{-1}; other bands at 1435m, 1310vw, 1217m, 1191vw, 1181vw, 1172w, 1162vw, 1119m, 1090w, 1070vw, 1064sh, 1037w, 1028sh, 1013vw, 1004vw, 998vw, 967m, 934w, 843w, 838m, 831m, 810m, 750m, 745m, 717m, 713w, 702sh, 697m, 684vw, 639w cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 1·07, m, 3H, Me; 5·08, s, 5H, C_5H_5; 7·5, m, 15H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 18·2, s, Me; 87·0, s, diene skeleton; 89·8, s, C_5H_5; 113·7, 118·5, 2 x s, CN; 128·7 - 136·4, m, Ph, 167·9, m, diene skeleton; 203·9, d, *J*(CP) 18 Hz, CO; 222·5, d, *J*(CP) 9 Hz, RuC; CF_3 resonances not observed.

(ii) R_f=0·5 (135 mg, 60%) m.p. 176 - 177° (Found: C, 55·6; H, 3·0; N, 4·0; F, 15·8%; *M*(mass spectrometry), 710. $C_{33}H_{23}F_6N_2OPRu$ requires C, 55·9; H, 3·3; N, 4·0; F, 16·1%; *M*, 710). Infrared (CH_2Cl_2): ν(CO) 1969vs; ν(CN) (Nujol) 2220m, 2212m; ν(C=C) 1617s; ν(CF, major bands) 1343s, 1255s, 1142s cm^{-1}; other bands at 3086vw, 3058vw, 1441m, 1436w, 1224m, 1187w, 1169m, 1123m, 1108vw, 1098m, 1090w, 1073vw, 1059vw, 1040w, 1024vw, 1012vw, 1001w, 971vw, 966m, 930w, 852w, 845w, 832m, 811w, 754sh, 750w, 748m, 719m, 709m, 697m, 686vw, 680vw, 639w, 564vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·84, m, 3H, Me; 5·03, s, 5H, C_5H_5; 7·45, m, 15H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 21·8, d, *J*(CP) 2 Hz, Me; 89·8, s, C_5H_5; 106·7, s, 108·3, m, 109·8, m, 112·6, s, 115·2, m, 117·2, s, a mixture of CF_3, diene and CN resonances; 129·2 - 135·3, m, Ph; 166·5, s, C(2) 207·7, d, *J*(CP) 18 Hz, CO; 219·3, d, *J*(CP) 9 Hz, RuC.

Reaction of Ru[η^3-C(CN)$_2$C(Ph)C=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (13) with CO

A solution of the allylic complex (13) (130 mg, 0·20 mmol) in tetrahydrofuran (50 ml) was carbonylated in an autoclave (53 atm CO, 120°, 17 h). The yellow solution was taken to dryness, extracted with diethyl ether and crystallized from cyclohexane. Recrystallization (dichloromethane/cyclohexane) gave yellow *microcrystals* of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)(PPh_3)(\eta-C_5H_5)$ (9), (120 mg, 89%). This was identified by comparing its infrared and n.m.r. spectra with those of the fully characterized complex, described above. In the ^1H n.m.r. spectrum both isomers were present initially in solution.

Reaction of $Ru[\eta^3\text{-}C(CN)C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ *(13) with* $CNBu^t$.

(A) Under mild conditions A mixture of (13) (140 mg, 0·21 mmol) and $CNBu^t$ (200 mg, 2·4 mmol) in thf (50 ml) was heated in a 100 ml autoclave under nitrogen (50 atm, 70°, 17 h). Filtration, crystallization from cyclohexane, and recrystallization (dichloromethane/cyclohexane) yielded dark red *crystals* of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CNBu^t)(PPh_3)$-$(\eta\text{-}C_5H_5)$ (17) (140 mg, 89%) m.p. 231 - 233° (Found: C, 67·6; H, 4·6; N, 9·2%; *M*(mass spectrometry), 741. $C_{42}H_{34}N_5PRu$ requires C, 68·1; H, 4·6; N, 9·5%; *M*, 741). Infrared (CH_2Cl_2): $\nu(CN)$ 2224m, 2216m, 2209m; $\nu(CNBu^t)$ 2138s, $\nu(C{=}C)$ (Nujol) 1510m, 1503sh; other bands at 1301w, 1254w, 1224w, 1202m, 1180vw, 1163vw, 1150vw, 1096m, 1078m, 1062w, 1020vw, 1002vw, 991w, 828m, 812sh, 803m, 757vw, 748m, 740m, 733m, 714m, 688s, 679sh, 659m, 652w, 617vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·33, s, 9H, Me; 4·62, s, 5H, C_5H_5; 7·4, m, 20H, Ph; upon warming two new singlets appeared at 1·26 (Me) and 4·54 (C_5H_5) accounting for about 30% of the protons. ^{13}C n.m.r.: $\delta(CDCl_3)$ 30·5, s, Me; 58·1, s, *tert*-C; 73·8, s, C(1); 86·7, 87·0, 2 x s (ratio = 1:2·5) C_5H_5; 95·2, s, C(4); 113·4, 114·1, 114·5, 118·4, 4 x s, CN; 128·9 - 136·7, m, Ph, 151·7, s, br, RuCN; 178·1, s, C(2); 224·3, d, *J*(CP) 9 Hz, C(3).

(B) Under vigorous conditions A mixture of (13) (200 mg, 0·30 mmol) and $CNBu^t$ (150 mg, 1·8 mmol) in benzene (50 ml) was heated in a 100 ml autoclave under nitrogen (50 atm, 150°, 10 h). Reduction to dryness and extraction with light petroleum (2 x 20 ml) left a yellow residue which on crystallization (dichloromethane/hexane) gave yellow *crystals* of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CNBu^t)_2(\eta\text{-}C_5H_5)$ (18) (159 mg, 93%) m.p. 205 - 207° (Found: C, 62·0; H, 5·1; N, 15·0%; *M*(mass spectrometry), 562. $C_{29}H_{28}N_6Ru$ requires C, 62·0; H, 5·0; N, 15·0%; *M*, 562). Infrared (CH_2Cl_2) $\nu(CN)$ 2223m, 2216sh; $\nu(CNBu^t)$ 2162s, 2118s; $\nu(C{=}C)$ (Nujol) 1530m cm^{-1}; other

bands at 1286w, 1268vw, 1231m, 1228sh, 1195s, 1177vw, 1070vw, 1005w, 988w, 831w, 821vw, 802m, 768w, 738w, 715vw, 692m, 659w, 653vw, 618vw cm^{-1}. ^{1}H n.m.r.: δ(CDCl$_3$) 1·51, 1·61, 2 x s, 18H, Me; 4·57, s, 5H C_5H_5; 7·49, s, 5H, Ph. ^{13}C n.m.r.: δ(CDCl$_3$) 30·7, 31·4, 2 x s, Me; 58·2, 58·4, 2 x s, *tert*-C; 69·3, s, C(1); 84·6, s, C_5H_5; 90·8, s, C(4); 113·0, 113·3, 114·1, 117·6, 4 x s, CN; 128·0, 129·0, 131·8, 133·1, 4 x s, Ph; 152·3, s, RuCN; 179·7, s, C(2); 226·2, s, C(3).

Reaction of $Rh[\eta^2\text{-}C(CN)_2C(CN)_2](C{\equiv}CPh)(CO)(PPh_3)_2$ *with NCMe*

After heating $Rh(C{\equiv}CPh)(tcne)(CO)(PPh_3)_2$ (90 mg, 0·10 mmol) in acetonitrile (20 ml) at reflux point for 30 min a yellow *powder* was precipitated and identified as $Rh(C{\equiv}CPh)(tcne)(NCMe)(PPh_3)_2$ (22) (78 mg, 85%) m.p. >160° (dec.) (Found: C, 69·4; H, 4·8; N, 7·3%. $C_{52}H_{38}N_5P_2Rh$ requires C, 69·6; H, 4·3; N, 7·8%). Infrared (CH_2Cl_2) ν(CN), 2226m; ν(NCMe), 2137m; ν(C≡C) (Nujol) 2073vw cm^{-1}; other bands at: 1588w, 1433m, 1307vw, 1197w, 1187vw, 1178sh, 1149vw, 1085sh, 1081m, 1019vw, 991w, 750m, 739m, 734sh, 688s, 658w cm^{-1}. ^{1}H n.m.r.: δ(CDCl$_3$) 1·80, s, 3H, Me; 7·0 - 8·0, m, 30H, Ph. ^{13}C n.m.r.: δ(CDCl$_3$) 63 0, s, Me; 125·6 - 134·9, m, Ph. (NC carbon not detected).

Note - the presence of excess tcne did not affect the result of this reaction.

Irradiation of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ *(9)*

A solution of (9, 150 mg, 0·22 mmol) in 1,2 dimethoxyethane (50 ml) was irradiated for 2 h (Pen-ray high pressure mercury lamp, 50 w). The volume was reduced to 15 ml and light petroleum added to give orange *crystals* of $Ru[\eta^3\text{-}C(CN)_2C(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (13) (100 mg, 70%). This was identified from its infrared spectrum and by spotting on a t.l.c.

plate and comparing with an authentic sample (silica, 1:2 diethyl ether/light petroleum.

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CHAPTER FOUR

THE PREPARATION OF SOME σ-ACETYLIDE COMPLEXES

4.1 *INTRODUCTION*

The chemistry described in Chapters Two and Three required the synthesis of a number of new σ-acetylide complexes. While a variety of σ-acetylide complexes are known, the synthesis and chemistry of many systems has not been explored. The major routes to σ-acetylide complexes are:

(i) metathesis reactions of metal complexes with other metal acetylides:

e.g. $[CoCl_2(PPh_3)_2] + 4\ NaC{\equiv}CPh \xrightarrow{liq.NH_3} [Co(C{\equiv}CPh)_4(PPh_3)_2]^{2-}$ (ref. 1)

$Au_2C_2.NH_3 + 2KC{\equiv}CR \xrightarrow{liq.NH_3} [RC{\equiv}CAuC_2AuC{\equiv}CR]^{2-}$ (ref. 2)

$IrCl(CO)(PPh_3)_2 + Me_3SnC{\equiv}CPh \longrightarrow Ir(C{\equiv}CPh)(CO)(PPh_3)_2$ (ref. 3)

(ii) oxidative addition of an acetylene to a metal complex:

e.g. $Pt(\eta^2\text{-}ClC{\equiv}CPh)(PPh_3)_2 \longrightarrow$ *trans*-$PtCl(C{\equiv}CPh)(PPh_3)_2$ (ref. 4)

$[Ir(CO)_3(PR_3)_2]^+ + HC{\equiv}CPh \longrightarrow [IrH(C{\equiv}CPh)(CO)_2(PR_3)]^+$ (ref. 5)

(R = Et, Ph).

(iii) reaction of a halo-acetylene with an anionic metal complex:

e.g. $[M(CO)_3(\eta\text{-}C_5H_5)]^- + BrC{\equiv}CPh \longrightarrow M(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ (ref. 6)

(M = Cr, Mo, W)

(iv) deprotonation of isolated or non-isolated vinylidene complexes (described in Sections 1.3.4.1 and 1.3.5.1)

(v) reaction of a terminal acetylene with a metal halide in the presence of NEt_3 and a CuI catalyst:

e.g. *trans*-$PtCl_2(PEt_3)_2 + HC{\equiv}CH \xrightarrow{NEt3/CuI}$ *trans*-$Pt(C{\equiv}CH)_2(PEt_3)_2$ (ref. 7)

The acetylide complexes described in this chapter have been prepared by routes (ii), (iv) and (v). Ligand exchange reactions have led to a range of complexes with varying steric and electronic properties.

4.2 RESULTS AND DISCUSSION

The σ-acetylide complexes $Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1, R = Bu^t; 2, R = $CH_2CH_2C{\equiv}CH$) and $Ru(PPh_3)_2(\eta\text{-}C_5H_5)C{\equiv}CCH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (3) have been formed *via* vinylidene intermediates. Reactions of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with HC≡CR in methanol gave orange-red solutions of the vinylidene complexes which on deprotonation with NaOMe yielded the acetylide complexes as yellow solids. Complex (3) was formed when $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $HC{\equiv}C(CH_2)_2C{\equiv}CH$ were reacted together in a 2:1 ratio. These complexes were identified by their spectral and micro-analytical data. In the infrared spectrum ν(C≡C) appears at *c*. 2100 cm^{-1} as a medium band. In the ^{13}C n.m.r. spectrum the α-carbon of the acetylide group appears between 95 and 115 p.p.m. with coupling to phosphorus, while the β-carbon appears as a singlet between 100 and 125 p.p.m. The binuclear acetylide complex (3) had singlets due to the CH_2 (δ2·51) and C_5H_5 (4·22) protons in the ^1H n.m.r. spectrum. These data distinguishes complex (3) from $Ru(C{\equiv}CCH_2{}^*CH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)$ (2) which had a triplet [1·90, J(HH) 2·4 Hz], triplet of triplets [2·14, J(HH) 2, J(PH) 8 Hz], multiplet (2·64) and singlet (4·22) assigned to CH, $CH_2{}^*$, CH_2 and C_5H_5 respectively. (Other data are described in the Experimental section). A variety of other complexes have been prepared similarly.[8]

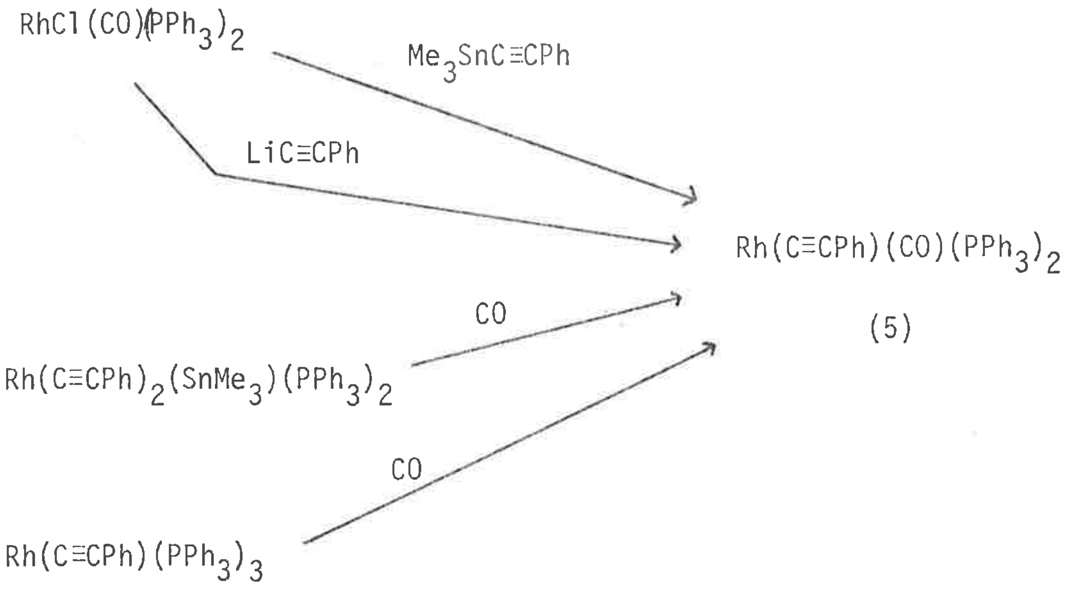
A reaction of $WCl(CO)_3(\eta\text{-}C_5H_5)$ with HC≡CPh and CuI in $HNEt_2$ gave $W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)$ (4) as a yellow powder (82%).[6] The copper iodide catalyst was essential for the reaction and suggests the formation of a copper acetylide compound which undergoes a metathesis reaction with $WCl(CO)_3(\eta\text{-}C_5H_5)$:

$$CuI + HC{\equiv}CPh \rightarrow [CuC{\equiv}CPh] \xrightarrow{WCl(CO)_3(\eta\text{-}C_5H_5)} \underset{(4)}{W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)}$$

The $HNEt_2$ medium was also necessary for the reaction, presumably as a proton 'sponge'. Complex (4) was identified by comparing its spectral and physical data with literature values[6] (see Experimental). Previously complex (4) was prepared from reactions of $[W(CO)_3(\eta\text{-}C_5H_5)]K$ with BrC≡CPh (28%) or $[PhC{\equiv}CPPh_3]Br$ (45%).

A reaction of $IrCl(CO)(PPh_3)_2$ with CO in the presence of $BPh_4{}^-$ or $PF_6{}^-$ gives $[Ir(CO)_3(PPh_3)_2]^+$.[5,9] Treatment of the salt with HC≡CPh gives an oxidative addition product which on deprotonation gives $Ir(C{\equiv}CPh)(CO)(PPh_3)_2$.[5] It was not possible to prepare $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ (5) by the same series of steps as the intermediate complexes could not be isolated. This result can be attributed to the general lower stability of Rh(III) complexes compared with Ir(III) complexes. A 'one pot' reaction of $RhCl(CO)(PPh_3)_2$, HC≡CPh and CO in NaOMe/MeOH solution, however, gave

$Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ (5) in 86% yield. If the reaction was attempted in the absence of CO, only starting material was recovered. This suggests that the reaction proceeds *via* $[Rh(CO)_3(PPh_3)_2]^+$, which is analogous to the intermediate isolated in the formation of $Ir(C{\equiv}CPh)(CO)(PPh_3)_2$.[3] A variety of other syntheses of $Rh(C{\equiv}CPh)(CO)(PPh_3)_2$ are known (Scheme 1).



Scheme 1

Ligand exchange reactions [for example used above in the synthesis of (5)] have yielded a variety of new σ-acetylide complexes. Reactions of (i) PMe_3 with $Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ gave $Ru(C{\equiv}CR)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$ [R = Bu^t (6), Me (7)] (ii) $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with L gave $Ru(C{\equiv}CPh)(L)(PPh_3)(\eta\text{-}C_5H_5)$ [L = CO (8), $CNBu^t$ (9)] and (iii) $Os(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ with dppe gave $Os(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$ (10). These complexes were identified by their physical and spectral data (see Experimental). These reactions proceed in the same manner as ligand exchange reactions of similar halide complexes.[10,11]

4.3 EXPERIMENTAL

General experimental conditions have been described in Chapter Two. Literature methods were used in the preparation of $RuCl(PPh_3)_2(\eta-C_5H_5)$,[12] $WCl(CO)_3(\eta-C_5H_5)$,[13] $RhCl(CO)(PPh_3)_2$,[14] $Ru(C{\equiv}CMe)(PPh_3)_2(\eta-C_5H_5)$, $Ru(C{\equiv}CPh)(PPh_3)_2(\eta-C_5H_5)$ and $Os(C{\equiv}CPh)(PPh_3)_2(\eta-C_5H_5)$.[8]

Preparation of σ-Acetylide Complexes

(A) $Ru(C{\equiv}CBu^t)(PPh_3)_2(\eta-C_5H_5)$ *(1)* 3,3-Dimethylbutyne (20 drops, excess) was added to a suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (230 mg, 0·32 mmol) in methanol (50 ml), and the mixture was heated briefly at reflux point to form a red solution. After cooling, addition of sodium (*c.* 40 mg, 0·002 g atom) resulted in a rapid change in colour, with deposition of light yellow *crystals* which were collected and recrystallized (dichlromethane/methanol) to give pure $Ru(C{\equiv}CBu^t)(PPh_3)_2(\eta-C_5H_5)$ (1) (210 mg, 86%), m.p. 215 - 218° (Found: C, 73·7; H, 5·8%; *M*(mass spectrometry), 772. $C_{47}H_{44}P_2Ru$ requires C, 73·1; H, 5·7%; *M*, 772). Infrared: ν(C≡C) 2120m; other bands at 1595w, 1578vw, 1248m, 1204sh, 1191w, 1164w, 1108w, 1097s, 1091s, 1074w, 1031w, 1011w, 1001w, 860w, 835m, 806s, 761sh, 755s, 748s, 737s, 722m, 698vs, 688s, 664w, 616vw, 540vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·20, s, 9H, Me; 4·18, s, 5H, C_5H_5; 7·15, m, 7·58, m, 30H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 33·0, s, Me; 85·2, s, C_5H_5; 120·4, s, ≡C; 127·1 - 139·8, m, Ph (other carbons not detected).

(B) $Ru(C{\equiv}CCH_2CH_2C{\equiv}CH)(PPh_3)_2(\eta-C_5H_5)$ *(2)* A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1·5 g, 2·07 mmol) NH_4PF_6 (330 mg, 2·02 mmol) and 1,5 hexadiyne (200 mg, 2·56 mmol) in methanol (120 ml) was heated at reflux point for 5 min. Yellow *microcrystals* were deposited on addition of sodium (*c.* 100 mg, 0·004 g atom), which on recrystallization

(dichlomethane/methanol) gave pure $Ru(C{\equiv}CCH_2CH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)$ (2) (1·38 g, 85%) m.p. >160° (dec.) (Found: C, 73·6; H, 5·4%. $C_{47}H_{40}P_2Ru$ requires C, 73·3; H, 5·3%). Infrared (Nujol): ν(C≡C) 2100m cm^{-1}; other bands at 3292m, 1583vw, 1571vw, 1431s, 1310vw, 1273w, 1249vw, 1186w, 1162vw, 1155vw, 2001vw, 1092s, 1083m, 1069w, 1025w, 1008w, 997w, 912vw, 842vw, 831w, 801m, 756w, 747s, 740sh, 721vw, 696vs, 681w, 654w, 638w, 617vw cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 1·90, t, *J*(HH) 2·4 Hz, 1H, ≡CH; 2·14, tt, *J*(PH) 8 Hz, *J*(HH) 2 Hz, $RuC{\equiv}CCH_2$; 2·64, m, 2H, $\underline{CH_2}C{\equiv}CH$; 4·22, s, 5H, C_5H_5; 7·1 - 7·5, m, 30H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 20·7, s, $\underline{C}H_2C{\equiv}CH$; 23·3, s, $RuC{\equiv}C\underline{C}H_2$; 68·1, s, ≡CH; 84·8, s, C_5H_5; 85·3, s, $\underline{C}{\equiv}CH$; 95·3, t, *J*(CP) 25 Hz, RuC; 109·1, s, $RuC{\equiv}\underline{C}$; 125·5 - 141·5, m, Ph.

(C) $Ru(PPh_3)_2(\eta\text{-}C_5H_5)C{\equiv}CCH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (3) A solution of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1·15 g, 1·58 mmol), $HC{\equiv}CCH_2CH_2C{\equiv}CH$ (63 mg, 0·81 mmol) and NH_4PF_6 (263 mg, 1·61 mmol) was heated at reflux point in methanol (200 ml) for 0·25 h. The reaction mixture was decanted hot from some unreacted starting material (123 mg, 11%) and sodium (*c.* 60 mg, 0·003 g atom) added with the subsequent precipitation of $Ru(PPh_3)_2(\eta\text{-}C_5H_5)\text{-}C{\equiv}CCH_2CH_2C{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5).0{\cdot}5MeOH$ (3) as a yellow *powder* (502 mg, 43%), m.p. 153 - 155° (Found: C, 71·0; H, 4·4%. $C_{88}H_{74}P_4Ru_2.0{\cdot}5CH_3OH$ requires C, 72·2; H, 5·2%). Infrared (Nujol): ν(C≡C) 2100m, 2095sh cm^{-1}; other bands at 3050m, 1586vw, 1480m, 1437s, 1309vw, 1244vw, 1182w, 1159vw, 1154vw, 1089m, 1083sh, 1068vw, 1027w, 1000w, 851vw, 832w, 813sh, 805m, 753m, 742m, 738m, 702sh, 697s, 682sh cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 2·51, s, 4H, CH_2; 3·47, s, 1·5H, $\underline{Me}OH$; 4·22, s, 10H, C_5H_5; 7·1, 7·5, m, 60H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 25·6, s, CH_2; 84·7, s, C_5H_5; 91·0, t, *J*(CP) 27 Hz, RuC; 112·0, s, ≡C; 127·2 - 141·7, m, Ph.

(D) $W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)$ (4) A mixture of $WCl(CO)_3(\eta\text{-}C_5H_5)$ (300 mg, 0·81 mmol), $PhC\equiv CH$ (100 mg, 0·98 mmol) and CuI (5 mg) was reacted together in $HNEt_2$ (25 ml) for 8 h in the dark. The mixture was taken to dryness, extracted with diethyl ether, filtered and crystallized from hexane. All manipulations were carried out under anaerobic and light-free conditions. Complex (4) was obtained as yellow *crystals* (290 mg, 82%) m.p. 129 - 131° (lit.[6] 142 - 143°) [*M*(mass spectrometry), 434. $C_{16}H_{10}O_3W$ requires *M*, 434]. Infrared (CH_2Cl_2): ν(C≡C) 2105m; ν(CO) 2040s, 1954vs cm^{-1} [lit. ν(C≡C) 2110, KBr; ν(CO) 2040, 1950, $CHCl_3$]; other bands at (Nujol) 1597w, 1488m, 1427w, 1419w, 1212w, 1178vw, 1069w, 1064w, 1012w, 1003w, 931vw, 906w, 860vw, 850vw, 838m, 831m, 755s, 693m, 665m cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 5·62, s, 5H, C_5H_5; 7·24, m, 5H, Ph (lit. 5·76 and 7·07 - 7·53 respectively, $CDCl_3$). ^{13}C n.m.r.: δ($CDCl_3$) 73·0, s, ≡C; 91·8, s, C_5H_5; 129·3, s, WC; 126·4, 127·2, 128·1, 131·2, 4 x s, Ph; 211·8, s, CO.

(E) $Rh(C\equiv CPh)(CO)(PPh_3)_2$ (5) CO was slowly bubbled through a mixture of $RhCl(CO)(PPh_3)_2$ (500 mg, 0·72 mmol) and $PhC\equiv CH$ (80 mg, 0·79 mmol) in NaOMe/MeOH (*c*. 100 mg of sodium in 25 ml of methanol). After 1·5 h bubbling was ceased and the reaction was allowed to proceed under a CO atmosphere for 18 h. A yellow *powder* was collected, washed with methanol, and identified as $Rh(C\equiv CPh)(CO)(PPh_3)_2$ (5) (470 mg, 86%) m.p. >140°(dec) (lit.[15] 151 - 154, dec). Infrared (Nujol): ν(C≡C) 2094w; ν(CO) 1958vs cm^{-1}; [lit.(Nujol) 2092 and 1958 cm^{-1} respectively].

Ligand Exchange Reactions

(A) $Ru(C\equiv CBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)$ with PMe_3 A reaction of $Ru(C\equiv CBu^t)$-$(PPh_3)_2(\eta\text{-}C_5H_5)$ (1·05 g, 1·36 mmol) with PMe_3 (250 mg, 3·3 mmol) in

petroleum spirit (100 - 120° boiling fraction, 20 ml) in a sealed ampoule (170°, 6 h) yielded a yellow solution, which on crystallization from light petroleum gave yellow *crystals* of $Ru(C{\equiv}CBu^t)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$ (6) (580 mg, 72%) m.p. 164 - 165° (Found: C, 65·4; H, 6.6%; *M*(mass spectrometry), 586. $C_{32}H_{38}P_2Ru$ requires C, 65·6; H, 6·5%; *M*, 586). Infrared (Nujol): $\nu(C{\equiv}C)$ 2082s cm^{-1}; other bands at 1594vw, 1582vw, 1437s, 1424m, 1353m, 1306vw, 1395vw, 1292w, 1277vw, 1274m, 1268w, 1253m, 1195w, 1182w, 1155vw, 1118vw, 1098w, 1092w, 1085s, 1065vw, 1051vw, 1022w, 1003w, 990w, 949s, 932m, 928m, 850w, 840w, 824m, 798m, 785s, 751w, 748m, 741s, 735sh, 716m, 710m, 691sh, 688vs, 677w, 666m, 658sh, 610vw, 583vw cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·10, s, 9H, CCH_3; 1·20, d, *J*(PH) 9 Hz, 9H, PCH_3; 4·43, s, 5H, C_5H_5; 7·3 - 7·7, m, 15H, Ph. ^{13}C n.m.r.: 22·1, d, *J*(CP) 29 Hz, PCH_3; 29·7, s, $C\underline{C}H_3$; 33·2, s, CH_3; 82·5, t, *J*(CP) 2 Hz, C_5H_5; 89·0, ABq, *J*(AB) 24·5 Hz, RuC; 116·5, s, $\equiv\underline{C}C$; 127·0 - 141·6, m, Ph.

(B) $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ with PMe_3 Using the method described in (A), $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (380 mg, 0·52 mmol) and PMe_3 (10 mg, 0·13 mmol) gave $Ru(C_2Me)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$ (7) as yellow *crystals* (160 mg, 56%) m.p. 169 - 170° (Found: C, 63·5; H, 6·0; *M*(mass spectrometry), 544. $C_{29}H_{32}P_2Ru$ requires C, 64·1; H, 5·9%; *M*, 544). Infrared (Nujol): $\nu(C{\equiv}C)$ 2100s cm^{-1}; other bands at 1586vw, 1570vw, 1434s, 1417w, 1295w, 1277w, 1275w, 1177vw, 1155vw, 1098vw, 1082m, 1067vw, 1022vw, 1000vw, 993vw, 987vw, 979vw, 962sh, 946s, 928m, 922sh, 849vw, 833w, 813w, 792m, 752m, 742w, 738m, 720m, 710w, 698m, 691sh, 687s, 676vw, 668w, 658w cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ 1·17, d, *J*(PH) 9 Hz, 9H, PCH_3; 1·95, t, *J*(PH) 3 Hz, 3H, $\equiv CCH_3$; 4·48, s, 5H, C_5H_5; 7·3 - 7·7, m, 15H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 7·3, s, $\equiv C\underline{C}H_3$; 22·3, d, *J*(PH) 28 Hz, PCH_3; 82·2, s, C_5H_5; 94·1, ABq, *J*(AB) 23 Hz, RuC; 101·4, s, $\equiv\underline{C}CH_3$; 125·8 - 141·1, m, Ph.

(C) Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) with CO A solution of Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (2·16 g, 2·73 mmol) in tetrahydrofuran (50 ml) was carbonylated in an autoclave (50 atm CO, 105°, 4 days). Addition of ethanol (20 ml) to the solution, and removal of part of the solvent afforded a fine light yellow precipitate, which was recrystallized (dichloromethane/methanol) to give pure Ru(C≡CPh)(CO)(PPh$_3$)(η-C$_5$H$_5$) (8) as yellow *microcrystals* (1·44 g, 95%), m.p. 218 - 220° (Found: C, 68·5; H, 4·5%; *M*, 546. $C_{31}H_{25}OPRu$ requires C, 68·1; H, 4·6%; *M*, 546). Infrared (CHCl$_3$): ν(C≡C) 2097s; ν(CO) 1967vs; other bands at (Nujol) 1598m, 1592sh, 1578vw, 1570w, 1491s, 1213w, 1193w, 1179w, 1166w, 1154w, 1096s, 1067w, 1018w, 1014w, 1002m, 998sh, 973w, 912w, 857w, 846w, 838w, 814s, 766s, 759sh, 756s, 743m, 724w, 704sh, 697s, 692s, 582w, 565w cm^{-1}. ^{1}H n.m.r. δ(CDCl$_3$) 5·05, s, 5H, C$_5$H$_5$; 6·97, m, 5H, CH$_2$<u>Ph</u>; 7·40, m, 15H, PPh$_3$. ^{13}C n.m.r.: δ(CDCl$_3$) 87·2, s, C$_5$H$_5$; 100·1, d, *J*(CP) 24 Hz, RuC; 112·7, s, <u>C</u>Ph; 124·2 - 137·4, m, Ph; 203·7, d, *J*(CP) 22 Hz, CO.

(D) Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) with CNBu^t A solution of Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0·25 mmol) and Bu^{t}NC (4 drops, *c.* 40 mg, 0·5 mmol) in tetrahydrofuran (20 ml) was heated in an autoclave under nitrogen (7 atm, 150°, 16 h). Addition of ethanol (15 ml) and evaporating to *c.* 10 ml afforded a product on cooling, which was filtered, washed with MeOH and light petroleum, and dried to give pure Ru(C≡CPh)(CNBu^t)(PPh$_3$)(η-C$_5$H$_5$) (9) as fine yellow *crystals* (120 mg, 77%), m.p. 175 - 177° (Found: C, 70·2; H, 5·6; N, 2·2%; *M*, 601. $C_{35}H_{34}NPRu$ requires C, 70·6, H, 5·6; N, 2·3%; *M*, 601). Infrared (CHCl$_3$): ν(C≡C) 2128s, ν(CN) 2088s; other bands at (Nujol) 1600s, 1592sh, 1579w, 1491s, 1372m, 1232w, 1210m, 1187vw, 1175w, 1161vw, 1107sh, 1101m, 1091m, 1068w, 1032w, 1012w 1001w, 905w, 836m, 833sh, 811w, 793m, 761s, 749s, 723w, 704m, 693vs, 620vw, 595vw, 554vw, 533vw cm^{-1}. ^{1}H n.m.r.: δ(CDCl$_3$) 1·12, s, 9H, Me; 4·82, s, 5H, C$_5$H$_5$;

6·97, s, 5H, Ph; 7·42, m, 15H, PPh_3. ^{13}C n.m.r.: δ($CDCl_3$) 30·8, s, $\underline{C}Me_3$; 56·2, s, $\underline{C}Me_3$; 84·2, s, C_5H_5; 111·2, d, *J*(CP) 26 Hz, Ru$\underline{C}$≡C; 111·8, s, $\underline{C}Bu^t$; 123·2 - 139·2, m, C_6H_5; 159·6, d, *J*(CP) 26 Hz, Ru$\underline{C}NBu^t$.

(E) Os(C≡CPh)(PPh_3)$_2$(η-C_5H_5) with dppe A mixture of Os(C≡CPh)(PPh_3)$_2$(η-C_5H_5) (190 mg, 2·2 mmol) and dppe (200 mg, 5 mmol) was heated in refluxing decalin (40 ml) for 4 h. The resulting solution was added to a column of alumina, the decalin washed through with light petroleum, and the product eluted with benzene/ethanol (49:1). Partial evaporation, and addition of ether, caused precipitation of yellow *crystals*, which were collected and washed with ether to give pure Os(C≡CPh)(dppe)(η-C_5H_5) (10) (140 mg, 86%), m.p. 135 - 137° (Found: C, 62·1; H, 4·5%; *M*, 750. $C_{39}H_{30}OsP_2$ requires C, 62·4; H, 4·0%; *M*, 750). Infrared (Nujol): ν(CC) 2090s; other bands at 1596sh, 1590m, 1312m(br), 1185m, 1173m, 1111m, 1096s, 1077w, 1025w, 996w, 970w(br), 873w, 832w, 810w, 791w, 752w, 741s, 727s, 703w, 689s, 669w, 663m cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 2·31, m, 2·58, m, 4H, CH_2; 4·78, s, 5H, C_5H_5; 7·33, m, 25H, Ph.

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CHAPTER FIVE

THE PREPARATION AND CHEMISTRY OF SOME HYDRIDE COMPLEXES

5.1 INTRODUCTION

The nature of the M-H bond in transition metal hydride complexes has long been the subject of theoretical interest to chemists. The hydrido moiety, once thought to be unique, has been found to behave similarly to halide or alkyl species. Many studies of the stereochemistry and structures of hydride complexes have been made, in addition to extensive investigations of their chemistry, not least because of their role as intermediates in catalytic hydrogenation or hydroformylation reactions.

Main group metal hydrides such as $LiAlH_4$ are well known and have proved a convenient source of H^- in synthetic chemistry. The first report of a transition metal hydride species was that of CuH in 1844.[1] In the early 1930's the preparations of $H_2Fe(CO)_4$ and $HCo(CO)_4$ appeared[2] and since then hydride complexes of most transition metals have been reported.

A variety of preparative routes can be used in the formation of metal hydride complexes and have been the subject of comprehensive reviews.[3] These include (i) exchanging a leaving group (usually halide) with H^- from a main group hydride (e.g. $LiAlH_4$ or $NaBH_4$), (ii) oxidative addition of H_2 or HX to a metal complex (iii) protonation of neutral or ionic complexes (iv) β-hydride elimination from alcohols in the presence of base. The latter route, first used by Chatt and Shaw,[4] has proved a convenient and high yield route to several cyclopentadienyl-iron, -ruthenium and -osmium hydride complexes.

The hydride complex, $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$, was first prepared from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $LiAlH_4$.[5] This synthesis has proved rather tedious, particularly for large scale preparations. Brief reflux of a variety of cyclopentadienyl-iron, -ruthenium and -osmium halide complexes in NaOR/ROH or NEt_3/MeOH led to precipitation of the pure hydride complexes in high yield. Some reactions of the metal-hydrogen bond with CS_2, CO_2 and HX have also been investigated.

Initial investigations of this chemistry were made jointly with Dr. R.C. Wallis.

5.2 RESULTS

Reactions of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, $RuCl[P(OPh)_3](PPh_3)(\eta\text{-}C_5H_5)$ (1), $RuCl(dppe)(\eta\text{-}C_5H_5)$, $RuCl(sp)(\eta\text{-}C_5H_5)$ (2) [sp = $P(C_6H_4CH{=}CH_2\text{-}o)Ph_2$], $FeCl(dppe)(\eta\text{-}C_5H_5)$ and $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ in a solution of refluxing NaOMe/MeOH gave the corresponding hydride complexes (3) - (8) (Table 1). Complex (3), which was also prepared using NaOEt/EtOH or NEt_3/MeOH, was characterized by comparing its spectral data with literature values [^1H n.m.r. (CS_2) -11·83, t, *J*(PH) 34Hz, RuH; 4·11, s, C_5H_5; lit.[5] -11·73 (34Hz), 4·04 respectively. Infrared ν(RuH) 1950 (CS_2); lit.[5] 1950 cm^{-1}. M^+ at *m/e* 692].

Table 1. Some infrared and ^{1}H n.m.r. data of relevant hydride complexes. Complexes (9) - (11) have been included for comparison.

Compound	ν(M-H)	δ(M-H)
$HFe(dppe)(\eta-C_5H_5)$ (7)	1830, 1880 (Nujol) 1840 (CH_2Cl_2)	-16·1(C_6D_6)
$HFe[P(OPh)_3]_2(\eta-C_5H_5)$ (9)^A	1920 (Nujol)	-14·05^B
$HRu(PPh_3)_2(\eta-C_5H_5)$ (3)	1970 (Nujol) 1950 (CS_2)	-11·13(C_6D_6) -11·73 (CS_2)
$HRu[P(OPh)_3](PPh_3)(\eta-C_5H_5)$ (4)	1960 (Nujol) 1951 (CS_2)	-11·80(C_6D_6)
$HRu(dppe)(\eta-C_5H_5)$ (5)	1911, 1945 (Nujol) 1944 (CS_2)	-13·26(C_6D_6) -13·86 (CS_2)
$HRu(CO)(PPh_3)(\eta-C_5H_5)$ (10)^C	(under CO)	-11·58 (CS_2)
$HRu(CNBu^t)(PPh_3)(\eta-C_5H_5)$ (11)^D	1980 (Nujol) 1976 (CS_2)	-11·36(C_6D_6)
$HOs(PPh_3)_2(\eta-C_5H_5)$ (8)	2067 (Nujol) 2060 (CS_2)	-13·98 (CS_2) -14·57(C_6D_6)

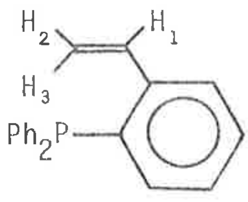
A, ref. 6; B, solvent not given; C, ref. 7; D, ref. 8.

The iron complex (7) has been reported previously[9] and was identified from its physical data, while complexes (4), (5) and (8) were identified by microanalytical and spectral data. In the infrared spectra ν(MH) appears between 1920 and 2060 cm^{-1}, while in the ^{1}H n.m.r. spectra the hydride proton resonates between δ -11·8 and -16 p.p.m. with coupling to phosphorus (Table 1 and Experimental). In the solid state spectra of the dppe complexes [(5) and (7)] ν(MH) appears as two broad absorptions, while in solution only one absorption is present.

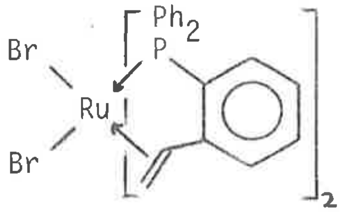
Of particular interest is the reaction of RuCl(sp)(η-C_5H_5) (2) with NaOMe/MeOH. Complex (2) is formed in a reaction of RuCl(PPh_3)$_2$-(η-C_5H_5) and sp. In the ^{1}H n.m.r. spectrum the olefinic protons appear at higher field than in the free ligand, thus indicating that the olefin is π-bonded to the metal (Table 2).[10] The ^{13}C and ^{31}P n.m.r. indicate that one isomer is present (see Experimental). A reaction of (2) with NaOMe/MeOH gives the hydride complex (6) in two isomeric forms (the mixture was identified by its spectral and microanalytical data). The ^{1}H n.m.r. spectrum is complex (Figure 1) but indicates that the olefin is bonded to the metal (Table 2), and that there has been no addition of H^- or MeO^- to the olefin. The hydride resonances appear as two doublets of doublets at δ-9·60 and -8·56 [J(PH) 31Hz, J(H3H) 2 Hz]. The ^{13}C and ^{31}P n.m.r. spectra further indicated that two isomers were present. The olefinic carbons of the minor isomer appear as two doublets [34·9, CH_2; 49·0, CH; J(CP) = 5 Hz], while the major isomer has two singlets (36·2, CH_2; 51·1, CH). This suggests that the isomers differ in the position of the olefinic group. Resonances at δ82·3 and 84·1 are assigned to the C_5H_5 groups of the minor and major isomers respectively, while a small singlet at δ 83·2 is assigned to an unidentified impurity. Chlorination of (6) with $CDCl_3$ regenerates the chloride (2) as a single isomer.

A reaction of HRu(sp)(η-C_5H_5) with CS_2 gave a separable mixture of two dark red complexes. The mass spectra indicated that 1:1 adducts of formulation HRu(CS_2)(sp)(η-C_5H_5) (13) had formed. While the minor isomer could not be identified further, the other product was shown to contain a $CHCH_3$ group from its ^{1}H n.m.r. spectrum [δ1·90, d, CH_3; 3·28, q, CH, J(HH) 6·5 Hz]. Cyclopentadienyl and phenyl protons were also present (δ4·87, s and 7·0-7·4, m, respectively) but no resonances were present in the

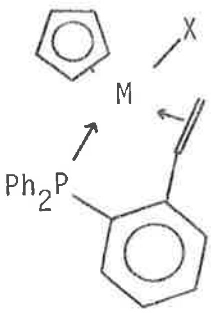
Table 2 ^{1}H n.m.r. data for the olefinic group of the sp ligand. Complex (9) is included for reference and is used as a basis for assignment.*



sp



(12)



(2) M=Ru, X=Cl

(6) M=Ru, X=H

(17) M=Os, X=Br

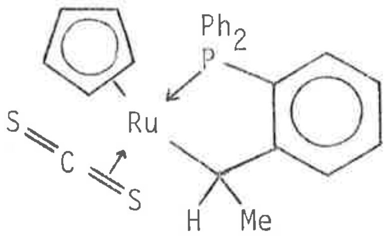
Compound	δH(1)	δH(2)*	δH(3)*	$J(12)$	$J(13)$	$J(23)$
sp	A	4·99	5·45	11·0	17·5	1·3
$RuBr_2(sp)_2$ (12)^B	3.30	2·08	3·11	9·0	12·5	≤ 1
RuCl(sp)(η-C_5H_5) (2)	5·40	3·04	C	9·0	9·0	5·0
RuH(sp)(η-C_5H_5) (5)^D	C	1·75	2·73	E	E	E
RuH(sp)(η-C_5H_5) (5)^F	C	1·44	2·96	E	E	E
OsBr(sp)(η-C_5H_5) (17)^D	5·31	3·15	4·17	9·0	9·0	5·0
OsBr(sp)(η-C_5H_5) (17)^F	5·47	2·92	4·28	9·0	9·0	5·0

A, under phenyl; B, ref. 10; C, under C_5H_5; D, major isomer;
E, complex coupling, cannot be assigned; F, minor isomer.

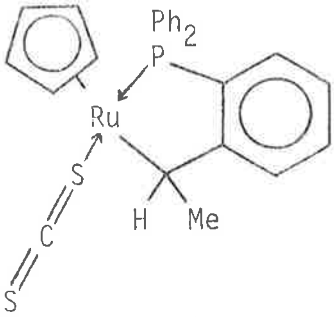
*[The assignment of H(2) and H(3) has been made on the basis of $J(13)$ being greater than $J(12)$.[10] When $J(12)$ equals $J(13)$ the resonance at lower field is arbitrarily assigned to H(3) as this is the most common occurrence].

Ru-H region (*c.* −12 p.p.m.) or the SCHS region (13·65 - 9·85 p.p.m.[11]). This implies that the hydride proton has transferred onto the CH_2 group of the sp ligand. In the ^{13}C n.m.r. spectrum singlets at δ27·4 and 84·3 are assigned to methyl and cyclopentadienyl groups, respectively, while a broad multiplet (123·2 - 138·4) is assigned to phenyl carbons. A doublet at δ51·3 (*J* = 11 Hz) may be due to CH with coupling to phosphorus, although no phosphorus coupling was observed in the ^{1}H n.m.r. spectrum. The apparent doublet may in fact be two singlets, which could be assigned to CH and CS. Two other doublets appear at δ145·9 [*J*(CP) = 15 Hz] and 150·6 [*J*(CP) = 6 Hz] and may be assigned to phenyl or CS carbons.

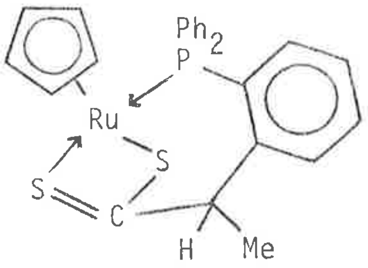
From the n.m.r. data the structure of the major isomer of (13) could feasibly be any of (13A) - (13C). The infrared data, however, precludes (13A) as no strong $\nu(CS_2)$ absorptions are present in the region 955 - 1235 (asymmetric stretch) and 632 - 653 cm^{-1} (symmetric stretch).[11,12]



(13A)

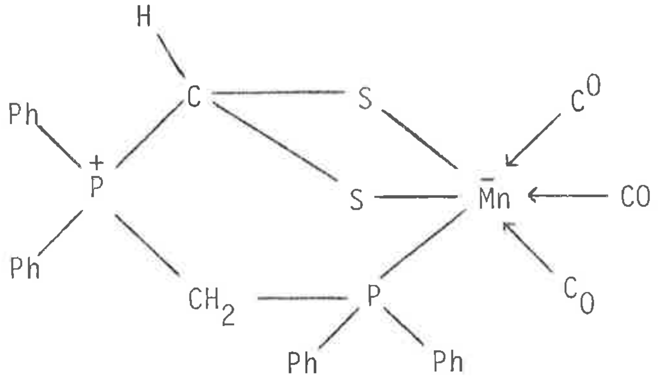


(13B)



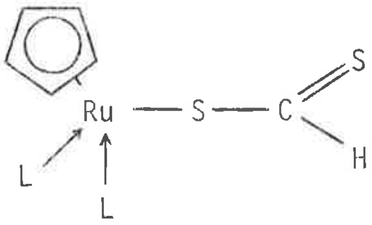
(13C)

Similarly (13B) is eliminated as no $\nu(CS_2)$ absorption appears at *c.* 1500 cm^{-1}. Absorptions in the infrared spectrum at 1091m, 917s, and 751m cm^{-1} can be assigned to the asymmetric stretching, symmetric stretching, and bending modes, respectively, of the dithioformate group of complex (13C). Complex (14),[13] formed in a reaction of $HMn(CO)_3(dppm)$ with CS_2, shows some similarity to (13C) and exhibits low energy ν(CS) absorptions (818, 652 cm^{-1}). A structural determination is currently in progress, and will be needed before (13) can be fully characterized.*



(14)

A dithioformate complex, (15), was formed in a reaction of $HRu(dppe)(\eta\text{-}C_5H_5)$ with CS_2. In the ^1H and ^{13}C n.m.r. spectra the



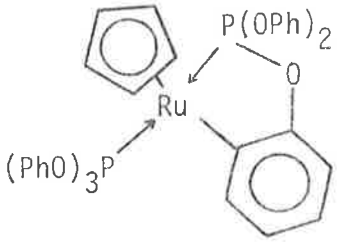
(15) LL = dppe
(18) L = PPh_3

expected methylene, cyclopentadienyl and phenyl peaks were observed (see Experimental). The SCHS group was identified by the expected[11,12] low field ^1H n.m.r. resonance at δ10·61, and a resonance at δ176·5 p.p.m. in the ^{13}C n.m.r. spectrum. In the infrared spectrum ν(CS) appears at

*(see Appendix)

976vs cm^{-1} and in the mass spectrum a molecular ion is observed at *m/e* 642.

A reaction of $RuCl[P(OPh)_3]_2(\eta-C_5H_5)$ with NaOMe/MeOH gave $\overline{Ru[(C_6H_4O)P}(OPh)_2[P(OPh)_3](\eta-C_5H_5)$ (16). This was characterized by comparison with



(16)

literature data[14] and from its ^{13}C n.m.r. spectrum (see Experimental).

The hydride complexes react with $CHCl_3$, $CDCl_3$, $CHBr_3$ and CCl_4, as expected, to give the corresponding halide complexes. Reactions of $HRu(PPh_3)_2(\eta-C_5H_5)$ (3) with HI or HBr gave the iodide and bromide complexes respectively, which were converted back to (3) in refluxing NaOMe/MeOH.

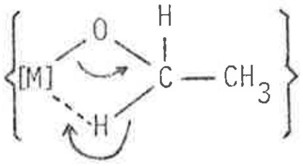
The hydride complex $HRu(PPh_3)_2(\eta-C_5H_5)$ (3) is stable as a dry solid at room temperature, but in solution is quite air sensitive. The complex is stable to heat (200°) and undergoes ligand exchange with dppe under vigorous conditions (200°) to give $HRu(dppe)(\eta-C_5H_5)$ (5).

Ligand exchange reactions of $RuCl(PPh_3)_2(\eta-C_5H_5)$ with $P(OPh)_3$ and $OsBr(PPh_3)_2(\eta-C_5H_5)$ with sp gave $RuCl[P(OPh)_3](PPh_3)(\eta-C_5H_5)$ (1) and $OsBr(sp)(\eta-C_5H_5)$ (17) respectively. These complexes were identified from spectral and microanalytical data (see Experimental). Complex (1) had a small peak at *m/e* 822 in its mass spectrum, presumably formed by disproportionation of (1) to give $\{RuCl[P(OPh)_3]_2(\eta-C_5H_5)\}^+$ in the mass spectrometer. Complex (17) was formed as a mixture of two isomers which were separated by chromatography. In the ^1H n.m.r. spectra the protons of the olefinic groups of both isomers appear at much higher field than the free ligand (Table 2), thus indicating that the group is π-bonded to the metal.*

5.3 *DISCUSSION*

A variety of cyclopentadienyl-iron, -ruthenium and -osmium halide complexes have been converted to the corresponding hydride complexes [(3) - (8)] by refluxing in methanol or ethanol in the presence of base. These conversions are believed to proceed *via* a hydride transfer mechanism, which is common for iridium and platinum complexes[15]:

e.g. $[M]—Cl + CH_3CH_2OH + OH^- \longrightarrow$



$\longrightarrow [M]—H + CH_3CHO.$

An independent report describing the reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with $MeO^-/MeOH$ appeared[16] after this work had been completed.

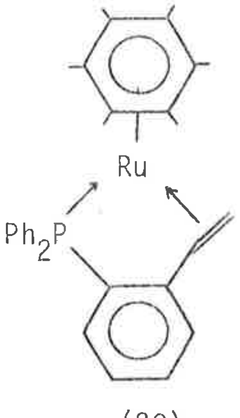
Halogenation of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (3) with CHX_3 (X=Cl, Br) or HX (X = Br,I) gave the halide complexes $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$. Reactions of these halide complexes with NaOMe/MeOH also gave (3) under similar conditions to the chloride.

In the reaction of $RuCl(sp)(\eta\text{-}C_5H_5)$ (2) with NaOMe/MeOH it was thought that MeO^- or H^- might interact with the olefinic group. Instead, however, the hydride complex $HRu(sp)(\eta\text{-}C_5H_5)$ (6) formed, which reverted to the chloride complex (2) on treatment with $CDCl_3$.

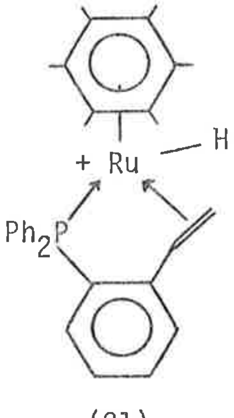
Reactions of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$[8] and $HRu(dppe)(\eta\text{-}C_5H_5)$ with CS_2 gave thioformate complexes (18) and (15) respectively. Sulphur-bonded thioformate complexes, formed in reactions of hydride complexes with CS_2, have been reported for manganese, rhenium,[3] platinum[17] and iron[18] complexes.

*(see Appendix)

While RuCl(sp)(η-C_5H_5) (2) was present as only one isomer, HRu(sp)(η-C_5H_5) (6) and OsBr(sp)(η-C_5H_5) (17) have two distinct isomeric forms according to their n.m.r. spectra. Isomerism involving the sp ligand has been noted previously for $RuCl_2(sp)_2$(19)[10] and other complexes.[19] The bromide form of (19) is present as only one isomer and indicates how small changes can influence the orientation of the olefinic group quite markedly. Structural studies of the two isomers of (17) are in progress and should reveal information about the orientation of the sp ligand.* A reaction of Ru(sp)(η^6-C_6Me_6) (10) with H^+ gave the hydrido cation (21) and another minor product.[20] The identity of the second product



(20)



(21)

is not known, but may be similar to the minor isomer of HRu(sp)(η-C_5H_5) (6).

A reaction of $RuCl[P(OPh)_3]_2(\eta\text{-}C_5H_5)$ with NaOMe/MeOH gave $\overline{Ru[(C_6H_4O)P}(OPh)_2][P(OPh)_3](\eta\text{-}C_5H_5)$ (15), while a reaction of $RuCl[P(OPh)_3]$-$(PPh_3)(\eta\text{-}C_5H_5)$ (1) under the same conditions gave $HRu[P(OPh)_3](PPh_3)(\eta\text{-}C_5H_5)$ (4). It is not understood why an *ortho*-metallated product is not formed in the reaction of (1). The mass spectra of complexes (1) and (4) both have a peak at *m/e* 738, assigned to an *ortho*-metallated ion (22). A peak

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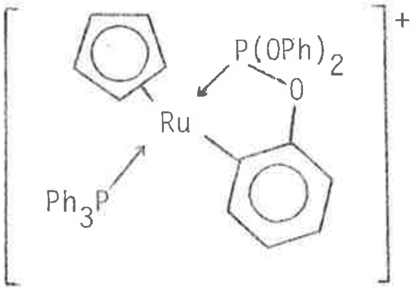
*(see Appendix)



(22)

at $(M-2H)^+$ was not observed in the spectrum of $HRu(PPh_3)_2(\eta-C_5H_5)$ (3), suggesting that *ortho*-metallation does not take place as readily with the PPh_3 ligand. *Ortho*-metallation of $RuCl[P(OPh)_3]_2(\eta-C_5H_5)$ has been observed previously in its mass spectrum and in a reaction with $NEtCy_2$.[14]

A comparison of ν(MH) and δ(MH) values for $HML_2(\eta-C_5H_5)$ systems (Table 1) shows an expected[21] increase in stretching frequency with metal atomic weight (Figure 2). No other trends are apparent at this stage.

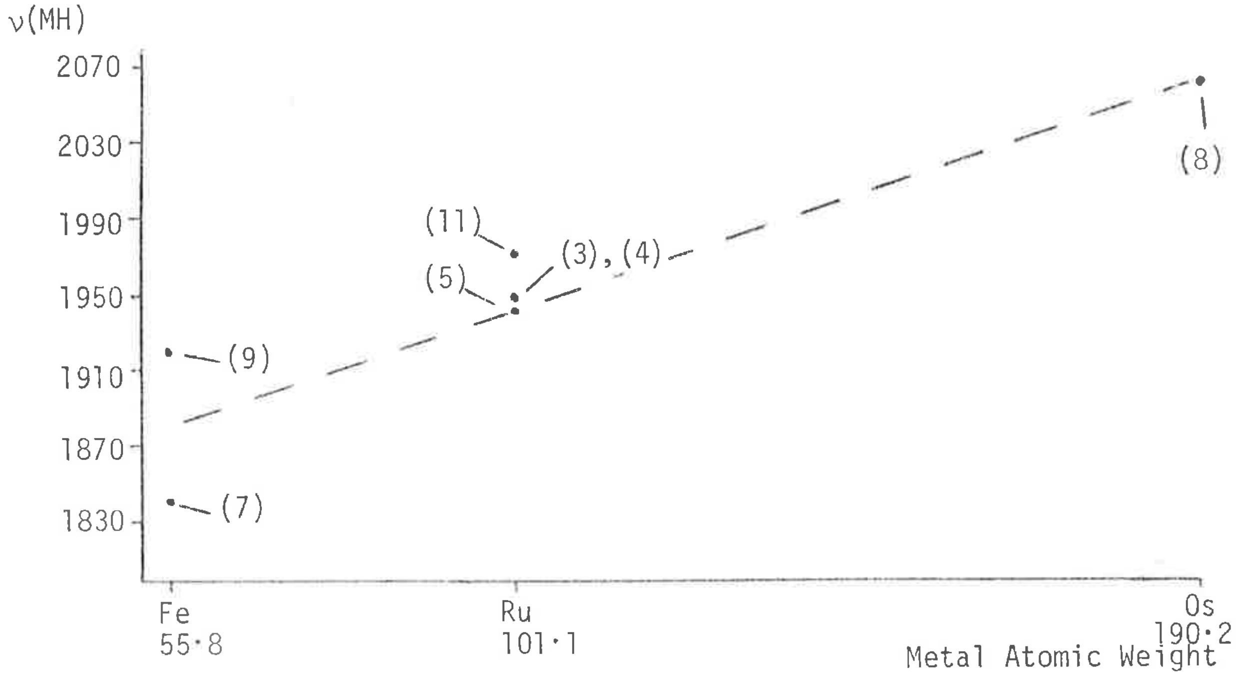


Figure 2 The variation in ν(M-H) absorptions as the metal is changed.

Ligand exchange of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (3) with CO[22] and dppe to give $HRu(CO)(PPh_3)(\eta\text{-}C_5H_5)$ and $HRu(dppe)(\eta\text{-}C_5H_5)$ respectively required vigorous conditions (140° and 200° respectively). In contrast much milder conditions were used in the preparation of $RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (40°)[8] and $RuCl(dppe)(\eta\text{-}C_5H_5)$ (80°).[23] The chloride complex, $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, is known to lose PPh_3 readily, and this is attributed to the strong steric interaction between the PPh_3 groups.[24] Replacement of Cl with H is expected to lessen this interaction and would explain the increased resistance of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ to ligand exchange.

A reaction of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ with CO_2 (140°, 30 atm) gave only starting material, while a reaction of $H(N_2)Co(PPh_3)_3$ with CO_2 gave a formate complex, $Co(OOCH)(PPh_3)_3$, under mild conditions.[25]

5.4 EXPERIMENTAL

Literature methods were used in the preparations of $RuCl[P(OPh)_3]_2(\eta\text{-}C_5H_5)$[14], $RuCl(dppe)(\eta\text{-}C_5H_5)$[23] and $FeCl(dppe)(\eta\text{-}C_5H_5)$.[9] The sp ligand was kindly donated by Dr. M.A. Bennett (Australian National University).

Preparation of Starting Materials

(A) $RuCl[P(OPh)_3](PPh_3)(\eta\text{-}C_5H_5)$ (1) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (304 mg, 0·42 mmol) and $P(OPh)_3$ (154 mg, 0·50 mmol) was refluxed in decalin (7 ml) for 2 min. Upon cooling orange *crystals* were collected and recrystallized from CH_2Cl_2/light petroleum yielding $RuCl[P(OPh)_3](PPh_3)(\eta\text{-}C_5H_5).0{\cdot}4CH_2Cl_2$ (250 mg, 73%) m.p. 174 - 178° (Found: C, 62·2; H, 4·5%. $C_{41}H_{35}ClO_3P_2Ru.0{\cdot}4CH_2Cl_2$ requires C, 61 5; H, 4·5%). Infrared (Nujol) ν(PO) 1209s, 1187vs, 1156s cm^{-1}; other bands at 1584s, 1476s, 1426m, 1303vw, 1281vw, 1081m, 1065w, 1043vw, 1019vw, 1014w, 993w, 986w, 904s, 896s, 879vs, 822m, 796m, 766s, 756s, 746m, 741w, 731m, 723w, 715m, 700w, 690m, 681s, 674vw, 608m, 606sh, 589w, 584sh cm^{-1}. ^1H n.m.r.:

δ($CDCl_3$) 4·22, d, *J*(PH) 1·0 Hz, 5H, C_5H_5; 5·25, s, 0·8H, CH_2Cl_2; 6·78 - 7·92, m, 30H, PPh. ^{13}C n.m.r.: δ($CDCl_3$) 53·5, s, CH_2Cl_2; 82·3, d, *J*(CP) 4 Hz, C_5H_5; 121·8 - 138·5, m, PPh; 152·3, d, *J*(CP) 12 Hz, POC.

(B) RuCl(sp)(η-C_5H_5) (2) (with R.C. Wallis) A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (726 mg, 1·0 mmol) and sp (288 mg, 1·0 mmol) in petroleum spirit (100 - 120° boiling fraction, 45 ml) was heated under reflux for 2 h. Filtration of the warm reaction mixture and cooling afforded a yellow-orange *powder* which was recrystallized (diethyl ether) to give yellow/orange *crystals* of RuCl(sp)(η-C_5H_5) (2) (455 mg, 93%) m.p. 252 - 255° (Found: C, 61·2, H, 4·5%; *M*(mass spectrometry) 490. $C_{25}H_{22}$-ClPRu requires C, 61·3, H, 4·5%; *M*, 490). Infrared: (Nujol) 1313w, 1269sh, 1259w, 1237w, 1226w, 1210vw, 1190w, 1177w, 1160m, 1130vw, 1102sh, 1099s, 1092m, 1088sh, 1071m, 1027w, 1008vw, 997m, 990w, 971vw, 960vw, 940vw, 932vw, 847vw, 835sh, 829sh, 822m, 813m, 803vw, 783w, 771s, 758s, 750s, 745sh, 740sh, 728w, 699vs, 687sh. ^1H n.m.r. : δ($CDCl_3$): (see Table 2) 3·04, 1H, H(2); 4·65, s, 5H, C_5H_5 [H(3) resonance under C_5H_5]; 5·40, 1H, H(1) 7·35 - 7·96, m, 14H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 51·1, s, CH_2; 69·8, s, CH; 83·0, s, C_5H_5; 127·9 - 136·2, m, Ph. ^{31}P n.m.r.: δ($CDCl_3$) 71·9, s; relative to PPh_3.

(C) OsBr(sp)(η-C_5H_5) (17) A reaction of $OsBr(PPh_3)_2(\eta-C_5H_5)$ (300 mg, 0·35 mmol) with sp (110 mg, 0·38 mmol) in petroleum spirit (80 - 100° boiling fraction, 50 ml) in an autoclave (60 atm N_2, 200°, 20h) gave an orange product. Elution on a preparative t.l.c. plate (3:2 diethyl ether/light petroleum) gave $OsBr(PPh_3)_2(\eta-C_5H_5)$ (Rf = 0·8, 11 mg, 4%) and OsBr(sp)(η-C_5H_5) (17) as two isomers: (i) (R_f = 0·7) as orange *crystals* from dichloromethane/methanol (97 mg, 45%) m.p. 216 - 218° (Found: C, 48·4; H, 3·6%; *M*(mass spectrometry), 625. $C_{25}H_{22}BrOsP$ requires

C, 48·2; H, 3·6%; *M*, 625). Infrared (Nujol): ν(C=C) 1587w cm^{-1}; other bands at 1714w(br), 1310vw, 1248vw, 1188vw, 1161w, 1156w, 1131vw, 1099m, 1092m, 1080w, 1071vw, 1029vw, 1001vw, 973vw, 967vw, 956vw, 948vw, 922vw, 830vw, 820w, 787vw, 759m, 753m, 748m, 723vw, 701sh, 698s, 686vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) (couplings in Table 2) 3·15, 1H, H(2); 4·17, 1H, H(3); 4·88, s, 5H, C_5H_5; 5·31, 1H, H(1); 7·4, m, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 32·1, s, CH_2; 51·6, s, CH; 83·1, s, C_5H_5; 126·6 - 134·9, m, Ph.

(ii) (R_f = 0·6) as orange *crystals* from dichloromethane/methanol (10 mg, 5%) m.p. 224 - 235^0 (Found: C, 49·9; H, 3·7%; *M*(mass spectrometry), 625. $C_{25}H_{22}BrOsP$ requires C, 48·2; H, 3·6%; *M*, 625). Infrared (Nujol): ν(C=C) 1587w cm^{-1}; other bands at 1438s, 1310w, 1248w, 1206vw, 1186vw, 1154m, 1143w, 1100w, 1092m, 1080m, 1028w, 1001w, 965vw, 955vw, 925w, 829w, 818w, 770m, 754m, 746w, 703s, 697s cm^{-1}; ^{1}H n.m.r.: δ($CDCl_3$) (couplings in Table 2) 2·92, 1H, H(2); 4·28, 1H, H(3); 4·89, s, 5H, C_5H_5; 5.47, 1H, H(1); 7·4, m, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 34·3, s, CH_2; 52·7, s, CH; 83·1, s, C_5H_5; 126·6 - 134·9, m, Ph.

(D) RuBr(PPh$_3$)$_2$(η-C$_5$H$_5$) A suspension of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0·29 mmol) in methanol (20 ml) was reacted with HBr (0·5 ml, 48% solution, excess). After 2 h the product was collected as an orange *powder* (166 mg, 75%), [recrystallization from CH_2Cl_2/MeOH gave $RuBr(PPh_3)_2(\eta\text{-}C_5H_5) . CH_2Cl_2$] m.p. 155 - 165° (Found: C, 58·5; H, 4·3; *M*(mass spectrometry), 771. $C_{41}H_{35}BrP_2Ru.CH_2Cl_2$ requires: C, 59·0; H, 4·4%; *M*, 771). Infrared: (Nujol) 1585w, 1570vw, 1433s, 1311w, 1197vw, 1188w, 1159vw, 1101vw, 1089s, 1059vw, 1026w, 1006w, 998m, 845w, 830m, 798m, 750m, 745m, 739s, 699vs, 688sh, 618vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 4·12, s, 5H, C_5H_5; 5·29, s, 2H, CH_2Cl_2; 7·12 - 7·40, m, 30H, PPh. ^{13}C n.m.r.: δ($CDCl_3$) 81·7, s, C_5H_5; 127·7 - 139·8, m, PPh.

Preparation of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ *(3)*

(A) With NaOMe/MeOH (Method A) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1·0 g, 1·4 mmol) and sodium metal (*c.* 200 mg, 0·009 g atom) was refluxed in methanol (50 ml) until all the starting material had disappeared (*c.* 1 h). A yellow *powder* precipitated from solution and was identified as $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (3), (900 mg, 94%); [*M*(mass spectrometry), 692; Calculated for $C_{41}H_{36}P_2Ru$: *M*, 692]. Infrared (Nujol): ν(RuH) 1970 cm^{-1}. ^{1}H n.m.r.: δ(C_6D_6) -11·13, t, *J*(PH) 33·7 Hz, 1H, RuH; 4·49, s, 5H, C_5H_5; 7·0, 7·5, m, 30H, PPh. ^{13}C n.m.r.: δ(C_6D_6) 82·0, t, *J*(CP) 2 Hz, C_5H_5; 127·3 - 141·7, m, Ph.

(B) With NaOEt/EtOH Using the above procedure with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (440 mg, 0·61 mmol), sodium metal (*c.* 40 mg, 0·002 g atom) and ethanol (25 ml) the hydride complex was collected (300 mg, 72%) and identified by comparing the infrared spectrum with that of an authentic sample.

(C) With NEt_3*/MeOH* A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1·04 g, 1·4 mmol) in NEt_3 (6 ml, 43 mmol) and methanol (50 ml) was refluxed for 4 h yielding $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (750 mg, 76%). This was identified by infrared and n.m.r. data.

(D) From $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ *(X = Br, I).* Using *Method A* $RuBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0·13 mmol) or $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ (150 mg, 0·18 mmol) was reacted with sodium metal (*c.* 40 mg, 0·002 g atom) in methanol (25 ml) to afford the hydride complex (57 mg, 64% and 92 mg, 72% respectively). This was identified by melting point and infrared data.

Preparation of Other Hydride Complexes

(A) $HRu[P(OPh)_3](PPh_3)(\eta-C_5H_5)$ (4) Using *Method A*, (4) was obtained (290 mg, 88%) from $RuCl[P(OPh)_3](PPh_3)(\eta-C_5H_5)$ (2) (345 mg, 0·45 mmol), sodium metal (*c.* 40 mg, 0·002 g atom) and methanol (30 ml), m.p. 70° (dec.) (Found: C, 66·4; H, 4·9%; *M*(mass spectrometry), 740. $C_{41}H_{36}O_3P_2Ru$ requires C, 66·6; H, 4·9%; *M*, 740). Infrared: (CS_2) ν(RuH) 1957m; ν(PO) (Nujol) 1220m, 1197vs, 1184vs, 1159sh, 1154m, cm^{-1}; other bands at 1626vw, 1586s, 1428s, 1301vw, 1280vw, 1095vw, 1083m, 1061w, 1016m, 997w, 899vs, 875s, 859vs, 817vw, 807vw, 791m, 765vs, 737w, 715s, 682vs, 657vw, 611m, 607m, 588w cm^{-1}. ^1H n.m.r.: $\delta(C_6D_6)$ -11·80, dd, *J*(PH) 32·5 Hz, *J*(PH) 38·2 Hz, 1H, RuH; 4·33, s, 5H, C_5H_5; 6·97 - 7·92, m, 30H, Ph. ^{13}C n.m.r.: $\delta(C_6D_6)$ 82·5, s, C_5H_5; 122·3 - 134·7, m, Ph; 153·8, d, *J*(CP) 7 Hz, POC.

(B) $HRu(dppe)(\eta-C_5H_5)$ (5) Using *Method A*, (5) was obtained (150 mg, 80%) from $RuCl(dppe)(\eta-C_5H_5)$ (200 mg, 0·33 mmol), sodium metal (*c.* 40 mg, 0·002 g atom) and methanol (50 ml), m.p. 170° (dec.) (Found C, 65·8; H, 5·3%; *M*(mass spectrometry), 566. $C_{31}H_{30}P_2Ru$ requires: C, 65·8; H, 5·4%; *M*, 566). Infrared: ν(RuH) (CS_2) 1944; (Nujol) 1911m, 1945m cm^{-1}; other bands at 1578vw, 1563vw, 1428s, 1297w, 1167w, 1146vw, 1109vw, 1089s, 1080s, 1057w, 1015w, 987w, 979vw, 867w, 812vw, 800m, 788m, 778m, 740s, 732sh, 699s, 687s, 674sh, 665m, 644vw cm^{-1}. ^1H n.m.r.: $\delta(C_6D_6)$ -13·26, t, *J*(PH) 34·2 Hz, 1H, RuH; 2·0, m, 4H, CH_2; 4·76, s, 5H, C_5H_5; 7·2, 7·6, 8·0, m, 20H, PPh. ^{13}C n.m.r.: $\delta(C_6D_6)$ 31·9, d, *J*(CP) 24 Hz, CH_2; 80·2, s, C_5H_5; 125·4 - 145·8, m, Ph.

(C) $HRu(sp)(\eta-C_5H_5)$ (6) Using *Method A*, $RuCl(sp)(\eta-C_5H_5)$ (300 mg, 0·61 mmol) was converted to (6) (242 mg, 87%) after reacting with sodium metal (*c.* 40 mg, 0·002 g atom) in methanol (30 ml) for 1 h, m.p. >140° (dec.)

(Found C, 65·2; H, 5·2%; *M*(mass spectrometry), 456. $C_{25}H_{23}PRu$ requires: C, 65·9; H, 5.1%; *M*, 456). Infrared (Nujol): ν(RuH) 1958m cm^{-1}; other bands at 1582w, 1577sh, 1179vw, 1169w, 1155vw, 1102vw, 1093m, 1068w, 1023vw, 1010vw, 992vw, 888vw, 827vw, 801w, 795sh, 780vw, 760w, 753m, 743m, 720vw, 701s, 695s, 682vw cm^{-1}. ^1H n.m.r.: δ(C_6D_6) -9·60, dd, *J*(PH) 31 Hz, *J*[H(3)H] 2 Hz, RuH; -8·56, dd, *J*(PH) 32 Hz, *J*[H(3)H] 2 Hz, RuH* (*denotes the minor isomer) see Table 2 and Figure 1 for the olefinic region; 4·36, m, 4·57, s, 4·69, s, 4·79, s, 6H, C_5H_5 + CH; 7·0 - 8·2, m, 14H, Ph; (further assignment cannot be made at this stage; Ru* is the minor isomer). ^{13}C n.m.r.: δ(C_6D_6) 26·2, s, CH_2; 34·9, d, *J*(CP) 5 Hz, CH_2*; 49·0, d, *J*(CP) 5 Hz, CH*; 51·1, s, CH; 82·3, s, C_5H_5*; 83·2, s, unassigned; 84·1, s, C_5H_5; 124·3 - 136·3, m, Ph. ^{31}P n.m.r.: δ(C_6D_6) 76·7, s, RuP; 88·2, s, RuP*; relative to PPh_3.

(D) HFe(dppe)(η-C_5H_5) (7) Complex (7) was prepared by refluxing FeCl(dppe)(η-C_5H_5) (40 mg, 0·07 mmol) with sodium metal (*c.* 40 mg 0·002 g atom) in methanol (15 ml). After 0·5 h the black suspension had given way to a pale yellow solution, which on cooling yielded FeH(dppe)(η-C_5H_5) as a yellow/white *powder* (30 mg, 80%), m.p. 138 - 150° (lit.[9] 146 - 156°). Further spectral data is in Table 1.

(E) HOs(PPh_3)$_2$(η-C_5H_5) (8) Complex (8) was prepared by *Method A* from OsBr(PPh_3)$_2$(η-C_5H_5) (310 mg, 0·36 mmol), sodium metal (*c.* 40 mg, 0·002 g atom) and methanol (40 ml) as pale yellow *microcrystals* (240 mg, 85%), m.p. 164° (dec.) (Found C, 63·1; H, 4·5; *M*(mass spectrometry), 782. $C_{41}H_{36}P_2Os$ requires: C, 63·1; H, 4·7%; *M*, 782). Infrared: (CS_2) ν(OsH) 2060m cm^{-1}; other bands at (Nujol) 1577vw, 1563vw, 1296w, 1168m, 1136vw, 1090vw, 1077s, 1074s, 1058m, 1016w, 993w, 827w, 806w, 740m, 736s, 728s, 725sh, 697sh, 690vs, 681s, 673sh, 656vw, 630vw cm^{-1}. ^1H n.m.r.: δ(C_6D_6) -13·98,

t, *J*(PH) 28·3 Hz, 1H, OsH; 4·41, s, 5H, C_5H_5; 6·90 - 7·56, m, 30H, PPh. ^{13}C n.m.r.: δ(C_6D_6) 77·2, s, C_5H_5; 125·0 - 143·1, m, PPh.

Reaction of RuCl[P(OPh)$_3$]$_2$(η-C$_5$H$_5$) with NaOMe/MeOH

A solution of RuCl[P(OPh)$_3$]$_2$(η-C_5H_5) (37 mg, 0·05 mmol) was heated at reflux point for 4 h in a sodium methoxide solution (sodium metal, *c*. 40 mg, 0·002 g atom, in methanol, 15 ml). Upon cooling $\mathrm{Ru\overline{[(C_6H_4O)P}(OPh)_2]}$-[P(OPh)$_3$](η-$C_5H_5$) (15) (27 mg, 76%) was isolated and identified from its melting point (110 - 120°, lit.[14] 116 - 118°) and by comparing its ^{1}H n.m.r. spectrum with that of an authentic sample (4·28, s, 5H, C_5H_5; 7·2, m, 30H, Ph). ^{13}C n.m.r.: δ($CDCl_3$) 84·2, t, *J*(CP) 3 Hz, C_5H_5; 110·8, d, *J*(CP) 16·5 Hz, RuC; 120·4 - 129·9, m, Ph; 152·3, d, *J*(CP) 7·5 Hz, POC.

Reactions of CS$_2$

(A) With HRu(dppe)(η-C$_5$H$_5$) (5) A stirred solution of HRu(dppe)-(η-C_5H_5) (130 mg, 0·23 mmol) in CS_2 (15 ml) yielded orange *crystals* after standing for 2 d (the reaction is 80% complete after 3 h by n.m.r.). The product was recrystallized from dichloromethane/hexane giving Ru(SCHS)-(dppe)(η-C_5H_5).0·25CH_2Cl_2 (15) (120 mg, 79%), m.p. 214 - 216° (Found: C, 58·8; H, 4.6%; *M*(mass spectrometry), 642. $C_{32}H_{30}P_2S_2Ru$.0·25CH_2Cl_2 requires: C, 58·6; H, 4.6%; *M*, 642). Infrared: (Nujol) ν(CS) 976vs cm^{-1}; other bands at 1427m, 1221s, 1168w, 1144w, 1083s, 1057w, 1014w, 864m, 833vw, 821vw, 811w, 796m, 784vw, 776vw, 742s, 726w, 686vs, 669m, 643vw cm^{-1}. ^{1}H n.m.r.: δ($CDCl_3$) 2·4, m, 4H, CH_2; 4·82, s, 5H, C_5H_5; 5·29, s, 0·5H, CH_2Cl_2; 7·4, m, 30H, Ph; 10·74, s, 1H, CHS. ^{13}C n.m.r.: δ($CDCl_3$) 27·2, t, *J*(CP) 23 Hz, CH_2; 82·1, s, C_5H_5; 127·1 - 133·9, m, Ph; 176·5, s, CHS.

(B) With HRu(sp)(η-C_5H_5) (6) A reaction of (6) (70 mg, 0·15 mmol) with CS_2 (20 ml) over 2 d gave a dark red solution. After loading onto a preparative t.l.c. plate two isomers of $Ru(CS_2)[CH(CH_3)C_6H_4PPh_2](\eta\text{-}C_5H_5)$ (13) were isolated (2:3 diethyl ether/cyclohexane): (i) (Rf ≃ 0·7) as a dark red *powder* (42 mg, 51%) from dichloromethane/hexane, m.p. 202 - 204° (Found: C, 58·5; H, 4.4%; *M*(mass spectrometry), 532. $C_{26}H_{23}PRuS_2$ requires C, 58·7; H, 4.4%; *M*, 532). Infrared (Nujol): $\nu(CS_2)$ 1096sh, 1091m, 917s, 754sh, 751m cm^{-1}; other bands at 1312w, 1278vw, 1262vw, 1197vw, 1186vw, 1179w, 1106vw, 1070vw, 1057vw, 1026sh, 1022w, 1009w, 1000vw, 986w, 978w, 957vw, 850w, 831w, 824vw, 809m, 793vw, 764w, 740w, 700s, 683vw, 642vw cm^{-1}. ^1H n.m.r. $\delta(CDCl_3)$ 1·90, d, *J*(HH) 6·5 Hz, 3H, CH_3; 3·28, q, *J*(HH) 6·5 Hz, 1H, CH; 4·87, s, 5H, C_5H_5; 7·0 - 7·4, m, 14H, Ph. ^{13}C n.m.r.: $\delta(CDCl_3)$ 27·4, s, CH_3; 51·3, d, *J* = 11 Hz, CH; 84·3, s, C_5H_5; 123·2 - 138·4, m, Ph; 145·9, d, *J*(CP) = 15Hz, 150·6, d, *J*(CP) = 6 Hz, unassigned. (ii) (Rf ≃ 0.8) as a red powder (2 mg, 2%) from dichloromethane/hexane [*M* (mass spectrometry), 532. $C_{26}H_{23}PRuS_2$ requires *M*, 532]. (Not enough product was available for further identification.)

Reaction of HRu(PPh$_3$*)*$_2$*(*η*-C*$_5$*H*$_5$*) with CO*$_2$

A solution of $HRu(PPh_3)_2(\eta\text{-}C_5H_5)$ (300 mg, 0·43 mmol) in petroleum spirit (50 ml, 80 - 100° boiling range) was heated with CO_2 in an autoclave (30 atm CO_2, 140°, 17 h). On cooling yellow *crystals* were collected and identified as starting material (230 mg, 77%) by infrared spectroscopy.

Reaction of HRu(sp)(η*-C*$_5$*H*$_5$*) (6) with CDCl*$_3$

A solution of (6) in C_6D_6 within an n.m.r. tube was reacted with $CDCl_3$ at room temperature. The spectrum of (6) disappeared over 1 h with concomitant formation of peaks due to $RuCl(sp)(\eta\text{-}C_5H_5)$ (2). This crystallized from solution and was identified by its melting point (252 - 255°) and n.m.r. spectrum.

Ligand exchange of $HRu(PPh_3)_2(\eta-C_5H_5)$ (3) with dppe.

After heating a mixture of $HRu(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0·29 mmol) and dppe (130 mg, 0·33 mmol) in petroleum spirit (80 - 100° fraction, 50 ml) in a nitrogen filled autoclave (50 atm, 200°) for 17 h, a yellow solution was obtained. This was filtered and the volume reduced to give yellow *crystals* of $HRu(dppe)(\eta-C_5H_5)$ (5), (130 mg, 79%). The product was identified by comparing its infrared and n.m.r. spectra with those of an authentic sample.

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CHAPTER SIX

THE N.M.R. AND MASS SPECTRAL DATA OF SOME CYCLOPENTADIENYL METAL COMPLEXES

6.1 INTRODUCTION

The preparation of a large number of cyclopentadienyl-ruthenium complexes have now been reported in the literature.[1] The ^{13}C-n.m.r. spectra of many of these complexes, together with those of some related complexes of other metals, have been recorded by Dr. R.C. Wallis and myself. Relevant data has been summarised in tables for the purpose of trying to understand any systematic trends which may exist, particularly in the position of the cyclopentadienyl resonances, as the metal, ligand or β-substituent is changed. It is hoped that a better understanding of the electronic properties of the complexes will be gained and lead to some predictability about their chemistry. A review of ^{13}C n.m.r. data for organometallic complexes has recently appeared.[2]

The mass spectra of the neutral complexes described in this thesis have displayed some systematic trends and are discussed briefly.

6.2 N.M.R. DATA

The n.m.r. spectra were routinely recorded using Fourier transform techniques. Approximately 0·1 molar solutions gave satisfactory ^{13}C n.m.r. spectra in overnight runs using 10 mm tubes. If non-protonated carbon centres were present (e.g. CO, CN, C≡C etc.) a 15 - 25° pulse angle gave best results, combined with the use of a delay (*c.* 5 sec.) between pulses. These techniques allow sufficient relaxation for good spectra after about 10,000 pulses and do not require relaxation reagents.

Except where indicated the spectra were recorded in $CDCl_3$ and are measured relative to tetramethylsilane in p.p.m. Broad band proton decoupling was used routinely except where off-resonance experiments were required for assignment purposes.

While the spectrometer can reliably measure chemical shifts to within ±0·2 p.p.m., factors such as solvent and concentration also have an effect on the measurement. A systematic study of these factors has not been made at this stage. When comparing two compounds in the same solvent at about the same concentration, a difference in the carbon chemical shift of a particular group (e.g. CO, C_5H_5) of less than one p.p.m. is not considered to be a significant change. It has been most helpful to gather as many similar compounds as possible together and change one substituent systematically. Tables 1 - 8 summarise this data.

6.2.1 The Effect of Changing the Halide Substituent

The data in Table 1 indicates that changing from Cl to Br has little effect on the C_5H_5 or CO resonances. The iodide substituent shifts the proton resonances of C_5H_5 downfield and the carbon resonances upfield, while it has no impact on the carbonyl resonances of $FeX(CO)_2(\eta\text{-}C_5H_5)$ complexes. The fluoride group on $RuF(PPh_3)_2(\eta\text{-}C_5H_5)$ shifts the proton C_5H_5 resonance considerably downfield from the other halide complexes.

It was expected that an increase in the electronegativity of the halide would deplete the electron density on the cyclopentadienyl group thus shifting the resonances to lower field. This trend is observed only for the cyclopentadienyl carbons as I → Br and for the cyclopentadienyl protons as Cl → F. Other factors appear to be operating which over-ride this trend in other cases; these are not understood at this stage.

Table 1 Some halide complexes and their cyclopentadienyl and carbonyl resonances

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	$\underline{C}O$	ref.
$FeCl(CO)_2(\eta\text{-}C_5H_5)$	4·98	85·9	213·3	3
$FeBr(CO)_2(\eta\text{-}C_5H_5)$	5·05	85·9	213·5	3
$FeI(CO)_2(\eta\text{-}C_5H_5)$	5·07	84·7	213·6	3
$RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·89	86·0	203·8	4[A]
$RuBr(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·88	86·2	203·5	B
$RuF(PPh_3)_2(\eta\text{-}C_5H_5)$	4·56	-	-	5
$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$	4·10	81·5	-	6[A]
$RuBr(PPh_3)_2(\eta\text{-}C_5H_5)$	4·12	81·7	-	B
$RuI(PPh_3)_2(\eta\text{-}C_5H_5)$	4·18	78·3	-	B
$OsCl(PPh_3)_2(\eta\text{-}C_5H_5)$	4·31	78·0	-	7
$OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$	4·31	78·3	-	8[A]

A, source of preparation only; B, this thesis.

6.2.2 *The Effect of Changing the Metal*

From the data in Table 2 it is evident that the ^{13}C chemical shift of the C_5H_5 group increases as the metal is changed from iron to ruthenium, and decreases to a larger extent in changing from ruthenium to osmium. This trend (i.e. $Fe < Ru > Os$), while not linear (e.g. $Fe < Ru < Os$), may be correlated with lanthanide contraction from Ru → Os. The proton chemical shifts of the C_5H_5 and methyl groups, however, follow a different trend and, except for the hydride complexes, increase down the group.

The ^{13}C chemical shifts of groups bonded to the metal (e.g. CO, CH_3) move to higher field down the group [the PMe_3 complexes have different halide groups (Cl and Br), but the data in Table 1 suggests that this will have little effect on the chemical shift]. This trend, which is quite consistent and large (10 - 37 p.p.m.), is inexplicably different from that observed for the cyclopentadienyl carbon resonances.

6.2.3 *The Variation in Cyclopentadienyl Chemical Shift as the Ligands are Varied*

In general the data in Tables 3 and 4 indicates that the cyclopentadienyl carbons move to lower field as the ligands become less basic. For $RuCl(L)(PPh_3)(\eta\text{-}C_5H_5)$ the trend is $PMe_3 < CNBu^t < PPh_3 \sim P(OMe)_3 < P(OP)_3 < CO$, while for $RuCl(L)_2(\eta\text{-}C_5H_5)$ the resonances increase in the order dpae $< (PMe_3)_2$ $<$ dppe $< (PMePh_2)_2 < (PPh_3)_2 \sim (AsPh_3)_2 \sim [P(OMe)_3]_2 < [P(OPh)_3]_2 < (CNBu^t)_2$. The order of basicity observed by Tolman[19] [i.e. $PMe_3 > PMePh_2 > AsPh_3 \sim PPh_3$ $CNBu^t > P(OMe)_3 > P(OPh)_3 > CO$] follows the same trend as the data above in most instances and thus the cyclopentadienyl carbon resonances can be used as a general indicator of ligand basicity. A notable exception is $CNBu^t$ which in mono-substituted derivatives lies between PMe_3 and PPh_3, whereas in disubstituted derivatives it is at lower field than found for any other ligands tried. In the bis-substituted

Table 2. A variety of iron-, ruthenium- and osmium-cyclopentadienyl complexes and some of their ^1H and ^{13}C n.m.r. chemical shifts.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	other		ref.
			^1H	^{13}C	
$Fe(\eta-C_5H_5)_2$	4·04^A	67·9	-	-	9
$Ru(\eta-C_5H_5)_2$	4·55	70·1	-	-	10
$Os(\eta-C_5H_5)_2$	4·57^A	63·9^B	-	-	9
$FeMe(CO)_2(\eta-C_5H_5)$	4·70^A	85·3	-0·11(CH_3)	218·4(CO) -23·5(CH_3)	11,12
$RuMe(CO)_2(\eta-C_5H_5)$	5·13^A	87·4	0·29(CH_3)	200·8(CO) -33·2(CH_3)	11,13
$FeMe(CO)(PPh_3)(\eta-C_5H_5)$	4·29	84·2^C	-0·18(CH_3)	222·5(CO) -22·3(CH_3)	14,15
$RuMe(CO)(PPh_3)(\eta-C_5H_5)$	4·80	87·2	0·07(CH_3)	206·6(CO) -29·6(CH_3)	13
$RuBr(PPh_3)_2(\eta-C_5H_5)$	4·12	81·7	-	-	D
$OsBr(PPh_3)_2(\eta-C_5H_5)$	4·31	78·3	-	-	8^E
$RuH(PPh_3)_2(\eta-C_5H_5)$	4·49^B	82·0^B	-	-	D
$OsH(PPh_3)_2(\eta-C_5H_5)$	4·41^B	77·2^B	-	-	D
$RuBr(CO)(PPh_3)(\eta-C_5H_5)$	4·88	86·2	-	203·5(CO)	D
$OsBr(CO)(PPh_3)(\eta-C_5H_5)$	5·00	82·6	-	184·2(CO)	4^E
$RuCl(PMe_3)_2(\eta-C_5H_5)$	4·44	77·3	-	-	16
$OsBr(PMe_3)_2(\eta-C_5H_5)$	4·57	72·3	-	-	17
$Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$	4·32	85·4	-	-	18^E
$Os(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$	4·39	81·5	-	-	18^E
$\{Ru[\overline{C(CH_2)_3O}](PPh_3)_2(\eta-C_5H_5)\}PF_6$	4·82	91·2	-	300·5(α-C)	D
$\{Os[\overline{C(CH_2)_3O}](PPh_3)_2(\eta-C_5H_5)\}PF_6$	4·97	88·4	-	263·4(α-C)	D

A, in CCl_4; B, in C_6D_6; C, solvent not given; D, this thesis;

E, source of preparation only.

Table 3 The cyclopentadienyl chemical shifts of some $RuCl(L)(PPh_3)(\eta\text{-}C_5H_5)$ complexes arranged in ascending order of ^{13}C chemical shift.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	ref.
$RuCl(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$	4·30	79·4	16
$RuCl(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$	4·53	80·9	10
$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$	4·10	81·5	6[A]
$RuCl[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$	4·49	81·6	20
$RuCl[P(OPh)_3](PPh_3)(\eta\text{-}C_5H_5)$	4·22	82·3	B
$RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·89	86·0	4[A]

A, source of preparation only; B, this thesis.

Table 4 The cyclopentadienyl chemical shifts of some $RuCl(L)_2(\eta\text{-}C_5H_5)$ complexes arranged in ascending order of ^{13}C chemical shift.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	ref.
$RuCl(dpae)(\eta\text{-}C_5H_5)$	4·51	73·2	21
$RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$	4·44	77·3	16
$RuCl(dppe)(\eta\text{-}C_5H_5)$	4·69	77·9	8[A]
$RuCl(PMePh_2)_2(\eta\text{-}C_5H_5)$	4·32	80·2	22
$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$	4·10	81·5	6[A]
$RuCl(AsPh_3)_2(\eta\text{-}C_5H_5)$	4·10	81·6	21
$RuCl[P(OMe)_3]_2(\eta\text{-}C_5H_5)$	4·84	81·6	20
$RuCl[P(OPh)_3]_2(\eta\text{-}C_5H_5)$	4·05	82·1	5[A]
$RuCl(CNBu^t)_2(\eta\text{-}C_5H_5)$	4·73	83·9	10

A, source of preparation only.

systems the $AsPh_3$ complex is virtually at the same chemical shift as that for PPh_3 while the other arsine ligand, dpae, is inexplicably at higher field than dppe by 4·7 p.p.m.. More study of these systems is required before these trends can be properly understood.

The proton resonances of the cyclopentadienyl groups in Tables 3 and 4 show no observable trends.

As more PPh_3 ligands are added to $MMe(CO)_2(\eta\text{-}C_5H_5)$ (Table 5) the chemical shifts of the cyclopentadienyl protons and carbons move to higher field. This is expected for carbon resonances from the trend in Tables 3 and 4. The methyl carbons (Table 5), however, move to lower field as more phosphine ligands are added. This was not expected as the presence of a more electron-rich ligand should increase the electron density on the methyl group and move it to higher field. No observable trend was present for the methyl protons.

Table 5 Some iron- and ruthenium-methyl complexes and the effect of changing the ligand on the C_5H_5, CO, and CH_3 resonances.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	$C\underline{H}_3$	$\underline{C}H_3$	CO	ref.
$FeMe(CO)_2(\eta\text{-}C_5H_5)$	$4{\cdot}70^A$	85·3	$-0{\cdot}11^A$	-23·5	218·4	11,12
$FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·29	$84{\cdot}2^B$	-0·18	$-22{\cdot}3^B$	$222{\cdot}5^B$	14,15
$RuMe(CO)_2(\eta\text{-}C_5H_5)$	$5{\cdot}13^A$	87·4	$0{\cdot}29^A$	-33·2	200·8	11,13
$RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·80	87·2	0·07	-29·6	206·6	13
$RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$	$4{\cdot}36^C$	$84{\cdot}8^C$	$0{\cdot}97^C$	$-26{\cdot}5^C$	-	4^D

A, in CCl_4; B, solvent not given; C, in C_6D_6; D, source of preparation only.

6.2.4 *The Variation in the Metal-Bonded Carbon Resonance*

The α-bonded carbon resonances in Table 6 vary dramatically from -26·5 to 359·0 p.p.m.. The methyl group is at significantly higher field than any other (-26·5 p.p.m.). At the opposite extreme the vinylidene complex (8) has an extremely deficient α-carbon with a chemical shift of 359·0 p.p.m. The metal-bonded carbons of the vinyl complexes [(4) and (5)] resonate at 182·2 and 193·1 p.p.m. respectively and the acetylide α-carbon of (2) resonates at 116·1 p.p.m.; these chemical shifts are about 20 - 50 p.p.m. down-field from those of comparable organic systems. The α-bonded carbon resonance shows coupling to ligands and metals possessing a spin, which, with the characteristic chemical shifts observed, gives much valuable information about the nature of the complexes. This data has proved to be very important in the identification of these systems.

Table 6 An arrangement of α-carbon resonances of $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ complex in ascending order of chemical shift

Complex	no.	$C_5\underline{H}_5$	$\underline{C}_5H_5$	α-C	ref.
[Ru]Me^A	(1)	4·36	84·8	-26·5	4^B
[Ru]C≡CPh	(2)	4·32	85·4	116·1	18^B
[Ru][$\overline{CH(CH_2)_3O}$]^A	(3)	4·21	86·7	148·7	C
[Ru]C(E)=CH(E)	(4)	4·15	86·3	182·2	23^B
[Ru]C(OMe)=CHPh^A	(5)	4·52	86·2	193·1	C
{[Ru][$\overline{C(CH_2)_3O}$]}PF_6	(6)	4·82	91·2	300·5	C
{[Ru][C(OMe)CH_2Ph]}PF_6	(7)	4·84	92·0	308·7	C
{[Ru][C=CHPh]}PF_6	(8)	5·27	95·2	359·0	18

[Ru] = $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$; E = CO_2Me; A, in C_6D_6; B, source of preparation only; C, this thesis.

6.2.5 *The Variations in Metal-Acetylide Carbons*

The metal bonded acetylide carbons in Tables 7 and 8 appear between 91·6 and 129·3 p.p.m. while the β-carbons appear between 68·3 and 114·7 p.p.m. In most instances the resonances are at lower field than organic acetylenes (67 - 92 p.p.m.[26]).

As the electronegativity of the β-substituent of $Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ increases the α- and β-carbons and the cyclopentadienyl resonances all increase in chemical shift ($Me<Ph<C_6F_5{\sim}CO_2Me$). When one of the ligands of $Ru(C{\equiv}CPh)(L)(PPh_3)(\eta\text{-}C_5H_5)$ is made less basic ($PPh_3>CNBu^t>CO$) the α-carbons move to higher field (116·1, 112·2, 100·1 respectively). Such a well defined trend is not observed for the β-carbons (114·7, 111·8, 112·8 respectively), or the cyclopentadienyl carbons (85·4, 84·2, 87·3 respectively). While no direct comparisons can be made between iron and ruthenium complexes in Tables 7 and 8, the data indicates that the α-carbons of iron complexes appear at higher field. This is evident for $Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)$ and $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (112·6 and 91·6 respectively). While the ligands differ, the dppe ligand has basic properties similar to two PPh_3 ligands, and for $Ru(C{\equiv}CPh)(L)_2(\eta\text{-}C_5H_5)$ the change from one to the other did not affect the shift of the α-carbon. The α-carbon of $Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$ appears at 116·8 p.p.m. while that of $Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ is at 100·1 p.p.m. If the ruthenium complex had two CO ligands, making the complexes directly comparable, it is expected that the resonance would move to higher field thus widening the gap between the iron and ruthenium α-carbon resonances.

Table 7. Some σ-acetylide complexes and the changes in the α- and β-carbon resonances as the β-substituents are changed.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	α-C	β-C	ref.
$Fe(C{\equiv}CCH)(dppe)(\eta\text{-}C_5H_5)$	4·28	79·7	105·7	68·3	24
$Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)$	4·17	78·8	112·6	97·5	24
$Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$	4·78	82·6	116·1	112·0	18^A
$Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·23	84·5	91·6	105·2	18^A
$Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·32	85·4	116·1	114·7	18^A
$Ru(C{\equiv}CC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·35	86·0	B	B	18^A
$Ru(C{\equiv}CCO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·37	86·1	C	C	18^A

A, source of preparation only; B, under phenyl (127·2 - 140·7 p.p.m.); C, under phenyl (127·2 - 140·4 p.p.m.).

Table 8. Some σ-acetylide complexes and their chemical shifts for a variety of ligands.

Complex	$C_5\underline{H}_5$	$\underline{C}_5H_5$	α-C	β-C	ref.
$Fe(C{\equiv}CPh)(CO)_2(\eta\text{-}C_5H_5)$	4·98	85·4	116·8	88·8	22^A
$Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·32	85·4	116·1	114·7	18^A
$Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$	4·78	82·6	116·1	112·0	18^A
$Ru(C{\equiv}CPh)(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$	4·82	84·2	112·2	111·8	B
$Ru(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)$	4·99	87·3	100·1	112·8	B
$Ru(C{\equiv}CMe)(PMe_3)(PPh_3)(\eta\text{-}C_5H_5)$	4·48	82·2	94·1	101·4	B
$Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$	4·23	84·5	91·6	105·2	18^A

A, source of preparation only; B, this thesis

6.3 MASS SPECTRAL DATA

The cyclopentadienyl metal complexes described in this thesis generally give mass spectra with strong molecular ions (see Experimental in Chapters 1-5) and a variety of daughter ions. Cationic complexes are an exception to this and give unusual spectra which have not been interpreted at this stage.

The complexes generally form ions due to the loss of at least one ligand, and sometimes due to the loss of the substituent group. A characteristic pattern is observed for complexes containing the $Ru(PPh_3)(\eta-C_5H_5)$ moiety. These are summarised in Table 9 and some structures for the ions are suggested. Peaks are also observed for PPh_3^+ and its daughter ions. In complexes containing the $Ru(C\equiv CR)(PPh_3)(\eta-C_5H_5)$ moiety an organic ion is usually found at *m/e* 300 - 400 which can be assigned to $[R-C\equiv C-PPh_3]^+$.

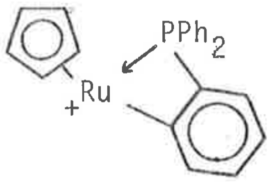
6.4 EXPERIMENTAL

Preparation of $RuBr(CO)(PPh_3)(\eta-C_5H_5)$

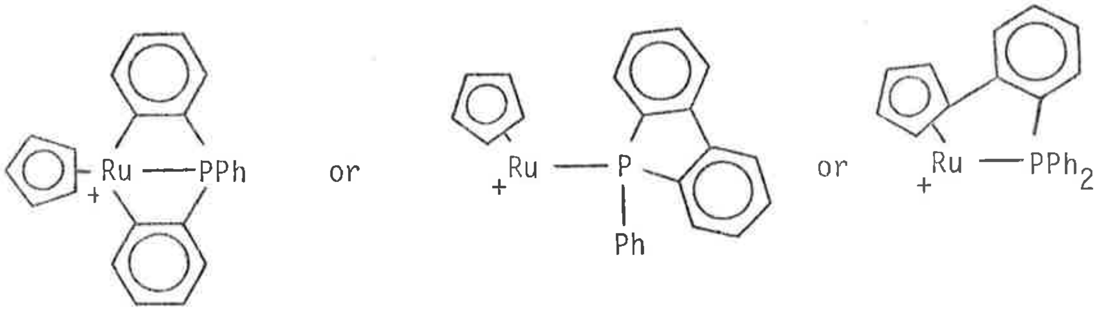
Carbonylation of $RuBr(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0·26 mmol) in benzene (15 ml) in an autoclave (30 atm CO, 110°, 2·5 d) gave $RuBr(CO)(PPh_3)(\eta-C_5H_5)$ as orange *crystals* after evaporation and crystallization from dichloromethane/ethanol (122 mg, 88%) m.p. 231 - 234° (Found: C, 54·0; H, 3·7%; *M*(mass spectrometry), 537. $C_{24}H_{20}BrOPRu$ requires C, 53·7; H, 3·8%; *M*, 537). Infrared (CH_2Cl_2): ν(CO) 1921vs cm^{-1}; other bands at (Nujol) 1434s, 1311vw, 1185w, 1159w, 1097s, 1073vw, 1029w, 1012vw, 1000w, 993vw, 976vw, 837m, 814m, 751s, 708m, 697s, 563w cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 4·88, s, 5H, C_5H_5; 7·4, m, 15H, Ph. ^{13}C n.m.r.: δ($CDCl_3$) 86·2, s, C_5H_5; 128·2 - 136·8, m, Ph; 203·5, d, *J*(CP) 22 Hz, CO.

Table 9 Ions present in the mass spectra of $Ru(PPh_3)(\eta\text{-}C_5H_5)$ complexes.

m/e	Structure	no
429	$Ru(PPh_3)(\eta\text{-}C_5H_5)^+$	(9)
428	$[(9) - H]^+$	(10)
427	$[(9) - 2H]^+$	(11)
362	$[Ru(PPh_3)\text{-}2H]^+$	(12)
352	$Ru(Ph)(\eta\text{-}C_5H_5)$	(13)
350	$[(13) - 2H]^+$	(14)
275	$Ru(PPh)(\eta\text{-}C_5H_5)$	(15)
244	$Ru(Ph)(\eta\text{-}C_5H_5)$	(16)
232	$Ru(\eta\text{-}C_5H_5)_2$	(17)
167	$Ru(\eta\text{-}C_5H_5)$	(18)



(10)



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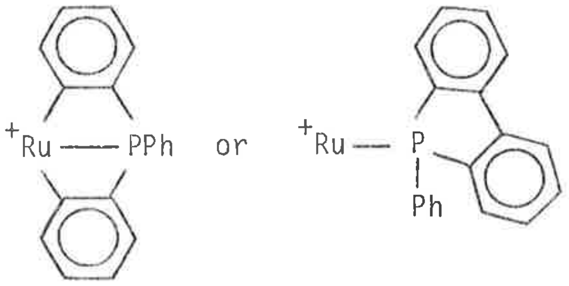

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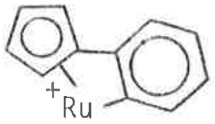

(14)

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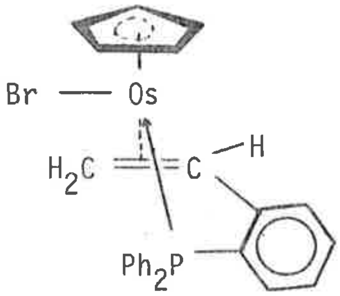
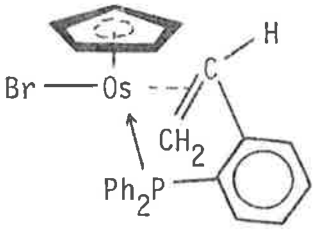
APPENDIX

Recent structural studies have shed new light on the major isomers of OsBr(sp)(η-C_5H_5) (Figure 1) and the product from the reaction of HRu(sp)(η-C_5H_5) with CS_2 (Figure 2). These complexes were discussed in Chapter 5.

The styryl group of the sp ligand in OsBr(sp)(η-C_5H_5) was found to lie almost parallel with the Os-Br bond:



A consideration of models indicated that the other isomer would most likely have the styryl group in a position perpendicular to the Os-Br bond:



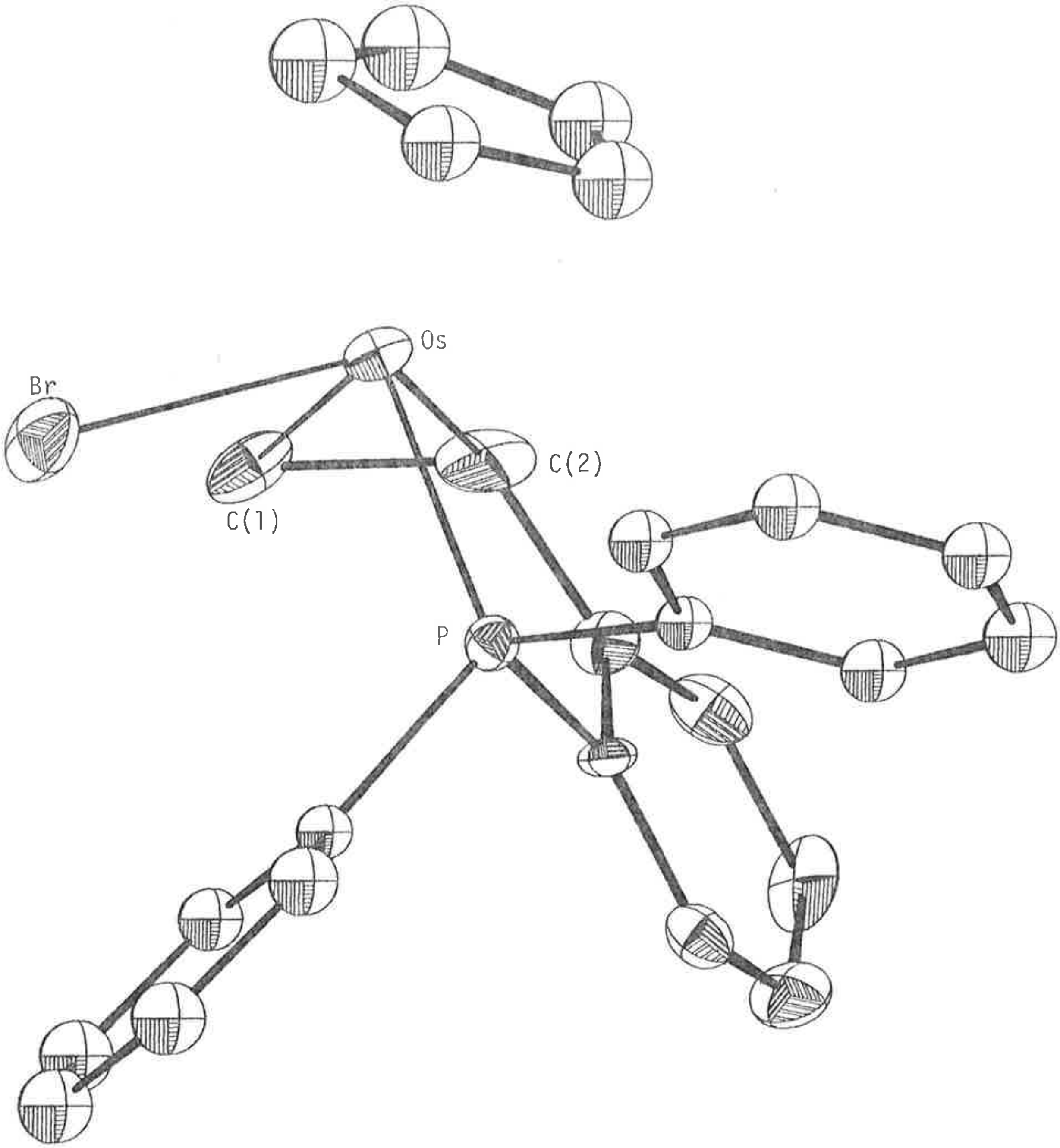


Figure 1. Structure of OsBr(sp)(η-C_5H_5) (by T.W. Hambley and M.R. Snow). Selected bond lengths: Os-C(1), 2·249(14); Os-C(2), 2·182(19); C(1)-C(2), 1·618(26)Å. R = 3·9%.

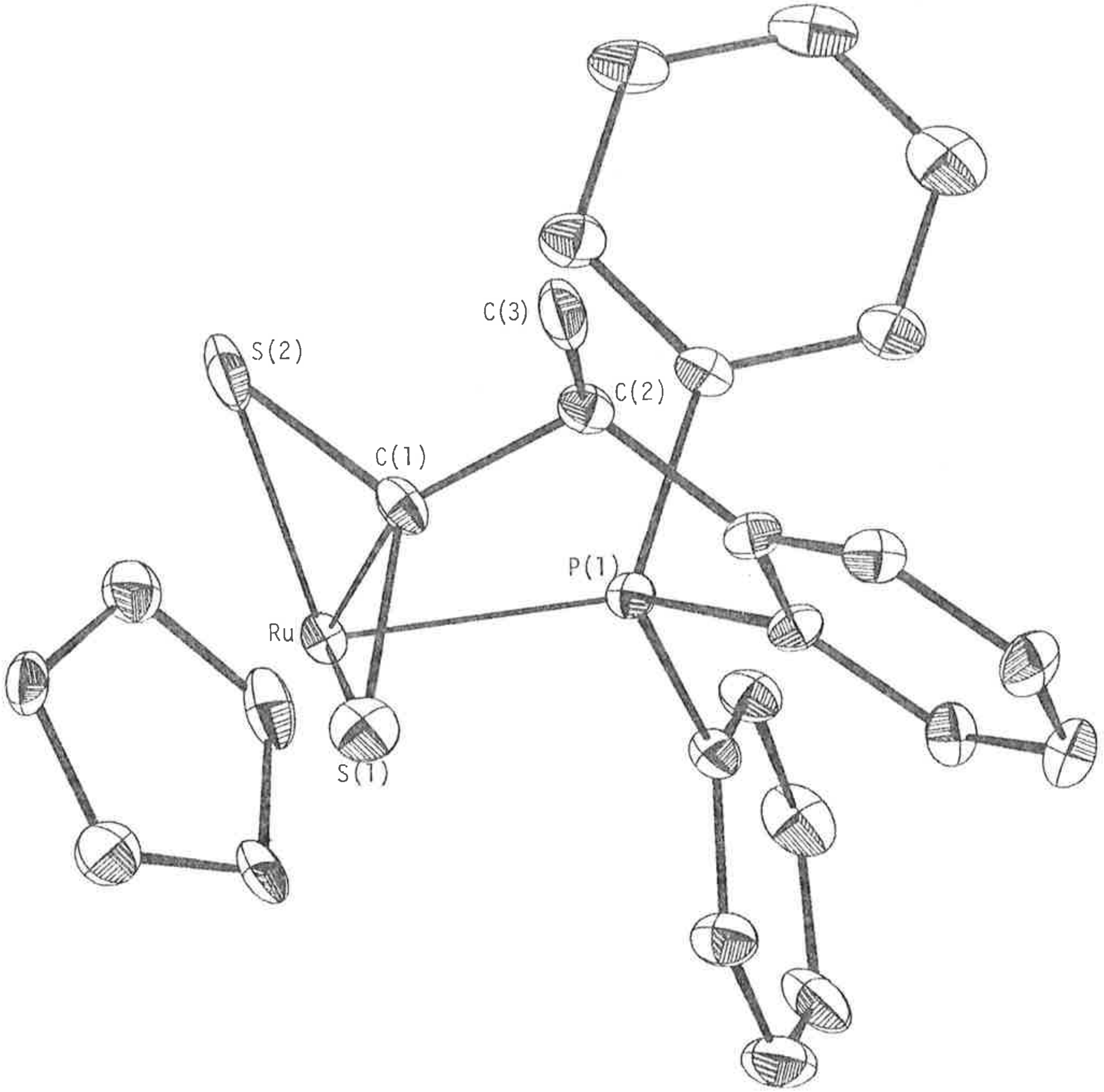
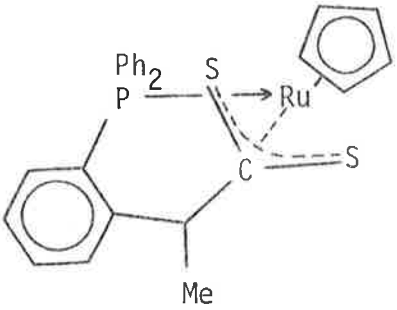
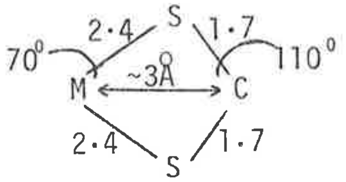


Figure 2. Structure of $Ru(\eta^3\text{-}S_2\overline{C)[P(C_6H_4C}HMe\text{-}\mathit{o})Ph_2](\eta\text{-}C_5H_5)$ (by T.W. Hambley and M.R. Snow). Selected bond lengths: Ru-S(1), 2·426(1); Ru-S(2), 2·418(1); Ru-C(1), 2·175(4); C(1)-S(1), 1·728(4); C(1)-S(2), 1·722(4); C(1)-C(2), 1·537(6); C(2)-C(3), 1·514(6)Å. Selected bond angles: S(1)-C(1)-S(2), 121·3(2); S(1)-Ru-S(2), 76·7(1)°. R = 2·7%.

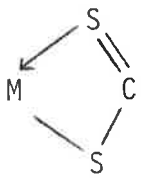
In the reaction of $HRu(sp)(\eta\text{-}C_5H_5)$ with CS_2 two dark red isomers were isolated. The major isomer was shown structurally to have a substituted dithioformate group which is η^3-bonded to the metal:



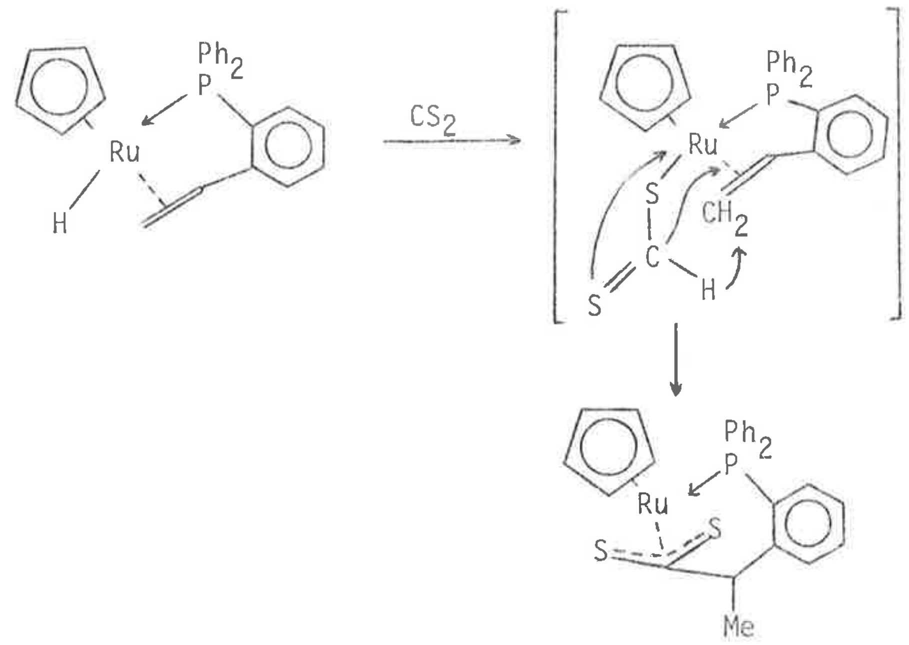
A consideration of models indicated that little strain had to be placed on the system for the CS_2 group to interact with the metal. Of particular interest was the observation that the central carbon atom is within bonding distance of the metal (2·18Å) [this is similar to M-C bonds of the η^3-allylic complexes described in Chapter 3 (*c.* 2·14Å)]. Previous structural studies of chelated dithioformato complexes that I know of show only bonding to the metal *via* the sulphur atoms.[1-3] These have a metal-carbon bond distance of about 3Å (the M-C distance is not normally reported and is being calculated for other systems):



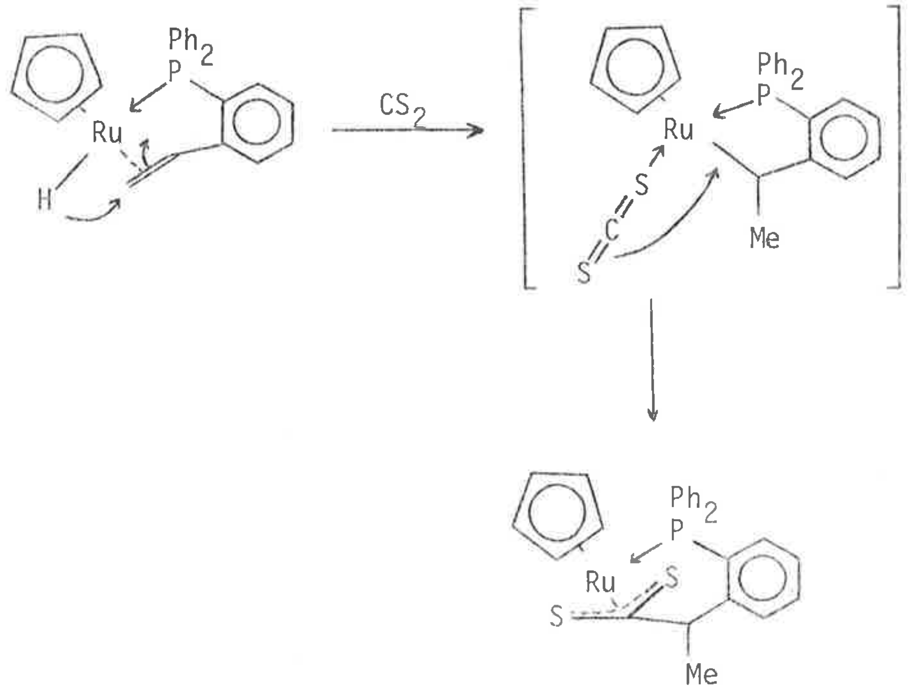
(typical bond distances and angles)



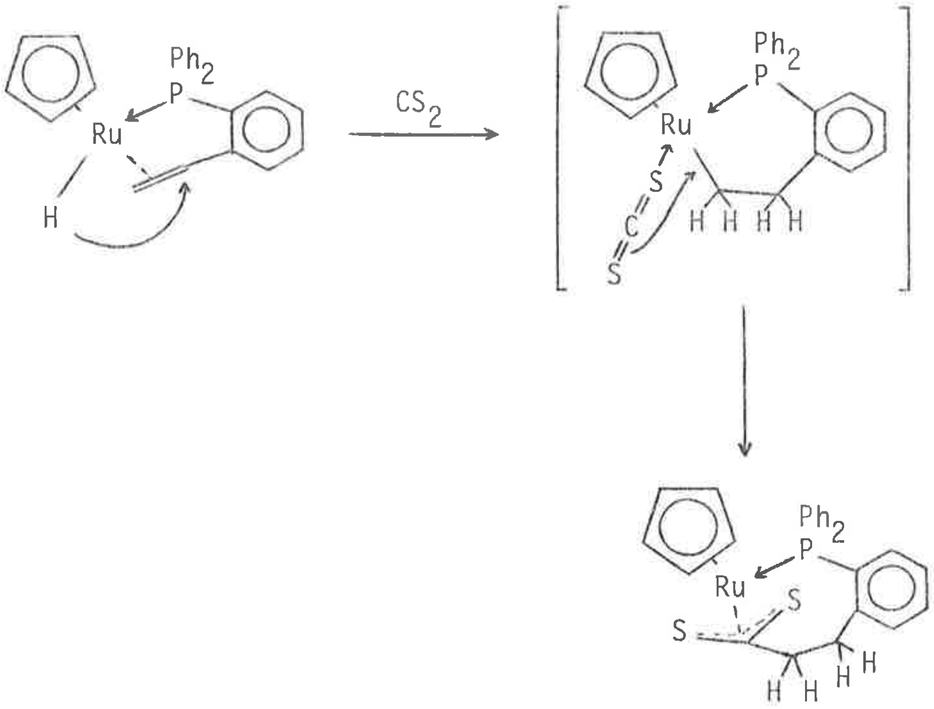
The product is possibly formed *via* a σ-bonded thiocarbonate intermediate which undergoes insertion of C=C into the C-H bond:



Alternatively attack of CS_2 could lead to a hydride shift onto CH_2 of the olefinic group which is followed by insertion of CS_2 into the M-C bond:



The shift of a hydride group onto the sp ligand has been observed previously[4], while insertion of CS_2 into M-C bonds is well known.[1,2] If indeed this mechanism does take place then the minor isomer may be the product of an initial hydride shift onto CH:



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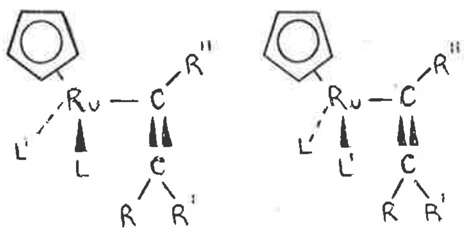
APPENDIX II

Three isomers were observed for Ru[C(OEt)=CHPh](CO)(PPh_3)(η-C_5H_5) (43) (page 89). These may arise from *cis/trans* isomerism about the olefinic bond or by the formation of diastereomers (43a) and (43b). The latter are possible if the vinyl group does not lie in the symmetry plane of the Ru(CO)(PPh_3)(η-C_5H_5) moiety.



	L	L'	R	R'	R''
(43)	CO	PPh_3	H	Ph	OEt
(9)	CO	PPh_3	CN	CN	C(Ph)=$C(CN)_2$
(17)	$CNBu^t$	PPh_3	CN	CN	C(Ph)=$C(CN)_2$
(18)	$CNBu^t$	$CNBu^t$	CN	CN	C(Ph)=$C(CN)_2$
(25)	CO	PPh_3	CN	CN	C(Me)=$C(CF_3)_2$

The observation of isomers for Ru{C[=$C(CN)_2$]C(Ph)$C(CN)_2$}(L)(PPh_3)(η-C_5H_5) (L = CO, 9; L = $CNBu^t$, 17) (page 134) and Ru{C[=$C(CN)_2$]C(Me)$C(CF_3)_2$}(CO)-(PPh_3)(η-C_5H_5) (25) (page 145) can be explained by the formation of diastereomers (9a,b), (17a,b) and (25a,b) respectively. This is possible if there is no plane of symmetry in the butadienyl ligand, which is shown to be the case by the X-ray structure of complex (17). The formation of two isomers of Ru{C[=$C(CN)_2$]C(Ph)=$C(CN)_2$}$(CNBu^t)_2$(η-C_5H_5) (18) (page 134) may also be explained in terms of diastereoisomerism, with the formation of (18a) and (18b). Alternatively, the olefin bonds may be coplanar but the butadienyl group is forced to lie outside of the symmetry plane of the Ru$(CNBu^t)_2$(η-C_5H_5) group by steric restrictions. Inequivalence of the $CNBu^t$ ligands results if the barrier to rotation about Ru-C is high. Similarly the pairs of isomers reported for Ru[$\overline{C=C(Ph)C(CN)_2C}(CN)_2$](dppe)-($\eta$-$C_5H_5$) (8) and Ru{C[=$C(CN)_2$]C(Ph)$C(CN)_2$}(dppe)($\eta$-$C_5H_5$) (12) (page 135) can also be explained in this manner. Isomerism of the dimethylene fragment of the dppe ligand has been observed in other systems and may also offer a plausible explanation for the isomers found for complexes (8) and (12)

It is also possible that the diene fragment can adopt a *cisoid* or *transoid* orientation in solution. This would offer an alternative explanation for the isomers observed in the formation of Ru{C[=$C(CN)_2$]C(Ph)=$C(CN)_2$}[$P(OMe)_3$](PPh_3)(η-C_5H_5) (10) (page 135).