SOME ASPECTS OF ORGANOTRANSITION METAL CHEMISTRY

by

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ERRATA

1. Throughout text, 2,2′-bipyridyl should be replaced by 2,2′-bipyridine.
2. Page 3, line 18: missing bracket.
3. Page 11, line 10: similarly, as
4. Page 17, line 27: reference 52.
5. Page 21, line 3, replace first phrase with: Crystals of (<u>43</u>) and (<u>44</u>) decomposed in the X-ray beam and, therefore, were not suitable for a structural study.
6. Page 35, line 1: "band" should be replaced by "peak".
7. Page 43 in <u>General conditions</u>: Microanalyses were by the Canadian Microanalytical Service, New Westminster, British Columbia.
8. Page 61 at end of (h): The PF_6^- salt has been prepared previously.[40]
9. Pages 139 and 141: references 33 and 61 are the same.
10. Page 160, line 9: tetrahydrofuran

SUMMARY

The chemistry of metal vinylidene and acetylide complexes has been a very active field of research for the past decade. In Chapter 1, previous work in this area is surveyed, and some reactions of ruthenium and osmium complexes are described. The β-carbon of transition metal acetylides has been shown to have a pronounced nucleophilic character, and this fact is used to synthesise a range of new vinylidene complexes. Electrophiles employed include organic halides, aryldiazonium and tropylium cations. The reactivity of the vinylidenes towards small nucleophiles has been examined, and that of the first aryldiazovinylidene complex made, $[Ru\{C{=}CPh(N{=}NPh)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$, has been investigated in some detail. Nucleophiles such as PPh_3, $Ph_2P(CH_2)_2PPh_2$, H^- or MeO^- readily cleave the C-N bond, regenerating the starting acetylide complex, $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$. Reaction with water or carbonylation affords $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$, and reaction with methanol gives $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$. Reaction with iodomethane affords $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$, whilst the diazo group can be methylated with $[Me_3O][SbCl_6]$; cyclomanganation with $Mn(CH_2Ph)(CO)_5$ gives $[Ru\{C{=}CPh[\overline{N{=}NC_6H_4Mn}(CO)_4\text{-}2]\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$. The FAB mass spectra of these complexes have proved useful in assignment, and these are discussed.

Much of the work on complexes containing the $Ru(L)_2(\eta\text{-}C_5H_5)$ group has been carried out for L = PPh_3. Chapter 2 describes results obtained when the bidentate phosphines dppm $[CH_2(PPh_2)_2]$ and dppe $[Ph_2P(CH_2)_2PPh_2]$ replace the triphenyl phosphine ligands. In the case of dppm, sequential replacement of the PPh_3 groups involves an intermediate monodentate dppm complex and careful choice of reaction conditions allows the isolation of the compound $RuCl(\eta^1\text{-dppm})(PPh_3)(\eta\text{-}C_5H_5)$. The crystal structure of this complex is discussed and some of its chemistry presented. The metal hydrides, $Ru(H)(L_2)(\eta\text{-}C_5H_5)$ (L_2 = dppe, dppm) were prepared; insertion of dimethyl acetylenedicarboxylate into the Ru-H bond affords the σ-vinyl complexes $Ru\{C(CO_2Me){=}C(H)(CO_2Me)\}(L_2)(\eta\text{-}C_5H_5)$. The crystal structure of the dppe example was determined, and this is compared with related vinyl structures.

Cyclopentadienyl ruthenium phosphine chemistry has proved both extensive and varied, and elucidation of much of this work has been aided by crystallographic investigations. Chapter 3 collects together the existing structural data of this type of complex and includes the results of six structures determined by the author.

Chapter 4 contains some chemistry of the cluster carbonyl $Ru_3(CO)_{12}$ with *N*-donor ligands. A survey of previous work in this area is followed by an account of results obtained by the author. Despite the great deal of work done in the field of metal cluster chemistry in the last few years, relatively little attention has been

given to the reactions of $Ru_3(CO)_{12}$ with *N*-heterocycles. Reaction of $Ru_3(CO)_{12}$ with bipy affords $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$, which has an unusual $Fe_3(CO)_{12}$-type structure. Reaction with the substituted pyridine NC_5Cl_5 leads not to substitution, but to the hexanuclear carbido cluster $Ru_6C(\eta\text{-toluene})(CO)_{14}$. Reactions with pyrazoles afford the oxidative addition products $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3HR_2\text{-}3,5)(CO)_{10}$ ($R = H,Me,CF_3$); the structure of the CF_3 example was determined and is discussed. The N=N bond is cleaved in the reaction between $Ru_3(CO)_{12}$ and azobenzene, which gives $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (among other products). Electron transfer catalysed substitution reactions, which had proved successful with $Ru_3(CO)_{12}$, were also used to give substitution products of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ containing tertiary phosphines, $P(OMe)_3$ and *m*-xylyl isocyanide. Structural studies of some of the products show that initial substitution occurs at an outer Ru; as with $Ru_3(CO)_{12}$, phosphines substitute equatorially and isocyanides axially. The ligands dppm and dppe span the non-bonding Ru...Ru vector. The probable course of these reactions is discussed.

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.

I consent to this thesis being made available for photocopying and loan.

MARK G. HUMPHREY

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ABBREVIATIONS

In general

Å	angstroms
acac	acetylacetonate
A.R.	analytical reagent
Ar	aryl
atm	atmospheres
bipy	2,2′-bipyridyl
bqH	benzo[*h*]quinoline
Bu^i	isobutyl
Bu^n	normal butyl
Bu^s	secondary butyl
Bu^t	tertiary butyl
ca	*circa*
calcd.	calculated
Cp	cyclopentadienyl
Cy	cyclohexyl
d	days
deb	*p*-diethynylbenzene
dec.	decomposed
dmad	dimethyl acetylenedicarboxylate
dpompyr	*N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine
dppa	1,2-bis(diphenylphosphino)acetylene
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
E_a	activation energy
EI	electron impact
e.s.d.	estimated standard deviation

Et	ethyl
ETC	electron transfer-catalysed
eV	electron volts
FAB	fast atom bombardment
fac	*facial*
g	grams
GC	gas chromatography
h	hours
HOMO	highest occupied molecular orbital
IR	infrared
kJ	kilojoules
kV	kilovolts
L	ligand
lit.	literature value
LUMO	lowest unoccupied molecular orbital
M	metal
M	molecular ion or molarity
mA	milliamperes
mbar	millibars
Me	methyl
mer	*meridional*
mg	milligrams
MHz	Megahertz
min	minutes
ml	millilitres
mmol	millimoles
m.p.	melting point
MS	mass spectrometry
m.u.	mass units

m/z	mass per unit charge
NMR	nuclear magnetic resonance
p	page
PcH_2	phthalocyanine
Ph	phenyl
1,10-phen	1,10-phenanthroline
pp	pages
ppn	bis(triphenylphosphine)iminium
Pr^i	isopropyl
psi	pounds per square inch
py	pyridine
pzH	pyrazole
R	alkyl or aryl
R-DAB	1,4-diaza-1,3-butadiene (with nitrogen substituent R)
ref.	reference
$salenH_2$	*N*,*N*´-ethylenebis(salicylidenimine)
sec.	seconds
thf	tetrahydrofuran
TLC	thin layer chromatography
tpp	tetraphenylporphyrinato
vol.	volume
X	anion
xy	xylyl

For infrared spectroscopy

br	broad
cm^{-1}	wavenumbers (reciprocal centimetres)
m	medium

s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak

For nuclear magnetic resonance spectroscopy

d	doublet
dd	doublet of doublets
dt	doublet of triplets
Hz	Hertz
J	coupling constant
m	multiplet
ppm	parts per million
q	quartet
t	triplet

CHAPTER ONE

INTRODUCTION

It is well known that transition metals can stabilise reactive organic species by complexation. The acetylene tautomer vinylidene, $H_2C{=}C{:}$, is one such species. Its calculated lifetime is *ca* 10^{-11} sec.,[1] which agrees with a value of *ca* 10^{-10} sec. deduced from trapping experiments;[2] however, it is stable as a ligand in a transition metal complex. The first vinylidene complex was obtained from diphenylketene and $Fe_2(CO)_9$ in 1966,[3,4] but rapid development of this area did not occur until rational routes to these complexes had been developed, in the mid to late 1970's. This field of chemistry, together with that of the related propadienylidene ligand ($H_2C{=}C{=}C{:}$), has been reviewed;[5] however, the considerable interest in this area since that survey warrants an examination of results published since then. For the purpose of brevity, this is restricted to mononuclear vinylidene metal complexes, the area of this author's work; binuclear vinylidene complexes, propadienylidene complexes and cluster complexes are mentioned only when they are derived from, or react to form, mononuclear vinylidene complexes. Following the procedure of Bruce and Swincer,[5] classification is by the metal present.

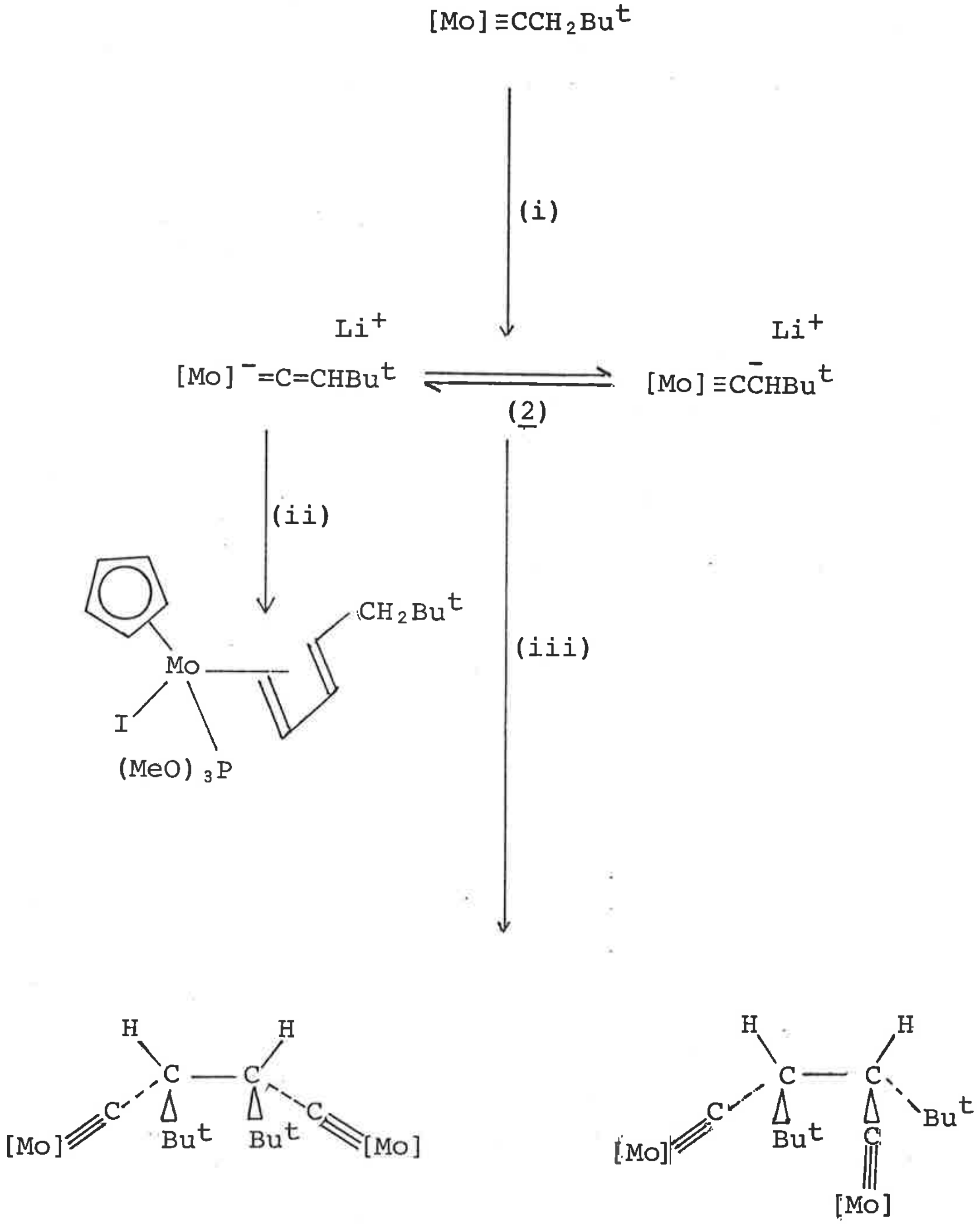
New Chemistry of Vinylidene Complexes

A. Molybdenum and Tungsten

Rearrangement of a terminal alkyne to a vinylidene is a common reaction on transition metals; upon coordination the relative thermodynamic stabilities of the acetylene and the vinylidene are reversed.[6] The terminal alkyne→coordinated vinylidene rearrangement has been shown to occur on molybdenum;[7] reaction of PhC≡CH with [Mo(NCMe)(dppe)-(η-C_7H_7)][PF_6] gave [Mo(C=CHPh)(dppe)(η-C_7H_7)][PF_6] (<u>1</u>), which was readily deprotonated to give the η^1-alkynyl complex Mo(C≡CPh)(dppe)(η-C_7H_7). The anionic ambident molybdenum complex Li[Mo(CCHBu^t){P(OMe)$_3$}$_2$(η-C_5H_5)] (<u>2</u>) added electrophiles at both the molybdenum and β-carbon;[8] with allyl halides, it behaved like a vinylidene with the negative charge centred on the metal, affording Mo-(η^4-1,3-$C_4H_5CH_2Bu^t$)(I){P(OMe)$_3$}(η-C_5H_5), containing a 1,3-diene ligand. It also reacted with the one-electron oxidants [Fe(η-C_5H_5)$_2$][BF_4] or CuI to give the biscarbynes (<u>3</u>) and (<u>4</u>) as a mixture of the *meso*-form and an *RS*-pair (see Scheme 1).

The coordinatively-unsaturated complex *fac*-W(CO)$_3$(thf)-(dppe) also reacted with terminal alkynes, to give neutral vinylidene complexes of the type *mer*-W(C=CHR)(CO)$_3$(dppe) [R = CO_2Me (<u>5</u>), Ph (<u>6</u>).[9] The initially-formed π-bonded alkyne is suggested to rearrange to a meridional vinylidene because of the unfavourable four-electron two-centre $d\pi$-$\pi_\perp$ conflict in these d^6 complexes. Protonation of (<u>6</u>) with $HBF_4.OMe_2$, followed by addition of [NEt_4]Cl generated the neutral Fischer-type carbyne (<u>7</u>). Methylation of (<u>2</u>) with [Me_3O][BF_4] and deprotonation with alumina afforded the alkyl(aryl) vinylidene (<u>8</u>).[10]

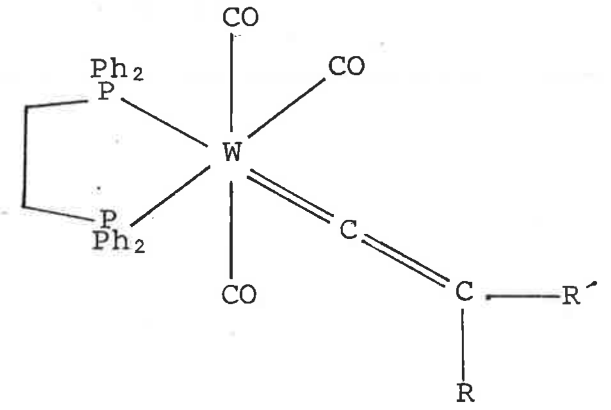
Irradiation of W(CO)$_6$ with terminal alkynes in hydrocarbon solvents formed active polymerisation catalysts for the synthesis of poly(acetylenes); catalytically-active vinylidene complexes formed by rearrangement of



(3); *meso*-form

(4); one of the *RS*-pair

<u>Scheme 1</u>. [Mo] = $Mo\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$. Reagents: (i) Bu^nLi; (ii) $CH_2{=}CHCH_2I$; (iii) CuI or $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$.



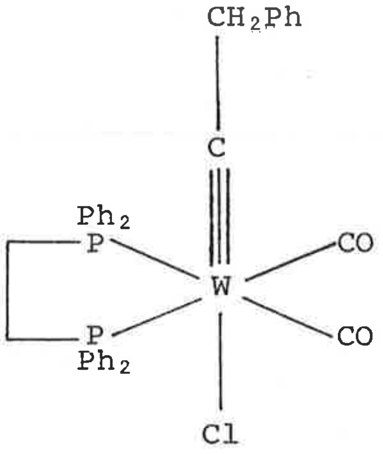
(5) R = CO_2Me
R´ = H

(6) R = Ph
R´ = H

(8) R = Ph
R´ = Me

η^2-alkyne complexes were suggested to be intermediates in the formation of the poly(acetylenes).[11]

Addition of electrophiles to the β-carbon of an acetylide group affords vinylidene ligands. Alkylation of $[W(C{\equiv}CBu^t)(CO)_5]^-$ with FSO_3Me or $[Et_3O][BF_4]$ gave the deep green complexes $W(C{=}CBu^tR)(CO)_5$ [R = Me (9), Et (10)].[12] These complexes did not undergo further alkylation; however, as with (6), protonation in the presence of halide ions ($[NMe_4]I$) afforded the carbyne complexes *trans*-$W({\equiv}CCHBu^tR)$-$(I)(CO)_4$ [R = Me (11), Et (12)]. Transformation of acetylide complexes into carbyne complexes was also achieved in a single step; double β-protonation of $[W(C{\equiv}CR)(CO)_5]^-$ (R = Ph, Bu^t) in the presence of I^- afforded $W({\equiv}CCH_2R)(I)(CO)_4$ (13). Addition of CO_2 to the β-carbon of Li[*fac*-$W(C{\equiv}CR)$-$(CO)_3(dppe)$] (R = Me,Bu^n) followed by methylation yielded *mer*-$W\{C{=}C(R)CO_2Me\}(CO)_3(dppe)$ (14);[13] ion-pair formation at the β-carbon was suggested as a kinetic mediator in this system, as a similar reaction was not observed with



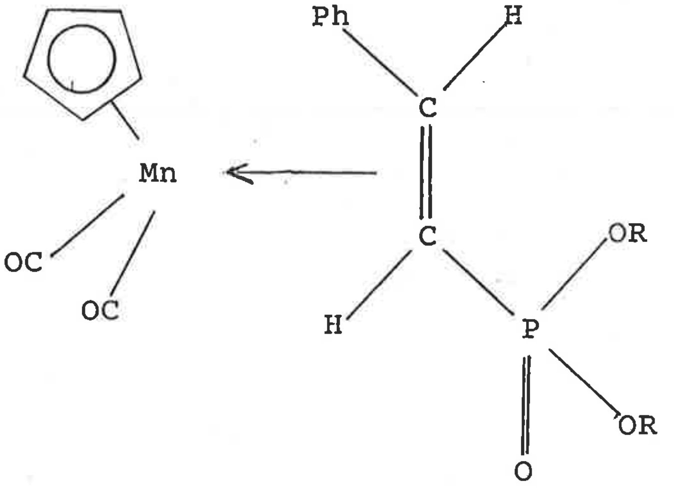
(7)

the $[ppn]^+$ salt.

Solvolysis of presumed vinylidene intermediates by alcohols is believed to be responsible for the formation of Fischer-type carbene complexes $W\{C(OR')CH_2R\}(CO)_5$ from the reaction between chemically- or photochemically-generated coordinatively-unsaturated '$W(CO)_4$' and terminal alkynes.[14]

B. Manganese and Rhenium

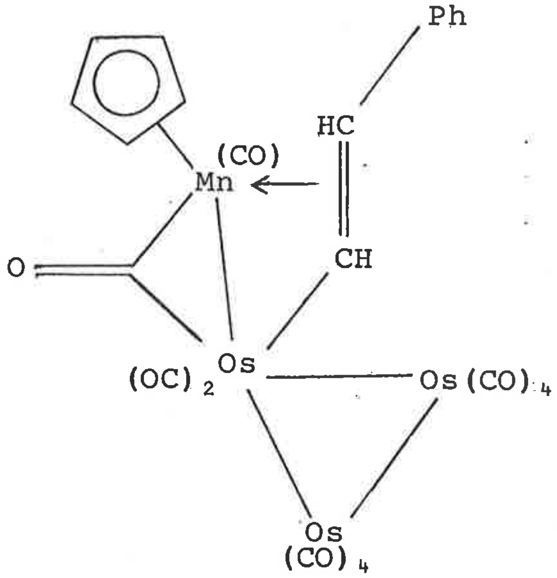
The manganese vinylidene complex $Mn(C{=}CHPh)(CO)_2$-$(\eta$-$C_5H_5)$ reacted with $P(OR)_3$ (R = Et or Ph) to afford $Mn\{\eta^2$-$PhCH{=}CHP(O)(OR)_2\}(CO)_2(\eta$-$C_5H_5)$ [R = Et (15), Ph (16)] in a reaction interpreted as an unusual variant of the Arbuzov reaction occurring in the coordination sphere of a transition metal, accompanied by rearrangement of the organic ligand from vinylidene to η^2-alkene.[15] The analogous reactions between $Mn(C{=}CHR)(CO)_2(\eta$-$C_5H_5)$ (R = Ph, CO_2Me, $CBu^t{}_2OH$) and PPh_2R' (R' = Ph,Me) gave vinylphosphonium ylide complexes $\bar{M}n\{C(\overset{+}{P}Ph_2R')=CHR\}(CO)_2(\eta$-$C_5H_5)$ (not all combinations of R,R').[16] The tetranuclear mixed-metal



(15) R = Et

(16) R = Ph

cluster complex $MnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}(\eta\text{-}C_5H_5)$ (17) was obtained from the reaction between $Mn(C{=}CHPh)(CO)_2$-$(\eta\text{-}C_5H_5)$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$;[17] although stable in polar solvents, it rapidly decomposed in non-polar solvents to give triosmium clusters.



(17)

The coordinatively-unsaturated complex $Mn(thf)(CO)_2(\eta-C_5H_5)$ reacted with *p*-diethynylbenzene (deb) to give $Mn(deb)(CO)_2(\eta-C_5H_5)$ (18) and $\{Mn(CO)_2(\eta-C_5H_5)\}_2(deb)$ (19).[18] When (18) and (19) were treated with PhLi, followed by HBr, they afforded the vinylidene complexes $Mn(C{=}CHC_6H_4C{\equiv}CH)(CO)_2(\eta-C_5H_5)$ (20) and $\{(\eta-C_5H_5)(OC)_2Mn(C{=}CH)\}_2C_6H_4$, respectively; the terminal acetylene in (20) was reduced by LiBr and HCl in ether, affording $Mn(C{=}CHC_6H_4CBr{=}CH_2)(CO)_2(\eta-C_5H_5)$. Complex (20) added PPh_3 in the same way as the other manganese vinylidene complexes above, and afforded the analogous vinylphosphonium ylide complex $\overset{-}{Mn}\{C(\overset{+}{P}Ph_3){=}CHC_6H_4C{\equiv}CH\}(CO)_2(\eta-C_5H_5)$.

Addition of $[Bu^tS]^-$ to $Mn(C{=}C{=}CPh_2)(CO)_2(\eta-C_5H_4Me)$ and subsequent protonation afforded $Mn\{C{=}CHC(Ph)_2SBu^t\}(CO)_2(\eta-C_5H_4Me)$, together with $Mn\{C(SBu^t)C(H){=}CPh_2\}(CO)_2(\eta-C_5H_4Me)$; nucleophilic attack on the allenylidene group occurs at both the α- and γ- carbons.[19]

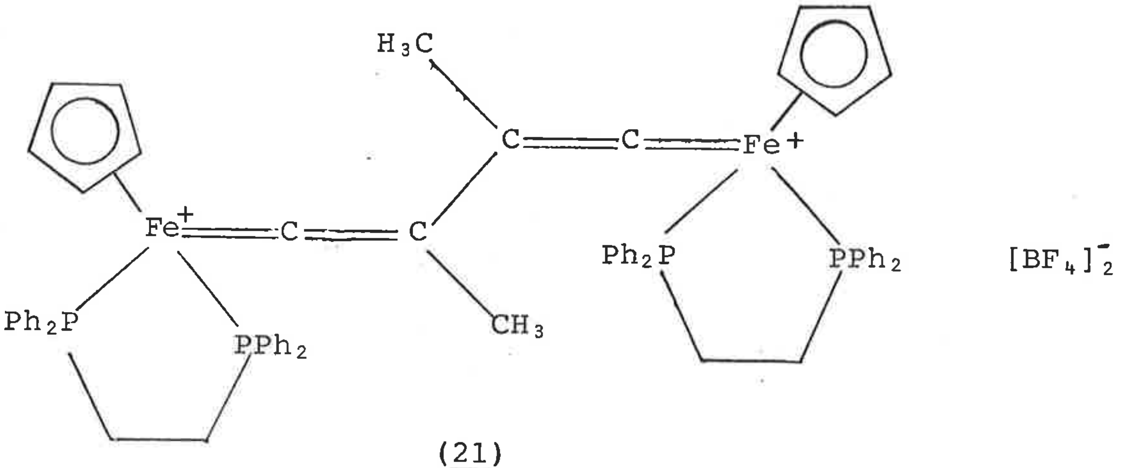
Terminal acetylenes reacted with *trans*-$[ReCl(N_2)(dppe)_2]$ to give the neutral vinylidene complexes *trans*-$[ReCl(C{=}CHR)(dppe)_2]$ (R = Ph,Et or CO_2Et), by the familiar alkyne-to-vinylidene rearrangement.[20]

C. Iron, Ruthenium and Osmium

Addition of organocuprate reagents to iron-vinylidenes gave alkenyliron complexes.[21] Thus, the reaction between $[Fe(C{=}CMe_2)(CO)(PPh_3)(\eta-C_5H_5)]^+$ and $Li_2[Cu(CN)R_2]$ (R = Ph, $CH{=}CH_2$) afforded $Fe\{C(R){=}CMe_2\}(CO)(PPh_3)(\eta-C_5H_5)$. The unsymmetrical vinylidene $[Fe(C{=}CMePh)(CO)(PPh_3)(\eta-C_5H_5)]^+$ reacted with $Li_2[Cu(CN)Me_2]$ to give the *Z* (93%) and *E* (7%)

isomers of Fe{C(Me)=CMePh}(CO)(PPh$_3$)(η-C$_5$H$_5$); the stereospecificity presumably arises because the addition reaction takes place preferentially *trans* to the more bulky vinylidene substituent.

The reaction of [Fe(C=CHMe)(dppe)(η-C$_5$H$_5$)][BF$_4$] with iodosobenzene yielded [Fe(μ-C$_4$Me$_4$)(dppe)$_2$(η-C$_5$H$_5$)$_2$][BF$_4$]$_2$ (21), by an oxidative coupling of the vinylidene ligands.[22]



(21)

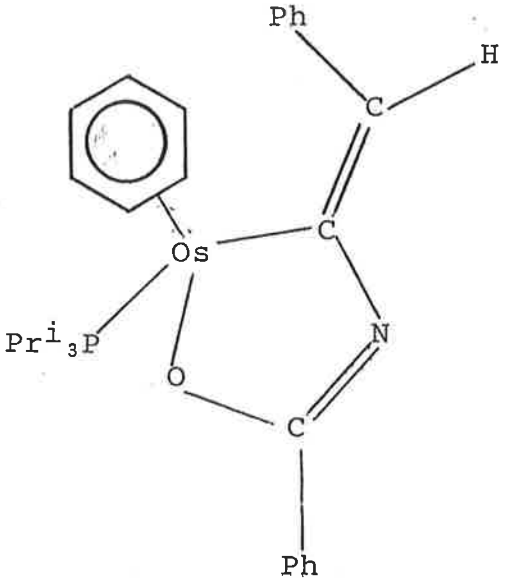
This contrasts with the oxidative coupling of the anionic molybdenum vinylidene complex (12), which occurred without hydrogen loss.

The non-rigid behaviour of iron- and ruthenium-vinylidene complexes with chelating phosphines was investigated by variable temperature ^{31}P NMR spectroscopy.[23] The preferred geometry of the complexes in solution was found to be the one in which the plane of the vinylidene moiety is perpendicular to the plane containing the α-carbon, the metal atom and the centroid of the cyclopentadienyl ring; the barrier of rotation is about 9-10 kcal/mol.

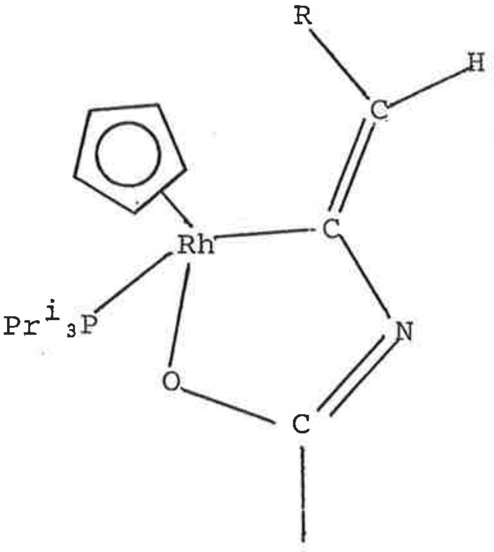
A range of disubstituted vinylidene complexes was prepared by reacting the nucleophilic σ-acetylide complexes M(C≡CR)(L$_2$)(η-C$_5$H$_5$) (M = Fe,Ru; L = PPh$_3$, L$_2$ = dppe) with organic halides;[24] the analogous reactions with the isoelectronic cyanide ligand in cyano complexes $M(CN)L_n$ have been long known.[25]

The osmium vinylidene complexes $[Os(C{=}CHR)(CO)(PPh_3)(\eta\text{-}C_5Me_5)][BF_4]$ ($R = Bu^t,Ph$) were prepared from the iodo-complexes by halogen abstraction with $AgBF_4$ followed by treatment with the terminal acetylene; $Os(I)(CO)_2(\eta\text{-}C_5Me_5)$ gave $[Os(CO)_3(\eta\text{-}C_5Me_5)][BF_4]$ by the same procedure.[26]

The arene-ruthenium complexes $RuCl_2(L)(\eta\text{-}C_6Me_6)$ ($L = PMe_3,PMe_2Ph$) reacted at room temperature with $NaPF_6$ and $RC{\equiv}CH$ ($R = H,Bu^t,Ph$) in methanol to afford the (alkoxy)alkylcarbene complexes $[RuCl\{C(OMe)CH_2R\}(L)(\eta\text{-}C_6Me_6)][PF_6]$ probably *via* a vinylidene intermediate;[27] the arene-ruthenium vinylidenes are considerably more reactive than the analogous cyclopentadienylruthenium vinylidenes. The arene-osmium complex $Os(C{=}CHPh)(PPr^i{}_3)(\eta\text{-}C_6Me_6)$ and the isoelectronic $Rh(C{=}CHR)(PPr^i{}_3)(\eta\text{-}C_5H_5)$ ($R = H,Ph$) reacted with benzoyl azide to give the metallaheterocycles (<u>22</u>), (<u>23</u>) and (<u>24</u>), respectively;[28] for the osmium complex,



(<u>22</u>)



(<u>23</u>) R = H

(<u>24</u>) R = Ph

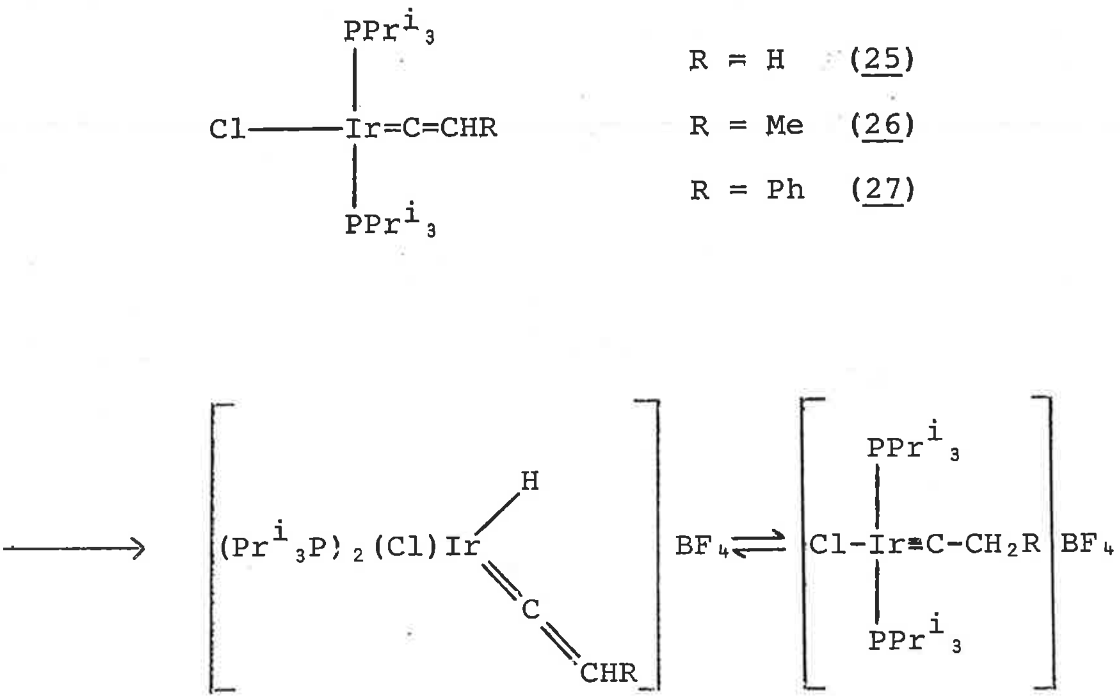
the initial *Z*-isomer thermally rearranged to the *E*-isomer.

Reaction between $K_2[Ru(tpp)]$ (tpp = 5,10,15,20-tetraphenylporphyrinato dianion) and $Cl_2C{=}C(C_6H_4Cl\text{-}4)_2$ afforded the vinylidene complex $Ru\{C{=}C(C_6H_4Cl\text{-}4)_2\}(tpp)$.[29]

D. Other metals

Square-planar vinylidene complexes were obtained from the reactions between *trans*-$[RhCl(RC{\equiv}CH)(PPr^i{}_3)_2]$ (R = H,Me,Ph) and pyridine in benzene.[30] The analogous iridium complexes *trans*-$[Ir(C{=}CHR)(Cl)(PPr^i{}_3)_2]$ (R = H,Me,Ph) were prepared similarly as the first vinylidene iridium complexes. The iridium reactions are slower than their rhodium counterparts and a five-coordinate hydrido-acetylide intermediate was isolated, the first time that the conversion $M(\eta^2\text{-}RC_2H) \rightarrow M(C{=}CHR)$ has been shown to occur in two steps *via* the oxidative-addition intermediate $MH(C_2R)$; this route to vinylidene formation was analysed theoretically by Silvestre and Hoffmann, and considered energetically prohibitive.[6] These iridium-vinylidene complexes were protonated at the β-carbon, affording carbyne complexes *via* a hydrido-vinylidene intermediate (Scheme 2).[31]

The reaction between $TaCl_2(\eta\text{-}C_5Me_5)_2$ and vinylmagnesium bromide gave the hydrido-vinylidene complex $Ta(H)(C{=}CH_2)(\eta\text{-}C_5Me_5)_2$ (28); the NMR data support a structure with all atoms of the $[Ta(H)(C{=}CH_2)]$ moiety in the same plane.[32] Reaction of (28) with CO afforded $Ta(CH{=}CH_2)(CO)(\eta\text{-}C_5Me_5)$, which regenerated (28) upon photolysis; water and methanol reacted with (28) to liberate ethylene, giving $Ta(H)(O)(\eta\text{-}C_5Me_5)_2$ and $Ta(H)(\eta^2\text{-}CH_2O)(\eta\text{-}C_5Me_5)_2$, respectively.



Scheme 2

The most successful preparative routes to metal vinylidene complexes are:

(i) reaction of a metal complex, containing a suitable leaving group, with a terminal acetylene, and

(ii) protonation or alkylation of a metal acetylide. This Chapter explores reactions of type (ii), using electrophiles such as organic halides, aryldiazonium and cycloheptatrienyl cations, and examines the reactivity of some of the resulting vinylidenes. The use of fast atom bombardment (FAB) mass spectrometry proved useful in characterisation of these complexes and these spectra are discussed.

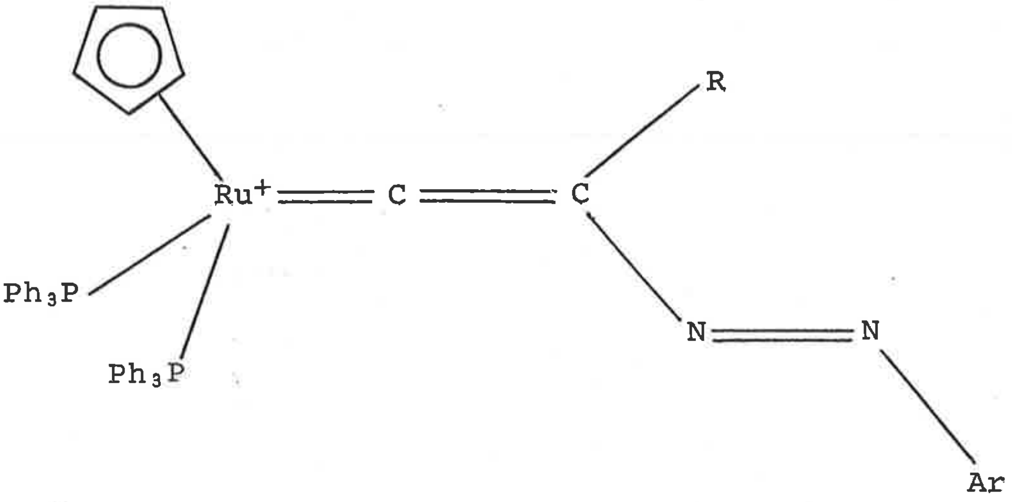
RESULTS AND DISCUSSION

As was mentioned above, one of the characteristic reactions of transition metal σ-acetylide complexes, $M(C\equiv CR)(L)_n$, is their protonation or alkylation to give the related vinylidene complexes $[M(C{=}CRR')(L)_n]^+$ (R′ = H or alkyl).[5] This ready addition of electrophiles to the β-carbon of the acetylide fragment is consistent with theoretical findings that electron density in the HOMO is localised on this carbon.[33] It is surprising, therefore, that other electrophilic reagents have not been found to react in a similar fashion with transition metal σ-acetylide complexes. Other types of reaction, in particular, cycloaddition of electron-deficient olefins,[34,35] probably proceed *via* initial reaction at the β-carbon, but do not afford vinylidene complexes.

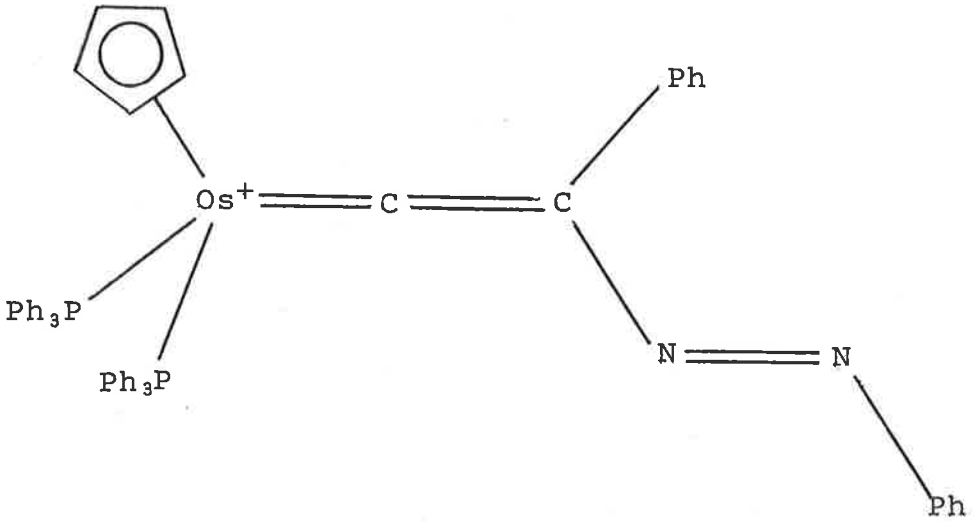
This Chapter describes reactions of some ruthenium and osmium σ-acetylides with electrophilic aryldiazonium and tropylium cations and organic halides and some reactions of the resulting aryldiazo-, cycloheptatrienyl- and alkyl- vinylidenes.

1. Preparation and properties of aryldiazo- and cycloheptatrienyl- vinylidene complexes

Addition of $[ArN_2][X]$ (X = PF_6 or BF_4) to an equimolar amount of $Ru(C\equiv CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ in diethyl ether or tetrahydrofuran resulted in an immediate colour change from yellow to bright red. Suitable work-up procedures gave red crystalline solids which were identified in each case as the salts $[Ru(C{=}CRN{=}NAr)(PPh_3)_2(\eta\text{-}C_5H_5)][X]$ by elemental microanalyses, from their spectral properties,



	R	Ar		R	Ar
(29)	Ph	Ph	(36)	Ph	$C_6H_4NO_2$-4
(30)	Me	Ph	(37)	Me	$C_6H_4NO_2$-4
(31)	C_6F_5	Ph	(38)	Ph	$C_6H_3Cl_2$-2,4
(33)	Ph	$C_6H_3Me_2$-3,4	(39)	Me	$C_6H_3Cl_2$-2,4
(34)	Me	$C_6H_3Me_2$-3,4	(40)	Ph	C_6H_4OMe-4
(35)	C_6F_5	$C_6H_3Me_2$-3,4	(41)	Me	C_6H_4OMe-4



(32)

and, in one case, by a single-crystal X-ray diffraction study. Complexes (29) - (41) were obtained in this manner (anions omitted from diagrams).

Their IR spectra contain medium intensity bands between 1550-1600 cm^{-1} assigned to ν(C=C) and ν(N=N) modes, and the usual strong broad absorptions of the respective anions at *ca* 1050 cm^{-1} for the ν(BF) absorption of $[BF_4]^-$ and *ca* 840 cm^{-1} for the ν(PF) band of the $[PF_6]^-$ anion. In the ^{1}H NMR spectra the C_5H_5 resonances occur as singlets at δ *ca* 5.3, and other resonances are characteristic of the various functional groups present in R and Ar. The ^{13}C NMR spectra contain C_5H_5 resonances at δ *ca* 95, characteristic of cationic complexes; most informative were the resonances of the α- and β-carbons of the vinylidene ligand, which were found at δ *ca* 360 and 120 ppm, respectively. The former appeared as a triplet by coupling with the two ^{31}P nuclei, and its low-field position is typical for vinylidene complexes. These signals are relatively weak, however, and were not always located, even with the aid of paramagnetic relaxation reagents [$Cr(acac)_3$ or $Fe(acac)_3$] and delayed pulse techniques. The crystal structure of one example of this new class of vinylidene, $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$, was determined.

X-ray structure of $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)]$-$[BF_4]$ (33)

The structure of the cation in (33) is shown in Figure 1, and confirms the presence of the aryldiazovinylidene ligand. The Ru-C(42) distance of 1.823(9)Å is the shortest

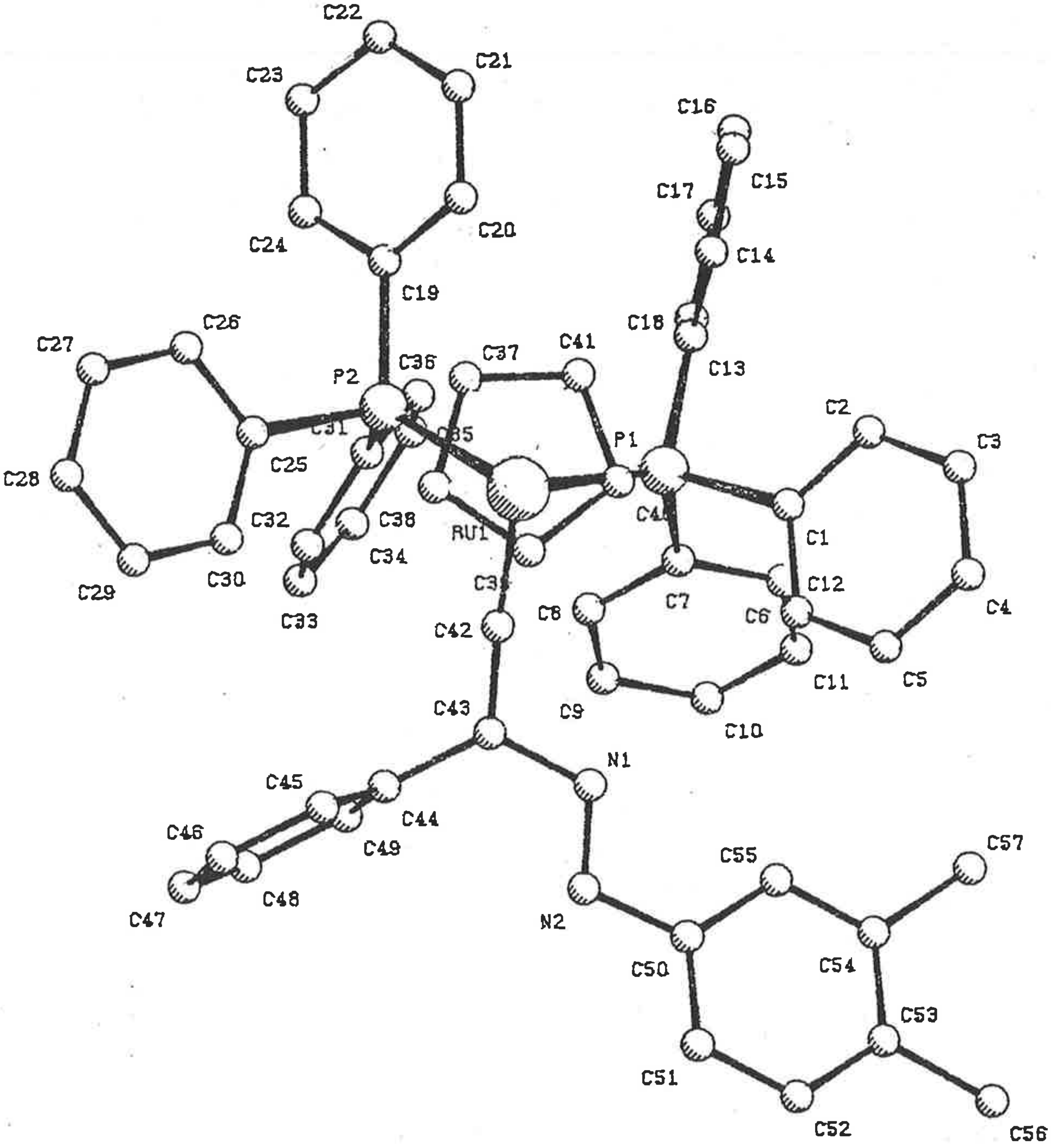


Figure 1: PLUTO plot of the structure of the cation in $[Ru\{C{=}CPh(N{=}NC_6H_3Me_2\text{-}3,4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (33).

such separation in a cyclopentadienylruthenium complex (Table 5, Chapter 3), while the C(42)-C(43) distance of 1.34(1) and angles about the β-carbon [C(42)-C(43)-N(1) 114.4(8), C(42)-C(43)-C(Ph) 121.4(8), C(Ph)-C(43)-N(1) 124.2(7)°] indicate a normal C=C double bond and relatively little distortion from a trigonal sp^2-hybridised C(43). The Ru-C(42)-C(43) system is nearly linear [169.9(7)°]. The aryldiazo group has the *trans* configuration usually found, with no significant differences in bond parameters from those found in *trans*-azobenzene,[36] e.g. N(1)=N(2) 1.27(1), N(2)-C(Ar) 1.42(1)Å, N(1)-N(2)-C(Ar) 113.0(7)°.

Reactivity of $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>29</u>)

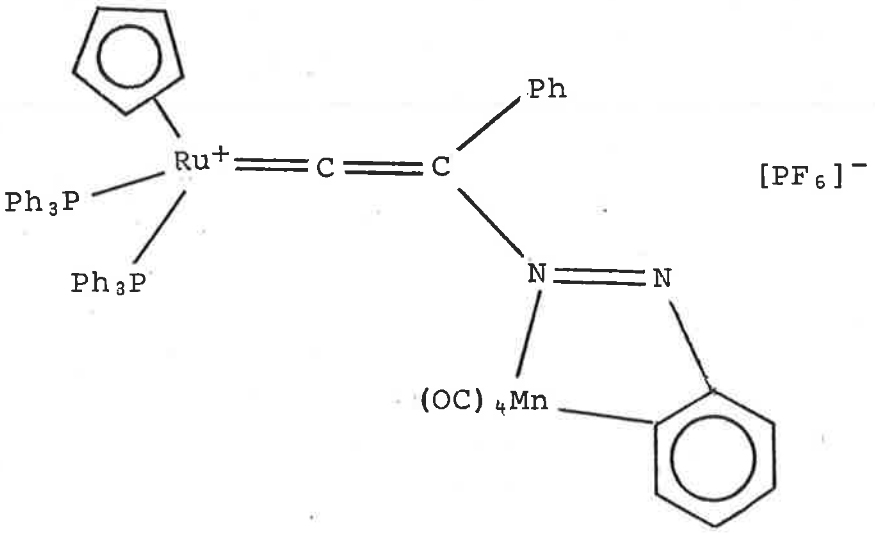
The formation of aryldiazovinylidene complexes represents a facile synthesis of the C=C-N=N system and formation of a C-N bond. However, studies of the reactivity of one of these novel complexes, (<u>29</u>), indicated that the C-N bond is readily broken, regenerating the original metal acetylide complex. Thus, with PPh_3 or dppe, complex (<u>29</u>) afforded $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (50-80% recovery) and white organophosphorus compounds tentatively identified as $R_3P{=}NPh$.

Reagents which have been shown to react with $[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ gave similar products with the aryldiazovinylidene complex. Thus, after heating in refluxing aqueous tetrahydrofuran, complex (<u>29</u>) gave $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ in 70% yield. Similarly, a lower yield of $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ was obtained in refluxing methanol. Displacement of the vinylidene ligand occurred under CO (45 atm, 100°C, 16 h); $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ was isolated in 37% yield, while a similar reaction with H_2, followed by treatment with a chlorinated solvent, afforded $RuCl(PPh_3)_2(\eta-C_5H_5)$. With iodomethane, the disubstituted vinylidene complex $[Ru(C{=}CMePh)(PPh_3)_2(\eta-C_5H_5)]^+$ was formed. In all of these cases, TLC examination of the solutions left after isolating the metal-containing complexes showed them to contain complex mixtures from which no pure compounds could be isolated and characterised.

Reactions between (<u>29</u>) and $K[BH(CHMeEt)_3]$ (*K*-Selectride) or NaOMe afforded only $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$, recovered in very small amount (5-15%). Attempted protonation (with $HPF_6.OEt_2$) gave only a partial hydrolysis product, the salt $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta-C_5H_5)][PO_2F_2]$, characterised on the basis of strong bands at 1590 $[\nu(C{=}C)+\nu(N{=}N)]$, 1057 $[\nu(PO)]$ and 847 cm^{-1} $[\nu(PF)]$.

The diazo function in complex (<u>29</u>) was alkylated with $[Me_3O]^+$. This slow reaction afforded yellow-brown $[Ru(C{=}CPhN{=}NMePh)(PPh_3)_2(\eta-C_5H_5)]^{2+}$, isolated as the mixed $[PF_6]^-/[SbCl_6]^-$ salt. Characterisation of this complex was aided by the N*Me* resonance found at $\delta 1.57$ in the ^1H NMR spectrum.

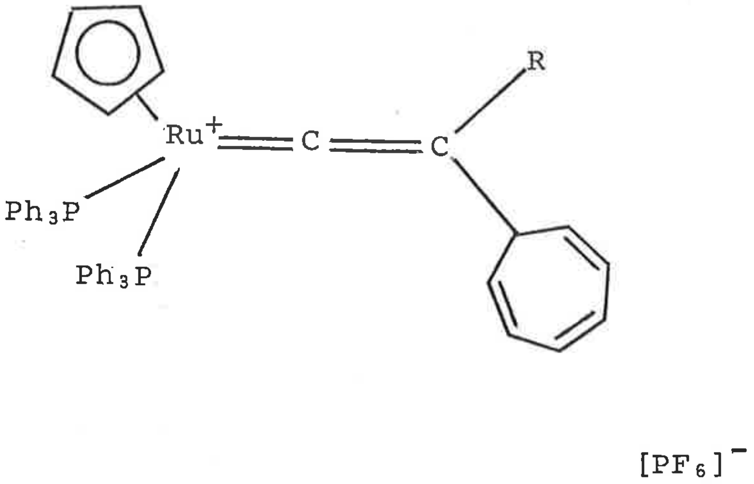
A characteristic reaction of aryldiazo groups is their cyclometallation which occurs on reaction with many metal substrates. The reaction between (<u>29</u>) and $Mn(CH_2Ph)(CO)_5$ afforded a purple complex, characterised as the metallated complex (<u>42</u>). The IR spectrum contains three $\nu(CO)$ absorptions at 2080, 1999 and 1959 cm^{-1}, confirming the presence of the $Mn(CO)_4$ group, while the fast atom bombardment mass spectrum contains a parent ion and related fragment ions. X-ray quality crystals could not be obtained.



(42)

Preparation of cycloheptatrienylvinylidene complexes

Addition of a solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ in dichloromethane to a suspension of $[C_7H_7][PF_6]$ in the same solvent produced a red solution; work-up afforded orange crystals of $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (43) in high yield. A related air-stable complex was obtained from $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (44).



(43) R = Ph

(44) R = Me

These compounds were characterised by elemental microanalysis and various spectroscopic studies. They are insoluble in light petroleum, diethyl ether and water, slightly soluble in methanol and ethanol, more soluble in tetrahydrofuran, acetone and chloroform, and very soluble in dichloromethane and dimethyl sulphoxide.

The IR spectra are characterised by medium to strong absorptions between 1640-1650 cm^{-1} arising from the C=C double bonds of the vinylidene and cycloheptatrienyl groups, and strong broad ν(PF) bands at *ca* 840 cm^{-1} from the $[PF_6]^-$ anion. The ^{1}H NMR spectra contain sharp singlets at δ *ca* 5.2 assigned to the C_5H_5 protons, and three multiplets between δ5.3-6.5 assigned to six vinylic protons (three sets of two equivalent nuclei each) of the cycloheptatrienyl group. The remaining proton resonates at δ2.85 and 2.34 for (43) and (44), respectively, and is coupled to two of the vinyl protons, thus appearing as a triplet. The phenyl protons are found in the usual aromatic region, between δ7-8.

In the ^{13}C NMR spectra, the methine carbon resonates at δ36.4 (43) or 34.4 (44); the three sets of signals from the vinylic carbons are found between δ122-126 and at δ133 and are assigned, together with the methine resonance, by off-resonance decoupling experiments. The phenyl resonances are found as multiplets between δ128-136 and exhibit splitting patterns consistent with coupling to two ^{31}P nuclei. The C_5H_5 resonances are singlets at δ94.4 (43) or 93.6 (44) while the metal-bonded carbons in (43) and (44) give triplets at δ347 and 352, respectively, the low-field chemical shift being consistent with their extremely electron-deficient nature, and similar to those found for other vinylidene complexes. For (43), the β-carbon resonance was not conclusively identified and probably lies under the phenyl multiplets. Crystals of (43) or (44) suitable for X-ray structural determination could not be obtained, due to decomposition in the X-ray beam; however, the analogous complex [Ru{C=CPh(C_7H_7)}(dppe)-(η-C_5H_5)][PF_6] (45) was prepared and crystallographically characterised.[37]

X-ray structure of [Ru{C=CPh(C_7H_7)}(dppe)(η-C_5H_5)][PF_6] (45)

The structure of the cation in (45) is shown in Figure 2. As the metal coordination for this complex is discussed in more detail in Chapter 3, discussion here will be restricted to the vinylidene ligand.

The Ru-C distance of 1.848(9)Å in (45) is very short, as in (33) (*vide supra*). The C=C bond length [1.32(1)Å] implies a bond order of *ca* two, and is similar to those of the localised C=C bonds in the C_7 ring [1.29(2)-1.32(1)Å]. The Ru-C(33)-C(34) system is almost linear [174.9(6)°]. The X-ray structure confirms the presence of the non-planar, tub-shaped cycloheptatrienyl group. Steric congestion in (45) is reduced by the almost orthogonal arrangement of the phenyl ring planes.

Reactivity of cycloheptatrienylvinylidene complexes

The addition of sodium methoxide to (43) afforded the parent acetylide complex, Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5). The cycloheptatrienyl group was lost as the substituted cycloheptatriene, C_7H_7OMe; although this compound could not be isolated in a pure state, mass spectral evidence of its identity was obtained (a species showing a parent ion at *m/z* 122, calculated for C_7H_7OMe).

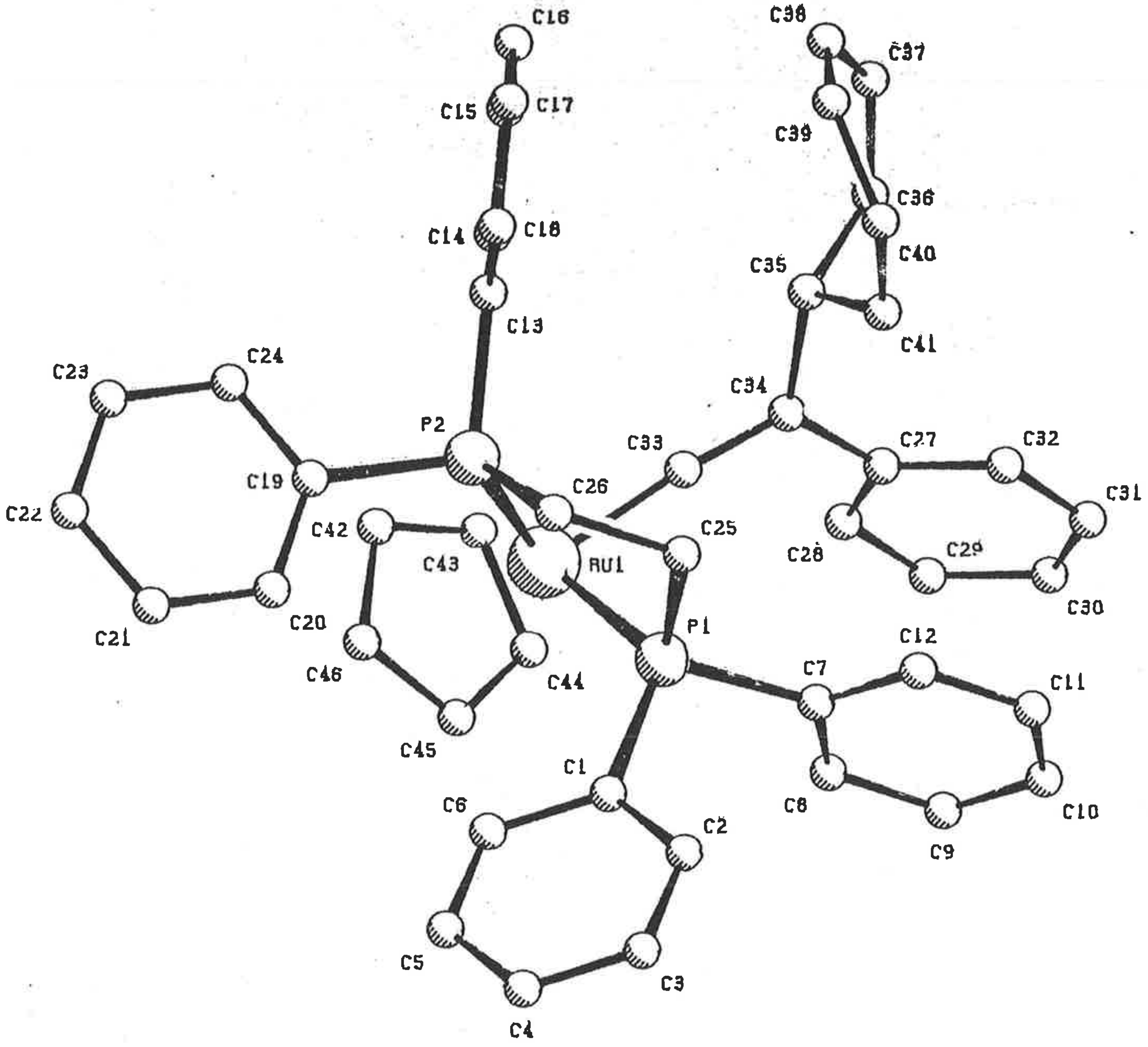


Figure 2: PLUTO plot of the structure of the cation in [Ru{C=CPh(C_7H_7)}(dppe)(η-C_5H_5)][PF_6] (45).

Other reactions also resulted in ready displacement of the C_7H_7 group; as above, probably as the appropriately substituted cycloheptatriene.[38] Attempts to add hydride (using $K[BHBu^s{}_3]$) or methanol to (<u>43</u>) or water to (<u>45</u>), gave respectively $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and $[Ru(CO)(dppe)(\eta\text{-}C_5H_5)]^+$, formed by displacement of the C_7H_7 group from the cycloheptatrienyl-vinylidene complexes, followed in the latter cases by subsequent transformation of the acetylide in the presence of a trace of acid generated in the reaction, or present in the tropylium salt despite precautions taken to dry this material *in vacuo*. The observed reactions presumably result from the high stability of the $[C_7H_7]^+$ cation and its consequent ready displacement, and parallel the corresponding reactions with aryldiazovinylidene complexes.

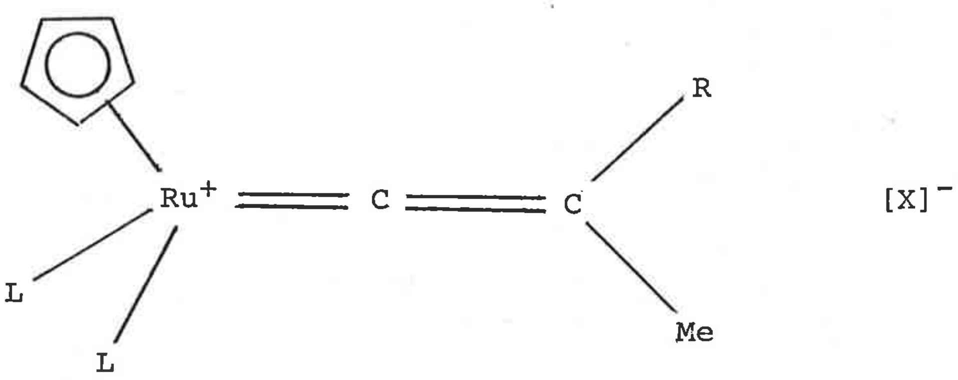
<u>Preparation of $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$ (46)</u>

Addition of a suspension of $[MeCO][SbCl_6]$ in diethyl ether to a suspension of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ in the same solvent produced a red solution. The solvent was removed and the resultant red-orange powder was left under nitrogen overnight during which time the solid turned green. The major product, obtained after chromatography, was identified as $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$ (<u>46</u>) on the basis of its spectral properties and microanalysis. The IR spectrum contains a medium strength absorption at 1655 cm^{-1} assigned to the C=C double bond of the vinylidene ligand, and a strong band at 346 cm^{-1} arising from $\nu(SbCl)$ of the $[SbCl_6]^-$ anion. The ^1H NMR spectrum has the usual resonances arising from the cyclopentadienyl (δ5.28, singlet) and phenyl (δ7.26, multiplet) groups. The FAB mass spectrum was most informative (*vide infra*); a strong molecular cation (*m/z* 827) readily losing the added electrophile to give an ion corresponding to the molecular ion of the parent acetylide (*m/z* 792). The FAB mass spectra of this and some other vinylidene complexes prepared are discussed in more detail later. Final confirmation of the identity of (46) was obtained by its preparation, as a $[PF_6]^-$ salt, by a rational route;[39] addition of Cl_2 to $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ resulted in the formation of the cationic halovinylidene complex.

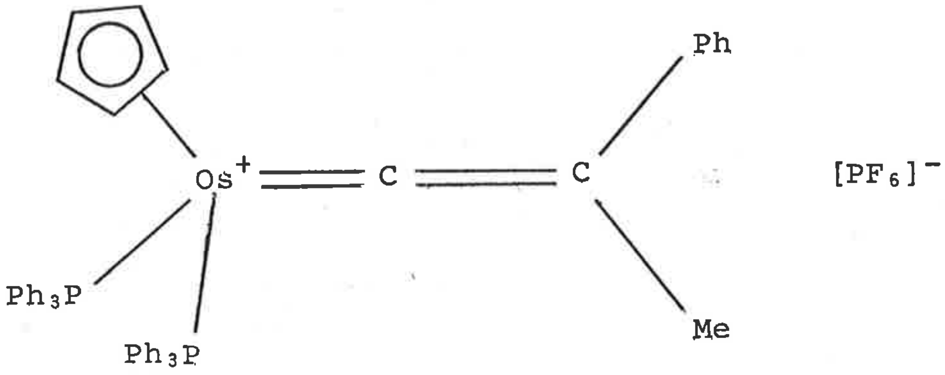
2. Preparation and properties of alkylvinylidene complexes

Several years ago, Davies *et al*[24] reported that alkylvinylidene complexes could be obtained by reacting iron and ruthenium σ-acetylide complexes with primary alkyl halides (MeI, EtI and $PhCH_2Br$). Independently, a study of the reactions of some ruthenium and osmium acetylides with alkyl halides has been made, and these results, which largely complement those of the Oxford group, are described below, together with reactions of some of the resulting vinylidene complexes with methyl lithium.

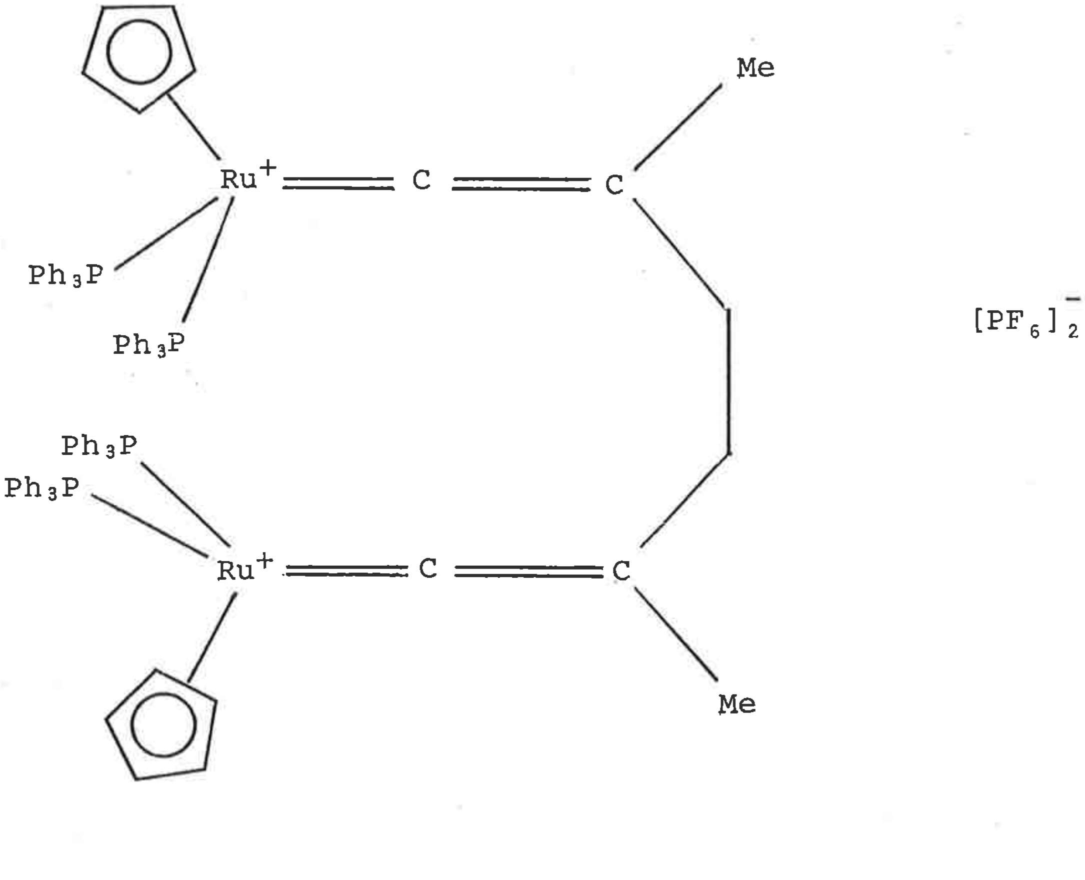
Heating a mixture of $Ru(C{\equiv}CR)(L_2)(\eta\text{-}C_5H_5)$ and excess iodomethane in refluxing dichloromethane overnight afforded red solutions; suitable work-up procedures (involving Schlenk techniques due to the oxidative sensitivity of the products) afforded pink-, orange- or buff-coloured powders of the corresponding vinylidene complexes [(47) - (58)], isolable as the iodide or (by metathesis) hexafluorophosphate salts. These complexes were identified by elemental microanalyses, from their spectral properties, and, in the case of (48), by a single-crystal X-ray diffraction study; (47) and (53)



	R	L_2	X
(<u>47</u>)	Ph	$(PPh_3)_2$	PF_6
(<u>48</u>)	Ph	$(PPh_3)_2$	I
(<u>50</u>)	Ph	dppm	I
(<u>51</u>)	Ph	dppe	PF_6
(<u>52</u>)	Ph	$(CNBu^t)(PPh_3)$	PF_6
(<u>53</u>)	Me	$(PPh_3)_2$	PF_6
(<u>54</u>)	Me	$(PPh_3)_2$	I
(<u>55</u>)	C_6H_4F-4	$(PPh_3)_2$	PF_6
(<u>56</u>)	C_6F_5	$(PPh_3)_2$	I
(<u>57</u>)	$(CH_2)_2C_2H$	$(PPh_3)_2$	PF_6


Os$^+$
C
C
Ph
Me
Ph$_3$P
Ph$_3$P
[PF$_6$]$^-$

(<u>49</u>)


Ru$^+$
C
C
Me
Ph$_3$P
Ph$_3$P
[PF$_6$]$_2^-$
Ph$_3$P
Ph$_3$P
Ru$^+$
C
C
Me

(<u>58</u>)

had been obtained previously by methylation of the appropriate acetylide using $[Me_3O][PF_6]$.[40]

Their IR spectra contain medium intensity bands between 1630-1700 cm^{-1} assigned to $\nu(C{=}C)$ from the vinylidene group and, in the case of the $[PF_6]^-$ salts, a strong broad absorption at *ca* 840 cm^{-1} for $\nu(PF)$. In the ^1H NMR spectra, the C_5H_5 resonances occur as singlets in the range δ *ca* 5.1 - 5.5 and the phenyl groups occur in the usual place; the methyl groups occur as singlets from δ1.25 - 2.25. Other resonances are characteristic of the various functional groups in the individual complexes. The ^{13}C NMR spectra of (48) and (54) were obtained; the cyclopentadienyl resonances are found at δ *ca* 94, similar to those in the aryldiazovinylidene complexes (*vide supra*), and the methyl groups' resonances at δ *ca* 12.5. The β-carbons resonate at δ125.3 (48) and δ117.5 (54); the α-carbon was only detected for the former complex, and is found at the usual strongly deshielded downfield position for this carbon, at δ354, as a triplet with coupling to the two phosphines. The crystal structure of (48) was determined, and is discussed below.

X-ray structure of $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]I$ (48)

The structure of the cation in (48) is shown in Figure 3, and confirms the presence of the methylphenylvinylidene ligand. As with the X-ray structures of the other vinylidene complexes in this Chapter, discussion is limited to the vinylidene ligand geometry. The Ru-C(6) distance of 1.863(10)Å and the C=C double bond value of 1.293(15)Å are comparable to values found for the other ruthenium vinylidene structures; a slight bending at the α-carbon occurs to give a Ru-C(6)-C(7) angle of 172.8(11)°. Angles about the β-carbon

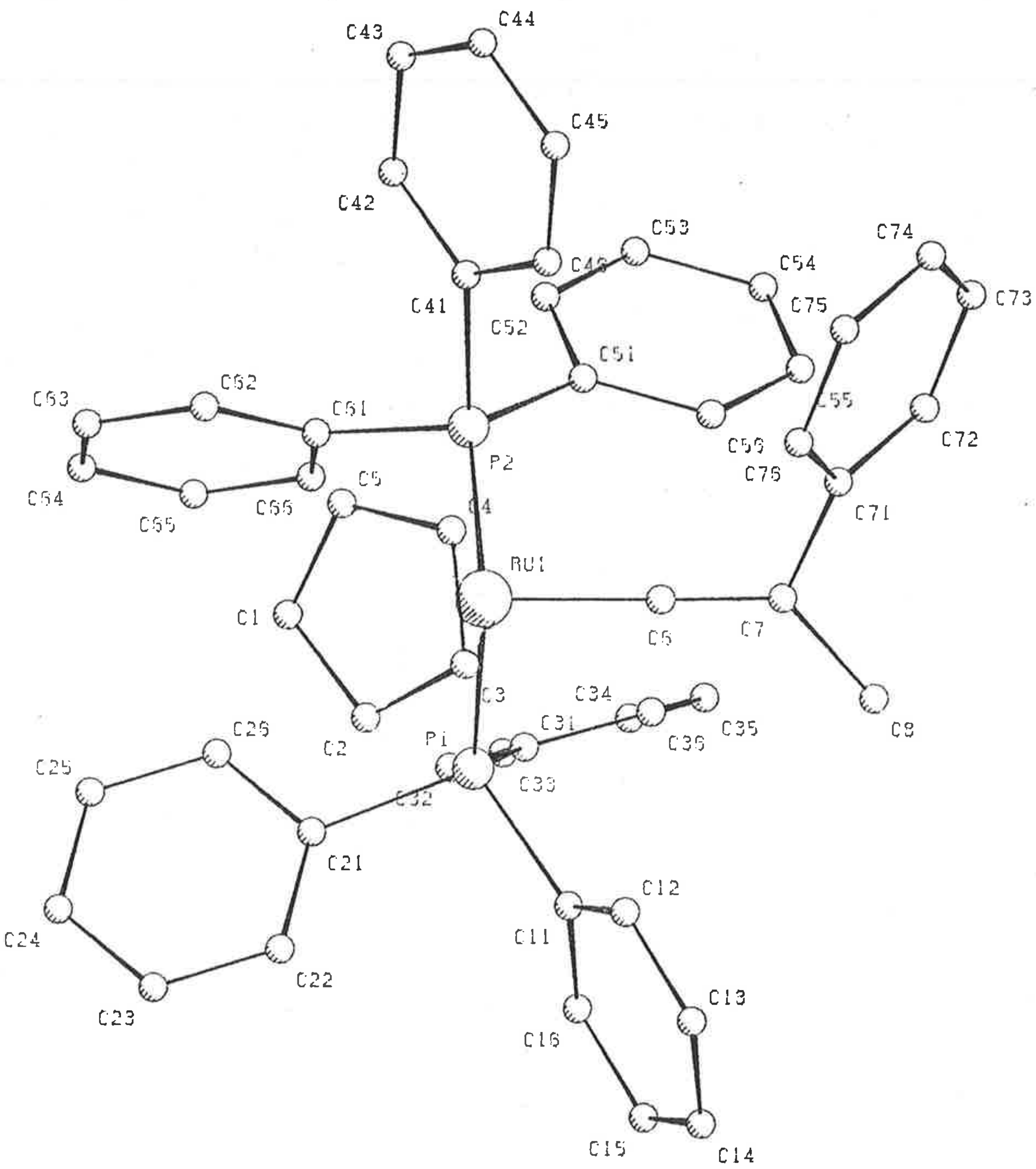


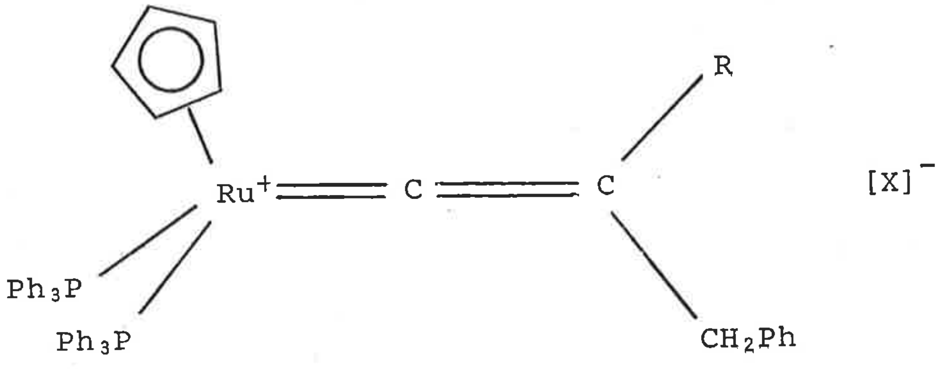
Figure 3: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the structure of the cation in [Ru(C=CMePh)$(PPh_3)_2$-(η-C_5H_5)]I (48).

[C(6)-C(7)-Me 117.0(11)° and C(6)-C(7)-Ph 125.1(12)°] indicate that there is relatively little distortion from trigonal geometry at C(7). Structural parameters for some ruthenium-vinylidene complexes are collected in Table 1.

Reactions of ruthenium acetylides with other organic halides

The successful reaction of Group VIII metal acetylides with iodomethane prompted the natural extension of this synthesis to other organic halides; if successful, these reactions would generate a much wider range of vinylidene complexes than would be available *via* cationic alkylating agents.

Reactions between ruthenium acetylides and primary organic halides were uniformly successful. Thus, reaction between $Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ (R = Me,Ph) and benzyl bromide in refluxing chloroform overnight afforded the

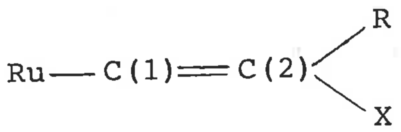


(59) R = Ph, X = PF_6

(60) R = Me, X = Br

TABLE 1

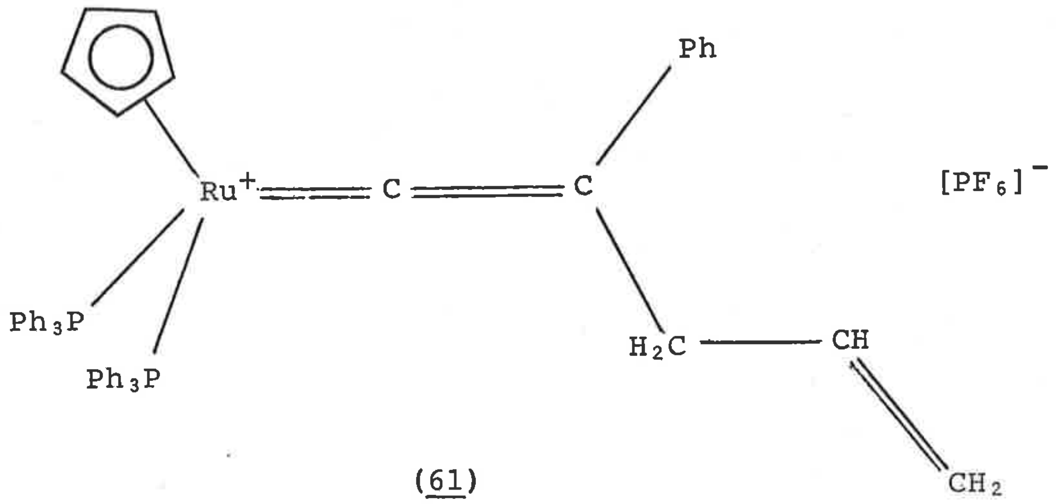
Structural parameters for some ruthenium vinylidene complexes



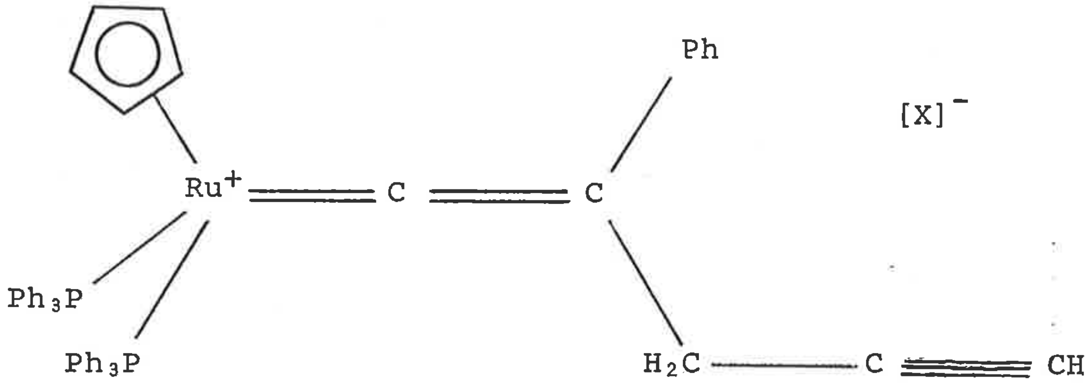
R	X	Bond distances (Å)		Bond angles (°)			Ref.
		Ru-C(1)	C(1)-C(2)	Ru-C(1)-C(2)	C(1)-C(2)-R	C(1)-C(2)-X	
Ph	C_7H_7	1.848(9)	1.32(1)	174.9(6)	121.1(6)	118.1(7)	this work
Me	H	1.845(7)	1.313(10)	180(2)	125.1(6)	-	41
Me	Ph	1.863(10)	1.293(15)	172.8(1)	117.0(11)	125.1(12)	42
Ph	$N{=}NC_6H_3Me_2$	1.823(9)	1.34(1)	169.9(7)	121.4(8)	114.4(8)	this work
C_6H_4Br-4	Br	1.85(1)	1.31(2)	169.4(14)	126.8(15)	116.8(13)	43

corresponding benzylvinylidene complexes, (59) and (60), in good (>60%) yield, characterised from their spectral data and microanalysis. The IR spectra contain the usual ν(C=C) bands [and ν(PF) in the case of (59)]; the ^{1}H NMR spectra have resonances at δ *ca* 3.5, assigned to the methylene groups, together with resonances characteristic of the cyclopentadienyl and phenyl groups. In the ^{13}C NMR spectrum of (59), the methylene carbon was detected at δ32.4, the cyclopentadienyl (δ94.6) and phenyl (δ127 - 138) in their usual regions, and the α-carbon (δ349.0) in its customary downfield position, coupled to the two phosphorus nuclei.

Similar reactions between $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ and primary halides with unsaturated functional groups, allyl chloride and propargyl bromide, also afforded vinylidene complexes [(61) - (63)], characterised as before. However, analogous reactions with primary organic dihalides gave varying degrees of substitution of halide; thus, with 1,3-dibromopropane, only (64) was obtained and with diiodomethane, (65) was isolated, although the organic halide was present in excess. Complexes (64) and (65) were characterised on the basis of their IR, ^{1}H NMR and [in the case of (64)] ^{13}C NMR spectra; (64) has the usual bands and resonances in the IR and ^{1}H NMR spectra, together with three multiplets at δ2.4 - 3.3, assigned to the three methylene groups. The ^{13}C NMR spectrum of (64) contains three signals at δ25 - 34 arising from the methylene groups; the cyclopentadienyl resonance occurs at δ 94.4. The IR spectrum of (65) contains bands assigned to ν(C=C) and ν(PF); in the ^{1}H NMR spectrum, the methylene group is found as a singlet at δ2.7. The dppe analogue of (64) was prepared similarly.

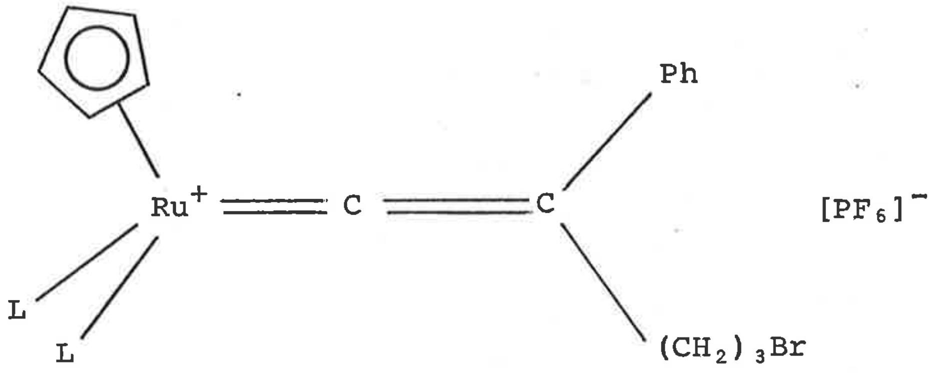


(61)



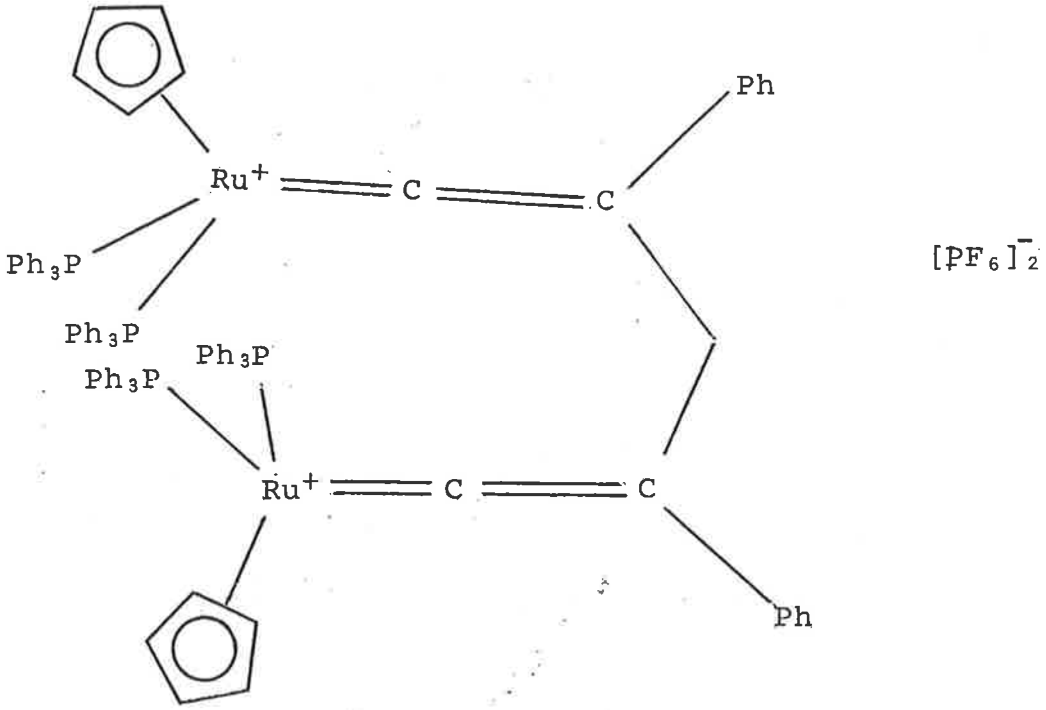
(62) X = Br

(63) $X = PF_6$



(64) L = PPh$_3$

(66) L$_2$ = dppe

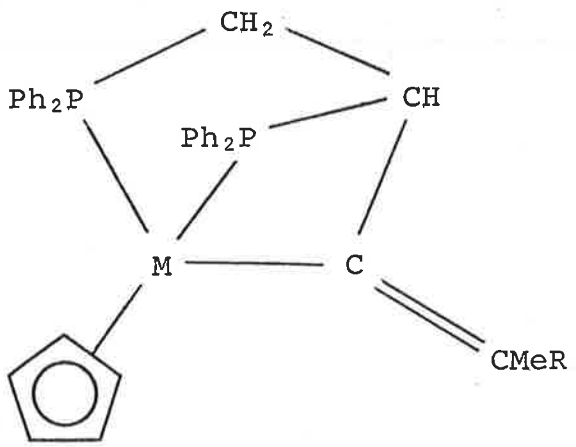


(65)

Reaction of $Ru(C\equiv CPh)(PPh_3)_2(\eta-C_5H_5)$ with iodoform produced a complex mixture of at least eight products, and was not pursued further, and with the fluorocarbon CF_3I led to decomposition and a ruthenium mirror being deposited on the reaction vessel. The synthesis could not be extended to secondary or tertiary halides; bromocyclopropane and 2-bromo-2-methylpropane both afforded $RuBr(PPh_3)_2(\eta-C_5H_5)$ (55% and 90% respectively), the former accompanied by a small amount (13%) of $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (the metal carbonyl cation is the oxidation product of all of the alkylvinylidenes synthesized).

<u>Reactions of some alkylvinylidenes with methyl lithium</u>

The α-carbon of metal vinylidene complexes is extremely electron deficient; the reactions of the iron complex $[Fe(C{=}CH_2)(CO)(PPh_3)(\eta-C_5H_5)]^+$ with reagents HX have been studied in some detail, and involve addition of the nucleophilic X^- to the α-carbon with concomitant proton addition to the β-carbon, to afford in most cases iron-carbene complexes.[44] The iron complex $[Fe(C{=}CMe_2)(dppe)(\eta-C_5H_5)]^+$ (<u>67</u>) adds H^- to the α-carbon to give the vinyl product $Fe(CH{=}CMe_2)(dppe)(\eta-C_5H_5)$.[45] However, (<u>67</u>) reacted with $NaN(SiMe_3)_2$ or KOH to give (<u>68</u>) by an intramolecular addition of the deprotonated dppe ligand to the α-carbon.[46] In view of these results, it is perhaps not surprising that whereas methyl lithium did not react with $[Ru(C{=}CMe_2)(PPh_3)_2(\eta-C_5H_5)]^+$ or $[Ru(C{=}CMePh)(PPh_3)_2(\eta-C_5H_5)]^+$, it afforded (<u>69</u>) on reaction with $[Ru(C{=}CMePh)(dppe)(\eta-C_5H_5)]^+$; the bulky phosphines restrict attack at the α-carbon to the intramolecular nucleophile. The mass spectrum of complex (<u>69</u>)



(68) M = Fe, R = Me

(69) M = Ru, R = Ph

contains a band corresponding to the molecular ion; its ^1H NMR spectrum shows differences when compared with (68) in the resonances of the methylene and methine protons. Thus, an X-ray diffraction study of (69) was undertaken to verify its identity.

X-ray structure of $Ru\{C(=CMePh)CH(PPh_2)CH_2PPh_2\}(\eta-C_5H_5)$ (69)

The structural study confirms the identity of the product (Figure 4). The bicyclic ligand occupies three coordination positions, with the $\eta-C_5H_5$ ligand completing the distorted octahedral environment of the metal. The Ru-C(Cp) distances [range 2.204(6) - 2.235(6), av. 2.222Å] are within the overall range of similar distances (Chapter 3). The two Ru-P distances [2.239(1), 2.241(2)Å] are *ca* 0.006Å shorter than those in several other dppe complexes. The Ru-C(6) separation [2.149(5)Å] is one of the longest Ru-C(sp^2) distances reported. Within the vinyl ligand, the C(6)-C(10) single bond is 1.534(7)Å, while the C(6)=C(7) double bond is 1.329(3)Å.

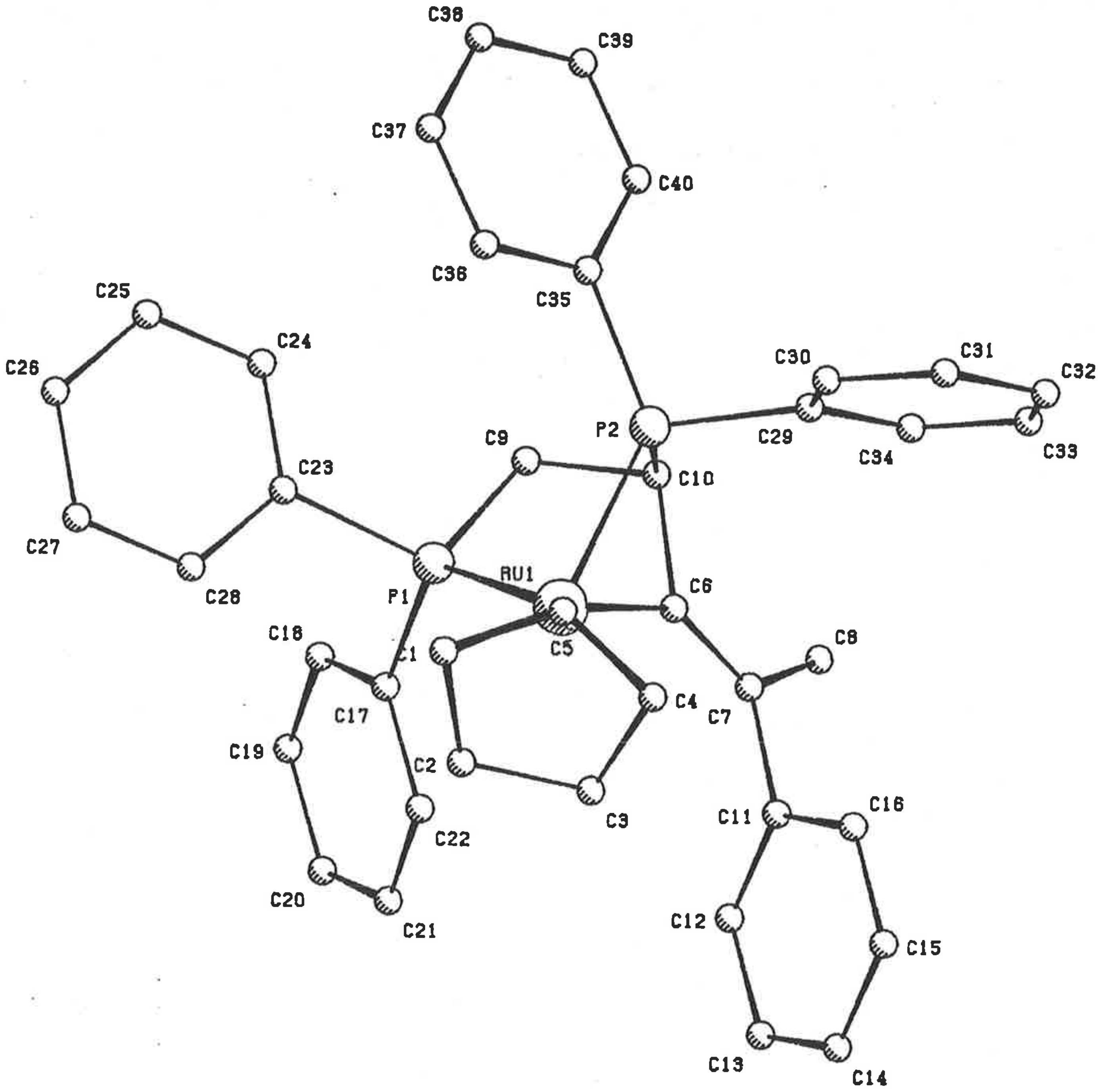


Figure 4: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru\{C(=CMePh)CH(PPh_2)CH_2PPh_2\}$-$(\eta$-$C_5H_5)$ (69).

Angles subtended at the metal atom by the three ligand atoms are all <90° [P(1)-Ru-P(2) 85.1(1), P(1)-Ru-C(6) 74.3(2), P(2)-Ru-C(6) 64.8(1)°], while those about C(6) show the influence of the small ring size: the intraring angle Ru-C(6)-C(10) is 100.6(3)°, while Ru-C(6)-C(7) has opened to 136.9(4), and C(10)-C(6)-C(7) is nearly normal at 122.5(5)°. The four-membered ring is folded about the Ru-C(10) vector [dihedral Ru-C(6)-C(10)/Ru-P(2)-C(10) 47.5°; *c.f.* 47.4° in (68)].

The above data confirm the strained nature of the bicyclic chelate system, which appears to be relieved by unusual lengthening of the Ru-C σ-bond and by unusually large deformations about C(6). Comparison with the iron analogue (68), which is not isomorphous with (69), shows that the Fe-C(Cp) [2.108Å, av] and Fe-C(6) [2.030(7)Å] distances are about 0.12Å shorter, and the Fe-P [2.150(2), 2.164(2)Å] are about 0.08Å shorter, than those found in (69). The angles within the four- and five-membered rings are generally similar, except for those about the metal atoms, which contract (by *ca* 2° for P-M-P or *ca* 4° for P-M-C angles) or about C(10), which increase by 0.7 - 2.5° in the ruthenium complex. The most significant difference between the two complexes is found in the C(6)-C(10) separation, which is 0.11Å longer in the iron derivative. It is evident that the presence of the larger ruthenium atom allows ring strain to be reduced as a result of increased atom separation.

FAB mass spectra of vinylidene complexes

The technique of ionisation of substrates by fast atom bombardment (FAB) has extended the utility of mass spectrometry to the analysis of both high molecular weight and ionic materials. Its application to organometallic molecules was demonstrated in the first account,[47] and a wide variety of studies have been described and reviewed.[48,49] FAB ionisation is admirably suited to ruthenium vinylidene complexes, and the spectra obtained from complexes described in this Chapter are analysed below.

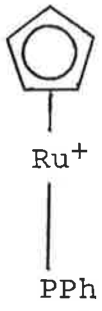
All positive ion spectra contain ions corresponding to the cation. The aryldiazovinylidenes studied by this technique were $[Os(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (32), $[Ru\{C{=}C(C_6F_5)N{=}NC_6H_3Me_2\text{-}3,4\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (35) and $[Ru(C{=}CMeN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (37); the osmium complex also has a matrix adduct ion at highest *m/z* value. Two major fragmentation routes for the molecular cation are loss of PPh_3 and of the aryldiazo fragment, which latter parallels the chemistry; in the case of (35), loss of arylnitrene also occurs, while with (37), loss of N_2 gives an ion at *m/z* 958. The base peaks are centred on *m/z* 427 ($[Ru(PPh_3)(C_5H_5)-nH]^+$) for the ruthenium complexes; for the osmium complex (32), the analogous ion at *m/z* 518 is found, but is exceeded in intensity by the phosphido ion $[Os(PPh_2)(C_5H_5)]^+$.

The spectrum of the cyclometallated complex $[Ru\{C{=}CPh\overline{N{=}NC_6H_4Mn}(CO)_4\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (42) was also obtained. In this, the highest mass ion corresponds to the cation, which then loses five fragments of 28 m.u. (four CO+N_2). An alternative fragmentation route involves loss of 4CO+Mn, with subsequent loss of N_2, N_2Ph, PPh_3 and Ph fragments; an ion at *m/z* 719 corresponds to the carbonyl cation $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$.

Although FAB mass spectra of the cycloheptatrienylvinylidene complexes (43) and (44) were not determined, spectra of analogues prepared subsequently were obtained; the molecular cations fragment by competitive loss of the two vinylidene substituents and in the two spectra obtained gave base peaks corresponding to $[Ru(PPh_3)(C_5H_5)]^+$ and $[Ru(dppe)(C_5H_5)]^+$. For the chlorovinylidene complex $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$ (46), the strong molecular cation loses the Cl^+ to give an ion corresponding to the parent acetylide $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]^+$ at *m/z* 792; subsequent fragmentation is by competitive loss of the phenylacetylide group and one of the phosphines to give finally $[Ru(PPh_3)(C_5H_5)]^+$ at *m/z* 429.

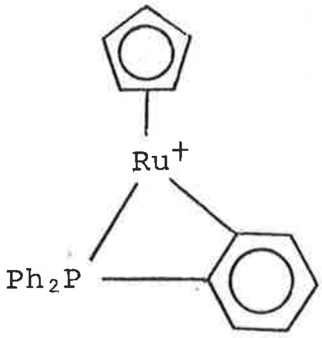
Of the alkylvinylidenes, FAB mass spectra of $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (47), $[Os(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (49), $[Ru(C{=}CMeCH_2CH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (57), $[Ru(C{=}CPhCH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (59), $[Ru(C{=}CPhCH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (63), $[Ru(C{=}CPhCH_2CH_2CH_2Br)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (64), $[CH_2\{(CPh{=}C)Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2][PF_6]_2$ (65) and $[Ru(C{=}CPhCH_2CH_2CH_2Br)(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (66) were obtained. In the osmium complex, the base peak corresponds to $[M\text{-}PPh_3]^+$; in all other cases it is $[Ru(PPh_3)(C_5H_5)]^+$. As with the aryldiazovinylidene complexes, loss of phosphine and fragmentation of the vinylidene ligand are the main fragmentation routes from the molecular ion. In the case of (65), the peak at highest mass (*m*/*z* 1744) corresponds to $[M+PF_6]^+$. In several spectra, the carbonyl-containing cation $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$ is present, probably owing to oxidation of the vinylidene ligand as previously observed.[5]

Comparisons with electron impact (EI) generated spectra cannot be direct, since these ionic complexes do not give EI spectra; however, spectra of related neutral complexes $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ are generally characterised by weak molecular ions, ready loss of X and PPh_3, with base peaks centred on *m*/*z* 427. It has previously been suggested that ions at *m*/*z* 427, 428 and 429 have the composition $[Ru(PPh_3)\text{-}(C_5H_5)\text{-}nH]^+$ (n = 2, 1 and 0, respectively), with structures



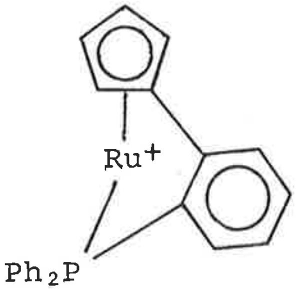
m/*z* 429

(A)



m/*z* 428

(B)



m/*z* 427

(C)

such as (A), (B) and (C); molecular complexes containing these structural fragments are known.[50] The FAB mass spectra contrast with the EI mass spectra in having increased relative intensities of ions containing two PPh_3 ligands and in preserving the Ru-element bond in the fragment X (in this case the Ru-C bond to the vinylidene ligand).

CONCLUSION

Ruthenium and osmium σ-acetylide complexes react with electrophiles to give the corresponding vinylidene complexes. Aryldiazonium cations afford aryldiazovinylidene complexes, whose reactivity toward nucleophiles is characterised by cleavage of the aryldiazo group; this functional group can be methylated or cyclomanganated. Analogously, tropylium ion affords cycloheptatrienylvinylidene complexes, the reactivity of which closely parallels that of the aryldiazovinylidene complexes. Primary organic halides give alkylvinylidenes, a reaction which could not be extended to secondary or tertiary halides. The FAB mass spectra of these vinylidenes proved useful in assignment; they differ from EI spectra of similar ruthenium complexes in favouring phosphine loss and preserving the Ru-vinylidene bond.

EXPERIMENTAL

General conditions

All reactions were run under nitrogen except those involving CO or H_2; no special precautions were taken to exclude air during work-up except in the preparation of alkylvinylidenes (Schlenk techniques), since most complexes proved to be stable as solids, and for short times in solution. Solvents were dried and distilled (thf from sodium diphenylketyl) before use. Pressure reactions were carried out in a small stainless steel laboratory autoclave (Carl Röth, Karlsruhe) of internal volume 100 ml, equipped with an internal glass liner. Structure solution and refinement details for $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ can be found in Chapter 3.

Instruments

Perkin-Elmer 683 double-beam spectrometer, NaCl optics except where indicated (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS 3074 mass spectrometer (mass spectra at 70 eV ionising energy, 8 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 6/1 dithiothreitol/dithioerythritol or 3-nitrobenzyl alcohol [for (42)]. The complexes were made up as *ca* 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials

The ruthenium and osmium acetylide complexes were prepared by the literature methods,[40,51,52] while the aryldiazonium salts were made by diazotisation of the appropriate substituted aniline with $NaNO_2/HBF_4$; $[PhN_2]$-$[PF_6]$, $[C_7H_7][PF_6]$ and $[MeCO][SbCl_6]$ were obtained from Cationics Inc., Cleveland, Ohio, and vacuum dried prior to use. $[Me_3O][SbCl_6]$ was obtained from Aldrich Chemical Company Inc., Milwaukee, Wisconsin; the $Mn(CH_2Ph)(CO)_5$ was prepared by reacting $[Mn(CO)_5]^-$ [from $Mn_2(CO)_{10}$+Na/Hg] with benzyl bromide. Alkyl halides were commercial products and used after removal of iodine (if necessary) and distillation.

Chromatography

In column chromatography, Florisil or silica was used as adsorbent; preparative TLC was on 20 x 20 cm plates coated with Kieselgel 60 GF_{254} (Merck, Darmstadt).

Preparation of aryldiazovinylidene complexes

(a) $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (29) - A suspension of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) in tetrahydrofuran (10 ml) was treated with an excess of a suspension of $[PhN_2][PF_6]$ in diethyl ether. A red-orange solution formed immediately. After stirring for 10 min, the solvent was removed *in vacuo*; a dichloromethane extract of the residue was filtered, and addition of methanol to the filtrate followed by slow evaporation afforded red crystals of $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (29) (226 mg, 86%), m.p. 177-181°C (dec.). (Found: C 63.1, H 4.4, N 2.7; $C_{55}H_{45}F_6N_2P_3Ru$ requires C 63.4, H 4.4, N 2.7%). IR (Nujol): $\nu(C{=}C) + \nu(N{=}N)$ 1585m, $\nu(PF)$ 835s(br) cm^{-1};

other bands at 1437m, 1408w, 1308w, 1233w, 1195w, 1155w, 1090w, 1075w, 1020w, 999w, 973w, 930w, 922w, 898w, 875w, 777w, 745w, 713w, 649s cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 5.28, s, 5H, C$_5$H$_5$; 7.26, m, 40H, Ph. ^{13}C NMR: δ(CDCl$_3$) 96.45, C$_5$H$_5$; 122.18, RuC=*C*; 128.86-133.83, Ph; 125.38, 153.49, 160.44, N=NPh; 362.01, t, *J*(CP) 15.8 Hz, RuC.

The following complexes were prepared similarly:

(b) [Ru(C=CMeN=NPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]. 0.5CH$_3$OH (30) - from Ru(C≡CMe)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.274 mmol), as red-orange crystals (263 mg, 96%), m.p. 183-187°C (dec.). (Found: C 60.0, H 4.5, N 2.8; C$_{50}$H$_{43}$F$_6$N$_2$P$_3$Ru. 0.5CH$_4$O requires C 60.9, H 4.6, N 2.8%). IR (Nujol): ν(C=C) + ν(N=N) 1608m, ν(PF) 835s(br) cm^{-1}; other bands at 1438w, 1300w, 1220w, 1175w, 1146w, 1090m, 1070w, 1038s, 1000w, 973w, 878w, 852s, 825s, 776w, 746m, 738w, 720w, 700m, 688m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.91, s, 3H, Me; 3.48, s, 1.5H, MeO; 5.35, s, 5H, C$_5$H$_5$; 7.42, m, 35H, Ph.

(c) [Ru{C=C(C$_6$F$_5$)N=NPh}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$].CH$_3$OH (31) - from Ru(C≡CC$_6$F$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.226 mmol), as orange crystals (130 mg, 49%), m.p. 145-147°C (dec.). (Found: C 56.9, H 3.7, N 2.3; C$_{55}$H$_{40}$F$_{11}$N$_2$P$_3$Ru·CH$_4$O requires C 57.8, H 3.8, N 2.4%). IR (Nujol): ν(C=C) + ν(N=N) 1590m, ν(PF) 835s(br) cm^{-1}; other bands at 1514m, 1494m, 1440m, 1415w, 1308w, 1161w, 1151w, 1090m, 1080w, 1018w, 998w, 984w, 941w, 900w, 764m, 746m, 717w, 693s cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.47, s, 3H, OMe; 5.49, s, 5H, C$_5$H$_5$; 7.32, m, 35H, Ph. ^{13}C NMR: δ(CDCl$_3$) 97.54, C$_5$H$_5$; 122.49, RuC=*C*; 128.90-133.20, Ph. 44 mg (22%) Ru(C≡CC$_6$F$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$) was recovered.

(d) $[Os(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (32), from $Os(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (80 mg, 0.091 mmol), as orange crystals (96 mg, 93%), m.p. 202-205°C (dec.). (Found: C 58.10, H 4.04, N 2.49; $C_{55}H_{45}F_6N_2OsP_3$ requires C 58.40, H 4.01, N 2.48%). IR (Nujol): ν(C=C) + ν(N=N) 1593s, ν(PF) 839s(br) cm^{-1}; other bands at 1445w, 1440m, 1418w, 1311w, 1242m, 1200w, 1158w, 1093m, 1072w, 1028w, 1024w, 1019w, 1001w, 937w, 922w, 907w, 779w, 752w, 748w, 718m, 699m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 5.43, s, 5H, C_5H_5; 7.23, m, 40H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 93.58, C_5H_5; 122.20, OsC=*C*; 128.39-134.93, Ph; 124.30, 153.38, 158.99, N=NPh.

(e) $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (33) was prepared from $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) and $[3,4\text{-}Me_2C_6H_3N_2][BF_4]$ (56 mg, 0.253 mmol) in dichloromethane (10 ml). The yellow solution became red immediately. After stirring for 5 min, the volume was reduced to 5 ml and the solution filtered into diethyl ether (100 ml), precipitating $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)][BF_4]$ (33) as an orange powder (224 mg, 88%), m.p. 144-146°C (dec.). This was crystallised from a dichloromethane/methanol mixture as the 0.67 methanol solvate. (Found: C 66.4, H 5.0, N 2.7; $C_{57}H_{49}BF_4P_2Ru.0{\cdot}67CH_4O$ requires C 66.3, H 5.0, N 2.7%). IR (Nujol): ν(C=C) + ν(N=N) 1588s, 1575m, ν(BF) 1060s(br) cm^{-1}; other bands at 1488w, 1472m, 1442s, 1434s, 1418w, 1315w, 1285w, 1241w, 1223m, 1190w, 1161w, 1150w, 999m, 889w, 856m, 839m, 826m, 798w, 752m, 747m, 720w, 695s, 673m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.14, s, 3H, Me; 2.29, s, 3H, Me; 3.48, s, 2H, MeO; 5.32, s, 5H, C_5H_5; 7.07-7.40, m, 38H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 19.57, Me; 96.06, C_5H_5; 125.43, RuC=*C*; 128.68-135.82, Ph; 119.88, 123.02, 151.97, 160.14, $N{=}NC_6$.

(f) $[Ru(C{=}CMeN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (34), from $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.274 mmol) and $[3,4\text{-}Me_2C_6H_3N_2][BF_4]$ (60 mg, 0.274 mmol), as an orange powder (225 mg, 87%), m.p. 182-184°C (dec.). (Found: C 65.6, H 5.1, N 2.9; $C_{52}H_{47}BF_4P_2Ru$ requires C 65.8, H 5.0, N 3.0%). IR (Nujol): ν(C=C) + ν(N=N) 1617s, ν(BF) 1042s(br) cm^{-1}; other bands at 1442m, 1372s, 1321w, 1312w, 1289w, 1281w, 1247w, 1208w, 1190w, 1172w, 1160w, 1098m, 1075m, 1062m, 1028m, 1001w, 888w, 853w, 839w, 825w, 762w, 747w, 727w, 702w, 698m, 668w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.92, s, 3H, C=CMe; 2.18, s, 3H, Me; 2.31, s, 3H, Me; 5.38, s, 5H, C_5H_5; 7.27, m, 33H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 7.02, C=CMe; 19.47, Me; 95.72, C_5H_5; 128.57-138.30, Ph; 119.58, 122.71, 151.69, 155.98, $N{=}NC_6$.

(g) $[Ru\{C{=}C(C_6F_5)N{=}NC_6H_3Me_2\text{-}3,4\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (35). Following the method in (a) above, $Ru(C{\equiv}CC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.227 mmol) and $[3,4\text{-}Me_2C_6H_3N_2][BF_4]$ (50 mg, 0.227 mmol) afforded a red-orange solution. The solvent was removed *in vacuo* and a dichloromethane extract of the residue was chromatographed (silica TLC plates; 1:1 acetone/light petroleum eluant), giving seven bands. The major band, red (R_f 0.60), was crystallized (dichloromethane/methanol), affording $[Ru\{C{=}C(C_6F_5)N{=}NC_6H_3Me_2\text{-}3,4\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4].MeOH$ (35) (146 mg, 58%), m.p. 166-167°C (dec.). (Found: C 61.47, H 4.17, N 2.47; $C_{57}H_{44}BF_9P_2Ru.CH_4O$ requires C 61.44, H 4.27, N 2.47%). IR (Nujol): ν(C=C) + ν(N=N) 1597s, ν(BF) 1072s(br) cm^{-1}; other bands at 1517m, 1493s, 1482m, 1440m, 1435m, 1415m, 1310m, 1281w, 1268w, 1238w, 1189w, 1164m, 1090s, 985s, 939w, 882w, 859w, 850m, 838m, 824m, 747s, 718m, 695s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.12, s, 3H, Me; 2.28, s, 3H, Me; 3.46, s, 3H, OMe; 5.55, s, 5H, C_5H_5; 7.25, m, 33H, Ph. ^{13}C NMR: δ($CDCl_3$) 19.47, Me; 97.37, C_5H_5; 128.57-139.66, Ph; 120.06, 123.27, 151.53, N=NC_6.

(h) [Ru(C=CPhN=$NC_6H_4NO_2$-4)(PPh_3)$_2$(η-C_5H_5)][BF_4].0·1CH_3OH (36), from Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.253 mmol) and [4-$O_2NC_6H_4N_2$][BF_4] (60 mg, 0.253 mmol), and crystallised (dichloromethane/methanol) as maroon crystals (180 mg, 69%), m.p. 203-205°C (dec.). (Found: C 63.81, H 4.18, N 3.79; $C_{55}H_{44}BF_4N_3O_2P_2Ru$.0·1$CH_4O$ requires C 64.13, H 4.18, N 4.07%). IR (Nujol): ν(C=C) + ν(N=N) 1605w, 1582m, 1565m, ν(NO) 1525m, 1338s, ν(BF) 1050s(br) cm^{-1}; other bands at 1438s, 1418w, 1295w, 1282w, 1261m, 1192w, 1181w, 1162w, 1154m, 1107w, 1090s, 1071s, 997m, 972s, 922w, 901w, 867m, 853w, 842w, 823w, 765w, 745m, 729m, 695s cm^{-1}. ^1H NMR: δ($CDCl_3$) 3.47, s, 0.3H, OMe; 5.39, s, 5H, C_5H_5; 7.0-8.1, m, 39H, Ph + C_6H_4. ^{13}C NMR: δ($CDCl_3$) 96.99, C_5H_5; 122.60, 124.37, N=NC_6; 128.57-134.09, Ph + C_6H_4.

(i) [Ru(C=CMeN=$NC_6H_4NO_2$-4)(PPh_3)$_2$(η-C_5H_5)][BF_4].0·5CH_2Cl_2 (37), from Ru(C≡CMe)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.274 mmol) and [4-$O_2NC_6H_4N_2$][BF_4] (65 mg, 0.274 mmol), and crystallised (dichloromethane/methanol) as red crystals of the 0.5 dichloromethane solvate (233 mg, 85%), m.p. 218-220°C (dec.). (Found: C 60.61, H 4.29, N 4.17; $C_{50}H_{42}BF_4N_3O_2P_2Ru$.0·5$CH_2Cl_2$ requires C 60.10, H 4.29, N 4.16%). IR (Nujol): ν(C=C) + ν(N=N) 1608w, 1597w, 1582m, ν(NO) 1517m, 1337s, ν(BF) 1037s(br) cm^{-1}; other bands at 1438m, 1418w, 1368s, 1357m, 1291w, 1230w, 1178m, 1148m, 1115w, 1105w, 1091m, 1078w, 1052m, 999w, 862w, 841w, 825w, 762w, 755w, 744m, 718w, 702w, 691m cm^{-1}. ^1H NMR: δ($CDCl_3$) 1.95, s, 3H, Me; 5.32, s, 1H, CH_2Cl_2; 5.47, s, 5H, C_5H_5; 7.0-8.3, m, 34H, Ph + C_6H_4.

(j) [Ru(C=CPhN=NC$_6$H$_3$Cl$_2$-2,4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$].0·25Et$_2$O (38), from Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.253 mmol) and [2,4-Cl$_2$C$_6$H$_3$N$_2$][BF$_4$] (66 mg, 0.253 mmol) as a red powder (234 mg, 85%), m.p. 191-194°C (dec.). (Found: C 62.62, H 4.26, N 2.49; C$_{55}$H$_{43}$BCl$_2$F$_4$N$_2$P$_2$Ru.0·25C$_4$H$_{10}$O requires C 62.79, H 4.28, N 2.62%). IR (Nujol): ν(C=C) + ν(N=N) 1582m, 1565m, ν(BF) 1071s(br) cm^{-1}; other bands at 1442w, 1437s, 1411w, 1402m, 1369s, 1353w, 1311w, 1279w, 1261w, 1243w, 1195w, 1182w, 1160w, 1091s, 1052s, 1035s, 995m, 919w, 900w, 855w, 838m, 822w, 791w, 758w, 746m, 695s, 683m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.18, t, *J*(HH) 7.6Hz, 1.5H, CH$_3$; 3.47, q, *J*(HH) 7.6 Hz, 1H, CH$_2$; 5.35, s, 5H, C$_5$H$_5$; 7.32, m, 38H, Ph + C$_6$H$_3$.

(k) [Ru(C=CMeN=NC$_6$H$_3$Cl$_2$-2,4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (39) from Ru(C≡CMe)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.274 mmol) and [2,4-Cl$_2$C$_6$H$_3$N$_2$][BF$_4$] (71.5 mg, 0.274 mmol), as an orange powder (169 mg, 62%), m.p. 124-126°C (dec.). (Found: C 60.14, H 3.96, N 2.66; C$_{50}$H$_{41}$BCl$_2$F$_4$N$_2$P$_2$Ru requires C 60.62, H 4.17, N 2.83%). IR (Nujol): ν(C=C) + ν(N=N) 1592m, ν(BF) 1053s(br) cm^{-1}; other bands at 1482m, 1441s, 1438s, 1400w, 1368m, 1355m, 1318w, 1280w, 1245w, 1225w, 1172m, 1091s, 1038s, 999m, 824w, 788w, 745m, 696s, 672w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.95, s, 3H, Me; 5.42, s, 5H, C$_5$H$_5$; 7.27, m. 33H, Ph + C$_6$H$_3$. ^{13}C NMR: δ(CDCl$_3$) 7.55, CH$_3$; 96.21, C$_5$H$_5$; 118.35, RuC=*C*; 127.13-134.58, Ph + C$_6$H$_3$; 148.11, 157.66, CCl.

(l) [Ru(C=CPhN=NC$_6$H$_4$OMe-4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (40), from Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (500 mg, 0.631 mmol) and [4-MeOC$_6$H$_4$N$_2$][BF$_4$] (140 mg, 0.631 mmol) as an orange powder (from dichloromethane/ethanol) (598 mg, 93%), m.p. 150-152°C (dec.). (Found: C 65.69, H 4.67, N 2.78; $C_{56}H_{47}BF_4N_2OP_2Ru$ requires C 66.34, H 4.67, N 2.76%). IR (Nujol): ν(C=C) + ν(N=N) 1605s, ν(BF) 1060s(br) cm^{-1}; other bands at 1504s, 1483s, 1438s, 1421m, 1395s, 1341w, 1320m, 1301w, 1287w, 1250s, 1210m, 1190w, 1163m, 1152m, 1030s, 1001m, 975w, 951w, 934m, 902m, 858m, 840s, 810w, 791w, 750s, 723m, 696s, 679s cm^{-1}. ^1H NMR: δ($CDCl_3$) 3.83, s, 3H, OMe; 5.31, s, 5H, C_5H_5; 7.32, m, 39H, Ph + C_6H_4. ^{13}C NMR: δ($CDCl_3$) 55.39, OMe; 96.04, C_5H_5; 113.67, RuC=*C*; 123.72, 128.62-134.81, Ph; 125.47, 148.01, 160.04, 160.97, N=NC_6; 364.54, t, J(CP) 15.3 Hz, RuC.

(m) $[Ru(C{=}CMeN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4].0{\cdot}5\text{-}EtOH$ (41) from $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.685 mmol) and $[4\text{-}MeOC_6H_4N_2][BF_4]$ (152 mg, 0.685 mmol) as maroon crystals (from dichloromethane/ethanol) (520 mg, 77%), m.p. >140°C (dec.). (Found: C 63.47, H 5.15, N 2.74; $C_{51}H_{45}BF_4N_2OP_2Ru.0{\cdot}5C_2H_6O$ requires C 63.55, H 4.92, N 2.85%). IR (Nujol): ν(C=C) + ν(N=N) 1608s, ν(BF) 1052s(br) cm^{-1}; other bands at 1505s, 1483s, 1442s, 1435s, 1420m, 1310m, 1296m, 1285w, 1252s, 1180s, 1175s, 1150m, 1000m, 938w, 876w, 847s, 839s, 825m, 810w, 785w, 770m, 749s, 723m, 697s, 685m, 660w cm^{-1}. ^1H NMR: δ($CDCl_3$) 1.21, t, *J*(HH) 7.1 Hz, 1.5H, CH_3CH_2; 1.91, s, 3H, Me; 3.69, q, *J*(HH) 7.1 Hz, 1H, CH_3CH_2; 3.85, s, 3H, OMe; 5.37, s, 5H, C_5H_5; 7.28, m, 34H, Ph + C_6H_4.

Reactions of $[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (29)

(a) With triphenylphosphine - A mixture of (29) (200 mg, 0.192 mmol) and PPh_3 (52 mg, 0.20 mmol) was heated in refluxing benzene for 26 h. The solvent was removed *in vacuo* and a dichloromethane extract of the residue was filtered; addition of methanol to the filtrate and concentration afforded yellow crystals of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (119 mg, 78%), identified on the basis of IR and TLC (R_f) by comparison with an authentic sample.[40]

(b) With 1,2-bis(diphenylphosphino)ethane - Similarly, (29) (200 mg, 0.192 mmol) and dppe (80 mg, 0.200 mmol) in refluxing benzene for 21 h afforded $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (80 mg, 53%) after a similar work-up, which was identified as above.

(c) With water - Complex (29) (200 mg, 0.192 mmol) was heated in a refluxing mixture of tetrahydrofuran (15 ml) and water (5 ml) for 2.5 d. The solvent was removed *in vacuo*. Addition of ethanol to a dichloromethane extract of the residue and concentration afforded $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ as a beige powder (116 mg, 70%), m.p. 118-120°C (dec.). (Found: C 58.49, H 4.27; $C_{42}H_{35}F_6OP_3Ru$ requires C 57.82, H 4.14%). IR (Nujol): ν(CO) 1980s(br), 1910m(br), ν(PF) 840s(br) cm^{-1}; other bands at 1589w, 1574w, 1482s, 1442s, 1436s, 1311w, 1262w, 1185w, 1170w, 1091s, 1072m, 1049w, 1028w, 999m, 929w, 742s, 721w, 695s cm^{-1}. (IR($CHCl_3$): ν(CO) 1986 cm^{-1} *c.f.* 1980 cm^{-1} in $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][BPh_4]$).[53] ^1H NMR: δ($CDCl_3$) 4.99, s, 5H, C_5H_5; 7.27, m, 30H, Ph.

(d) With methanol - A solution of (29) (200 mg, 0.192 mmol) in methanol (10 ml) was refluxed for 5 d. The light yellow crystals which had deposited were collected, dried and identified as $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (46 mg, 25%), on the basis of their IR and ^1H NMR spectra.[52] TLC of the filtrate revealed 12 bands which were not investigated further.

(e) With carbon monoxide - A solution of (29) (200 mg, 0.192 mmol) in tetrahydrofuran (30 ml) was carbonylated in an autoclave (47 atm, 100°C, 16 h). After cooling to room temperature, the CO was released. The red solution had become light yellow. The solvent was removed on a rotary evaporator and a dichloromethane extract of the residue was filtered into stirred diethyl ether, precipitating $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (61 mg, 37%) which was identified by comparison of its IR spectrum with that of an authentic sample (*vide supra*). TLC of the filtrate revealed 10 bands which were not worked up further.

(f) With dihydrogen - A solution of (29) (200 mg, 0.192 mmol) in dichloromethane (20 ml) was hydrogenated in an autoclave (50 atm, 100°C, 22 h). After cooling to room temperature, the hydrogen was released and the solvent removed on a rotary evaporator. A dichloromethane extract of the residue was chromatographed (silica, 1:1 acetone/light petroleum), and afforded seven bands; the major band (yellow, R_f 0.92) was identified as $RuCl(PPh_3)_2(\eta-C_5H_5)$ (30 mg, 22%), after crystallisation from dichloromethane/light petroleum, on the basis of its infrared and ^1H NMR spectra.[53]

(g) With iodomethane - A solution of (29) (200 mg, 0.192 mmol) in iodomethane (20 ml) was heated in an autoclave (47 atm N_2, 80°C, 20 h). After cooling to room temperature, the solution was reduced to dryness and a dichloromethane extract of the residue was filtered into diethyl ether, precipitating a light orange powder of $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]X$ (nature of anion unknown, probably a mixture of I^- and $[I_3]^-$)(130 mg), m.p. 178-181°C (dec.). (Found: C 59.10, H 4.37%). IR (Nujol): $\nu(C{=}C)$ 1696m, 1672s cm^{-1}; other bands at 1592m, 1587w, 1482s, 1438s, 1418w, 1317w, 1189w, 1162w, 1092s, 1055s, 1030s, 1014m, 999s, 882m, 873m, 838w, 820w, 783m, 751m, 721w, 702s, 697s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.93, s, 3H, Me; 5.16, s, 5H, C_5H_5; 7.05, m, 35H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 12.18, Me; 94.05, C_5H_5; 127.57-135.28, Ph. 17 mg of this salt was stirred in dichloromethane (5 ml) with NH_4PF_6 (5 mg, 0.031 mmol) for 30 min. The mixture was filtered into stirred ether, precipitating an orange powder identified as $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (12 mg) on the basis of its IR and ^1H NMR spectra.[40]

(h) With $Mn(CH_2Ph)(CO)_5$ - A mixture of (29) (250 mg, 0.240 mmol) and $Mn(CH_2Ph)(CO)_5$ (72 mg, 0.25 mmol) was heated in refluxing dichloromethane (10 ml) for 6 h. At this stage TLC indicated incomplete reaction; additional $Mn(CH_2Ph)(CO)_5$ (50 mg, 0.17 mmol) was added and the mixture refluxed for a further 21 h. The solution was cooled, the solvent was removed *in vacuo*, and a dichloromethane extract of the residue was chromatographed (silica: 1:1 acetone/light petroleum) affording five bands. The major band, purple (R_f 0.6), was crystallised from benzene/hexane as a purple powder, identified as $[Ru\{C{=}CPh\overline{N{=}NC_6H_4Mn}(CO)_4\text{-}2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (42) (52 mg, 18%), m.p. 138-140°C (dec.). (Found: C 57.71, H 3.83, N 2.14; $C_{59}H_{44}F_6MnN_2O_4P_3Ru$ requires C 58.67, H 3.67, N 2.32%).

IR (CH_2Cl_2): ν(CO) 2080m, 1999vs, 1959s cm^{-1}. ^1H NMR: δ($CDCl_3$) 5.19, s, 5H, C_5H_5; 7.27, m, 39H, Ph + C_6H_4.

(i) With $[Me_3O][SbCl_6]$. - A mixture of (29) (236 mg, 0.226 mmol) and $[Me_3O][SbCl_6]$ (121 mg, 0.226 mmol) was heated in refluxing chloroform (10 ml) for 18 h. The chloroform was removed *in vacuo*; extraction of the residue with dichloromethane, filtration, addition of ethanol and concentration afforded a yellow-brown powder which was recrystallised from dichloromethane/ethanol to give orange crystals of $[Ru(C{=}CPhN{=}NMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]$-$[PF_6][SbCl_6]$.EtOH (94 mg, 29%), m.p. 129-131°C (dec.). (Found: C 48.58, H 3.61, N 1.74; $C_{56}H_{48}Cl_6F_6N_2P_3RuSb.C_2H_6O$ requires C 48.46, H 3.79, N 1.95%). IR (Nujol): ν(N=N) + ν(C=C) 1609m, 1575m, 1564m, ν(PF) 840s(br) cm^{-1}; other bands at 1481m, 1441s, 1437s, 1418m, 1343m, 1263w, 1185w, 1161w, 1110w, 1090m, 1075w, 1025w, 999w, 933w, 886w, 775w, 742m, 718m, 692s cm^{-1}. ^1H NMR: δ($CDCl_3$)1.24, t, *J*(HH) 7 Hz, 3H, CH_3CH_2; 1.57, s, 3H, Me; 3.72, q, *J*(HH) 7 Hz, 2H, CH_3CH_2; 5.29, s, 5H, C_5H_5; 7.36, m, 40H, Ph.

(j) With $K[BH(CHMeEt)_3]$ (*K*-Selectride) A solution of (29) (200 mg, 0.192 mmol) in tetrahydrofuran (10 ml) was treated with *K*-Selectride (0.45 ml of a 0.5 *M* solution in tetrahydrofuran, 0.23 mmol). The solution was stirred for 16 h at which time two drops of ethanol were added. The solvent was then removed *in vacuo* and a dichloromethane extract of the residue was chromatographed (silica, 1:1 acetone/light petroleum), affording nine bands, one of which was identified as $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (4 mg, 3%) R_f 0.86, by TLC and IR.

(k) With sodium methoxide A suspension of (29) (200 mg, 0.192 mmol) in methanol (10 ml) was treated with sodium methoxide (0.2 ml of a 1 *M* solution in MeOH, 0.2 mmol). The resulting mixture was refluxed 2.5 h. After cooling to room temperature, the light yellow precipitate which had deposited was collected, washed with methanol and dried, and identified as $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (26 mg, 17%). TLC of the filtrate revealed eight bands which were not investigated further.

(l) With $HPF_6.OEt_2$. A solution of (29) (204 mg, 0.196 mmol) in dichloromethane (20 ml) was treated with $HPF_6.OEt_2$ (3 drops, excess), and stirred for 16 h. The solvent was then removed *in vacuo* and a dichloromethane extract of the residue was chromatographed (silica, 2:1 acetone/light petroleum), affording 3 bands, the major one of which was red (R_f 0.7) isolated as an orange powder from dichloromethane/diethyl ether, and identified as $[Ru(C{=}CPhN{=}NPh)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)][PO_2F_2]$ (84 mg, 43%), m.p. 156-158°C (dec.). (Found: C 66.10, H 4.59, N 2.78; $C_{55}H_{45}F_2N_2O_2P_3Ru$ requires C 66.20, H 4.55, N 2.81%). IR (Nujol): ν(C=C) + ν(N=N) 1590s, ν(PO) 1057s(br), ν(PF) 847m cm^{-1}; other bands at 1485m, 1439s, 1420s, 1310m, 1238m, 1197m, 1162w, 1155w, 1092s, 1080s, 1001m, 935w, 835w, 827w, 775w, 752s, 717s, 698s cm^{-1}. ^1H NMR: δ($CDCl_3$) 5.33, s, 5H, C_5H_5; 7.29, m, 40H, Ph.

Preparation of cycloheptatrienylvinylidene complexes

(a) $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (43) - A solution of $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1000 mg, 1.26 mmol) in dichloromethane (10 ml) was added to a suspension of vacuum-dried $[C_7H_7][PF_6]$ (300 mg, 1.27 mmol) in dichloromethane (10 ml), immediately giving a red solution, which was stirred for 20 min, and then evaporated to dryness. The residue was extracted with dichloromethane (5 ml), and the extract filtered into excess stirred diethyl ether to give a bright orange precipitate. Crystallisation (dichloromethane/ethanol) gave orange crystals of [Ru{C=CPh(C_7H_7)}(PPh_3)$_2$(η-C_5H_5)][PF_6] (43) (1051 mg, 81%), m.p. 170° (dec.). (Found: C 65.56, H 4.66; $C_{56}H_{47}F_6P_3Ru$ requires C 65.43, H 4.61%). IR (Nujol): ν(C=C) 1670s, ν(PF) 840vs(br) cm^{-1}; other bands at 1610w, 1593w, 1575w, 1480s, 1435s, 1395w, 1315w, 1184w, 1160w, 1090s, 1071w, 1020w, 1000m, 875m, 750(sh), 741m, 718m, 698s, 645w cm^{-1}. ^1H NMR: δ[$(CD_3)_2CO$] 2.85, t, *J*(HH) 11 Hz, 1H, CH; 5.25, s, 5H, C_5H_5; 5.34, m, 2H, =CH; 6.28, m, 2H, =CH; 6.53, m, 2H, =CH; 7.0-7.6, m, 35H, Ph. ^{13}C NMR: δ[$(CD_3)_2CO$] 36.42, s, CH; 94.44, s, C_5H_5; 123.99, s, =CH; 125.48, s, =CH; 132.68, s, =CH; 128-134, m, Ph; 346.95, t, *J*(CP) 16 Hz, RuC.

(b) [Ru{C=CMe(C_7H_7)}(PPh_3)$_2$(η-C_5H_5)][PF_6] (44) - A solution of Ru(C≡CMe)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.27 mmol) in diethyl ether (10 ml) and dichloromethane (10 ml) was treated with a suspension of [C_7H_7][PF_6] (excess) in diethyl ether. The yellow solution immediately became an orange suspension. After stirring for 15 min, the solvent was removed *in vacuo*. A dichloromethane extract of the residue was filtered; addition of methanol to the filtrate and concentration afforded orange crystals of [Ru{C=CMe(C_7H_7)}-(PPh_3)$_2$(η-C_5H_5)][PF_6] (44) (228 mg, 86%), m.p. 95-98°C (dec.). (Found: C 63.2, H 4.6; $C_{51}H_{45}F_6P_3Ru$ requires C 63.4, H 4.7%). IR (Nujol): ν(C=C) 1682m, ν(PF) 836s(br) cm^{-1}; other bands at 1609w, 1589w, 1572w, 1435m, 1315w, 1187w, 1160w, 1090m, 1033w, 996w, 875w, 756w, 741m, 692s cm^{-1}. ^1H NMR: δ($CDCl_3$)

1.90, s, 3H, Me; 2.34, t, *J*(HH) 5 Hz, 1H, CH; 5.09, s, 5H, C_5H_5; 5.25, m, 2H, =CH; 6.25, m, 2H, =CH, 6.48, m, 2H, =CH; 7.33, m, 30H, Ph. ^{13}C NMR: δ($CDCl_3$) 19.6, CH_3; 34.4, CH; 93.6, C_5H_5; 119.7, RuC=*C*; 122.0, 122.8, 125.2, =C; 128.3-136.1, Ph; 352.4, t, *J*(CP) 17 Hz, RuC.

Reaction of (43) with sodium methoxide

A suspension of $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (200 mg, 0.20 mmol) in methanol was treated with 0.93 *M* NaOMe solution (5 drops, excess). A yellow powder precipitated after *ca* 5 min. The solvent volume was reduced to 5 ml and the powder collected, washed (methanol) and dried, to give $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (143 mg, 93%), m.p. 201-203°C (dec.) *c.f.* lit.[40] 205°C (dec.). IR (Nujol): ν(C≡C) 2065 cm^{-1} *c.f.* lit.[40] ν(C≡C) 2068 cm^{-1}.

Preparation of $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$ (46)

A suspension of $[MeCO][SbCl_6]$ (879 mg, excess) in diethyl ether (10 ml) was added to $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) in the same solvent (10 ml). An immediate change from yellow suspension to red solution occurred. Evaporation afforded a red-orange solid which slowly changed to dark green overnight. The product was isolated by preparative TLC (silica gel, 1:1 acetone/light petroleum) from the largest of three green bands; crystallisation (benzene/ethanol) gave a green powder identified as $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5][SbCl_6]$ (121 mg, 41%) (46), m.p. 163-164°C (dec.). (Found: C 50.69, H 3.28; $C_{49}H_{40}Cl_7P_2RuSb$ requires C 50.66, H 3.47%). IR (KBr disc): ν(C=C) 1655m, ν(SbCl) 346s cm^{-1}; other bands at 3060w, 2922w, 2850w, 1481m, 1434s, 1418m, 1382w, 1361w, 1310w, 1188w, 1161w, 1089s, 1071w, 1025w, 999w, 832w, 821w, 781w, 740s, 693s, 614w, 551w, 532s, 520s, 512s, 500m, 461w, 422w cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 5.28, s, 5H, C_5H_5; 7.26, m, 35H, Ph.

Reactions of iodomethane

(a) With $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ - Method A A mixture of $Ru(C\equiv CPh)(PPh_3)_2(\eta-C_5H_5)$ (1190 mg, 1.50 mmol) and iodomethane (565 mg, 4.0 mmol) was heated in refluxing dichloromethane (50 ml) for 18 h. The dark red solution was cooled and NH_4PF_6 (261 mg, 1.60 mmol) added. The resulting mixture was stirred for 20 min and filtered into stirred diethyl ether (120 ml). The pink precipitate $[Ru(C{=}CMePh)(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (47), identified on the basis of IR and m.p. by comparison with an authentic sample,[40] was collected, washed (2 x 15 ml diethyl ether) and dried (570 mg, 40%). The yellow filtrate was reduced to dryness. Addition of methanol to a filtered dichloromethane extract and reduction of volume afforded yellow crystals of the starting material (500 mg, 42%).

Method B A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (250 mg, 0.32 mmol) and MeI (360 mg, 2.54 mmol) was heated in refluxing dichloromethane (10 ml) for 16 h. The solvent was removed *in vacuo*, and the residue extracted with a 3:2 dichloromethane/diethyl ether mixture (25 ml); filtration into stirred diethyl ether (100 ml) gave a pink powder of $[Ru(C{=}CMePh)(PPh_3)_2(\eta-C_5H_5)]I.CH_2Cl_2$ (48) (200 mg, 62%), m.p. 135-138°C (dec.). (Found: C 60.47, H 4.52; $C_{50}H_{43}IP_2Ru.CH_2Cl_2$ requires C 60.13, H 4.45%). IR (Nujol): $\nu(C\equiv C)$ 1690m, 1666s cm^{-1}; other bands at 1593m, 1576w, 1438s, 1432sh, 1414m, 1361m, 1312w, 1270m, 1183w, 1162w, 1111w, 1093s, 1076w, 1049w, 1028m, 1019w, 1015w, 999w, 938w, 913w, 874w, 860w, 851w, 842m, 823m, 760m, 755m, 745s, 730m, 702sh, 699s, 688s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 1.94, s, 3H, Me; 5.21, s, 5H, C_5H_5; 5.30, s, 2H, CH_2Cl_2; 6.95-7.56, m, 35H, Ph. ^{13}C NMR: δ($CDCl_3$) 12.67, Me; 94.45, C_5H_5; 125.34; RuC=*C*; 127.95-136.23, Ph; 353.66, t, *J*(CP) 15.8 Hz, RuC.

(b) With Os(C_2Ph)(PPh_3)$_2$(η-C_5H_5) - Using Method A, the reaction between Os(C_2Ph)(PPh_3)$_2$(η-C_5H_5) (189 mg, 0.22 mmol), MeI (130 mg, 0.92 mmol) and NH_4PF_6 (35 mg, 0.22 mmol) afforded [Os(C=CMePh)(PPh_3)$_2$(η-C_5H_5)][PF_6] (49) as a pink powder (160 mg, 71%), m.p. 193-197°C (dec.). (Found: C 57.4, H 4.1; $C_{50}H_{43}F_6OsP_3$ requires C 57.7, H 4.2%). IR (Nujol): ν(C=C) 1700m, 1681m, ν(PF) 840s(br) cm^{-1}; other bands at 1592m, 1576w, 1440m, 1415w, 1312w, 1187w, 1162w, 1118w(sh), 1092m, 1073w, 1050w, 1040w, 1015w, 1002w, 930w, 922w, 878w, 757m, 745m, 692s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 2.25, s, 3H, Me; 5.33, s, 5H, C_5H_5; 7.38, m, 35H, Ph.

(c) With Ru(C_2Ph)(dppm)(η-C_5H_5) - Using Method B, a mixture of Ru(C_2Ph)(dppm)(η-C_5H_5) (200 mg, 0.31 mmol) and MeI (130 mg, 0.92 mmol) gave [Ru(C=CMePh)(dppm)(η-C_5H_5)]I (50) as an orange powder (135 mg, 55%), m.p. 208-213°C (dec.). (Found: C 58.6, H 4.4; $C_{39}H_{35}IP_2Ru$ requires C 59.0, H 4.5%). IR (Nujol): ν(C=C) 1635m(br) cm^{-1}; other bands at 1594w, 1308w, 1160w, 1101m, 1048w, 1028w, 998w, 870w, 847w, 813w, 799w, 779w, 761m, 740m, 715w, 692m cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 1.28, s, 3H, Me; 4.97, m, 2H, CH_2; 5.84, s, 5H, C_5H_5; 7.43, m, 25H, Ph.

(d) With $Ru(C_2Ph)(dppe)(\eta$-$C_5H_5)$ - Using Method A, $Ru(C_2Ph)(dppe)(\eta$-$C_5H_5)$ (121 mg, 0.18 mmol), MeI (130 mg, 0.92 mmol) and NH_4PF_6 (30 mg, 0.18 mmol) gave $[Ru(C{=}CMePh)$-$(dppe)(\eta$-$C_5H_5)][PF_6]$ (51) as a pink powder (119 mg, 79%), m.p. 200-202°C (dec.). (Found: C 58.2, H 4.5; $C_{39}H_{30}F_6P_3Ru$ requires C 58.2, H 4.5%). IR (Nujol): $\nu(C{=}C)$ 1680w, 1651m(br), $\nu(PF)$ 838s(br) cm^{-1}; other bands at 1592w, 1572w, 1435m, 1418w, 1408w, 1098m, 1043w, 1023m, 872w, 800w, 754m, 741m, 710m, 695s, 669w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.25, s, 3H, Me; 2.89, s, 2H, CH_2; 3.08, s, 2H, CH_2; 5.54, s, 5H, C_5H_5; 6.59, 7.33, m, 25H, Ph.

(e) With $Ru(C_2Ph)(CNBu^t)(PPh_3)(\eta$-$C_5H_5)$ - Similarly, $Ru(C_2Ph)(CNBu^t)(PPh_3)(\eta$-$C_5H_5)$ (37 mg, 0.06 mmol), MeI (65 mg, 0.46 mmol) and NH_4PF_6 (10 mg, 0.06 mmol) gave $[Ru(C{=}CMePh)(CNBu^t)(PPh_3)(\eta$-$C_5H_5)][PF_6]$ (52) as a pink powder (13 mg, 28%), m.p. 160-162°C (dec.). (Found: C 56.5, H 4.8, N 1.8; $C_{37}H_{37}F_6NP_2Ru$ requires C 57.5, H 4.8, N 1.8%). IR (Nujol): $\nu(CN)$ 2190s, $\nu(C{=}C)$ 1660m, 1651m, $\nu(PF)$ 838s(br) cm^{-1}; other bands at 1591w, 1433w, 1094m, 1045w, 1022w, 753m, 746w, 703w, 691m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.11, s, 9H, CMe_3; 1.71, s, 3H, Me; 5.54, s, 5H, C_5H_5; 7.47, m, 20H, Ph.

(f) With $Ru(C_2Me)(PPh_3)_2(\eta$-$C_5H_5)$ - By Method A, $Ru(C_2Me)(PPh_3)_2(\eta$-$C_5H_5)$ (269 mg, 0.37 mmol), MeI (600 mg, 4.3 mmol) and NH_4PF_6 (57 mg, 0.35 mmol) gave $[Ru(C{=}CMe_2)$-$(PPh_3)_2(\eta$-$C_5H_5)][PF_6]$ (53) (207 mg, 63%) as an orange powder, identified by comparison (IR, m.p.) with an authentic sample.[40]

The iodide salt was obtained by Method B, a mixture of $Ru(C_2Me)(PPh_3)_2(\eta$-$C_5H_5)$ (200 mg, 0.26 mmol) and MeI (130 mg, 0.92 mmol) affording $[Ru(C{=}CMe_2)(PPh_3)_2(\eta-C_5H_5)]I$ (<u>54</u>) as an orange powder (172 mg, 77%), m.p. 197-199°C (dec.). (Found: C 61.7, H 4.8; $C_{45}H_{41}IP_2Ru$ requires C 62.0, H 4.7%). IR (Nujol): ν(C=C) 1701m cm^{-1}; other bands at 1587w, 1438s, 1436s, 1310m, 1241w, 1180w, 1162w, 1097m, 1090s, 1085sh, 1076sh, 1050w, 1022w, 1012w, 995w, 920w, 879w, 865w, 858w, 848w, 823w, 750s, 744s, 722s, 705(sh), 695s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.75, s, 6H, Me; 5.21, s, 5H, C_5H_5; 6.89-7.55, m, 30H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 12.18, Me; 93.56, C_5H_5; 117.52, $RuC{=}\mathit{C}$; 128.35-135.85, Ph.

(g) <u>With $Ru(C_2C_6H_4F\text{-}4)(PPh_3)_2(\eta-C_5H_5)$</u> - The reaction between $Ru(C_2C_6H_4F\text{-}4)(PPh_3)_2(\eta-C_5H_5)$ (100 mg, 0.12 mmol), MeI (130 mg, 0.92 mmol) and NH_4PF_6 (20 mg, 0.12 mmol) gave $[Ru\{C{=}CMe(C_6H_4F\text{-}4)\}(PPh_3)_2(\eta-C_5H_5)][PF_6].0{\cdot}25Et_2O$ (<u>55</u>) as a buff-coloured powder (86 mg, 72%), m.p. 200-201°C (dec.). (Found: C 61.2, H 4.3; $C_{50}H_{42}F_7P_3Ru.0{\cdot}25C_4H_{10}O$ requires C 62.0, H 4.5%). IR (Nujol): ν(C=C) 1684m, ν(PF) 840s(br) cm^{-1}; other bands at 1591w, 1440w, 1314w, 1235m, 1220m, 1188w, 1158m, 1094m, 1055m, 1015m, 1008m, 879w, 745m, 720w, 692s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.20, t, J(HH) 7 Hz, 1.5H, $C\mathit{H}_3CH_2$; 1.92, s, 3H, Me; 3.48, q, J(HH) 7 Hz, 1H, $CH_3C\mathit{H}_2$; 5.14, s, 5H, C_5H_5; 7.33, m, 34H, Ph + C_6H_4.

(h) <u>With $Ru(C_2C_6F_5)(PPh_3)_2(\eta-C_5H_5)$</u> - Using Method B, the reaction between $Ru(C_2C_6F_5)(PPh_3)_2(\eta-C_5H_5)$ (1000 mg, 1.13 mmol) and MeI (650 mg, 5.0 mmol) afforded $[Ru\{C{=}CMe(C_6F_5)\text{-}(PPh_3)_2(\eta-C_5H_5)]I$ (<u>56</u>) as an orange powder (475 mg, 41%), m.p. 120-123°C (dec.). IR (Nujol): ν(C=C) 1662m cm^{-1}; other bands at 1518s, 1491s, 1440s, 1418w, 1310w, 1185w, 1158w, 1115w, 1090m, 1061w, 1022m, 999w, 980m, 900w, 845w, 840w, 836w, 823w, 745m, 722w, 696s cm^{-1}.

(i) With $Ru\{C_2(CH_2)_2C_2H\}(PPh_3)_2(\eta-C_5H_5)$ - Using Method A, $Ru\{C_2(CH_2)_2C_2H\}(PPh_3)_2(\eta-C_5H_5)$ (197 mg, 0.26 mmol), MeI (130 mg, 0.92 mmol) and NH_4PF_6 (42 mg, 0.26 mmol) gave $[Ru(C{=}CMe\{(CH_2)_2C_2H\})(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (57) as an orange powder (150 mg, 63%), m.p. 150-152°C (dec.). (Found: C 61.1, H 4.5; $C_{48}H_{43}F_6P_3Ru$ requires C 62.1, H 4.6%). IR (Nujol): $\nu(\equiv CH)$ 3300w, $\nu(C{=}C)$ 1673m, $\nu(PF)$ 838s(br) cm^{-1}; other bands at 1588w, 1573w, 1435w, 1310w, 1181w, 1158w, 1089m, 1051w, 1018w, 998w, 758w, 740m, 720w, 694m, 685w(sh) cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.77, s, 3H, Me; 2.22, s, 4H, CH_2; 5.18, s, 5H, C_5H_5; 7.36, m, 30H, Ph; $\equiv CH$ not detected.

(j) With $\{(CH_2C_2)Ru(PPh_3)_2(\eta-C_5H_5)\}_2$ - Similarly, $\{(CH_2C_2)Ru(PPh_3)_2(\eta-C_5H_5)\}_2$ (85 mg, 0.060 mmol), MeI (130 mg, 0.92 mmol) and NH_4PF_6 (19 mg, 0.12 mmol) afforded $[\{(CH_2CMe{=}C)\text{-}Ru(PPh_3)_2(\eta-C_5H_5)\}_2][PF_6]_2.Et_2O$ (58) as an orange powder (65 mg, 61%), m.p. 159-163°C (dec.). (Found: C 59.6, H 4.3; $C_{90}H_{80}F_{12}P_6Ru_2.C_4H_{10}O$ requires C 61.0, H 4.9%). IR Nujol: $\nu(C{=}C)$ 1670m, $\nu(PF)$ 839s(br) cm^{-1}; other bands at 1590w, 1576w, 1438m, 1312w, 1175w, 1115w, 1092m, 1017w, 999w, 743m, 721w, 693s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.21, t, J(HH) 7 Hz, 3H, CH_3CH_2; 1.40, s, 6H, Me; 2.11, s, 4H, CH_2CH_2; 3.48, q, J(HH) 7 Hz, 2H, CH_3CH_2; 5.18, s, 10H, C_5H_5; 7.37, m, 60H, Ph.

Reactions of ruthenium acetylides with other organic halides

(a) A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (500 mg, 0.632 mmol) and benzylbromide (160 mg, 0.855 mmol) was heated in refluxing dichloromethane (10 ml) for 20 h. NH_4PF_6 (103 mg, 0.632 mmol) was added, and the mixture stirred for 30 min, before filtering into stirred diethyl ether (150 ml), precipitating a pink powder which was washed (diethyl ether) and dried, and identified as [Ru(C=CPhCH$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$)]-[PF$_6$] (59) (417 mg, 64%), m.p. 130-132°C (dec.). (Found: C 64.4 H 4.8; C$_{56}$H$_{47}$F$_6$P$_3$Ru requires C 65.4, H 4.6%). IR (Nujol): ν(C=C) 1655s, ν(PF) 841s(br) cm^{-1}; other bands at 1604w, 1594m, 1578w, 1497m, 1439s, 1418m, 1316w, 1312w, 1188m, 1161m, 1111w, 1092s, 1077m, 1038w, 1030m, 1021w, 1001m, 962m, 917w, 898w, 776w, 767w, 744s, 729s, 695s, 657m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.58, s, 2H, CH$_2$; 5.15, s, 5H, C$_5$H$_5$; 6.5-7.9, m, 40H, Ph. ^{13}C NMR: δ(CDCl$_3$) 32.4, CH$_2$; 94.6, C$_5$H$_5$; 126.8-138.3, m, Ph; 349.0, t, J(CP) 15.5 Hz, RuC.

(b) A mixture of Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (100 mg, 0.14 mmol) and benzyl bromide (32 mg, 0.19 mmol) was heated in refluxing dichloromethane (10 ml) for 20 h. After cooling, the solution was filtered into stirred diethyl ether (130 ml), affording an orange precipitate, [Ru(C=CMeCH$_2$Ph)(PPh$_3$)$_2$-(η-C$_5$H$_5$)]Br.0·5CH$_2$Cl$_2$ (60) (85 mg, 69%), m.p. 116-118°C (dec.). (Found: C 65.0, H 4.9; C$_{51}$H$_{45}$BrP$_2$Ru.0·5CH$_2$Cl$_2$ requires C 65.6, H 4.9%). IR (Nujol): ν(C=C) 1675m cm^{-1}; other bands at 1188w, 1155w, 1113w, 1101w, 1092m, 1075w, 1050w, 1030w, 1001w, 835w, 818w, 759m, 751m, 728w, 701s cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.75, s, 3H, Me; 3.35, s, 2H, CH$_2$; 5.26, s, 1H, 0.5CH$_2$Cl$_2$; 5.32, s, 5H, C$_5$H$_5$; 7.36, m, 35H, Ph.

(c) A mixture of Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.25 mmol), NH$_4$PF$_6$ (42 mg, 0.26 mmol) and allyl chloride was heated in refluxing dichloromethane (11 ml) for 36 h. The solvent was removed *in vacuo*, and a dichloromethane extract of the residue filtered into stirred diethyl ether to precipitate an orange powder of $[Ru(C{=}CPhCH_2CH{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (61) (191 mg, 77%), m.p. 104-106°C (dec.). (Found: C 64.1, H 4.6; $C_{52}H_{45}P_2Ru$ requires C 63.9, H 4.6%). IR (Nujol): ν(C=C) 1664m(br), ν(PF) 842s(br) cm^{-1}; other bands at 1595w, 1575w, 1440m, 1317w, 1191w, 1165w, 1115w(sh), 1093m, 1073w(sh), 1020w, 1001w, 922w, 878w, 749m, 699s cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.96, d, *J*(HH) 5 Hz, 2H, CH_2; 5.12, s, 5H, C_5H_5; 7.33, m, 35H, Ph; vinyl protons not located. ^{13}C NMR: δ($CDCl_3$) 30.97, CH_2; 94.62, C_5H_5; 117.70, RuC=*C*; 127-135, m, phenyl and vinyl carbons; Ru-C not located.

(d) A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.25 mmol) and HC_2CH_2Br (167 mg, 1.41 mmol) was heated in refluxing dichloromethane (13 ml) for 18 h. After cooling to room temperature, the solution was filtered into stirred diethyl ether (100 ml), precipitating a brown powder which was collected, washed (ether) and dried, and identified as $[Ru(C{=}CPhCH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)]Br$ (62) (81 mg, 35%), m.p. 164-168°C (dec.). (Found: C 67.0, H 5.0; $C_{52}H_{43}BrP_2Ru$ requires C 68.6, H 4.8%). IR (Nujol): ν(C≡C) 2102w, ν(C=C) 1663s(br) cm^{-1}; other bands at 1593m, 1576w, 1482s, 1438s, 1314w, 1294w, 1197w, 1186w, 1160w, 1111w, 1090m, 1075w, 1028w, 1000w, 943w, 891w, 841w, 817w, 760(sh), 749m, 744m, 724m, 695m cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.17, t, *J*(HH) 2.4 Hz, 1H, ≡CH; 3.07, d, *J*(HH) 2.4 Hz, 2H, CH_2; 5.26, s, 5H, C_5H_5; 7.1-7.3, m, 35H, Ph.

Alternatively, a mixture of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.63 mmol) and HC_2CH_2Br (334 mg, 2.81 mmol) was heated in refluxing dichloromethane (30 ml) for 40 h. After cooling to room temperature NH_4PF_6 (103 mg, 0.63 mmol) was added, and the resulting mixture was stirred for 15 min. It was then filtered into stirred diethyl ether (100 ml), precipitating a light brown powder which was dried and identified as $[\mathrm{Ru(C{=}CPhCH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)}][\mathrm{PF_6}]$ (63) (339 mg, 55%), m.p. 130-133°C (dec.). (Found: C 63.4, H 4.5; $\mathrm{C_{52}H_{43}F_6P_3Ru}$ requires C 64.0, H 4.4%). IR (Nujol): ν(C≡CH) 3295w, ν(C=C) 1654m(br), ν(PF) 844s(br) $\mathrm{cm^{-1}}$; other bands were similar to those found for the bromide salt.

(e) A mixture of $\mathrm{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}$ (100 mg, 1.26 mmol) and $\mathrm{BrCH_2CH_2CH_2Br}$ (1000 mg, 4.95 mmol) was heated in refluxing chloroform (13 ml) for 45 h. The solvent was removed *in vacuo* and $\mathrm{NH_4PF_6}$ (206 mg, 1.26 mmol) added to a dichloromethane extract (5 ml) of the residue. The mixture was stirred 20 min and filtered into stirred diethyl ether (100 ml), affording a pink precipitate of $[\mathrm{Ru\{C{=}C(\{CH_2\}_3Br)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)}][\mathrm{PF_6}]$ (64) (331 mg, 25%), m.p. 116-118°C (dec.). (Found: C 59.7, H 4.3; $\mathrm{C_{46}H_{46}BrF_6P_3Ru}$ requires C 59.0, H 4.4%). IR (Nujol): ν(C=C) 1660m, ν(PF) 837s(br) $\mathrm{cm^{-1}}$; other bands at 1590m, 1572w, 1434s, 1417w, 1402w, 1311w, 1263m(br), 1185w, 1169w, 1090s, 1027w, 999m, 971w, 925w, 745s, 720w, 694s $\mathrm{cm^{-1}}$. ^{1}H NMR: $\delta(\mathrm{CDCl_3})$ 1.76, m, 2H, $\mathrm{CH_2}$; 2.38, m, 2H, $\mathrm{CH_2}$; 3.26, m, 2H, $\mathrm{CH_2}$; 5.16, s, 5H, $\mathrm{C_5H_5}$; 7.34, m, 35H, Ph. ^{13}C NMR: $\delta(\mathrm{CDCl_3})$ 25.3, 31.2, 33.5, $\mathrm{CH_2}$; 94.4, $\mathrm{C_5H_5}$; 128.5-136.2, m, Ph; RuC and RuC=*C* not detected. $\mathrm{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}$ (569 mg, 57%) was recovered from the filtrate by removal of solvent, extraction with dichloromethane and crystallisation by addition of methanol.

(f) A mixture of Ru(C_2Ph)(PPh_3)$_2$(η-C_5H_5) (1000 mg, 1.26 mmol) and CH_2I_2 (1000 mg, 3.73 mmol) was heated in refluxing chloroform (11 ml) for 41 h. The solvent was removed *in vacuo* and NH_4PF_6 (206 mg, 1.26 mmol) added to a dichloromethane extract (5 ml) of the residue. The mixture was stirred 20 min and filtered into stirred diethyl ether (120 ml), affording a light brown precipitate of [CH_2{(CPh=C)-Ru(PPh_3)$_2$(η-C_5H_5)}$_2$][PF_6]$_2$ (<u>65</u>) (496 mg, 42%), m.p. 169-172°C (dec.). (Found: C 62.6, H 4.3; $C_{99}H_{82}F_{12}P_6Ru_2$ requires C 63.0, H 4.4%). IR (Nujol): ν(C=C) 1643m, ν(PF) 842s(br) cm^{-1}; other bands at 1591w, 1578w, 1442w, 1312w, 1210w, 1188w, 1165w, 1112w, 1092m, 1020w, 1001w, 961w, 747m, 722w, 698s cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.69, s, 2H, CH_2; 4.67, s, 10H, C_5H_5; 7.32, m, 70H, Ph. ^{13}C NMR: δ($CDCl_3$) 94.0, C_5H_5; 126.4-135.5, m, Ph; RuC, RuC=*C* and CH_2 not detected. Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5) (378 mg, 38%) was recovered from the filtrate by removal of solvent, extraction with dichloromethane, and crystallisation by addition of MeOH.

(g) A mixture of Ru(C_2Ph)(dppe)(η-C_5H_5) (500 mg, 0.75 mmol) and Br(CH_2)$_3$Br (400 mg, 1.98 mmol) was heated in refluxing chloroform (20 ml) for 48 h. At this stage TLC revealed the presence of unreacted acetylide; 200 mg (0.99 mmol) more Br(CH_2)$_3$Br was added and the mixture refluxed a further 20 h. After cooling to room temperature, NH_4PF_6 (122 mg, 0.753 mmol) was added and the mixture was stirred for 20 min. It was then filtered into diethyl ether (100 ml), precipitating a light orange powder which was washed (ether), dried and identified as [Ru(C=C{(CH_2)$_3$Br}Ph)(dppe)(η-C_5H_5)]-[PF_6] (<u>66</u>) (255 mg, 36%), m.p. 124-128°C (dec.). (Found: C 54.6, H 4.5; $C_{42}H_{38}BrF_6P_3Ru$ requires C 54.1, H 4.3%).

IR (Nujol): ν(C=C) 1665s, ν(PF) 840s(br) cm^{-1}; other bands at 1594m, 1578w, 1482s, 1438s, 1425m, 1421m, 1359w, 1340w, 1310w, 1270w, 1251w, 1205w, 1188w, 1162w, 1147w, 1131w, 1121w, 1101s, 1073w, 1028w, 1021w, 1010w, 1000w, 974w, 960w, 930w, 878s, 796m, 767m, 752s, 742s, 712s, 698s, 680s, 660m cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 1.61, m, 2H, CH_2; 2.91, m, 8H, 4xCH_2; 5.57, s, 5H, C_5H_5; 7.32, m, 25H, Ph. ^{13}C NMR: δ($CDCl_3$) 22.2, CH_2; 27.1, t, J(CP) 23.9 Hz, PCH_2; 31.0, 32.5, 2xCH_2; 91.6, C_5H_5; 126.8-135.9, Ph. The filtrate was reduced in volume; addition of dichloromethane and methanol followed by concentration afforded yellow crystals of Ru(C_2Ph)(dppe)(η-C_5H_5) (302 mg, 60%), identified by IR and m.p.[40]

(h) A mixture of Ru(C$\equiv$CPh)(PPh_3)$_2$(η-C_5H_5) (800 mg, 1.01 mmol) and 2-bromo-2-methylpropane (1900 mg, 13.87 mmol; purified by running down an alumina column and distilling before use) was heated in refluxing chloroform (25 ml) for 3.5 h. Upon cooling to room temperature orange crystals deposited. Addition of methanol (30 ml) to the filtrate and concentration afforded further product, identified as RuBr(PPh_3)$_2$(η-C_5H_5) by IR and m.p.,[54] with a combined yield of 700 mg (90%).

(i) A mixture of Ru(C$\equiv$CPh)(PPh_3)$_2$(η-C_5H_5) (750 mg, 0.947 mmol) and bromocyclopropane (1900 mg, 15.87 mmol) was heated in refluxing chloroform (25 ml) for 5 d. After cooling to room temperature, NH_4PF_6 (155 mg, 0.947 mmol) was added and the mixture stirred for 20 min. It was then filtered into stirred diethyl ether (100 ml), precipitating [Ru(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (109 mg, 13%), identified by IR and m.p. Ethanol was added to the filtrate, and concentration afforded an orange powder, identified as RuBr(PPh$_3$)$_2$(η-C$_5$H$_5$) (400 mg, 55%) by IR and m.p.

Reaction between [Ru(C=CMePh)(dppe)(η-C$_5$H$_5$)][PF$_6$] and LiMe

A suspension of [Ru(C=CMePh)(dppe)(η-C$_5$H$_5$)][PF$_6$] (65 mg, 0.079 mmol) in tetrahydrofuran (10 ml) at -63°C was reacted with LiMe (0.10 ml of a 1.4 *M* solution in ether, 0.14 mmol) at -63°C, when the pink suspension immediately formed a yellow solution. After allowing to warm to room temperature, solvent was removed *in vacuo*, and a benzene extract of the residue was eluted through silica (60 - 120 mesh) with dichloromethane. Addition of methanol and concentration afforded yellow crystals of Ru{PPh$_2$CH(C=CMePh)-CH$_2$PPh$_2$}(η-C$_5$H$_5$) (69) (31 mg, 58%), m.p. 168-170°C (dec.). (Found: C 70.0, H 5.5%, *M* (mass spectrometry) 680; C$_{40}$H$_{36}$P$_2$Ru requires C 70.7, H 6.3%, *M* 680). IR (Nujol): 1598m, 1575w, 1482m, 1438s, 1417w, 1280m, 1180w, 1165w, 1120m, 1101s, 1080m, 1027m, 1000m, 971w, 905w, 845m, 840m, 830w, 790m, 765w, 744w, 724w, 695s, 668w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.61, s, 3H, CH$_3$; 1.93, m, 1H, CH; 2.28, m, 2H, CH$_2$; 4.26, s, 5H, C$_5$H$_5$; 7.84, m, 25H, Ph.

The following FAB mass spectra were obtained (*m/z*, based on ^{79}Br, ^{102}Ru or ^{192}Os, assignment, relative intensity). Peaks marked with * are at the centre of multiplets which consist of the designated ion together with ions related by the loss of one or two H atoms.

(a) $[Os(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (32). 1141*, $[M + \text{matrix}]^+$, 17; 987*, $[M]^+$, 7; 959*, $[M - N_2]^+$, 12; 879*, $[1141 - PPh_3]^+$, 42; 825*, -, 10; 809*, $[Os(CO)(PPh_3)_2(C_5H_5)]^+$, 9; 781, $[Os(PPh_3)_2(C_5H_5)]^+$, 33; 757*, -, 12; 725*, $[M - PPh_3]^+$, 32; 697*, $[959 - PPh_3]^+$, 24; 620*, $[Os(C_2Ph)(PPh_3)(C_5H_5)]^+$, 64; 519*, $[Os(PPh_3)(C_5H_5)]^+$, 80; 442*, $[Os(PPh_2)(C_5H_5)]^+$, 100.

(b) $[Ru\{C{=}C(C_6F_5)N{=}NC_6H_3Me_2\text{-}3,4\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (35). 1015, $[M]^+$, 3; 896, $[M - (NC_6H_3Me_2)]^+$, 2; 882, $[M - (N_2C_6H_3Me_2)]^+$, 33; 863, $[882 - F]^+$, 4; 753*, $[M - PPh_3]^+$, 6; 691*, $[Ru(PPh_3)_2(C_5H_5)]^+$, 5; 634, $[M - PPh_3 - (NC_6H_3Me_2)]^+$, 5; 620, $[M - PPh_3 - (N_2C_6H_3Me_2)]^+$, 23; 601, $[620 - F]^+$, 7; 543, $[Ru(C_2C_6F_5)(PPh_2)(C_5H_5)]^+$, 80; 524, $[543 - F]^+$, 10; 429 - 427, $[Ru(PPh_3 - nH)(C_5H_5)]^+$, 100; 358*, $[Ru(C_2C_6F_5)(C_5H_5)]^+$, 23; 352, $[Ru(PPh_2)(C_5H_5)]^+$, 25; 287*, $[Ru(PPh_2)]^+$, 33; 244*, $[RuPh(C_5H_5)]^+$, 52; 210*, $[RuPPh]^+$, 21; 167, $[Ru(C_5H_5)]^+$, 20.

(c) $[Ru(C{=}CMeN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (37). 880, $[M]^+$, 15; 730, $[M - (N_2C_6H_4NO_2)]^+$, 7; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 4; 618*, $[M - PPh_3]^+$, 8; 428*, $[Ru(PPh_3)(C_5H_5)\text{-}H]^+$, 100.

(d) $[Ru\{C{=}CPh\overline{N{=}NC_6H_4Mn}(CO)_4\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (42). 1063, $[M]^+$, 51; 1035, $[M - CO]^+$, 3; 979, $[M - 3CO]^+$, 3; 951, $[M - 4CO]^+$, 6; 923, $[M - 4CO - N_2]^+$, 5; 897, $[M - Mn(CO)_4{+}H]^+$, 12; 869, $[897 - N_2]^+$, 5; 792, $[897 - N_2Ph]^+$, 50; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 37; 691*, $[Ru(PPh_3)_2(C_5H_5)]^+$, 24; 661, $[923 - PPh_3]^+$, 19; 529, $[897 - N_2Ph - PPh_3]^+$, 30; 453, $[Ru(C_2Ph)(PPh_2)(C_5H_5)]^+$, 55; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(e) $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$ (<u>46</u>). (Relative intensities not recorded). 827, $[M]^+$; 792, $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]^+$; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$; 530, $[Ru(C_2Ph)(PPh_3)(C_5H_5)]^+$; 429, $[Ru(PPh_3)(C_5H_5)]^+$.

(f) $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>47</u>). 807, $[M]^+$, 44; 742, $[M - C_5H_5]^+$, 2; 730, $[M - Ph]^+$, 3; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 4; 545, $[M - PPh_3]^+$, 88; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 350, $[Ru(PPh_2)(C_5H_5) - 2H]^+$, 55; 283, $[M - 2PPh_3]^+$, 56.

(g) $[Os(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>49</u>). 897, $[M]^+$, 41; 635, $[M - PPh_3]^+$, 100; 519, $[Os(PPh_3)(C_5H_5)]^+$, 42.

(h) $[Ru(C{=}CMeCH_2CH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>57</u>). 783, $[M]^+$, 18; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 2; 521, $[M - PPh_3]^+$, 65; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(i) $[Ru(C{=}CPhCH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>59</u>). 883, $[M]^+$, 25; 621, $[M - PPh_3]^+$, 47; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 359, $[M - 2PPh_3]^+$, 35.

(j) $[Ru(C{=}CPhCH_2C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>63</u>). 831, $[M]^+$, 12; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 3; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 3; 569, $[M - PPh_3]^+$, 33; 504, $[M - PPh_3 - C_5H_5]^+$, 23; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(k) $[Ru(C{=}CPhCH_2CH_2CH_2Br)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (<u>64</u>). 915, $[M]^+$, 5; 869, $[Ru(C{=}CPh_2)(PPh_3)_2(C_5H_5)]^+$, 13; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 30; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 9; 607, $[869 - PPh_3]^+$, 13; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(l) $[CH_2\{(CPh{=}C)Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2][PF_6]_2$ (<u>65</u>). 1744, $[M + PF_6]^+$, 0.1; 881, -, 4; 852, -, 11; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 13; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 7; 566, -, 13; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(m) $[Ru(C{=}CPhCH_2CH_2CH_2Br)(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (<u>66</u>). 787, $[M]^+$, 96; 565, $[Ru(dppe)(C_5H_5)]^+$, 100.

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CHAPTER TWO

Page

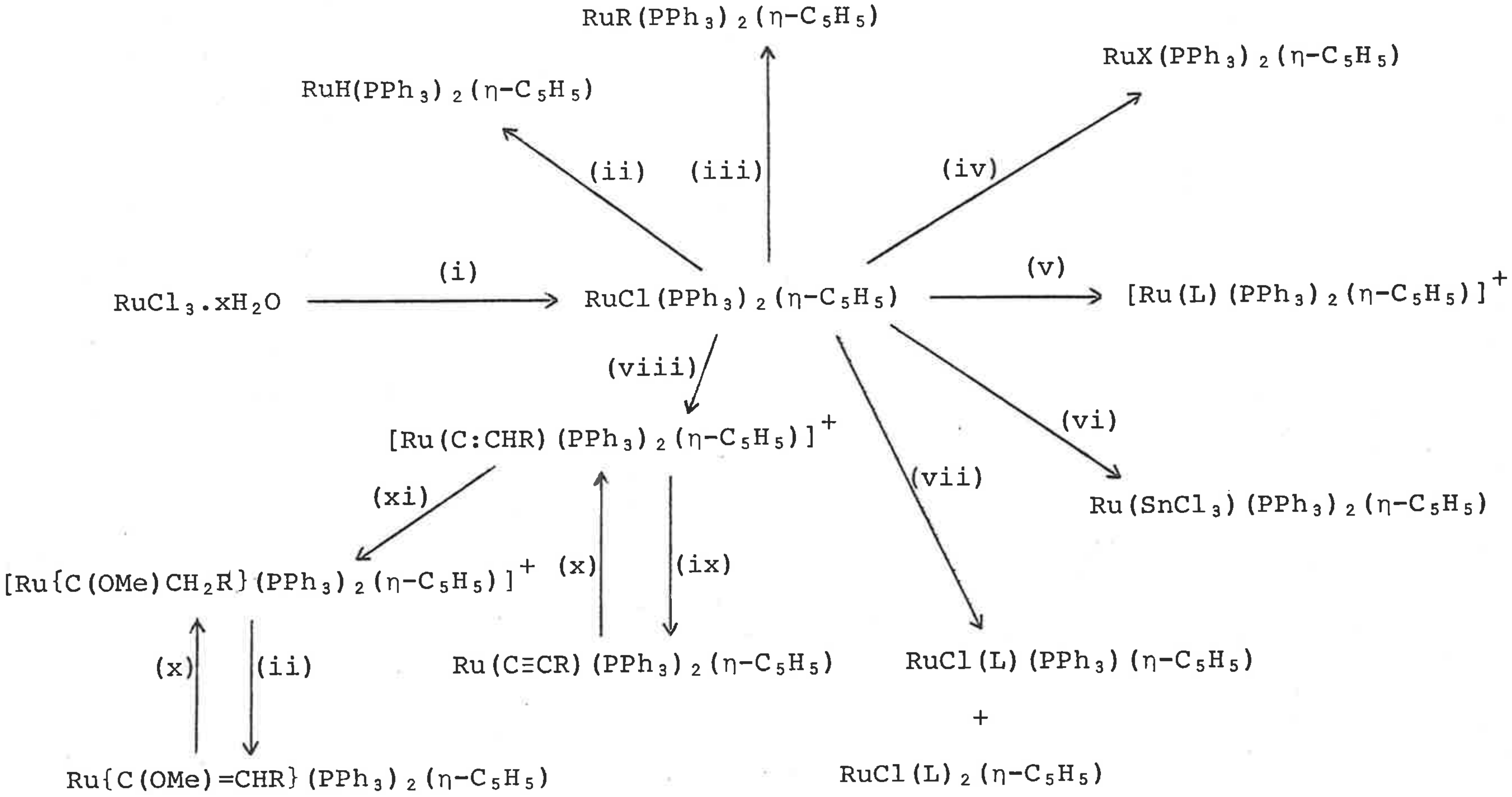
NEW CHEMISTRY OF CYCLOPENTADIENYLRUTHENIUM COMPLEXES CONTAINING DPPM OR DPPE

INTRODUCTION

There has been a great deal of interest in complexes containing the $Ru(PPh_3)_2(\eta-C_5H_5)$ moiety; this area has been reviewed,[1,2] and a summary of some of the reactions is given in the Scheme.

Considerably less interest has been shown in the chemistry of analogous complexes containing bidentate ligands such as $CH_2(PPh_2)_2$ (dppm) and $Ph_2P(CH_2)_2PPh_2$ (dppe). This is perhaps surprising in view of the fact that the tendency for loss or exchange of one of the PPh_3 ligands was recognised in early studies of the chemistry of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1).[3] Indeed, most other tertiary phosphine and phosphite derivatives can be obtained from (1) by suitable ligand exchange reactions.[4-10] However, the complexes thus obtained have generally only been used to establish the scope of a reaction originating in the $Ru(PPh_3)_2(\eta-C_5H_5)$ system (for example, refs. 9, 11, 12), although comparative studies with $Ru(PMe_3)_2(\eta-C_5H_5)$ indicated some differences in the chemistry with the smaller ligand.[8,13-15] This Chapter reports some results obtained with complexes containing dppm and dppe ligands.

The reaction between (1) and dppe in refluxing benzene afforded $RuCl(dppe)(\eta-C_5H_5)$ (2), while in refluxing methanol in the presence of NH_4PF_6, the salt $[Ru(PPh_3)(dppe)(\eta-C_5H_5)]PF_6$ was formed;[4] ^{31}P NMR studies of the former reaction by other workers are reported to show the intermediacy of $RuCl(PPh_3)(dppe)(\eta-C_5H_5)$, containing monodentate dppe.[16] Similar complexes were obtained with dppm, and in this case the reaction between $RuCl(dppm)(\eta-C_5H_5)$ (3) and carbon monoxide gave a relatively unstable



Scheme 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.

derivative characterized as $RuCl(CO)(\eta^1\text{-dppm})(\eta\text{-}C_5H_5)$ (4), containing monodentate dppm. Ready loss of CO reformed the chelate complex (3). The first part of this Chapter begins with a reinvestigation of the reaction between (1) and dppm; modification of the reaction conditions allowed the isolation of $RuCl(\eta^1\text{-dppm})(PPh_3)(\eta\text{-}C_5H_5)$ (5), which has a monodentate dppm ligand. The reactivity of this complex was examined in an attempt to make dppm-bridged heterobimetallic complexes.

The reaction between (1) and NaOMe in refluxing methanol affords the hydrido-complex $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ (6).[9] The second part of this Chapter looks at the analogous reactions with (2) and (3), and the reactions of the resultant complexes with dimethyl acetylenedicarboxylate (dmad).

RESULTS AND DISCUSSION

1. Some chemistry of $RuCl(\eta^1\text{-dppm})(PPh_3)(\eta\text{-}C_5H_5)$

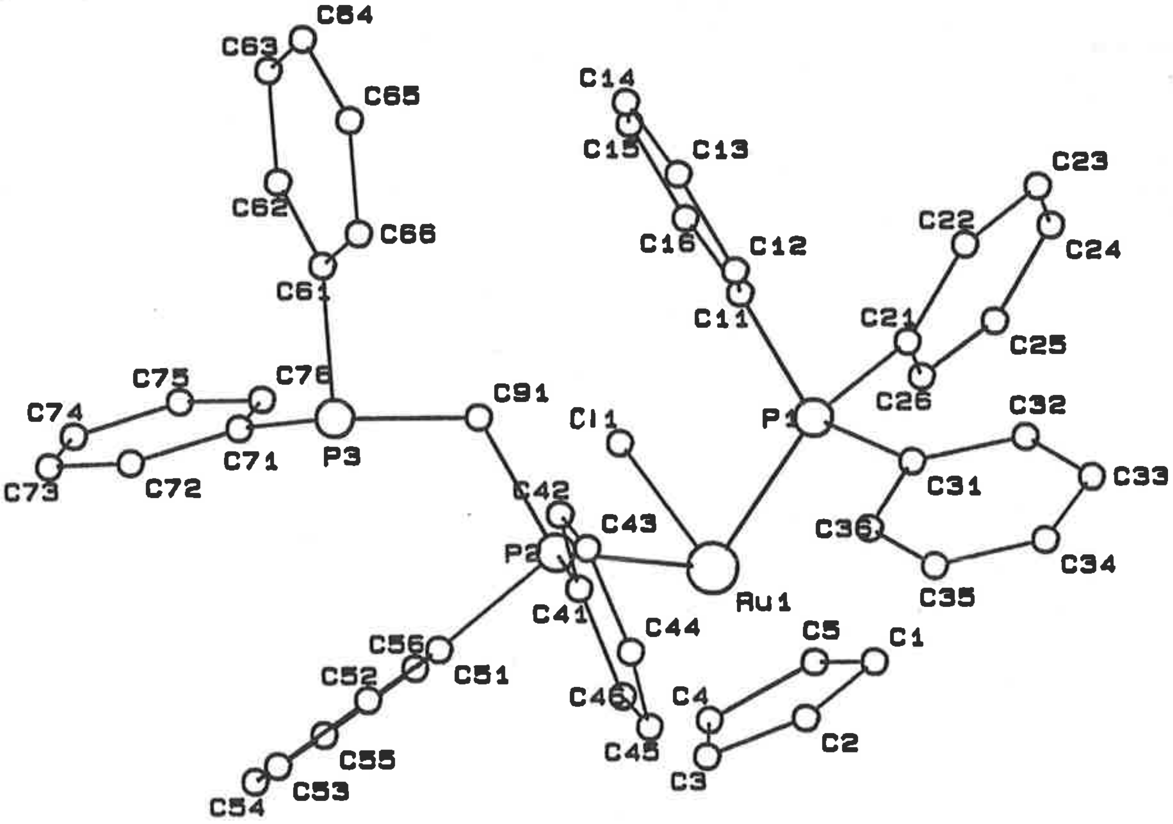
The course of the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1) and dppm is profoundly affected by the amount of solvent present. If mixtures containing about 200 ml benzene per millimole of each reactant are heated, exchange of dppm for the two PPh_3 ligands proceeds to completion, and $RuCl(dppm)(\eta\text{-}C_5H_5)$ (3) can be isolated.[4] In experiments where only about 9 ml benzene per millimole of each reactant is present, the exchange stops with precipitation of the orange complex $RuCl(PPh_3)(dppm)(\eta\text{-}C_5H_5)$ (5), containing a monodentate dppm ligand. This was readily characterized by elemental microanalyses, and from its ^{13}C and ^{31}P NMR spectra. The former contains a doublet of doublets at δ18.35, assigned to the methylene carbon of the dppm ligand showing different couplings to the coordinated (31 Hz) and free (17 Hz) ^{31}P nuclei. The ^{31}P NMR spectrum is quite unambiguous: resonances from the coordinated PPh_3 and PPh_2 nuclei occur at δ48.6 and 42.6, respectively, while the free PPh_2 group gives rise to a resonance at δ-23.4. In $Ru(dppm)_2(tpp)$ (tpp = tetraphenylporphyrinato), a difference of 45 ppm in the chemical shifts of free and coordinated ^{31}P nuclei was found.[17]

Relatively few complexes containing monodentate dppm have been described, the usual mode of coordination being as a chelating bidentate ligand, or bridging two metal centres. The complex $MoCl_2(CO)_2(dppm)_2$ contains one monodentate and one bidentate dppm ligand,[18] while in $Ru(dppm)_2(tpp)$, the central ruthenium is bonded to two axial monodentate dppm ligands.[17] Shaw's group has described several complexes of the type $MX_2(dppm)_2$ (M = Pd, Pt; X = CN, C_2Ph) containing mutually *cis* monodentate dppm ligands, which are useful precursors to unusual binuclear homo- and hetero-binuclear complexes.[19-21] Since complex (5) crystallized in well-formed blocks, the X-ray structure of this material was determined (Figure 1).

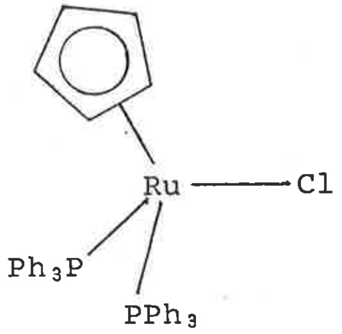
The ruthenium atom is bonded to a chlorine [Ru-Cl 2.445(3)Å], to the η^5-C_5H_5 ligand [Ru-C 2.174 - 2.220(8)Å], to PPh_3 [Ru-P 2.316(2)Å] and the dppm ligand by one of the two phosphorus atoms [Ru-P 2.319(2)Å]. The geometry around the metal is similar to other examples of complexes of this type that have been studied (Chapter 3); replacement of a PPh_3 (cone angle 145°) in (1) by the monodentate dppm ligand (cone angle estimated to be about the same as that of $PMePh_2$, 136°) results in a slight decrease in the P-Ru-P(A) angle [103.99(4) for (1) *vs* 97.07(8) for (5)] and a small increase in the P-Ru-Cl angle [89.05(3) for (1) *vs* 91.57(8) for (5)] [where P is a PPh_3-donor atom and P(A) is a second PPh_3-donor atom (1) or a dppm-donor atom (5)].

Comparison of the geometries about the coordinated and non-coordinated phosphorus atoms of the dppm ligand shows that the P-C(CH_2) and P-C(Ph) distances are similar in both cases. Coordination of phosphorus to the metal centre has little effect on the various C-P-C angles compared with those found in the free PPh_2 group. The phenyl rings of the PPh_2 and PPh_3 groups interleave to reduce the steric interaction between these two ligands and hence the effective cone angle.

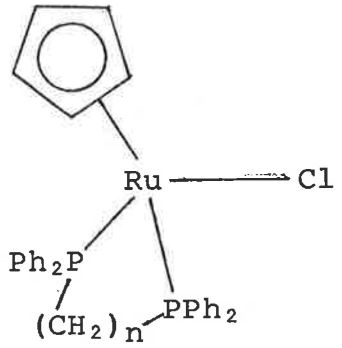
Several reactions of complex (5) were examined, with the unfulfilled intent of using it as an intermediate in the synthesis of heterometallic complexes containing μ-dppm



<u>Figure 1</u>: (by J.M. Patrick and A.H. White). PLUTO plot of the molecular structure of RuCl(η^1-dppm)(PPh$_3$)(η-C$_5$H$_5$) (<u>5</u>).

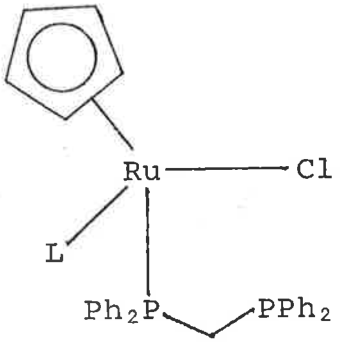


(1)



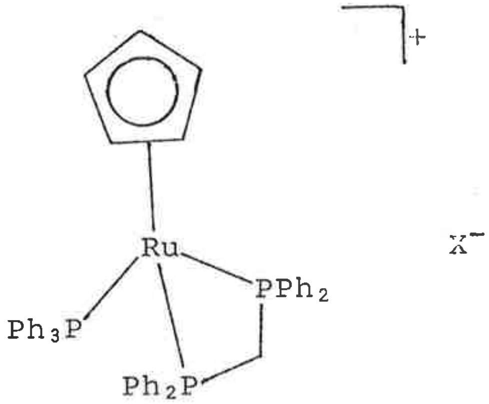
(2) n = 2

(3) n = 1



(4) L = CO

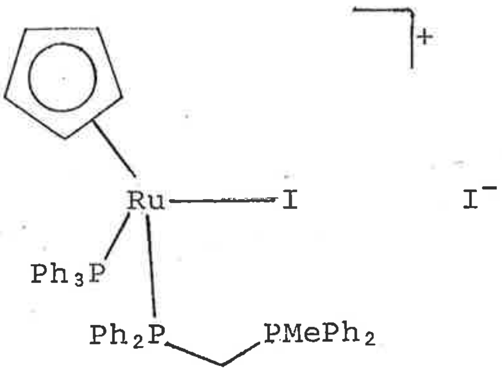
(5) L = PPh3



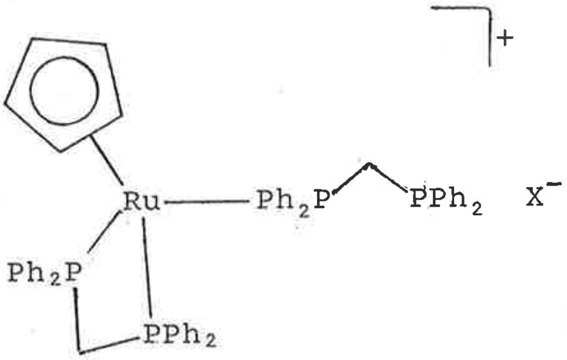
(7) X = Cl

(8) X = BF_4

(9) X = PF_6



(10)



(11) X = Cl

(12) X = PF_6

ligand(s). On heating in polar solvents such as acetonitrile, rapid isomerization occurred with expulsion of chloride ion from the first coordination sphere, to give the salt $[Ru(PPh_3)(dppm)(\eta-C_5H_5)]Cl$ (7), in which the dppm ligand is bidentate. This cation was more conveniently isolated as its tetrafluoroborate (8) or hexafluorophosphate (9) salt by running the reaction in the presence of these anions; the BF_4^- salt was also isolated from an attempt to methylate the free PPh_2 group with $[OMe_3][BF_4]$. The ^{13}C NMR spectrum of this cation contains a triplet resonance at δ45.3 ppm for the CH_2 group, while the two phosphorus nuclei of the dppm ligand, now equivalent, resonate at δ36.6 ppm in the ^{31}P NMR spectrum.

Although the methylation reaction with $[OMe_3]^+$ was unsuccessful, the reaction between (5) and MeI proceeded readily in refluxing benzene, with concomitant halogen exchange, to give $[RuI(PPh_3)(Ph_2PCH_2PMePh_2)(\eta-C_5H_5)]I$ (10). In the NMR spectra of this complex, characteristic ^1H resonances occur at δ2.34 (Me) and 5.07 (dt, CH_2 coupled to two different ^{31}P nuclei), and ^{13}C resonances are found at δ8.0 (Me) and 20.3 (CH_2).

The remaining PPh_3 ligand in (5) was readily displaced on heating in benzene to give (3). However, when this reaction was run in the presence of a molar equivalent of dppm, the new complex $[Ru(dppm)_2(\eta-C_5H_5)]Cl$ (11) was formed; as expected, this cation was more readily isolated as the PF_6^- salt (12), although the latter was too insoluble for satisfactory NMR spectra to be obtained. The cation is formulated as containing one monodentate and one bidentate dppm ligand. The ^{13}C NMR spectrum of the chloro complex (11) is consistent with this formulation, having CH_2 resonances at δ34.7 [dd, for the η^1-dppm ligand; two unequal J(CP)] and 38.45 [t, η^2-dppm; two equal J(CP)]. There is evidently no rapid intramolecular exchange between the η^1- and η^2-dppm ligands. A solution of (12) afforded crystals suitable for an X-ray study.

The anion in the structure is a 1:1 mixture of PF_6 and PO_2F_2, indicating some hydrolysis of the PF_6 had occurred. In the cation (Figure 2), the geometry about the metal is as found for other RuX(L)(L$'$)(η-C_5H_5) complexes (Chapter 3). The coordination of the η^2-dppm ligand is asymmetric, with Ru-P(1) and Ru-P(2) 2.295(3) and 2.325(3)Å, respectively; however, all other bonds and angles about P(1) are similar to their P(2) counterparts. The Ru-P(3) distance [2.323(2)Å] is experimentally identical to Ru-P(2). The bond distances in the η^1-ligand are comparable with those in the η^2-ligand; however, freed of the restrictions imposed by the $\overline{\text{Ru-P-C-P}}$ ring, the angles in the monodentate ligand differ significantly from those in the bidentate ligand. The Ru-P-C(CH_2) and P-C(CH_2)-P angles in the former [118.0(3) and 120.4(6)°, respectively] are markedly greater than those in the latter [97.5(3), 96.3(3) and 92.1(4)°, respectively]. The recently determined structure of $MoI_2(CO)_2$(η^1-dppm)(η^2-dppm) shows a similar variation in the η^2-dppm metal-phosphorus distances.[22]

All attempts to obtain binuclear derivatives from reactions of (5) with appropriate metal complexes were thwarted by the facile transfer of PPh_3 to the second metal complex with concomitant chelation of the dppm ligand. Thus, the only products identified from the reaction between (5) and $Fe_2(CO)_9$ were RuCl(dppm)(η-C_5H_5) (3) and $Fe(CO)_4(PPh_3)$.

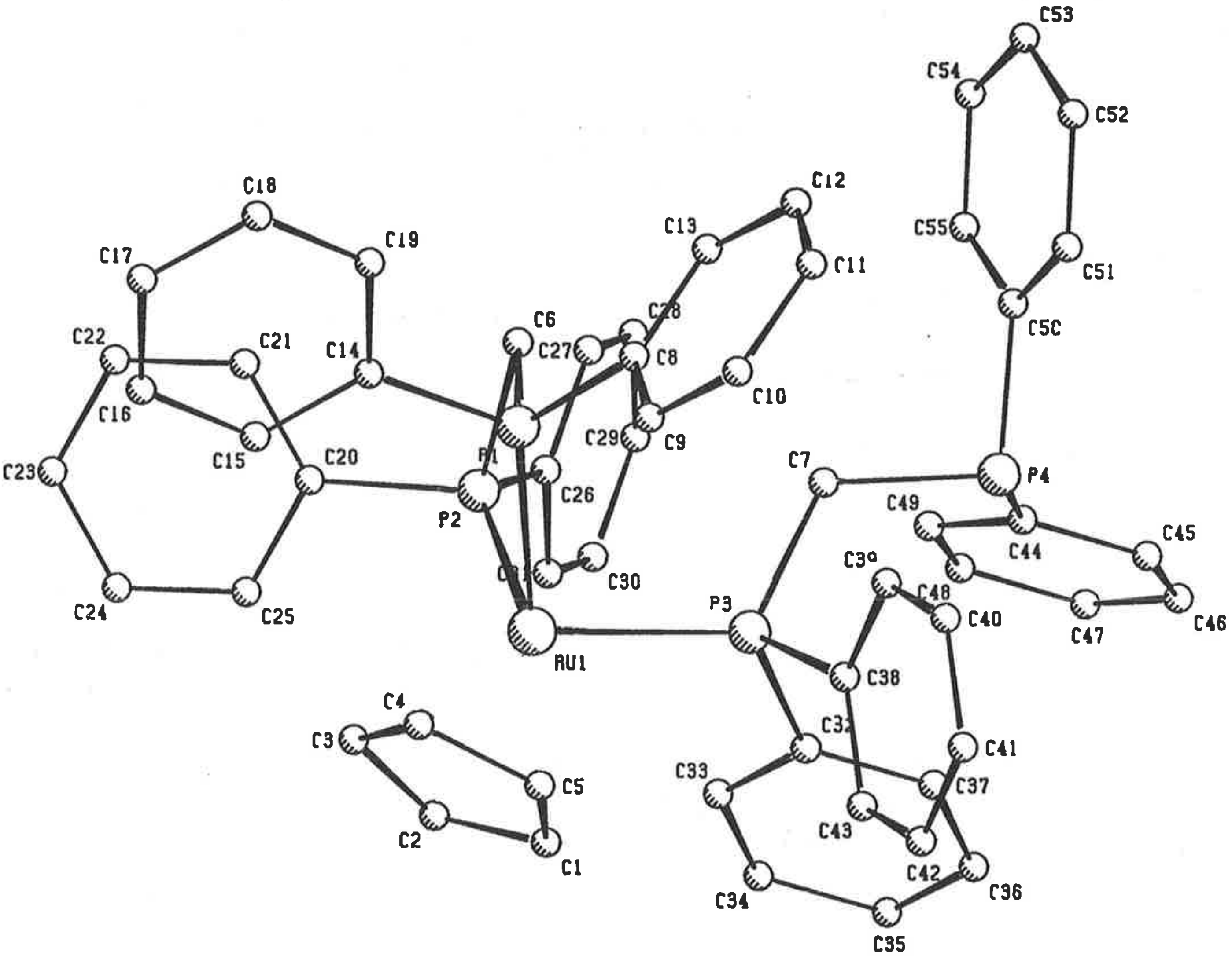


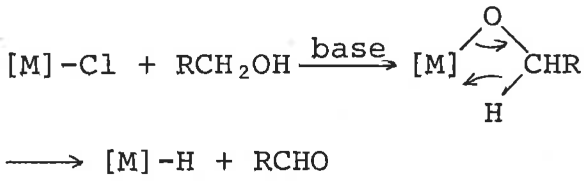
Figure 2: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the structure of the cation in $[Ru(\eta^1\text{-dppm})(\eta^2\text{-dppm})(\eta\text{-}C_5H_5)][\frac{1}{2}PF_6, \frac{1}{2}PO_2F_2]$.

The reaction with $Ru_3(CO)_{12}$ similarly afforded $Ru_3(CO)_{10}(PPh_3)_2$ (66%), that with $[RhCl(CO)_2]_2$ gave $RhCl(CO)(PPh_3)_2$ (93%), and that with $PdCl_2(NCPh)_2$ gave *trans*-$PdCl_2(PPh_3)_2$ (62%); in all cases the ruthenium-containing product was identified as (<u>3</u>).

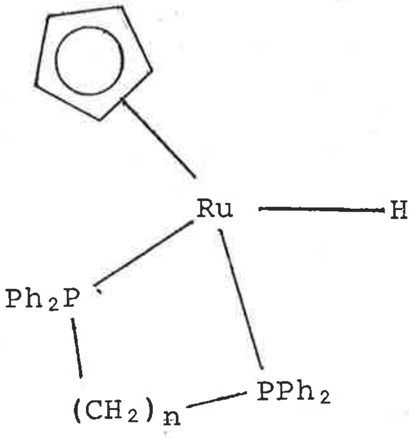
2. <u>Some chemistry of $Ru(H)(L_2)(\eta-C_5H_5)$ (L_2 = dppm, dppe)</u>

Brief heating of the complexes $RuCl(L_2)(\eta-C_5H_5)$ [L_2 = dppm (<u>3</u>), dppe (<u>2</u>)] in refluxing methanol containing sodium methoxide provided an excellent synthesis of the corresponding hydrides, $Ru(H)(L_2)(\eta-C_5H_5)$ [L_2 = dppm (<u>13</u>), dppe (<u>14</u>)]. The complexes were identified by microanalytical and spectroscopic data. The Nujol mull IR spectra contain medium-intensity ν(MH) absorptions [1941 cm^{-1} for (<u>13</u>), 1911 and 1945 cm^{-1} for (<u>14</u>)], while in the ^1H NMR spectra, the expected high-field signals for the metal-bonded proton are found at δ-11.00 for (<u>13</u>) and at δ-13.26 for (<u>14</u>), with appropriate coupling to ^{31}P nuclei. In the solid state Nujol spectrum of (<u>14</u>) and its iron analogue $Fe(H)(dppe)(\eta-C_5H_5)$,[41] ν(MH) appears as two broad absorptions, but in solution only one band is present.

The synthesis of these complexes proceeds by migration of a β-hydrogen of a first-formed alkoxy derivative to the metal atom, with concomitant elimination of the aldehyde:[23,24]

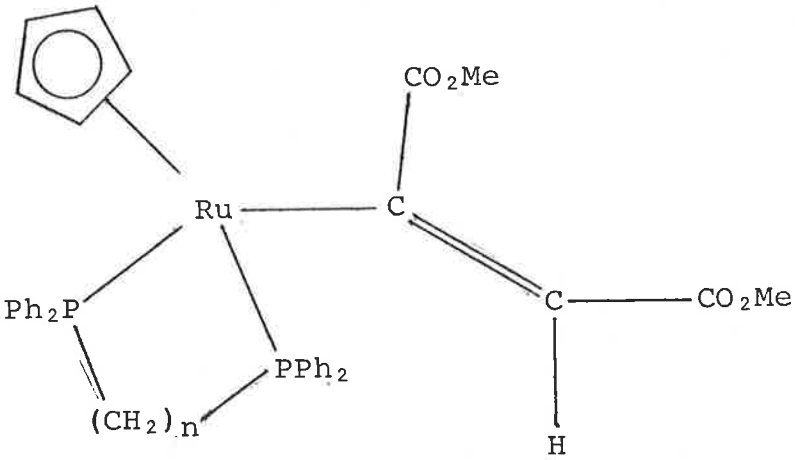


In these reactions, the hydride complex is precipitated, and can be filtered off; the solid complexes are air-stable, but in solution they oxidize readily. They are slightly soluble in methanol and ethanol, and more soluble in



(13) n = 1

(14) n = 2



(17) n = 1

(18) n = 2

benzene, diethyl ether and dichloromethane. In chloroform they rapidly react to form the corresponding chloro complexes, and in CS_2 form the insertion products $Ru[SC(=S)H](L_2)(\eta\text{-}C_5H_5)$.[9]

The availability of these hydrido complexes prompted the investigation of their reactions with $C_2(CO_2Me)_2$ (dmad). The related reaction between $Ru(H)(PPh_3)_2(\eta\text{-}C_5H_5)$ (6) and dmad afforded $Ru\{C(CO_2Me)=C(H)CO_2Me\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (15) by insertion of the alkyne into the Ru-H bond. The stereochemistry about the C=C bond was assigned as (*Z*), on the basis of NMR arguments, and its ready conversion to $\overline{Ru\{C(CO_2Me)=CHC(O}){OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ (16). However, it was recognised that the isolated complex was not necessarily the initial product, since a facile isomerisation might have occurred. In this regard, it is relevant to recall that the first-formed (*E*) adduct of dmad with $ReH(\eta\text{-}C_5H_5)_2$ isomerises on heating in benzene (Pt catalyst).[26]

As part of a detailed investigation of the reactions between dmad and selected ruthenium hydrido complexes,[27] the reactions of dmad with (13) and (14) were examined, affording yellow $Ru\{C(CO_2Me)=C(H)CO_2Me\}(L_2)(\eta\text{-}C_5H_5)$ [L_2 = dppm (17), dppe (18)], the latter as a hemi-ethanol solvate. Complex (17) decomposes over a period of hours in air, although complex (18), like (15), is quite stable in air. Both complexes are very soluble in chlorinated solvents, and only sparingly soluble in diethyl ether, ethanol or acetone; they are both insoluble in light petroleum.

The new complexes were characterised on the basis of elemental microanalyses and their IR, NMR and mass spectra.

Infrared absorptions are found for ν(C=O) [1705 and 1725 cm^{-1} in (17), 1695 cm^{-1} in (18)], ν(C=C) (1529 and 1531 cm^{-1}, respectively) and ν(C-O) [1192 and 1142 cm^{-1} (17), 1146 cm^{-1} (18)]. NMR resonances are assigned to OCH_3 [δ3.15 and 3.25 in (17), δ3.19 and 3.52 in (18)] and =CH groups (δ5.00 and 4.29, respectively), together with the expected cyclopentadienyl, methylene and phenyl resonances. In their mass spectra, molecular ions centred on *m/z* 694 (17) or 708 (18) decompose by loss of the vinyl and C_5H_5 groups. To help answer stereochemical questions in this system, the crystal structure of (18) was determined.

A molecule of (18) is shown in Figure 3, from which it is clear that the vinyl ligand carries the two CO_2Me groups in a mutually *cis* configuration. The ruthenium atom coordination is distorted octahedral [angles P(1)-Ru-P(2) 85.1, P(1)-Ru-C(32) 93.3(4), P(2)-Ru-C(32) 92.2(5)°]. The Ru-C(sp^2) distance [Ru-C 2.07(1) Å] is experimentally the same as that found in the related complex Ru{(*Z*)-C(CO_2Me)=C(H)CO_2Me}(CO)(PPh_3)(η-C_5H_5) (19) (Chapter 3).[27] The ruthenium is also bonded to the two phosphorus atoms of the chelating dppe ligand [Ru-P 2.271(4), 2.249(4) Å] and to the η-C_5H_5 group [Ru-C(Cp) 2.214-2.283(9), av. 2.25Å]. The two longest Ru-C(Cp) vectors are approximately *trans* to the shorter of the two Ru-P vectors.

In both (18) and (19), the C(CO_2Me)=CH(CO_2Me) groups show no significant differences from those found in related molecules such as Pd{(*E*)-C(CO_2Me)=CH(CO_2Me)}(C_2Ph)(PEt_3)$_2$,[28] Pt($C_6H_4PPh_2$){(*E*)-C(CO_2Me)=CH(CO_2Me)}(PPh_3),[29] RuCl{(*E*)-C(CO_2Me)=CCl(CO_2Me)}(CO)$_2$(PPh_3)$_2$,[30] *trans*-[PtH{(*Z*)-C(CO_2Me)=CH(CO_2Me)}($PBu^nBu^t_2$)$_2$][31] or [N(PPh_3)$_2$][Pt{(*Z*)-C(CO_2Me)=CCl(CO_2Pr^i)}Cl_2(CO)].[32]

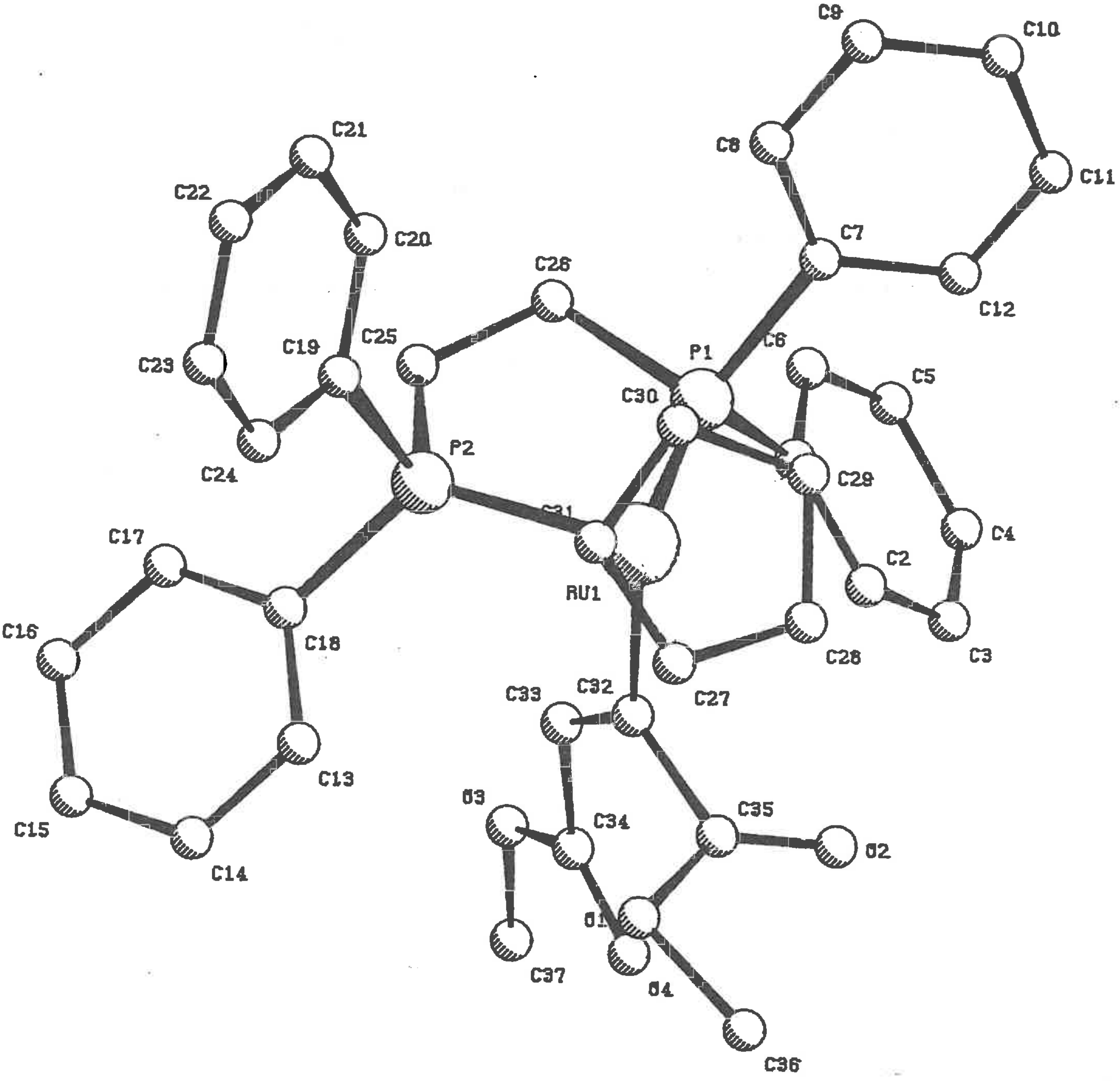


Figure 3: PLUTO plot of the molecular structure of $Ru\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ (<u>18</u>).

The structure determination of (<u>18</u>) unequivocally establishes the configuration of the vinyl ligand, and it seems likely that initial *cis* addition of the metal hydride to the alkyne occurs in this system, as has been found previously.[26]

EXPERIMENTAL

General experimental conditions were as described in Chapter 1. A nitrogen atmosphere was used routinely for (i) distilling solvents and (ii) carrying out reactions, but air was not excluded during work-up of the products.

^{31}P NMR spectra were recorded on a Bruker HX90E NMR spectrometer operating at 36.43 MHz relative to internal PPh_3 in $CDCl_3$. The conductivity measurements were made using a conductivity cell (cell constant = 0.174 cm^{-1}). The solutions were thermostatted in a water bath at 25°C and the resistance recorded using a Phillips PR9500 A.C. conductance bridge incorporating a cathode ray indicator for detection of the balance point. The concentration was *ca* 10^{-3} *M* using A.R. grade acetone; all conductance values obtained correspond to 1:1 electrolytes.[33] Structure solution and refinement details for Ru{(*E*)-C(CO_2Me)=CH-(CO_2Me)}(dppe)(η-C_5H_5) can be found in Chapter 3.

Starting materials

The complexes RuCl(PPh_3)$_2$(η-C_5H_5),[34] RuCl(dppe)(η-C_5H_5),[4] RuCl(dppm)(η-C_5H_5),[4] [RhCl(CO)$_2$]$_2$,[35] $PdCl_2(NCPh)_2$,[36] and $Ru_3(CO)_{12}$[37] were prepared by literature methods. Iodomethane was distilled before use; all other reagents were used as received.

Preparation of RuCl(η^1-dppm)(PPh_3)(η-C_5H_5) (5)

A mixture of RuCl(PPh_3)$_2$(η-C_5H_5) (5.00 g, 6.89 mmol) and dppm (2.65 g, 6.89 mmol) was heated in refluxing benzene (60 ml). After 4 h reflux, a yellow powder was collected and recrystallized from chloroform/ethanol to give orange crystals of RuCl(η^1-dppm)(PPh_3)(η-C_5H_5) (5)

(3.80 g, 65%), m.p. 220-224°C (dec.). (Found: C 67.2, H 5.2, Cl 4.9, P 11.0; $C_{48}H_{42}ClP_3Ru$ requires C 68.0, H 5.0, Cl 4.2, P 11.0%). IR (Nujol): 1585w, 1574w, 1569w, 1482m, 1434s, 1311w, 1183w, 1160w, 1130m, 1104(sh), 1097(sh), 1089s, 1069w, 1050w, 1031w, 1011w, 999w, 994w, 971w, 916w, 853(sh), 850w, 843(sh), 830m, 756s, 743s, 732s, 695s, 662w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.7, m, 2H, CH_2; 4.10, s, 5H, C_5H_5; 7.10, m, 35H, C_6H_5. ^{13}C NMR: $\delta(CDCl_3)$ 18.35, dd, $J(CPPh_2)$ 17.09 Hz, $J(CPPh_2Ru)$ 31.76 Hz, CH_2; 81.02, s, C_5H_5; 126-141, m, C_6H_5. ^{31}P NMR: $\delta(CDCl_3)$ -23.4, d, $J(PP)$ 17.1 Hz, CH_2PPh_2; 42.6, dd, $J(PP)$ 19.5 Hz, $J(PP)$ 41.5 Hz, $RuPPh_2$-; 48.6, d, $J(PP)$ 41.5 Hz, $RuPPh_3$.

Preparation of $[Ru(PPh_3)(dppm)(\eta\text{-}C_5H_5)]X$ [X = Cl (7), BF_4 (8)]

(a) X = Cl - A mixture of $RuCl(\eta^1\text{-dppm})(PPh_3)(\eta\text{-}C_5H_5)$ (500 mg, 0.66 mmol) and $NaBPh_4$ (50 mg, 0.15 mmol) was heated in refluxing acetonitrile (60 ml) for 16 h. Filtration and concentration followed by addition of diethyl ether afforded yellow crystals, which were recrystallized (dichloromethane/benzene) to give $[Ru(PPh_3)(dppm)(\eta\text{-}C_5H_5)]Cl$ (7) (98 mg, 20%), m.p. 252-254°C. (Found: C 66.9, H 5.1, N 0.0, P 10.6; $C_{48}H_{42}ClP_3Ru$ requires C 68.0, H 5.0, N 0.0, P 11.0%). IR (Nujol): 1630w(br), 1000w, 972w, 853(sh), 842w, 754(sh), 750m, 743w, 723s, 708(sh), 698s, 694(sh) cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 4.35, m, 2H, CH_2; 4.90, s, 5H, C_5H_5; 7.27, m, 35H, C_6H_5. ^{31}P NMR: $\delta(CDCl_3)$ 7.20, d, $J(PP)$ 36.6 Hz, PPh_2C; 52.94, t, $J(PP)$ 36.6 Hz, PPh_3. Conductivity (acetone): 139 Scm^{-2}.

(b) X = BF_4 - A mixture of RuCl(η^1-dppm)(PPh_3)(η-C_5H_5) (295 mg, 0.348 mmol) and [Me_3O][BF_4] (excess) was reacted in stirring benzene (50 ml) for 17 h. The white precipitate deposited was collected and recrystallized from dichloromethane/methanol to give yellow crystals of [Ru(PPh_3)(dppm)(η-C_5H_5)][BF_4] (<u>8</u>) (199 mg, 64%), m.p. 325°C. (Found: C 63.8, H 4.7; $C_{48}H_{42}BF_4P_3Ru$ requires C 63.0, H 4.6%). IR (Nujol): ν(BF) 1058vs(br) cm^{-1}; other bands at 1587w, 1574w, 1438s, 1310w, 1283w, 1187w, 1162w, 1100(sh), 1093(sh), 1090s, 1072w, 1036w, 1028(sh), 999w, 973(sh), 838m, 818w, 770w, 751m, 741m, 722m, 696s, 683(sh), 663w cm^{-1}. ^1H NMR: δ($CDCl_3$) 4.26, m, 2H, CH_2; 4.88, s, 5H, C_5H_5; 7.24, m, 35H, C_6H_5. ^{13}C NMR: δ($CDCl_3$) 45.31, t, *J*(CP) 24.4 Hz, CH_2; 84.48, s, C_5H_5; 128-139, m, C_6H_5.

<u>Preparation of [RuI(PPh_3)($Ph_2PCH_2PMePh_2$)(η-C_5H_5)]I (10)</u>

A mixture of RuCl(η^1-dppm)(PPh_3)(η-C_5H_5) (100 mg, 0.118 mmol) and excess iodomethane was heated in refluxing benzene (20 ml) for 3 h. After cooling and filtration, addition of 4:1 ether/hexane afforded orange crystals which were recrystallized from 1:3:4:1 benzene/acetone/ether/hexane to give [RuI(PPh_3)($Ph_2PCH_2PMePh_2$)(η-C_5H_5)]I (<u>10</u>) (53 mg, 42%), m.p. 141-143°C (dec.). (Found: C 55.3, H 4.4; $C_{49}H_{45}I_2P_3Ru$ requires C 54.4, H 4.2%). IR (Nujol): 1446w, 1410w, 1368w, 1312m(br), 1172w, 1160(sh), 1121w, 1108w, 1105w, 1089m, 1070w, 1028w, 997m, 898m, 843m(br), 810m, 771w, 754s, 743s, 727m, 697s cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.34, d, *J*(HP) 12.70 Hz, CH_3; 4.52, s, 5H, C_5H_5; 5.07, dt, *J*($HP_{a,b}$) 16.11 Hz, *J*(HP_c) 6.84 Hz, 2H, CH_2; 7.35, m, 35H, C_6H_5. ^{13}C NMR: δ($CDCl_3$) 7.98, d, *J*(CP) 54.93 Hz, CH_3; 20.34, t, *J*(CP) 32.96 Hz, CH_2; 81.86, s, C_5H_5; 127-136, m,

C_6H_5. Conductivity (acetone): 130 Scm^{-2}.

Preparation of [Ru(η^1-dppm)(η^2-dppm)(η-C_5H_5)]X [X = Cl (11), PF_6 (12)]

(a) X = Cl - A mixture of RuCl(η^1-dppm)(PPh_3)(η-C_5H_5) (2.37 g, 2.80 mmol) and dppm (1.08 g, 2.81 mmol) was heated in refluxing benzene (120 ml) for 135 h. Cooling afforded a white powder, which was recrystallized (dichloromethane/ether) to give [Ru(η^1-dppm)(η^2-dppm)(η-C_5H_5)]Cl (11) (1.03 g, 38%), m.p. 167-170°C (dec.). IR (Nujol): 1571w, 1438m, 1370w, 1310m, 1260w, 1161m, 1157(sh), 1119w, 1090m, 1027w, 999w, 741w, 725s, 696s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 5.12, s, 5H, C_5H_5; 7.28, m, 40H, C_6H_5; methylene protons not detected. ^{13}C NMR: δ($CDCl_3$) 34.71, dd, $J(CP_a)$ 21.97 Hz, $J(CP_b)$ 38.45 Hz, monodentate PCH_2P; 46.28, t, J(CP) 22.58 Hz, bidentate PCH_2P; 84.05, s, C_5H_5; 127-136, m, C_6H_5. Conductivity (acetone): 125 Scm^{-2}.

(b) X = PF_6 - A mixture of [Ru(η^1-dppm)(η^2-dppm)-(η-C_5H_5)]Cl (100 mg, 0.103 mmol) and NH_4PF_6 (50 mg, 0.307 mmol) was heated in refluxing methanol (40 ml) for 16 h. Cooling afforded a yellow powder which was recrystallised (dichloromethane/methanol) to give yellow crystals of [Ru(η^1-dppm)(η^2-dppm)(η-C_5H_5)][PF_6] (12) (83 mg, 75%), m.p. 257°C. (Found: C 61.4, H 4.7; $C_{55}H_{49}F_6P_5Ru$ requires C 61.2, H 4.5%). IR (Nujol): ν(PF) 839vs(br) cm^{-1}; other bands at 1588w, 1575w, 1440w, 1310w, 1160w, 1108w, 1092m, 1027w, 999w, 874(sh), 847(sh), 770w, 743w, 730m, 701(sh), 693s cm^{-1}. NMR spectra could not be obtained because of lack of solubility.

Reactions of RuCl(η^1-dppm)(PPh$_3$)(η-C$_5$H$_5$) with other metal complexes

(a) with [RhCl(CO)$_2$]$_2$ - RuCl(η^1-dppm)(PPh$_3$)(η-C$_5$H$_5$) (200 mg, 0.236 mmol) and [RhCl(CO)$_2$]$_2$ (45.9 mg, 0.118 mmol) were reacted in stirring benzene (50 ml) for 90 min. The solvent was removed in a vacuum and two products, A and B, were isolated by fractional crystallization from CHCl$_3$/light petroleum. Compound A was identified as RhCl(CO)(PPh$_3$)$_2$ (76 mg, 93%) by comparison of its m.p. and IR with those of an authentic sample.[38] Compound B was shown to be RuCl(dppm)(η-C$_5$H$_5$), also by comparison with an authentic sample (m.p. and ^{1}H NMR).

(b) with PdCl$_2$(NCPh)$_2$ - RuCl(η^1-dppm)(PPh$_3$)(η-C$_5$H$_5$) (200 mg, 0.236 mmol) and PdCl$_2$(NCPh)$_2$ (36.4 mg, 0.095 mmol) were reacted in benzene (50 ml) under stirring for 24 h. The solvent was removed in a vacuum and the residue washed with acetone (3 x 5 ml). Extraction with chloroform and crystallization by slow addition of acetone afforded yellow crystals of *trans*-PdCl$_2$(PPh$_3$)$_2$ (41 mg, 62%), identified by comparison with an authentic sample (m.p. and IR).[39]

(c) with Ru$_3$(CO)$_{12}$ - RuCl(η^1-dppm)(PPh$_3$)(η-C$_5$H$_5$) (271 mg, 0.320 mmol) and Ru$_3$(CO)$_{12}$ (200 mg, 0.320 mmol) were reacted in tetrahydrofuran (25 ml) for 15 min. The solvent was removed in a vacuum and partial evaporation of an acetone extract of the residue afforded purple crystals of Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$ (116 mg, 66%), identified by comparison with an authentic sample (m.p., IR and ^{1}H NMR spectra).[40]

Preparation of RuH(L_2)(η-C_5H_5) [L_2 = dppm (13), dppe (14)]

(a) L_2 = dppm - A mixture of RuCl(dppm)(η-C_5H_5) (1.00 g, 1.71 mmol) and sodium metal (*ca* 200 mg, 0.009 g. atom) was refluxed in methanol (50 ml) for 1 h. A yellow powder precipitated from solution and was identified as RuH(dppm)-(η-C_5H_5) (13) (520 mg, 55%), m.p. 185-186°C. (Found: C 65.0, H 5.5%, *M* (mass spectrometry) 552; $C_{30}H_{28}P_2Ru$ requires C 65.3, H 5.1%, *M* 552). IR (Nujol): ν(RuH) 1941s cm^{-1}; other bands at 3072(sh), 3049m, 1583w, 1571w, 1480s, 1435s, 1418(sh), 1379m, 1368(sh), 1358(sh), 1328w, 1307m, 1275w, 1182w, 1158w, 1100m, 1092m, 1075m, 1028w, 999w, 992w, 971w, 918w, 847w, 830w, 801w, 785w, 773w, 761w, 755(sh), 748m, 729s, 697s, 681(sh), 666w, 652w, 607w, 592w cm^{-1}. ^1H NMR: δ(C_6D_6) -11.00, dt, *J*(HP) 30.0 Hz, *J*(HH) 4 Hz, 1H, RuH; 3.83, m, 1H, CH; 4.72, m, 1H, CH; 4.97, s, 5H, C_5H_5; 7.06, 7.62, m, 20H, Ph. ^{13}C NMR: δ(C_6D_6)57.39, t, *J*(CP) 22.0 Hz, CH_2; 77.49, t, *J*(CP) 2.4 Hz, C_5H_5; 127-133, m, Ph.

(b) L_2 = dppe - A mixture of RuCl(dppe)(η-C_5H_5) (200 mg, 0.33 mmol) and sodium metal (*ca* 40 mg, 0.002 g. atom) was refluxed in methanol (50 ml) for 1 h. A yellow powder precipitated from solution and was collected, washed (methanol) and dried, and identified as RuH(dppe)(η-C_5H_5) (14) (150 mg, 80%), m.p. 170°C (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). IR (Nujol): ν(RuH) 1911s, 1945s cm^{-1}; other bands at 1428s, 1297w, 1167w, 1089s, 1080s, 1057w, 1015w, 987w, 867w, 800m, 788m, 778m, 740s, 732(sh), 699s, 687s, 674(sh), 665m cm^{-1}. ^1H NMR: δ(C_6D_6) - 13.26, t, *J*(HP) 34.2 Hz, 1H, RuH; 2.0, m, 2H, CH_2; 4.76, s, 5H, C_5H_5; 7.2, 7.6, 8.0, m, 20H, Ph. ^{13}C NMR: δ(C_6D_6) 31.9, d, *J*(CP) 24 Hz, CH_2; 80.2, s, C_5H_5; 125.4-145.8, m, Ph.

Preparation of Ru{(*E*) - C(CO_2Me)=CH(CO_2Me)}(L_2)(η-C_5H_5) [L_2 = dppm (17), dppe (18)]

(a) L_2 = dppm - A mixture of RuH(dppm)(η-C_5H_5), (240 mg, 0.35 mmol) and excess dmad (120 mg, 0.84 mmol) was heated in refluxing diethyl ether (60 ml) for 48 h. Cooling afforded yellow crystals of Ru{C(CO_2Me)=CH(CO_2Me)}-(dppm)(η-C_5H_5) (17) (113 mg, 32%), m.p. 86-90°C (dec.). (Found: C 59.79, H 4.86%, *M* (mass spectrometry) 694; $C_{36}H_{34}O_4P_2Ru$ requires C 62.25, H 4.90%, *M* 694). IR (Nujol): ν(C=O) 1725m, 1705s, ν(C=C) 1529m, ν(C-O) 1146s cm^{-1}; other bands at 1318w, 1244w, 1201m, 1120(sh), 1100m, 1071(sh), 1027w, 999w, 832w, 786w, 737w, 723w, 699s cm^{-1}. ^1H NMR: δ($CDCl_3$) 3.15, s, 3H, OMe; 3.25, s, 3H, OMe; 3.80, m, 2H, CH_2; 4.80, s, 5H, C_5H_5; 5.00, s, 1H, =CH; 7.35, m, 20H, Ph.

(b) L_2 = dppe - A mixture of RuH(dppe)(η-C_5H_5) (300 mg, 0.53 mmol) and dmad (150 mg, 1.06 mmol) was heated in refluxing diethyl ether for 15 h. The yellow crystals which separated on cooling were recrystallised ($CHCl_3$/EtOH) to give the hemi-ethanol solvate of (18) (223 mg, 69%), m.p. 170-174°C (dec.). (Found: C 61.73, H 5.36%, *M* (mass spectrometry) 708; $C_{37}H_{36}O_4P_2Ru.0{\cdot}5C_2H_6O$ requires C 62.38, 5.34%, *M* 708). IR (Nujol): ν(C=O) 1695s(br), ν(C=C) 1531s, ν(C-O) 1192s cm^{-1}; other bands at 3060m, 1585w, 1573w, 1482m, 1432s, 1321s, 1160(sh), 1107(sh), 1095m, 1072w, 1029m, 1000m, 958w, 935w, 915w, 868w, 857w, 831m, 802m, 782m, 744s, 709(sh), 697s, 665s, 658(sh), 641m, 628m, 617m cm^{-1}. ^1H NMR: δ($CDCl_3$) 1.18, t, *J*(HH) 7.2 Hz, 1.5H, CH_3CH_2; 2.73, m, 4H, PCH_2; 3.19, s, 3H, OMe; 3.52, s, 3H, OMe; 3.64, q, *J*(HH) 7.2 Hz, 1H, $CH_3\mathit{CH}_2$; 4.29, s, 1H, -CH=; 4.44, s, 5H, C_5H_5; 7.29, m, 20H, Ph. ^{13}C NMR: δ($CDCl_3$) 27.35, s, $\mathit{C}H_3CH_2$; 29.05, m, PCH_2; 50.05, s, OMe; 55.95, s, $CH_3\mathit{C}H_2$; 85.6, s,

C_5H_5; 128-134, m, Ph; 162.45, s, -CH=; 181.45, s, CO_2Me; 191.9, t, J(CP) 0.5 Hz, RuC.

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CHAPTER THREE

INTRODUCTION

The chemistry of complexes containing the $Ru(L)_2(\eta-C_5H_5)$ moiety has proved to be both extensive and varied. The elucidation of much of this work has been aided by crystallographic investigations, and at this stage it seems appropriate to examine existing structural data for cyclopentadienylruthenium phosphine complexes. Ru-ligand distances in these complexes have been tabulated and analysed.

In the course of synthetic investigations, described in Chapters 1 and 2, the author has determined the molecular structures of six complexes, $Ru(C{\equiv}CPh)(PPh_3)_2(\eta-C_5H_5)$ (1), $Ru(C{\equiv}CPh)(dppe)(\eta-C_5H_5)$ (2), $[Ru(C{=}CPhN{=}N-C_6H_3Me_2-3,4)(PPh_3)_2(\eta-C_5H_5)][BF_4]$ (3), $[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta-C_5H_5)][PF_6]$ (4), $Ru\{(Z)-C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)(\eta-C_5H_5)$ (5) and $Ru\{(E)-C(CO_2Me){=}CH(CO_2Me)\}(dppe)(\eta-C_5H_5)$ (6), and these data have been combined with those for other cyclopentadienylruthenium phosphine and phosphite complexes.

RESULTS AND DISCUSSION

A description of the structures solved by the author is followed by a consideration of the variation in Ru-ligand distances in cyclopentadienylruthenium phosphine and phosphite complexes. Description of some of the structures can be found in Chapter 1 [(3) and (4)] and Chapter 2 [(6)] alongside the relevant chemistry. Structure solution and refinement information is given in the Experimental section.

1. Description of Structures (1) - (6)

Plots of molecules of (1), (2), (5) and (6), and of the cations in (3) and (4) are given in Figures 1 - 6. As has been reported for other $RuX(L)_2(\eta-C_5H_5)$ compounds (see, e.g., refs. 1 and 2, *inter alia*), the coordination about the ruthenium atom in all six complexes can be considered to be distorted octahedral, with the C_5H_5 group occupying three facial sites and the other positions being taken up by two P atoms of the tertiary phosphine(s) [phosphine and CO for (5)] and the C atom of the unsaturated fragment.

Selected bond lengths for the six complexes are collected in Table 1. The separations of the five carbon atoms in the C_5 ring from the metal atom fall within the overall ranges found for related complexes. A discussion of ruthenium-cyclopentadienyl carbon bond distances in compounds of this type is given below.

C≡C triple bonds in (1) and (2) have lengths of 1.214(7) and 1.204(5)Å respectively, and fall within the range of values (1.18 - 1.25Å) reported for terminal alkynyl ligands.[4] The C=C bonds of the vinylidene ligands in (3) and (4) are 1.34(1) and 1.32(1) respectively, similar to the value of 1.31(1) found

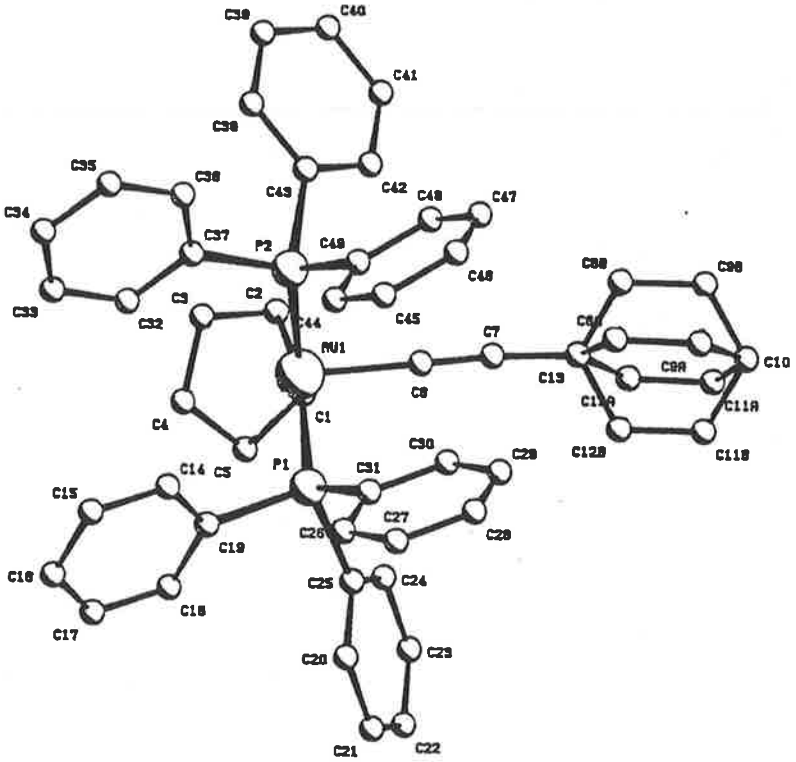


Figure 1: PLUTO plot of the molecular structure of Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$) (1), showing both orientations of the disordered phenyl group.

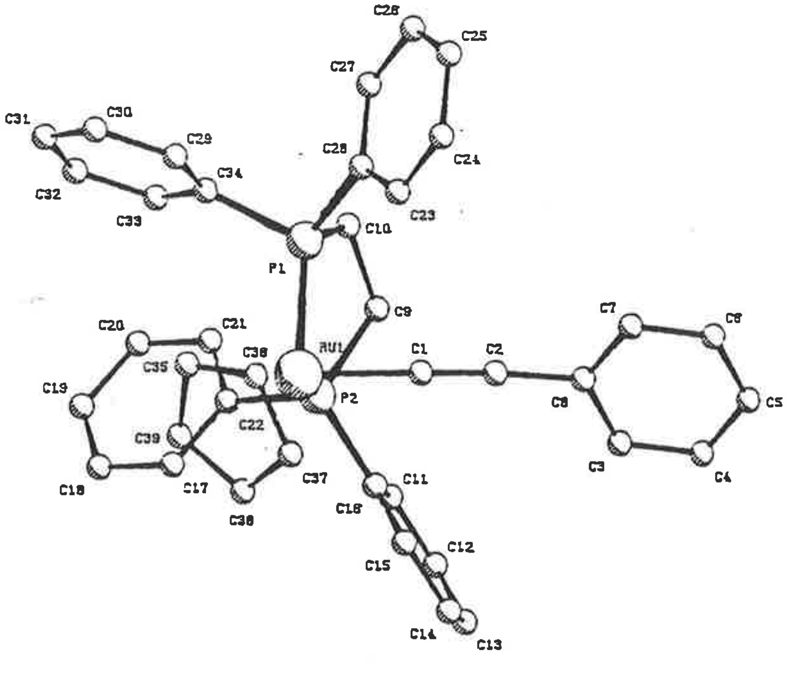


Figure 2: PLUTO plot of the molecular structure of Ru(C≡CPh)(dppe)(η-C$_5$H$_5$) (2).

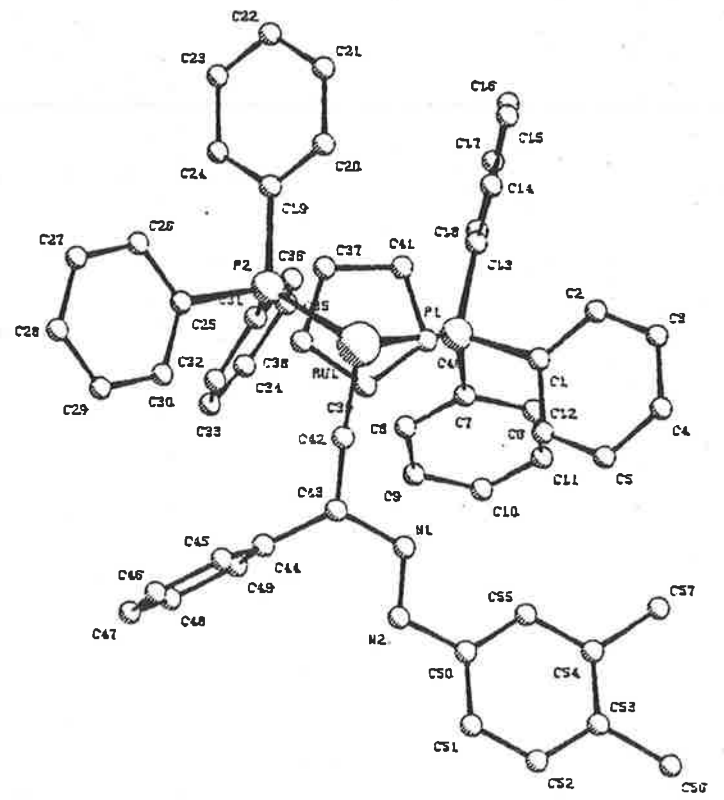


Figure 3: PLUTO plot of the structure of the cation in $[Ru\{C{=}CPh(N{=}NC_6H_3Me_2\text{-}3,4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (3).

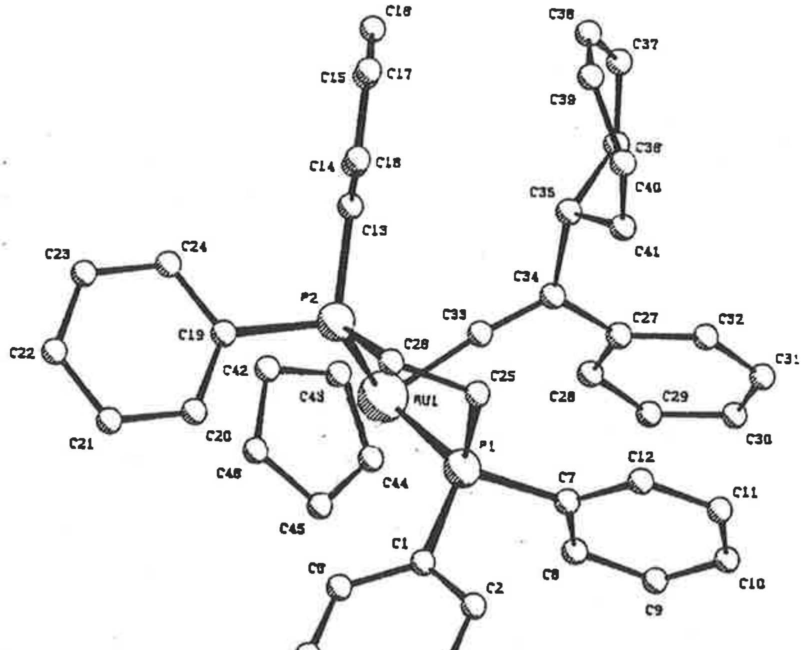


Figure 4: PLUTO plot of the structure of the cation in $[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (4).

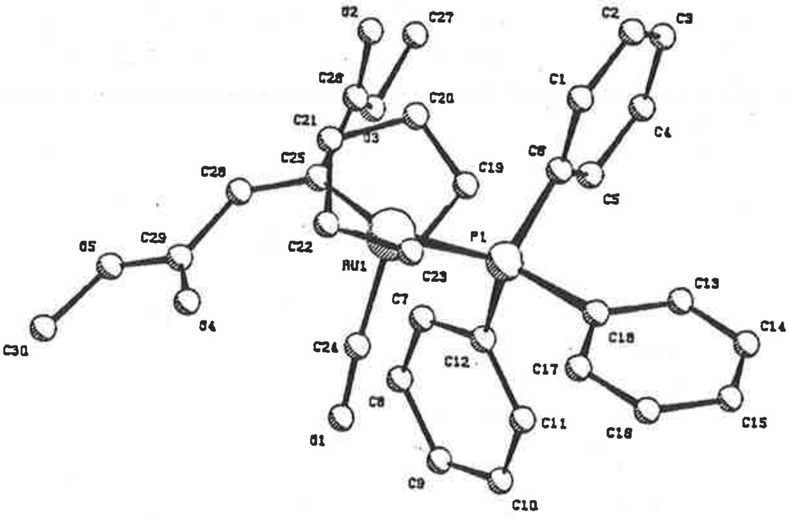


Figure 5: PLUTO plot of the molecular structure of $Ru\{(Z)-C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta-C_5H_5)$ (5).

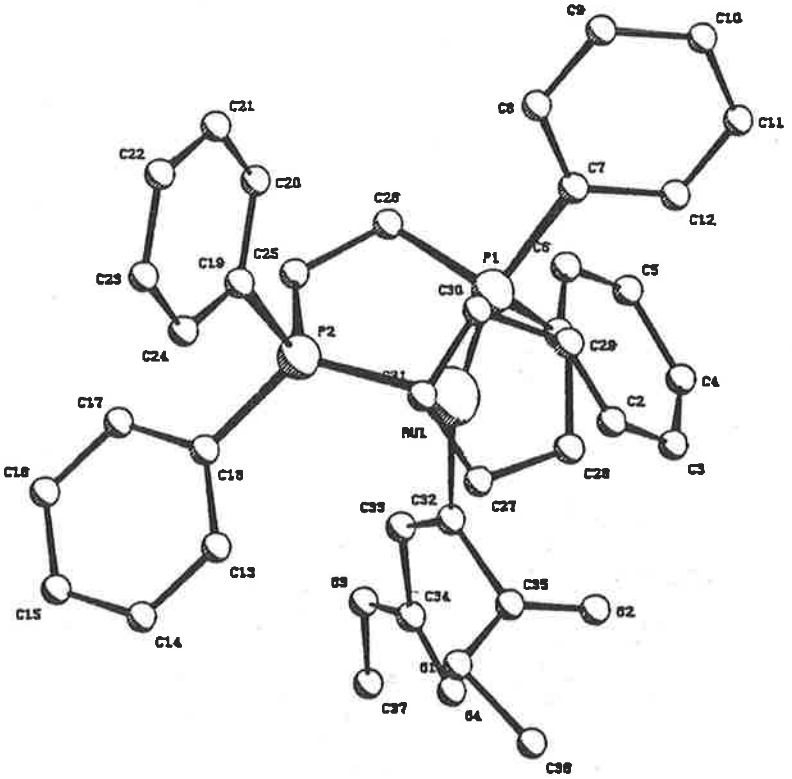
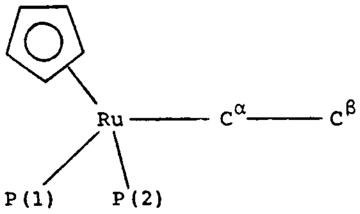


Figure 6: PLUTO plot of the molecular structure of $Ru\{(E)-C(CO_2Me)=CH(CO_2Me)\}(dppe)(\eta-C_5H_5)$ (6).

Table 1

Selected Bond Lengths (Å) for complexes of general formula Ru(R)(L)(L´)(η-C_5H_5).



	(1)	(2)	(3)	(4)	(5)	(6)
(R)	(C≡CPh)	(C≡CPh)	{C=CPh(N=N-$C_6H_3Me_2$-3,4)}	{C=CPh(C_7H_7)}	{C(CO_2Me)=C(H)-CO_2Me}	{C(CO_2Me)=C(H)-CO_2Me}
(L)(L´)	(PPh_3)$_2$	(dppe)	(PPh_3)$_2$	(dppe)	(CO)(PPh_3)	(dppe)
Ru-Cp 1	2.229(3) [2.229(3)][a]	2.261(4), 2.276(8)[b]	2.308(6)	2.250(5)	2.256(5)	2.235(8)
2	2.228(3) [2.228(3)]	2.260(5), 2.283(8)	2.263(6)	2.240(4)	2.250(7)	2.277(9)
3	2.242(4) [2.238(3)]	2.251(5), 2.265(9)	2.241(6)	2.259(4)	2.255(6)	2.283(9)
4	2.251(4) [2.256(3)]	2.245(5), 2.248(8)	2.273(6)	2.281(5)	2.263(7)	2.244(8)
5	2.243(4) [2.227(3)]	2.252(4), 2.255(9)	2.314(6)	2.276(6)	2.264(8)	2.214(8)
Ru-P(1)	2.307(1) [2.303(1)]	2.240(1)	2.362(3)	2.298(2)	2.310(2)	2.271(4)
Ru-P(2)	2.294(1) [2.285(1)]	2.250(1)	2.360(3)	2.305(2)	1.847(7)[d]	2.249(4)
Ru-C^{α}	2.017(5) [2.016(3)	2.009(3)	1.823(9)	1.848(9)	2.080(8)	2.071(12)
C^{α}-C^{β}	1.214(7) [1.215(4)]	1.204(5)	1.340(13)	1.319(13)	1.373(10)	1.433(21)
C^{β}-Ph	1.462(8) [1.456(4)] 1.418(8)[c]	1.444(5)	1.477(10)	1.483(9)	-	-
C^{β}-N	-	-	1.420(13)	-	-	-
N=N	-	-	1.272(10)	-	-	-
N-Ph	-	-	1.422(11)	-	-	-
C^{β}-C_7H_7	-	-	-	1.549(10)	-	-
C^{α}-CO_2Me	-	-	-	-	1.494(9)	1.472(21)
C^{β}-CO_2Me	-	-	-	-	1.462(10)	1.525(23)

All bracketed figures except a are 3σ.

[b] two orientations of Cp ring.

[a] values in square brackets from ref. 3, figures in brackets 9.5σ

[c] two orientations of Ph ring.

[d] P(2) ≡ CO

for the related complex $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$.[5] The C=C bonds of the vinyl groups in (5) and (6) have lengths of 1.37(1) and 1.43(2)Å respectively; a value of 1.37(2)Å was determined for the vinyl C=C bond in *trans*-$Pt(H)\{(Z)\text{-}C(CO_2Me){=}C(H)CO_2Me\}(PBu^nBu^t{}_2)_2$.[6] In the acetylides, the Ru-C≡C moiety is essentially linear [178.0(2)° for (1), 178.1(3)° for (2)], while in the vinylidenes, the Ru-C=C group is slightly bent [169.9(7)° for (3), 174.9(6)° for (4)].

2. Ru-P Distances in Cyclopentadienylruthenium Phosphine and Phosphite Complexes

The Ru-P distances in complexes (1) to (6) are given in Table 2, together with analogous data for other cyclopentadienylruthenium phosphine and phosphite compounds. Ru-P values have been collected elsewhere (e.g. refs. 48 - 51); in the case of *cis*-coordinated phosphines, distances in the range 2.20 - 2.39Å have been reported (*trans* phosphines have Ru-P bond lengths between 2.33 - 2.48Å).[52] The sum of the covalent radii of P and Ru is 2.43Å.[53] The present survey reveals values in the range 2.20 - 2.38Å (the quoted Ru-P distance in (*R*)-$[Ru(SnCl_3)\{(R)\text{-}Ph_2PCH(Me)CH_2PPh_2\}(\eta\text{-}C_5H_5)]$ of 2.888Å is anomalous and will not be discussed further).[9] The individual distances and their respective e.s.d.'s have been tabulated, rather than the mean values. In some eleven cases, the difference between Ru-P(1) and Ru-P(2) is significant. These differences are presumably due to crystal packing forces when P(1) and P(2) are spectroscopically equivalent, as in the case of $Ru(C{\equiv}CPh)\{(R)\text{-}Ph_2PCH(Me)CH(Me)PPh_2\}(\eta\text{-}C_5H_5)$.[17]

Table 2

Ruthenium-phosphorus bond distances in cyclopentadienylruthenium complexes.

(A) Haloruthenium complexes

Complex	Ru-P(1)	Ru-P(2)	Reference
$\mathrm{RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$	2.199(2)	2.234(2)	7
$\mathrm{RuCl(PMe_3)_2(\eta\text{-}C_5H_5)}$	2.273(6)	2.275(6)	8
	2.273(5)[a]	2.280(6)	
$(S)\text{-}\mathrm{[RuCl\{}(R)\mathrm{\text{-}Ph_2PCH(Me)CH_2PPh_2\}(\eta\text{-}C_5H_5)]}$	2.276(2)	2.278(2)	9, 10
$(S)\text{-}\mathrm{[RuCl(CO)(PPh_3)\{\eta\text{-}}(R)\mathrm{\text{-}C_5H_4menthyl\}]}$	2.310(2)		2
$\mathrm{RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)}$	2.311(3)		11
$(R)\text{-}\mathrm{[RuI(CO)(PPh_3)\{\eta\text{-}}(S,R,S)\mathrm{\text{-}(-)\text{-}C_5H_4neomenthyl\}]}$	2.313(4)		12
$\mathrm{RuCl(\eta^1\text{-}dppm)(PPh_3)(\eta\text{-}C_5H_5)}$	2.319(2)[b]	2.316(2)[c]	13
$\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_4C{\equiv}CCO_2Me)}$	2.326(2)	2.329(2)	14
$\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_5)}$	2.335(1)	2.337(1)	8

[a] Two independent molecules. [b] η^1-dppm. [c] $\mathrm{PPh_3}$

Table 2

(B) Ruthenium complexes with *C*-donor ligands (excluding CO,CN)

Complex	Ru-P(1)	Ru-P(2)	Reference
Ru{C(Ph)=C(Ph)C(Ph)=C(H)(Ph)}{P(OMe)$_3$}(η-C$_5$H$_5$)	2.220(2)		15
(*S*)-[RuMe{(*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$}(η-C$_5$H$_5$)]	2.229(2)	2.247(2)	16
Ru{C(=CMePh)CH(PPh$_2$)CH$_2$PPh$_2$}(η-C$_5$H$_5$)	2.239(1)	2.241(2)	62
Ru[C(O)C(Ph)=C(Ph)-η^2-{(*Z*)-C(Ph)=C(H)(Ph)}]{P(OMe)$_3$}(η-C$_5$H$_5$)	2.240(4)		15
Ru(C≡CPh)(dppe)(η-C$_5$H$_5$)	2.240(1)	2.250(1)	this work
(*R*)-[Ru(C≡CPh){(*R*)-Ph$_2$PCH(Me)CH(Me)PPh$_2$}(η-C$_5$H$_5$)]	2.241(2)	2.255(2)	17
Ru(1-σ-C$_8$H$_{13}$)(dppm)(η-C$_5$H$_5$)[a]	2.244(2)	2.252(2)	18
	2.259(2)[b]	2.250(2)	
Ru{C(CO$_2$Me)=C(H)CO$_2$Me}(dppe)(η-C$_5$H$_5$)	2.249(4)	2.271(4)	this work
Ru(1-σ-C$_8$H$_{13}$)(dppm)(η-C$_5$H$_5$)[c]	2.253(1)	2.258(1)	18
Ru(2-C$_6$H$_4$PPh$_2$)(PPh$_3$)(η-C$_5$H$_5$)	2.257(5)	2.284(5)	7
	2.277(5)[b]	2.295(5)	
Ru[C{=C(CN)$_2$}C(Ph)=C(CN)$_2$](dppe)(η-C$_5$H$_5$)	2.280(1)	2.340(1)	1
Ru(CHO)(CO)(PMe$_2$Ph)(η-C$_5$Me$_5$)	2.282(1)		19
Ru(2-C$_6$F$_4$N=NC$_6$F$_5$)(Ph$_2$PC$_6$H$_4$-η-C$_5$H$_4$)	2.283(3)		20
Ru[C{=C(CN)$_2$}C(Ph)=C(H)C$_6$H$_4$NO$_2$-4](dppe)(η-C$_5$H$_5$)	2.283(2)	2.319(3)	21
Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)	2.285(1)	2.303(1)	3
	2.294(1)	2.307(1)	this work
(*R*)-[Ru{C(OMe)CH$_2$Ph}{(*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$}(η-C$_5$H$_5$)][PF$_6$]	2.286(4)	2.299(4)	22
[Ru(C=C=CPh$_2$)(PMe$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]	2.289(2)	2.292(2)	23
(*S*)-[Ru(C=CHMe){(*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$}(η-C$_5$H$_5$)][PF$_6$]	2.289(2)	2.297(2)	22
[Ru(C=CHMe)(PMe$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]	2.293(2)	2.305(2)	5

Table 2 (B) continued

Complex	Ru-P(1)	Ru-P(2)	Reference
$Ru\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(NCMe)(PPh_3)(\eta\text{-}C_5H_5)$	2.297(2)		24
$Ru\{C(OPr^i){=}C(H)Ph\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.298(2)		25
$[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$	2.298(2)	2.305(2)	26
$Ru_2(\mu\text{-}C_8Ph_4)(PPh_3)_2(\eta\text{-}C_5H_5)_2$	2.308(2)	2.310(2)	27
$Ru\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.309(2)		24
$Ru\{C(H)(CO_2Me)C(CO_2Me)C{=}C(H)(Ph)\}(PPh_3)(\eta\text{-}C_5H_5)$	2.310(2)		27
$Ru\{C(CO_2Me){=}C(H)CO_2Me\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.310(2)		this work
$[Ru\{(CF_3)_2CC(Ph){=}CC(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(CF_3)_2C{=}C(CN)_2]$	2.314(6)	2.316(6)	28
$Ru[C\{{=}C(CN)_2\}C(Ph){=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.332(1)		24
$Ru\{C(CF_3){=}C(H)C(CF_3){=}C{=}C{=}C(H)(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$	2.335(3)		29
$[Ru\{C{=}CI(Ph)\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$	2.337(2)	2.356(2)	30
$[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]I$	2.341(3)	2.363(3)	31
$Ru[C\{{=}C(CN)_2\}C(Me){=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.347(1)		28
$[Ru\{C(OMe)Et\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$	2.347(2)	2.349(2)	31
$[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(\eta\text{-}C_5H_5)_2][PF_6]_2$	2.347(5)	2.368(5)	32
	2.354(5)	2.381(5)	
$[Ru\{C{=}CPh(N{=}NC_6H_3Me_2\text{-}3,4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$	2.360(3)	2.362(3)	26
$Ru[C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(H)(CF_3)](PPh_3)(\eta\text{-}C_5H_5)$	2.366(3)		33
$[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$	2.366(5)	2.366(5)	34
$[Ru(\eta^4\text{-}nbd)(PPh_3)(\eta\text{-}C_5H_5)][ClO_4]$	2.379(1)		35
$Ru[\eta^3\text{-}C(CF_3)_2C(Ph)C\{{=}C(CN)_2\}](PPh_3)(\eta\text{-}C_5H_5)$	2.411(2)		24

Table 2 (B) continued

Complex	Ru-P(1)	Ru-P(2)	Reference
$Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5).CuCl$	not given		36
$Ru\{\overline{C(CF_3)=C(CF_3)C(CF_3)}=C(H)(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$	not given		37
$Ru[C\{=C(CN)_2\}C(Ph)=C(CN)_2](CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$	not given		16
$Ru[\eta^3\text{-}C(CN)_2C(Ph)C\{=C(CN)_2\}](PPh_3)(\eta\text{-}C_5H_5)$	not given		16

[a] Orange isomer. [b] Two independent molecules. [c] Yellow isomer.

Table 2

(C) Other ruthenium complexes

Complex	Ru-P(1)	Ru-P(2)	Reference
Ru{NH=C(CF$_3$)N=C(CF$_3$)NH}{P(OMe)$_3$}(η-C$_5$H$_5$)	2.219(2)		39
	2.229(1)[a]		
Ru{N=C=C(CN)C(CN)=C(CN)$_2$}{P(OMe)$_3$}(PPh$_3$)(η-C$_5$H$_5$)	2.239(2)[b]	2.322(2)[c]	40
Ru(H)(dppf)(η-C$_5$H$_5$)	2.246(3)	2.263(4)	27
	2.258(3)[a]	2.265(3)	
[Ru(dppe)(η-C$_5$H$_5$)(μ-CN)Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]	2.265(4)[d]	2.327(3)[e]	41
	2.276(4)	2.337(3)	
(*S*)-[Ru(NCMe){(*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$}(η-C$_5$H$_5$)][PF$_6$]	2.28[h]		42
Ru{η^3-S$_2$CCH(Me)C$_6$H$_4$PPh$_2$}(η-C$_5$H$_5$)	2.288(1)		43
[Ru(C$_4$H$_6$)(PMe$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]	2.294(1)[a]	2.302(1)	57
	2.301(1)	2.298(1)	
[Ru(C$_3$H$_4$)(PMe$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$]	2.297(1)[a]	2.320(1)	57
	2.297(1)	2.321(1)	
[Ru(η^2-dppm)(η^1-dppm)(η-C$_5$H$_5$)][½PO$_2$F$_2$,½PF$_6$]	2.295(3)[f]	2.323(2)	14
	2.325(3)		
(*R*)-[Ru(NCMe)(CO)(PPh$_3$){η-(*S*,*R*,*S*)-(-)-C$_5$H$_4$neomenthyl}][PF$_6$]	2.324(3)		44
[Ru(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BPh$_4$]	2.327(1)	2.340(1)	3
[Ru(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)][Co(CO)$_4$]	2.347(13)	2.361(7)	45
Ru(CO)$_2$[P{C(O)Bu^t}$_2$](η-C$_5$Me$_5$)	2.404(1)		46,47
(*R*)-[Ru(SnCl$_3$){(*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$}(η-C$_5$H$_5$)]	2.888[h]		9

[a] Two independent molecules. [b] Trimethylphosphite. [c] Triphenylphosphine. [d] Dppe.

[e] Triphenylphosphines. [f] Bidentate dppm. [g] Monodentate dppm. [h] Mean value.

Table 2 has been divided into three parts. Part (A) considers the variations in Ru-P distances in haloruthenium complexes. The $d_{\text{Ru-P}}$ values broadly follow the trend of increasing with the cone angle[54] of the ligand, calculated for a constant M-P distance of 2.28Å, implying steric effects are significant in determining this parameter. Thus $d_{\text{Ru-P}}$ increases in the order L = $P(OMe)_3$ (107°) < PMe_3 (118°) < PPh_3 (145°) for the $CpRuL_2Cl$ complexes and L = CO (95°) ≅ η^1-dppm (136°) < PPh_3 (145°) for the $CpRu(L)(PPh_3)Cl$ complexes, where the figure in brackets is the cone angle of the ligand, and, as an approximation, the angle for $PMePh_2$ has been used for η^1-dppm. Maintaining the other ligands and replacing the cyclopentadienyl group with a η-$C_5H_4C{\equiv}CCO_2Me$ or menthylcyclopentadienyl group has no effect on this parameter; it is also insensitive to replacement of chloride by iodide.

Part (B) contains Ru-P distances for complexes incorporating *C*-donor ligands. Replacements of bis(phosphines) with a chelating phosphine decreases $d_{\text{Ru-P}}$ by approximately 0.06Å and, in general, the Ru-P separations are longer in cationic complexes than in neutral ones. This is probably the result of more efficient back-donation from the metal into the *C*-donor ligand; a similar phenomenon has been reported before.[3] The Ru-P distances increase as the π-accepting strength of the functional group increases. Recent theoretical calculations[55] and experimental results[56] suggest that back-donation into tertiary phosphines puts electron

<u>Table 3</u>

Ruthenium-chlorine bond distances in cyclopentadienylruthenium complexes.

Complex	Ru-Cl (Å)	Reference
$RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$	2.393(3)	7
$RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.396(6)	11
$RuCl(PPh_3)_2(\eta\text{-}C_5H_4C{\equiv}CCO_2Me)$	2.419(2)	14
(*S*)-$[RuCl(CO)(PPh_3)\{\eta\text{-}(R)\text{-}C_5H_4menthyl\}]$	2.425(2)	2
$RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$	2.440(5) 2.451(6)[a]	8
(*S*)-$[RuCl\{(R)\text{-}Ph_2PCH(Me)CH_2PPh_2\}(\eta\text{-}C_5H_5)]$	2.444(2)	9,10
$RuCl(\eta^1\text{-}dppm)(PPh_3)(\eta\text{-}C_5H_5)$	2.445(3)	13
$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$	2.453(2)	8

[a] Two independent molecules.

density into P-R σ*orbitals. Competition for electron density between PR_3 and good π-acceptors would lengthen the M-P bond and at the same time result in a decrease in the P-C bond length. However, the e.s.d.'s in the P-C bond lengths preclude any meaningful discussion on this point.

3. Ru-Cl Distances in Cyclopentadienylruthenium Phosphine and Phosphite Complexes

The Ru-Cl distances in the relevant complexes are listed in Table 3. Values for $d_{\text{Ru-Cl}}$ increase in the order $P(OMe)_3 < PMe_3 \cong PPh_3$ for the bis-ligand complexes and $CO < \eta^1\text{-dppm} \cong PPh_3$ for the (L)(PPh_3) complexes (*c.f.* $d_{\text{Ru-P}}$ series above). The variations in $d_{\text{Ru-Cl}}$ are smaller than those in $d_{\text{Ru-P}}$ for the chlororuthenium complexes, covering a range of 0.06Å for the former and 0.14Å for the latter. Substituting the cyclopentadienyl ring with a menthyl or $(C{\equiv}CCO_2Me)$ group leads to an increase in $d_{\text{Ru-Cl}}$ of 0.03Å for the former and a decrease of the same magnitude in the latter, yet both are electron donating substituents. In both cases, the cyclopentadienyl substituent is *trans* to the phosphine(s) but, as mentioned above, does not significantly affect the $d_{\text{Ru-P}}$ values.

4. Ru-C(Cp) Distances in Cyclopentadienylruthenium Phosphine and Phosphite Complexes

Series of ruthenium-cyclopentadienyl carbon distances are tabulated in Tables 4(A) - (D). In some cases, the cyclopentadienyl group has been constrained as a rigid pentagon. This naturally has some effect on individual Ru-C(Cp) distances, and I have indicated where this constraint has been applied.

Table 4(A)

Ru-cyclopentadienyl carbon bond distances in bis(triphenylphosphine) complexes.

Complex	Ru-C(1)	Ru-C(2)	Ru-C(3)	Ru-C(4)	Ru-C(5)[a]	Ru-C(av.)	Reference
$RuCl(PPh_3)_2(\eta-C_5H_5)$	2.220(3)	2.220(3)	2.210(3)	2.192(2)	2.194(4)	2.207	8
$Ru(C\equiv CPh)(PPh_3)_2(\eta-C_5H_5)$	2.227(3)	2.229(3)	2.228(3)	2.238(3)	2.256(3)	2.236	3
	2.243(4)	2.229(3)	2.228(3)	2.242(4)	2.251(4)	2.239	this work[c]
$[Ru(C=CMePh)(PPh_3)_2(\eta-C_5H_5)]I$	2.234(1)	2.256(12)	2.245(12)	2.239(13)	2.264(12)	2.248	3
$[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][BPh_4]$	2.244(2)	2.235(2)	2.239(2)	2.271(2)	2.265(2)	2.251	3
$[Ru\{C(OMe)Et\}(PPh_3)_2(\eta-C_5H_5)][PF_6]$	2.260(6)	2.247(7)	2.266(8)	2.243(7)	2.290(6)	2.261	31
$[Ru\{C=CBr(C_6H_4Br-4)\}(PPh_3)_2(\eta-C_5H_5)][Br_3]$[c]	2.231(12)	2.226(12)	2.273(12)	2.306(12)	2.280(11)	2.263	34
$[Ru\{C=CI(Ph)\}(PPh_3)_2(\eta-C_5H_5)][I_3]$	2.267(8)	2.250(5)	2.256(5)	2.277(6)	2.284(5)	2.267	30
$[Ru\{C=CPh(N=NC_6H_3Me_2-3,4)\}(PPh_3)_2(\eta-C_5H_5)][BF_4]$[c]	2.308(6)	2.263(6)	2.241(6)	2.273(6)	2.314(6)	2.280	this work
$Ru(C\equiv CPh)(PPh_3)_2(\eta-C_5H_5).CuCl$							36[b]
$[\{Ru(PPh_3)_2(\eta-C_5H_5)\}_2(\mu-C_{10}H_{12})][PF_6]_2$							38[b]
$[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][Co(CO)_4]$							45[b]
$[Ru(PPh_3)_2(\eta-C_5H_5)(\mu-NC)Ru(dppe)(\eta-C_5H_5)][PF_6]$							41[b]

[a] C(5) is approximately trans to X group. [b] Values not given. [c] Cp ring refined as a rigid group.

Table 4(B)

Ru-cyclopentadienyl carbon bond distances in $(PPh_3)(CO)$ complexes.

Complex	Ru-C(1)[a]	Ru-C(2)	Ru-C(3)	Ru-C(4)	Ru-C(5)	Ru-C(av.)	Reference
$Ru[C\{=C(CN)_2\}C(Me)=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.240(4)	2.217(4)	2.232(4)	2.264(4)	2.269(4)	2.244	28
$[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][BPh_4]$	2.244(2)	2.235(2)	2.239(2)	2.271(2)	2.265(2)	2.251	3
$Ru[C\{=C(CN)_2\}C(Ph)=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.249(5)	2.262(5)	2.235(5)	2.251(5)	2.283(6)	2.256	24
$Ru\{C=C(Ph)C(CF_3)_2(C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.273(7)	2.262(8)	2.254(9)	2.247(8)	2.252(7)	2.258	24
$Ru\{C(CO_2Me)=C(H)(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$[c]	2.255(6)	2.263(7)	2.264(8)	2.256(5)	2.250(7)	2.258	this work
$RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$[c]	2.298(20)	2.249(26)	2.241(22)	2.250(28)	2.265(31)	2.261	11
$[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][Co(CO)_4]$							45[b]

[a] C(1) and C(2) are approximately trans to PPh_3, C(3) and C(4) are approximately trans to X and C(5) is approximately trans to CO.

[b] Values not given.

[c] Cp ring refined as a rigid group.

Table 4(C)

Ru-cyclopentadienyl carbon bond distances in dppe complexes.

Complex	Ru-C(1)	Ru-C(2)	Ru-C(3)	Ru-C(4)	Ru-C(5)[a]	Ru-C(av.)	Reference
$Ru[C\{=C(CN)_2\}C(Ph)=C(H)(C_6H_4NO_2\text{-}4)](dppe)(\eta\text{-}C_5H_5)$	2.240(9)	2.243(10)	2.250(10)	2.235(12)	2.198(10)	2.233	21
$Ru\{C(CO_2Me)=C(H)(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$[c]	2.214(8)	2.235(8)	2.277(9)	2.283(9)	2.244(8)	2.251	this work
$Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)$[c]	2.261(4)	2.260(5)	2.251(5)	2.245(5)	2.252(4)	2.254	this work
$[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$[c]	2.250(5)	2.240(4)	2.259(4)	2.281(5)	2.276(6)	2.261	this work
$[Ru(dppe)(\eta\text{-}C_5H_5)(\mu\text{-}CN)Ru(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$							41[b]
$Ru[C\{=C(CN)_2\}C(Ph)=C(CN)_2](dppe)(\eta\text{-}C_5H_5)$							1[b]

[a] C(5) is approximately trans to X group. [b] Values not given. [c] Cp ring refined as a rigid group.

Table 4(D)

Ru-cyclopentadienyl carbon bond distances in chloride complexes.

Complex	Ru-C(1)	Ru-C(2)	Ru-C(3)	Ru-C(4)	Ru-C(5)	Ru-C(av.)	Reference
(*S*)-[RuCl{(*R*)-$Ph_2PCH(Me)CH_2PPh_2$}(η-C_5H_5)][e]	2.213(10)	2.207(9)	2.159(9)	2.161(9)	2.230(10)	2.194	9,10
RuCl(PMe_3)$_2$(η-C_5H_5)[c] [a]	2.17(2)	2.23(2)	2.20(2)	2.15(2)	2.23(2)	2.20	8
	2.24(2)[d]	2.21(2)	2.19(2)	2.21(2)	2.17(2)	2.20	
RuCl(η^1-dppm)(PPh_3)(η-C_5H_5)[b] [a]	2.220(7)	2.215(8)	2.210(8)	2.209(8)	2.174(8)	2.206	13
RuCl(PPh_3)$_2$(η-C_5H_5)[a]	2.220(3)	2.220(3)	2.210(3)	2.192(2)	2.194(4)	2.207	8
RuCl(PPh_3)$_2$(η-$C_5H_4C{\equiv}CCO_2Me$)[a] [f]	2.206(8)	2.224(7)	2.225(8)	2.195(8)	2.191(8)	2.208	14
(*S*)-[RuCl(CO)(PPh_3){η-(*R*)-C_5H_4menthyl}][b] [e]	2.249(9)	2.236(9)	2.207(10)	2.250(9)	2.245(9)	2.237	2
RuCl(CO)(PPh_3)(η-C_5H_5)[b] [e]	2.298(20)	2.249(26)	2.241(22)	2.250(28)	2.265(31)	2.261	11
RuCl{P(OMe)$_3$}$_2$(η-C_5H_5)[a]	2.266(11)	2.288(10)	2.281(10)	2.309(14)	2.266(14)	2.282	7

[a] C(5) is approximately trans to Cl.

[b] C(1) and C(2) are approximately trans to PPh_3.

[c] C(1) and C(3) are approximately trans to PMe_3; C(4) and C(5) are trans to Cl.

[d] Two independent molecules.

[e] C(3) and C(4) are approximately trans to Cl.

[f] C(3) has ($C{\equiv}CCO_2Me$) substituent.

In cases where the structure has been determined to the requisite degree of accuracy, some asymmetry is apparent in variations in the Ru-C(Cp) distances. This has been attributed to the relative *trans* effects of the ligands in some published examples; the larger *trans* effect of PMe_3 was considered responsible for the asymmetry in $[Ru(\eta^2\text{-}C_4H_6)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$[57] and the asymmetry in $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][BPh_4]$[3] was ascribed to the greater *trans* effect of CO. However, tabulation of examples of complexes of the type $Ru(X)(L)(L')(\eta\text{-}C_5H_5)$, where the L and L´ (= phosphines, CO) are held constant and the X group allowed to vary [Tables 4(A), 4(B) and 4(C)], shows that although variations in Ru-C(Cp) bond lengths do exist, they cannot readily be rationalised by *trans* effects; also, a five-sided figure occupying three coordination sites presents obvious difficulties. Consideration of the average ruthenium-cyclopentadienyl carbon bond distance overcomes part of the problem, that of localising the part of the cyclopentadienyl ligand that is *trans*. Assuming the effect of the PPh_3 ligands is constant, values in the Ru-C(av.) column of Table 4(A) indicate relative *trans*-effect strengths of the X ligands. As would be expected on the basis of their relative π-accepting strengths, halide and acetylide ligands exert a much weaker *trans*-effect than the vinylidene group, which is one of the best π-acceptors known.[72]

Table 4(D) considers the Ru-C(Cp) distances in chlororuthenium complexes. The Ru-C(av.) parameter seems largely insensitive to the nature of the tertiary phosphine; however, replacement by CO or $P(OMe)_3$ greatly increases the

Ru-C(av.) value. Substitution of the cyclopentadienyl ring with a ($C{\equiv}CCO_2Me$) group has no effect on the Ru-C(Cp) distances; the high e.s.d.'s in the structure of $RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)$ preclude a comparison with its menthylcyclopentadienyl analogue.

5. Ru-C Distances in Cyclopentadienylruthenium Phosphine and Phosphite Complexes (C = σ-bonded carbon ligand)

The chief interest in the author's structure determinations lies in the magnitude of the Ru-C(α) separations; an earlier survey[3] of Ru-C distances can now be extended to include the shorter Ru-C bonds found for the unsaturated ligands. For (1) and (2), values of 2.017(5) and 2.009(3)Å are consistent with single bonds from Ru^{II} to a C(*sp*) atom, and indicate a very low degree of metal to ligand back-bonding. In the palladium complex $Pd(C{\equiv}CC_6H_4C{\equiv}CH\text{-}2)(NCS)(PEt_3)_2$,[58] the Pd-C bond length is 1.952(7)Å, while in $Rh(C{\equiv}CPh)(tcne)(NCMe)(PPh_3)_2$, the Rh-C separation is 1.94(2)Å.[59] In contrast, the values found for the $Ru\text{-}C{=}CR_2$ bonds in (3) and (4) are significantly shorter, and suggest that considerable degrees of back-bonding from Ru to the α-carbon occur in these two complexes. The corresponding values for (5) and (6) are consistent with there being single bonds from Ru^{II} to a C(sp^2) atom.

The Ru-C bond lengths in $Ru(L_2)(\eta\text{-}C_5H_5)$ complexes are summarised in Table 5. Whilst a similar compilation has been presented before,[3] it is useful to extend the available data by inclusion of a number of examples which

Table 5

Ru-C distances in some cyclopentadienylruthenium complexes.

Complex	Ru-C(Å)	Reference	Δ[a]
$[Ru(C=CPhN=NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$	1.823(9)	this work	-0.11
$[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(\eta\text{-}C_5H_5)_2][PF_6]_2$	1.83(2)	32	-0.10
$(S)\text{-}[Ru(C=CHMe)\{(R)\text{-}Ph_2PCHMeCH_2PPh_2\}(\eta\text{-}C_5H_5)][PF_6]$	1.839(10)	22	-0.09
$[Ru\{C=CI(Ph)\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$	1.839(7)	30	-0.09
$[Ru(C=CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$	1.845(7)	5	-0.08
$[Ru\{C=CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$	1.848(9)	this work	-0.08
$[Ru\{C=CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$	1.85(1)	34	-0.08
$[Ru(C=CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)]I$	1.863(10)	31	-0.07
$[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][BPh_4]$	1.869(2)	3	-0.06
$[Ru(C=C=CPh_2)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$	1.884(5)	23	-0.05
$[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][Co(CO)_4]$	1.890(2)	45	-0.04
$(R)\text{-}[Ru\{C(OMe)CH_2Ph\}\{(R)\text{-}Ph_2PCHMeCH_2PPh_2\}(\eta\text{-}C_5H_5)][PF_6]$	1.93(2)	22	-0.07
$[Ru\{C(OMe)Et\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$	1.959(6)	31	-0.04
$Ru_2(\mu\text{-}C_8Ph_4)(PPh_3)_2(\eta\text{-}C_5H_5)_2$	1.982(7)	27	-0.02
$Ru_2(\mu\text{-}C_8Ph_4)(PPh_3)_2(\eta\text{-}C_5H_5)_2$	1.997(7)	27	0.0
$Ru(C\equiv CPh)(dppe)(\eta\text{-}C_5H_5)$	2.009(3)	this work	+0.08
$[Ru\{C(CF_3)_2CC(Ph)=CC(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)]_2\{\mu\text{-}(CF_3)_2C=C(CN)_2\}$	2.012(24)	28	+0.01
$\overline{Ru(2\text{-}C_6F_4N=N}C_6F_5)[PPh_2(C_6H_4\text{-}\eta\text{-}C_5H_5)]$	2.013(6)	60	+0.01
$Ru(C\equiv CPh)(PPh_3)_2(\eta\text{-}C_5H_5).CuCl$	2.016(9)	36	+0.09
$Ru(C\equiv CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$	2.016(3)	3	+0.09
	2.017(5)	this work	+0.09

Table 5 continued

Complex	Ru-C(Å)	Reference	a
$[\mathrm{Ru(dppe)(\eta\text{-}C_5H_5)(\mu\text{-}CN)Ru(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]}$	2.03(2)	41	+0.10
$\mathrm{Ru\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(NCMe)(PPh_3)(\eta\text{-}C_5H_5)}$	2.034(7)	24	+0.03
$\mathrm{Ru(CHO)(CO)(PMe_2Ph)(\eta\text{-}C_5Me_5)}$	2.036(4)	19	+0.04
$(R)\text{-}[\mathrm{Ru(C{\equiv}CPh)\{(}R\mathrm{)\text{-}Ph_2PCHMeCHMePPh_2\}(\eta\text{-}C_5H_5)}]$	2.038(7)	17	+0.11
$\mathrm{Ru[C(O)CPh{=}CPh\text{-}\eta^2\text{-}\{(}Z\mathrm{)\text{-}CPh{=}CHPh\}][P(OMe)_3](\eta\text{-}C_5H_5)}$	2.040(12)	15	+0.04
$\overline{\mathrm{Ru\{C(CF_3){=}C(CF_3)C(CF_3)}}\mathrm{{=}C(H)(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)}$	2.05	37	+0.05
$\mathrm{Ru_2(\mu\text{-}C_8Ph_4)(PPh_3)_2(\eta\text{-}C_5H_5)_2}$	2.051(7)	27	+0.05
$\mathrm{Ru\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}$	2.054(8)	24	+0.05
$\mathrm{Ru_2(\mu\text{-}C_8Ph_4)(PPh_3)_2(\eta\text{-}C_5H_5)_2}$	2.062(7)	27	+0.06
$\mathrm{Ru[C\{{=}C(CN)_2\}C(Ph){=}C(H)C_6H_4NO_2\text{-}4](dppe)(\eta\text{-}C_5H_5)}$	2.063(8)	21	+0.06
$[\mathrm{Ru\{C(CF_3)_2CC(Ph){=}CC(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)]_2\{\mu\text{-}(CF_3)_2C{=}C(CN)_2\}}$	2.066(20)	28	+0.07
$\overline{\mathrm{Ru(2\text{-}C_6H_4}}\mathrm{PPh_2)(PPh_3)(\eta\text{-}C_5H_5)}$	2.069(17)	7	+0.07
	2.091(17)[b]		+0.09
$\overline{\mathrm{Ru\{C(Ph){=}C(Ph)C(Ph)}}\mathrm{{=}C(H)(Ph)\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)}$	2.070(7)	15	+0.07
$\mathrm{Ru\{C(CO_2Me){=}C(H)CO_2Me\}(dppe)(\eta\text{-}C_5H_5)}$	2.071(12)	this work	+0.07
$\mathrm{Ru[C\{{=}C(CN)_2\}C(Ph){=}C(CN)_2](dppe)(\eta\text{-}C_5H_5)}$	2.074(3)	1	+0.07
$\mathrm{Ru[C\{{=}C(CN)_2\}C(Ph){=}C(CN)_2](CNBu^+)(PPh_3)(\eta\text{-}C_5H_5)}$	2.074(3)	38	+0.07
$\mathrm{Ru\{C(CO_2Me){=}C(H)CO_2Me\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}$	2.080(8)	this work	+0.08
$\mathrm{Ru\{C(O)NH_2\}(CO)_2(\eta\text{-}C_5H_5)}$	2.080(6)	61	+0.08
	2.084(7)		+0.08
$\mathrm{Ru\{C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(H)(CF_3)\}(PPh_3)_2(\eta\text{-}C_5H_5)}$	2.082(5)	33	+0.08
$\mathrm{Ru[C\{{=}C(CN)_2\}C(Ph){=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)}$	2.100(5)	24	+0.10

Table 5 continued

Complex	Ru-C(Å)	Reference	a
$Ru(1\text{-}\sigma\text{-}C_8H_{13})(dppm)(\eta\text{-}C_5H_5)$ (yellow isomer)	2.101(6)	18	+0.10
$Ru\{C(OPr^i)=C(H)Ph\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.103(6)	25	+0.10
$Ru[C\{=C(CN)_2\}C(Me)=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$	2.106(5)	24	+0.11
$Ru\{C(CF_3)=C(H)C(CF_3)=C=C=C(H)(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$	2.11(1)	29	+0.11
$Ru(1\text{-}\sigma\text{-}C_8H_{13})(dppm)(\eta\text{-}C_5H_5)$ (orange isomer)	2.119(6)	18	+0.12
$Ru\{C(=CMePh)CH(PPh_2)CH_2PPh_2\}(\eta\text{-}C_5H_5)$	2.149(5)	62	+0.15
$(S)\text{-}[RuMe\{(R)\text{-}Ph_2PCH(Me)CH_2PPh_2\}(\eta\text{-}C_5H_5)]$	2.169(6)	16	+0.07
$CH_2\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2$	2.18	63	+0.08
$[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(\eta\text{-}C_5H_5)_2][PF_6]_2$	2.30(2)	32	+0.30

a Δ = Ru-C(found) - Ru-C(calcd.) Calculated values from covalent radii sums: C(*sp*) 0.60, C(*sp*^{2}) 0.67, C(*sp*^{3}) 0.77, Ru^{II}1.33Å.

b Two independent molecules.

were either not available to or not used by the previous authors. The most obvious conclusion that can be drawn is that the experimentally determined bond lengths in the neutral complexes are, in general, somewhat longer than those calculated on the basis of covalent radii of 0.60, 0.67, 0.77 and 1.33Å for C(*sp*), C(sp^2), C(sp^3) and Ru^{II}, respectively, whereas in the cationic complexes, they are shorter by some 0.04 - 0.1Å.

It is difficult, if not impossible, to establish an internally consistent set of values for Ru-C(*sp*), Ru-C(sp^2) and Ru-C(sp^3) bond lengths in the absence of any back-bonding. Nevertheless, the results summarised in Table 5 strongly suggest that a considerable degree of back-bonding is occurring from the metal to the organic fragment in the case of CO, C=CRR′ and C(OR)R′. There appears to be no significant difference between ~~the~~ Ru-CO bond in [Ru(CO)-$(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and those in the neutral complexes of type $RuR(CO)(L)(\eta\text{-}C_5H_5)$. Finally, the Ru-C bonds in the four σ-phenylacetylide complexes are nearly 0.1Å longer than calculated, suggesting that rather than there being any multiple bonding between the metal and the α-carbon, there may be a relative deficiency of electron density in this region. These findings are consistent with theoretical calculations by Kostić and Fenske;[71] strong metal-ligand π-bonding with concomitant back-donation for the vinylidenes and carbenes where the π, π*, and p orbitals of the ligand interact strongly with metal based orbitals, and pure σ-bonding for the acetylides, as their π* level lies high above the filled metal-based orbitals.

CONCLUSION

Analysis of metal-ligand distances in cyclopentadienylruthenium phosphine and phosphite complexes has enabled some comments to be made regarding trends, but in cases where insufficient examples are available this must be tempered with caution. Nevertheless, some correlations can be made between metal-ligand parameters and cone angle and π-accepting strength of the ligands. The Ru-P distances show a dependence on cone angle of the phosphine or phosphite, but no variation upon substituting the cyclopentadienyl ring; they increase as the π-accepting strength of the functional group increases. The Ru-Cl parameter also varies as the cone angle of the ligand is changed, but to a lesser degree than the Ru-P value. The Ru-C(Cp) bond lengths exhibit some asymmetry, and to a limited extent this can be rationalised from the relative *trans*-effects of the ligands. Lastly, an ordering of Ru-C distances (where C is the terminal atom of a σ-bonded carbon donor ligand) shows that the Ru-C parameter is, in general, longer in neutral complexes and shorter in cationic complexes than that calculated on the basis of covalent radii; this result indicates the presence of back-bonding for the carbonyl, vinylidene and alkoxycarbene groups.

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1. The complexes Ru(C≡CPh)$(PPh_3)_2(\eta\text{-}C_5H_5)$ (1) and Ru(C≡CPh)(dppe)$(\eta\text{-}C_5H_5)$ (2) were prepared by the method of Bruce and Wallis.[64] The preparation of [Ru{C=CPh(N=N$C_6H_3Me_2$-3,4)}$(PPh_3)_2(\eta\text{-}C_5H_5)$]$[BF_4]$ (3) and the method of preparation of [Ru{C=CPh(C_7H_7)}(dppe)$(\eta\text{-}C_5H_5)$]$[PF_6]$ (4) are detailed in Chapter 1. A crystal of Ru{(*Z*)-C-(CO_2Me)=CH(CO_2Me)}(CO)$(PPh_3)(\eta\text{-}C_5H_5)$ (5) was supplied by Mr G.A. Koutsantonis and its preparation can be found elsewhere.[65] The preparation of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}-(dppe)$(\eta\text{-}C_5H_5)$ (6) is given in Chapter 2.

Crystallography

General techniques and details given below apply to structures determined by the author. Suitable crystals were grown from acetone (1), dichloromethane/pentane at -30°C (2), dichloromethane/methanol [(3) and (6)], and dichloromethane/ethanol (4).

They were then mounted on a glass fibre and coated with cyanoacrylate super glue. Lattice parameters were determined from a least-squares fit to the setting angles of 25 [22 for (6)] high angle reflections on an Enraf-Nonius CAD4 four-circle diffractometer using monochromated Mo-$K_{\bar{\alpha}}$ radiation.

Intensity data were measured using a ω-$(n/3)\theta$ scan where n was optimised by a ω/θ profile and scan analysis. The ω scan angles and horizontal counter apertures were varied according to $(A + B\tan\theta)°$ and $(C + D\tan\theta)$mm respectively, where A, B, C and D depend on the half-width of the individual reflection and the wavelength of radiation used. The intensity of three standard reflections were monitored every 60 minutes to check for crystal and machine stability. No crystal decomposition occurred for (1), (2), (3), (5) and (6); in the case of (4), the intensities had decreased by 43% at the completion of the data collection, but re-measurement of the orientation reflections indicated no significant change in the lattice parameters; a correction for this was applied using the programme SUSCAD,[66] assuming a linear decay.

Data reduction and application of Lorentz and polarization corrections were performed by SUSCAD. Absorption corrections were applied using the programme ABSORB;[67] crystal dimensions were determined with a microscope equipped with calibration scales.

Computing for all solution and refinement work was performed using the SHELX[68] system of programmes. Scattering factors for Ru were obtained from reference 69. Reflections with intensities $I<2.5\sigma(I)$ and systematically absent reflections were rejected, while equivalent reflections were averaged. Structures were solved by the heavy atom method to give the metal atom position, with all other non-hydrogen atoms being revealed in the Fourier difference maps of successive blocked-matrix least-squares refinements. Phenyl and cyclopentadienyl rings were included as rigid groups (C-C_{Ph} 1.395Å, C-C_{Cp} 1.42Å). Hydrogen atoms were placed in calculated positions (methylene C-H 0.97Å for (4); all other C-H in all structures 1.08Å). In the final

Table 6

Crystal data for complexes (1), (2) and (3).

	(1)	(2)	(3)
Formula	$C_{49}H_{40}P_2Ru$	$C_{39}H_{34}P_2Ru$	$C_{57}H_{49}BF_4N_2P_2Ru.0{\cdot}67CH_2Cl_2$
Formula weight	791.9	665.7	1069.3
Crystal size	0.38mm x 0.57mm x 0.15mm	0.35mm x 0.85mm x 0.63mm	0.51mm x 0.23mm x 0.05mm
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ variant, C_{2h}^5, No. 14	$P2_1/n$ variant, C_{2h}^5, No. 14	$P2_1/n$ variant, C_{2h}^5, No. 14
a(Å)	11.315(1)	14.642(4)	22.424(6)
b(Å)	17.376(4)	14.018(3)	10.215(5)
c(Å)	19.582(6)	16.490(4)	23.292(7)
α (deg.)	90.0	90.0	90.0
β (deg.)	92.36(1)	105.08(2)	104.64(2)
γ (deg.)	90.0	90.0	90.0
U (Å^3)	3845	3268	5160
Z	4	4	4
D_{calc} (g cm^{-3})	1.368	1.353	1.376
μ (Mo-$K_{\bar{\alpha}}$) (cm^{-1})	4.81	5.61	4.44
F(000), electrons	1632	1368	2196
Scan mode	$\omega:\frac{\theta}{3}$	$\omega:\theta$	$\omega:\frac{2\theta}{3}$
θ-range (deg.)	1.3-21	1.4-30	1.2-21
Refl. meas.	4505	6921	6010
Unique refls.	3674	5747	4451
Refls. used	3020	4841	2847
Final *R*	0.030	0.038	0.046
Weighting scheme, *k*	2.2	1.0	1.9
g	0.0001	0.0016	0.0008
Final R_w	0.033	0.048	0.049
Residual ρ (eÅ^{-3})	0.40	0.80	0.50
localised on	disordered phenyl group	disordered cyclopentadienyl group	diazophenyl group

Table 6 continued

Crystal data for complexes (4), (5) and (6).

	(4)	(5)	(6)
Formula	$C_{46}H_{41}F_6P_3Ru.0{\cdot}63CH_2Cl_2$	$C_{30}H_{27}O_5PRu$	$C_{37}H_{38}O_4P_2Ru$
Formula weight	955.4	599.6	707.7
Crystal size	0.075mm x 0.23mm x 0.35mm	0.14mm x 0.14mm x 0.08mm	0.50mm x 0.53mm x 0.56mm
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ C_i^1, No. 2	$P\bar{1}$ C_i^1, No. 2	$P2_1$ C_2^2, No. 4
a(Å)	11.67(3)	10.40(1)	9.33(1)
b(Å)	12.10(3)	11.22(1)	17.39(1)
c(Å)	15.98(4)	13.23(1)	10.36(1)
α(deg.)	76.6(2)	92.7(1)	90.0
β(deg.)	88.3(1)	110.6(1)	101.8(1)
γ(deg.)	86.8(1)	106.2(1)	90.0
U(Å^3)	2191	1371	1643
Z	2	2	2
D_{calc} (g cm^{-3})	1.448	1.452	1.430
μ(Mo-K$_{\bar{\alpha}}$) (cm^{-1})	5.56	6.20	5.70
F(000),electrons	973	600	732
Scan mode	ω:θ	ω:θ	$\omega{:}\frac{2\theta}{3}$
θ-range (deg.)	1.3-21	1.5-23	1.3-21
Refl. meas.	4155	2913	3750
Unique refls.	3809	2634	2194
Refls. used	3432	2520	2107
Final *R*	0.059	0.055	0.076
Weighting scheme, *k*	5.8	8.0	6.9
g	0.0005	0.0003	0.0012
Final R_w	0.069	0.068	0.085
Residual ρ (eÅ^{-3})	1.0	1.2	1.7
localised on	dichloromethane molecule	ruthenium	ruthenium

refinement cycles, the following weighting scheme was employed:

$$w = k/(\sigma^2(F_o) + |g||F_o|^2)$$

where the values of k and g were refined. The discrepancy factors R and R_w were determined as

$$R = \frac{\Sigma(||F_o| - |F_c||)}{\Sigma|F_o|}$$

$$R_w = \frac{\Sigma(||F_o| - |F_c||)\sqrt{w}}{\Sigma(|F_o|\sqrt{w})}$$

The structure of complex (6) was solved in the non-centrosymmetric space group $P2_1$; its configuration has been arbitrarily assigned as discrepancy factors for both possible configurations are not significantly different.

Bond lengths, valence angles, non-bonded distances and their standard deviations were all calculated using SHELX. Diagrams were plotted by PLUTO.[70] All programmes were implemented on the CYBER 173 computing system at the University of Adelaide.

A list of observed (F_o) and calculated (F_c) structure factors, and positional and thermal parameters for all atoms of all structures determined by the author are on microfiche in the back of this thesis.

Crystal data and relevant data collection parameters are collected in Table 6. Further information on structure solution and refinement is in Table 7.

Table 7

Further structure solution and refinement details.

	(1)	(2)	(3)	(4)	(5)	(6)
Types of hydrogen cyclopentadienyl (1) phenyl (2) methyl (3) methylene (4) methyne (5) vinyl (6)	(1) and (2) have a common thermal parameter.	(1) and (2) have a common thermal parameter, as does (4).	(1), (2) and (3) have a common thermal parameter.	(1), (2), (5) and (6) have a common parameter, as does (4).	(1) and (2) have a common thermal parameter as does (3), (4), and (6).	(1) and (2) have a common thermal parameter as does (3), and (6).
anisotropic thermal parameters	all non hydrogens, but phenyls in acetylide.	all non hydrogens, but Cp group.	all non hydrogens, but phenyls and fluorines.	all non hydrogens, but phenyls.	all non hydrogens, but Cp and phenyl carbons.	all non hydrogens but phenyls.
disorder	phenyl of acetylide group, modeled by two orientations (0.54, 0.46).	cyclopentadienyl group, modeled by two orientations (0.65, 0.35).	BF_4, modeled by three orientations (0.65, 0.25, 0.10).	-	-	-

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CHAPTER FOUR

INTRODUCTION

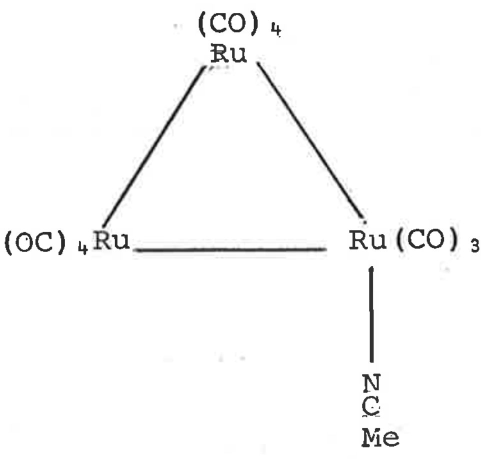
The chemistry of triosmium clusters with nitrogen-donor ligands has been examined in some detail.[1] By comparison, that of triruthenium clusters has been explored less thoroughly, and relatively few derivatives of $Ru_3(CO)_{12}$ containing *N*-donor ligands have been described. In most cases, this is the result of the use of harsh reaction conditions which leads to rapid break-up of the first formed cluster complexes. The much greater tendency of triruthenium clusters, as opposed to triosmium clusters, to undergo cluster fragmentation is due to a greater M-M bond strength for the heavier metal; the M-M bond enthalpies of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are 78 and 94 $kJmol^{-1}$, respectively.[2]

This Chapter commences with a literature survey of derivatives of $Ru_3(CO)_{12}$ containing *N*-donor ligands, classified according to the functional groups in the ligand. The last such review[3] contained work published up to 1980. The present survey incorporates results published up to the end of 1986.

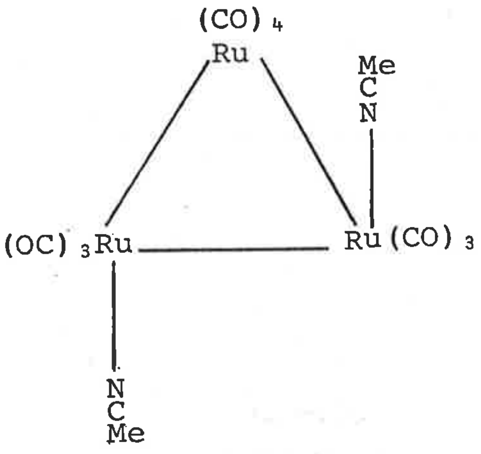
Reactions of $Ru_3(CO)_{12}$ with *N*-donor ligands

1. Nitriles

Triruthenium clusters with acetonitrile ligands have been used as starting materials for the synthesis of other compounds.[4,5] The acetonitrile ligands can be easily introduced by the action of trimethylamine-*N*-oxide on $Ru_3(CO)_{12}$, affording $Ru_3(CO)_{11}(NCMe)$ (1) and $Ru_3(CO)_{10}(NCMe)_2$ (2).



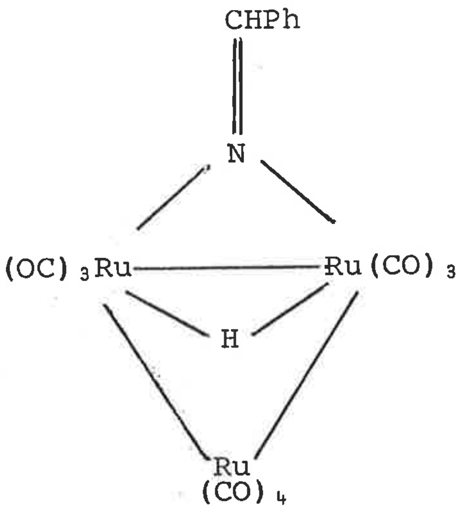
(1)



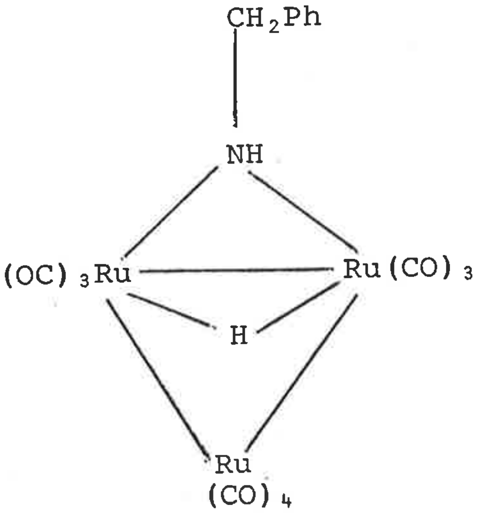
(2)

The structures of (1) and (2), featuring axial nitrile ligands, were assigned by comparison of their IR spectra with those of the analogous osmium complexes.[6,7] The acetonitrile ligands can be easily displaced by two-electron donors (*vide infra*), and use of these readily accessible precursors would be expected to afford other triruthenium clusters incorporating *N*-donor ligands not obtainable by thermal routes.

Reaction has been reported to occur between $Ru_3(CO)_{12}$ and benzonitrile only in the presence of acetic

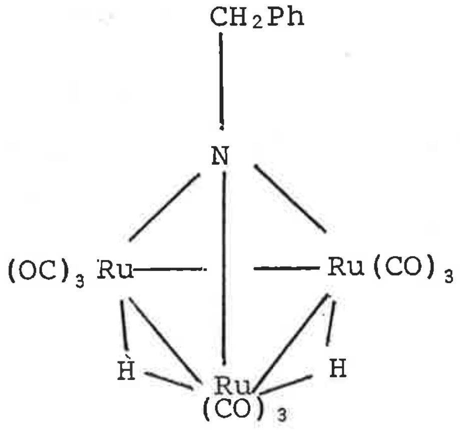


(3)



(4)

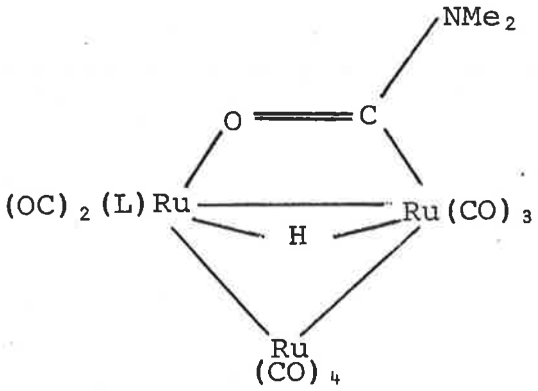
acid or molecular hydrogen.[8] In the former case, the reaction affords $Ru_4(\mu\text{-}H)_4(CO)_{12}$, $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CHPh)(CO)_{10}$ (3) and $Ru_3(\mu\text{-}H)(\mu\text{-}NHCH_2Ph)(CO)_{10}$ (4), the latter two by reduction of a coordinated benzonitrile ligand.[9]



(5)

Reaction under 110 atm of H_2 gave mainly (4), together with benzylamine, whereas reaction with H_2 at atmospheric pressure gave only (3). Hydrogenation of (3) afforded $Ru_3(\mu_3\text{-}NCH_2Ph)(\mu\text{-}H)_2(CO)_9$ (5);[10] recently, the imide-amide-nitrene transformations (3) $\rightleftarrows$ (4) $\rightleftarrows$ (5) have been shown to be reversible.

Further work with substituted benzonitriles bearing electron donating (-OMe) or electron withdrawing ($-NO_2$) groups in the *para* position indicated that the formation of complexes similar to (4) is significantly enhanced by an electron donor substituent; with an electron withdrawing group, only decomposition occurs.[12]



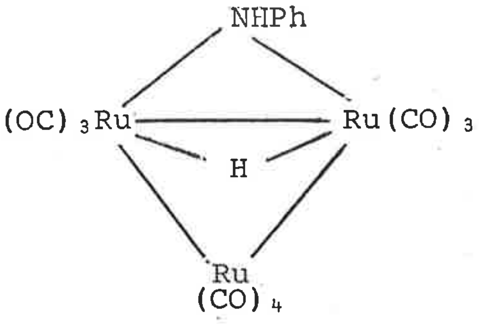
(6) L = CO

(12) L = P(OR)$_3$

R = Me,Et,Ph

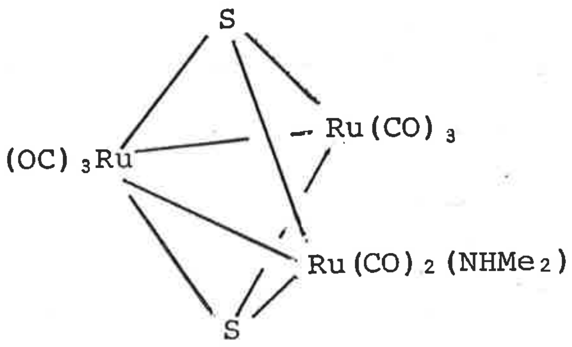
2. Amines

Dimethylamine reacted with Ru$_3$(CO)$_{12}$ at -30°C and afforded Ru$_3$(μ-H){μ-O=C(NMe$_2$)}(CO)$_{10}$ (6).[13,14]



(7)

Nucleophilic attack occurs at a carbonyl group to give the carbamoyl ligand. By contrast, the first product from the reaction between Ru$_3$(CO)$_{12}$ and aniline was Ru$_3$(μ-H)(μ-NHPh)(CO)$_{10}$ (7), formed by an oxidative addition of the N-H bond across a Ru-Ru bond.[15]



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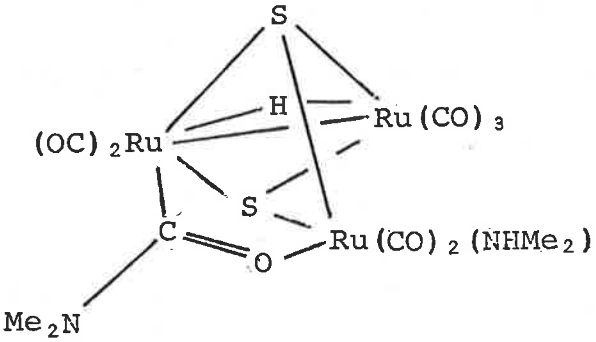
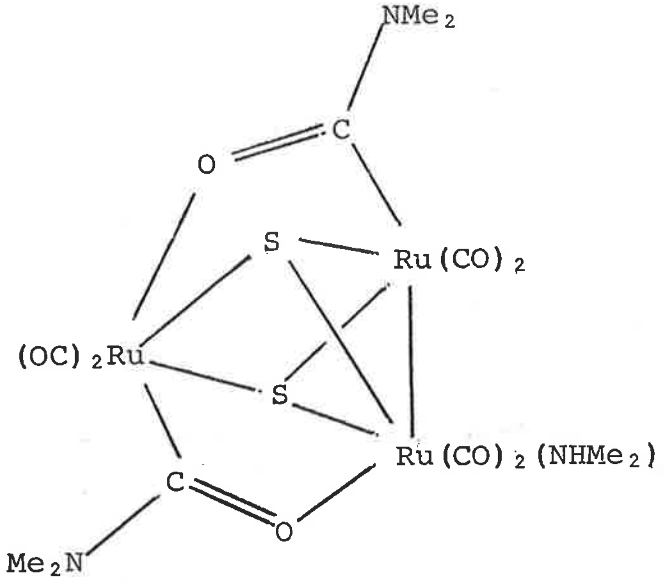
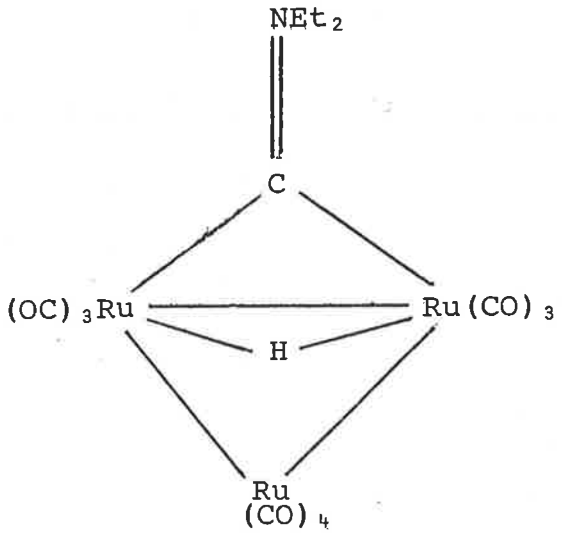


(9)

The reaction of $Ru_3(\mu_3-S)_2(CO)_9$ with dimethylamine was followed spectroscopically and found to proceed *via* the substitution product (8) to the carbamoyl-bridged complex (9) and thence to the bis(carbamoyl)-bridged complex (10).[16]



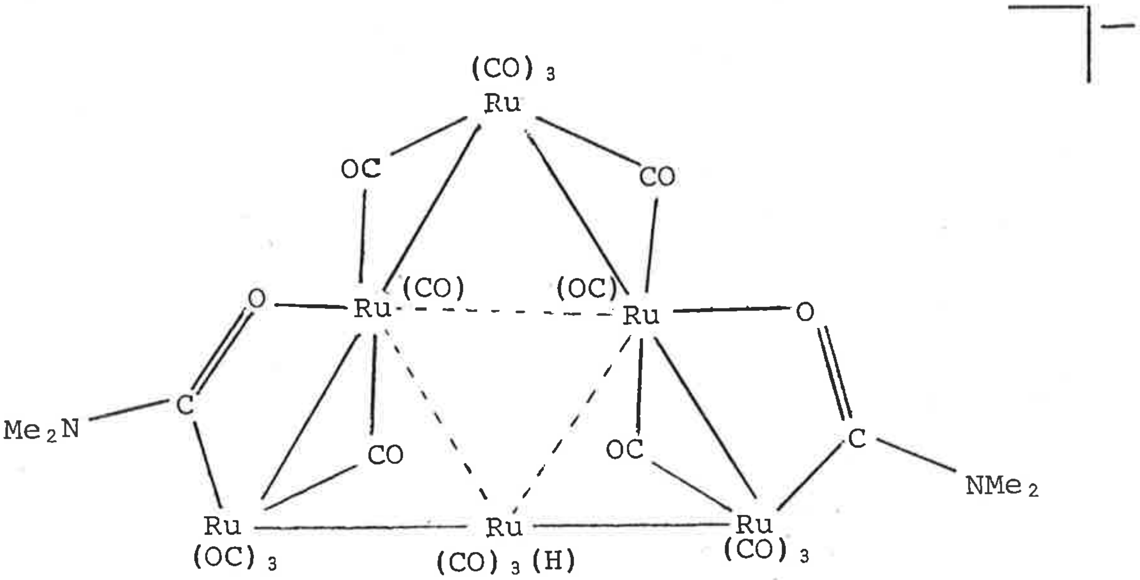
(10)



(<u>11</u>)

The halomethylidyne cluster $Ru_3(\mu_3\text{-}CBr)(\mu\text{-}H)_3(CO)_9$ reacted with diethylamine to give exclusively $Ru_3(\mu\text{-}CNEt_2)$-$(\mu\text{-}H)(CO)_{10}$ (<u>11</u>), either in the presence or absence of carbon monoxide, by nucleophilic substitution at the methylidyne carbon and intermolecular CO transfer; the presumed intermediate in this reaction, $Ru_3(\mu_3\text{-}CNEt_2)$-$(\mu\text{-}H)_3(CO)_9$, must be less stable than the final product because of the extra stabilisation associated with the $\mu\text{-}C^-{=}NR_2^+$ resonance form. It proved impossible to hydrogenate (<u>11</u>) to $Ru_3(\mu_3\text{-}CNEt_2)(\mu\text{-}H)_3(CO)_9$.[17]

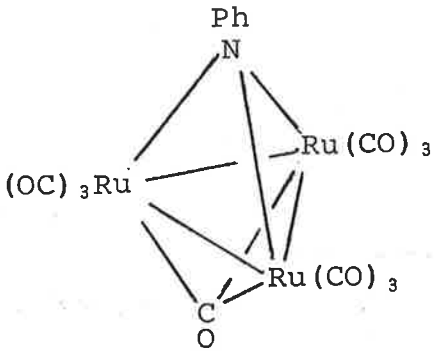
Reaction of $Ru_3(CO)_{12}$ with $C(NMe_2)_4$ gave the $[C(NMe_2)_3]^+$ salt of $[Ru_3\{\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}]^-$, believed to contain bridging carbonyl groups.[18] Acidification and phosphite substitution afforded (<u>12</u>).[19] Addition of base to a refluxing THF solution of (<u>6</u>) gave $[Ru_6(H)(\mu\text{-}O{=}CNMe_2)_2(\mu\text{-}CO)_4(CO)_{14}]^-$ (<u>13</u>), which was isolated as its $[AsPh_4]^+$ salt.[20]



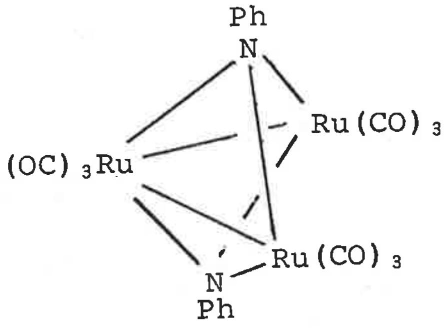
(<u>13</u>)

3. <u>Nitroarenes and nitrosoarenes</u>

Nitrobenzene reacted with $Ru_3(CO)_{12}$ at elevated temperatures and afforded $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9$ (<u>14</u>) and $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (<u>15</u>).[15,21,22] Nitrene-containing species have been proposed as intermediates in the catalytic reduction of nitrobenzene to aniline and isolation of polynuclear complexes with phenylnitrene groups such as, for example, (<u>14</u>) can be taken as indirect evidence for the involvement of such species in the catalytic reaction. In the presence of $Co_2(CO)_8$, the

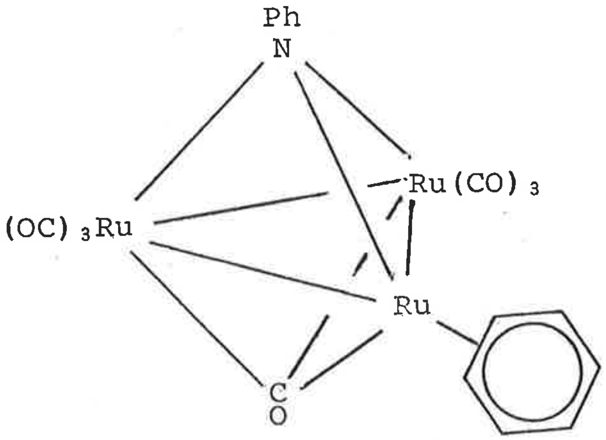


(14)



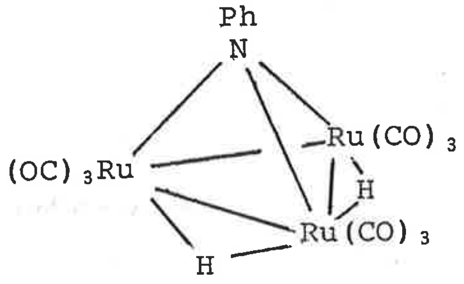
(15)

same reaction gave (15) and $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(CO)_6$-($\eta$-$C_6H_6$) (16), but not (14); small quantities of $Co_4(CO)_9$-(η-C_6H_6) were also isolated from the reaction system, and reaction of this complex with (14) produced (16), also in small quantities.[23]



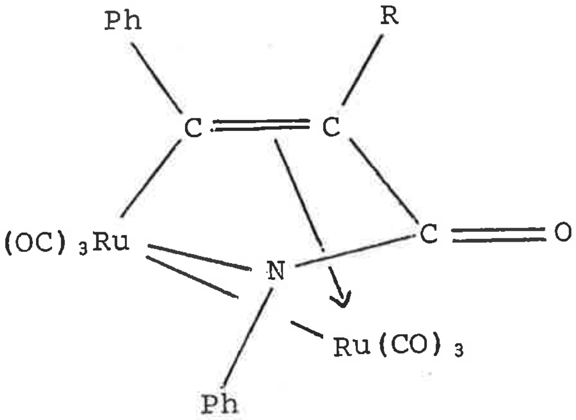
(16)

Hydrogenation of (<u>14</u>) afforded $Ru_3(\mu-H)_2(\mu_3-NPh)(CO)_9$ (<u>17</u>);[15,24] (<u>14</u>) reacted with diphenylacetylene to give



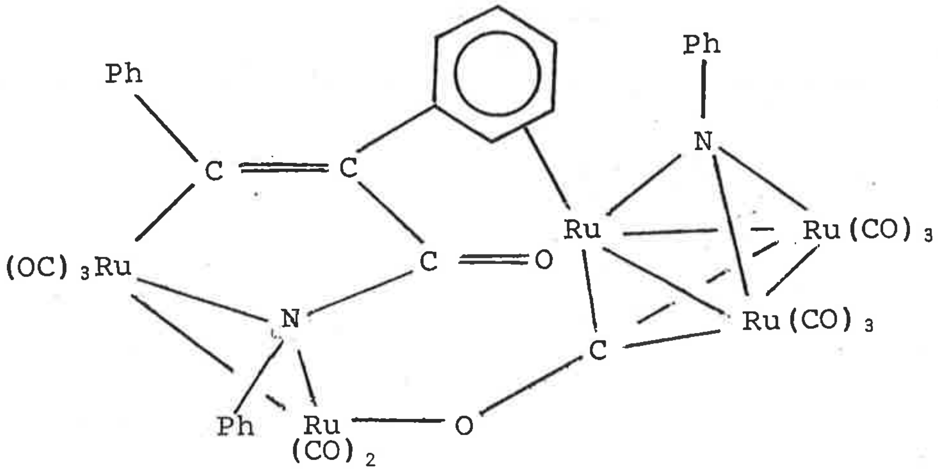
(<u>17</u>)

(<u>18</u>), (<u>20</u>) and (<u>21</u>) and with 1-phenylpropyne to give (<u>19</u>) by coupling of CO and the alkynes with the μ_3-nitrene. The complex (<u>18</u>) reacted further with PhC≡CPh and CO to form pentaphenylpyridone and 1,3,4-triphenylmaleimide, respectively.[25]

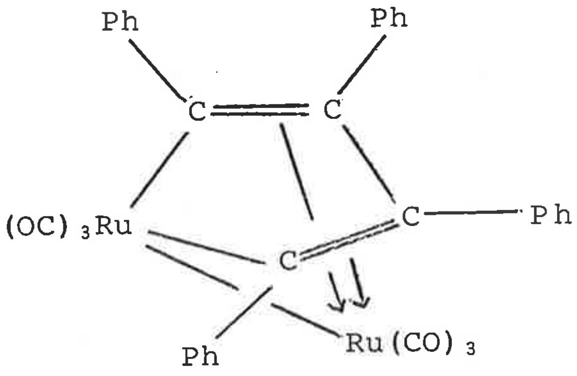


(<u>18</u>) R = Ph

(<u>19</u>) R = Me



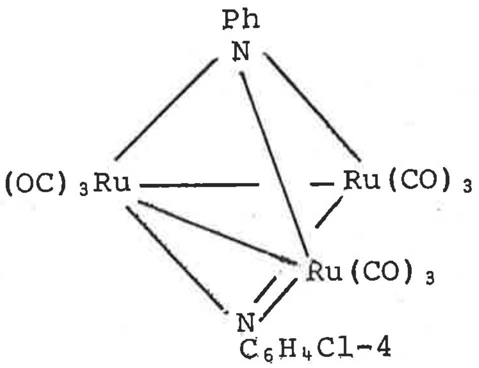
(<u>20</u>)



(<u>21</u>)

Carbonylation of (<u>14</u>) and (<u>15</u>) in acetonitrile at 140°C with 300psi of CO gave quantitative yields of $Ru_3(CO)_{12}$.[26] Phenyl isocyanate was shown by linked GC/MS to be the sole organic product from these reactions.

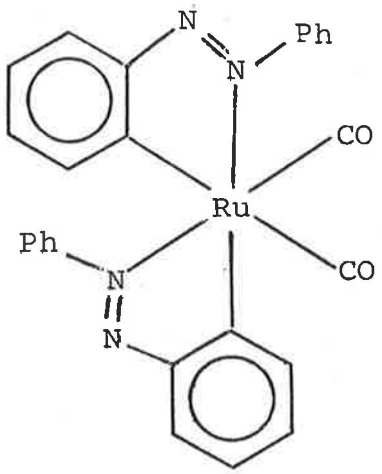
Reaction of $Ru_3(CO)_{12}$ with *para*-substituted nitrosoarenes gave analogues of (<u>14</u>) and (<u>15</u>); *p*-$ClC_6H_4NO_2$ reacted with (<u>14</u>) to afford (<u>22</u>).[27]



(22)

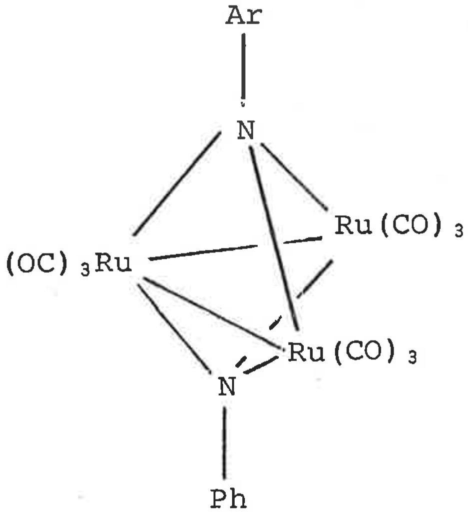
4. Azoarenes

In 1971, Stone *et al*[28] reported that the reaction between $Ru_3(CO)_{12}$ and azobenzene afforded three complexes; re-examination of this reaction showed that the products were (15), (23) and an uncharacterised black powder.[29]



(23)

There are three possible isomers for $Ru(CO)_2(C-N)_2$, where (C-N) is a chelating ligand with *C* and *N* donors; a different isomer is found in the product obtained from $Ru_3(CO)_{12}$ and benzo[*h*]quinoline (*vide infra*). Reaction between $Ru_3(CO)_{12}$ and $C_6F_5N{=}NC_6H_5$ afforded a complex with spectral properties similar to (15);[30] a systematic investigation of the reaction of $Ru_3(CO)_{12}$ and asymmetric



(24) Ar = C_6H_4Me-3

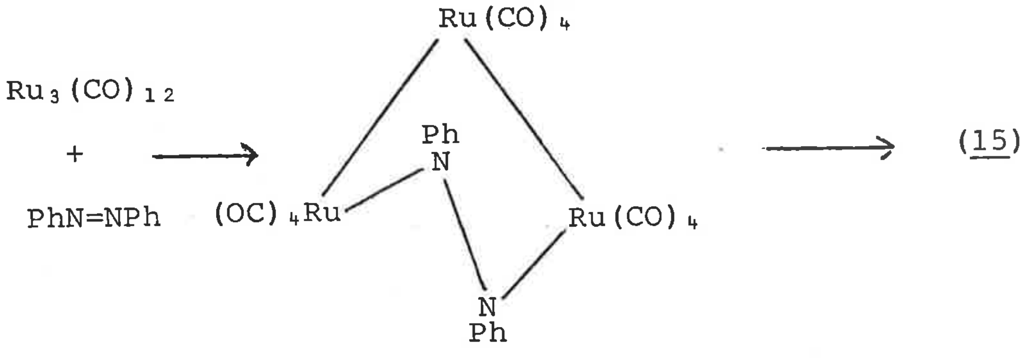
(25) Ar = $C_6H_4CF_3$-3

(26) Ar = C_6H_4F-3

(27) Ar = C_6H_4F-4

azoarenes $ArN{=}NC_6H_5$ showed only the mixed complexes $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}NC_6H_5)(CO)_9$ (24) - (27) were obtained.[29] The reaction between azotoluene and $Ru_3(CO)_{12}$ gave analogues of (15) and (23).

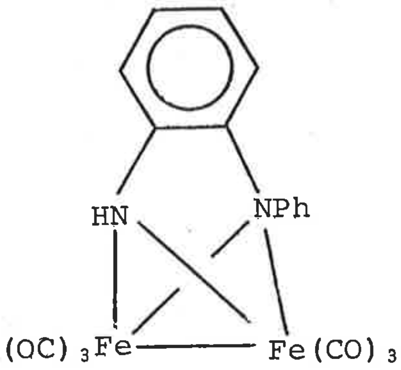
The formation of the trinuclear bis-arylimido complexes from azoarenes requires that the N=N double bond is cleaved at some stage of the reaction. It is likely that the first step of the transformation involves coordination of the azoarene to the cluster by the nitrogen atoms, perhaps giving an intermediate in which one of the M-M bonds is bridged by the azoarene such as (A) (Scheme 1). Slippage of the azoarene and further interaction with the third metal atom results in N-N bond cleavage, together with electron rearrangement following capping, leading to opening of the M_3 triangle. The intermediacy of (A) has not been established in the ruthenium system, but in an analogous reaction, $Os_3(CO)_{12-n}(CH_3CN)_n$ (n = 1 or 2) reacted with dimethyl azodicarboxylate to give $Os_3\{\mu_3\text{-}N(CO_2Me)NC(O)OMe\}(CO)_{11}$, which when heated in benzene afforded $Os_3\{\mu_3\text{-}N_2(C(O)OMe)_2\}(CO)_{10}$.[31,32] Stabilisation of this intermediate is aided by coordination of the ester carbonyl oxygen atoms.



(A)

Scheme 1

The eventual cleavage of the N-N bond is also consistent with the formation of the *o*-semidine derivatives such as (28), obtained from reactions between azobenzene and iron carbonyls.[33,34]

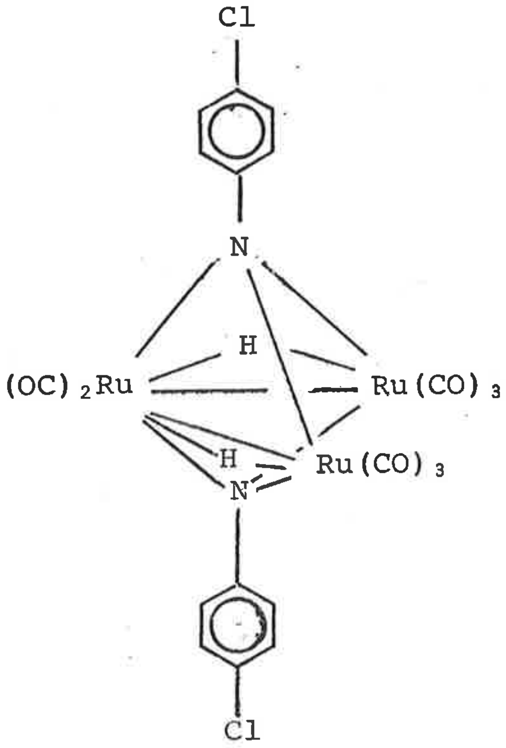


(28)

An alternative reaction can take place when one nitrogen is coordinated to one metal atom, namely the well-known cyclometallation reaction. Interaction of the aryl C-H bond with the cluster results in formation of an Ru-C bond and addition of the hydrogen atom to the cluster, as found with the aryldiazo complex $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}N{=}\dot{N}Ph)(CO)_8$ recently (*vide infra*). However, reaction with a second molecule of azoarene affords the mononuclear complexes such as (23), the hydrogen being eliminated with the other two metal carbonyl fragments; ruthenium carbonyl hydrides are unstable [$RuH_2(CO)_4$] or unknown [$Ru_2H_2(CO)_8$], and the possible cluster hydride, $Ru_4(\mu\text{-}H)_4(CO)_{12}$, reacted readily with azobenzene to give at least nine products.[29]

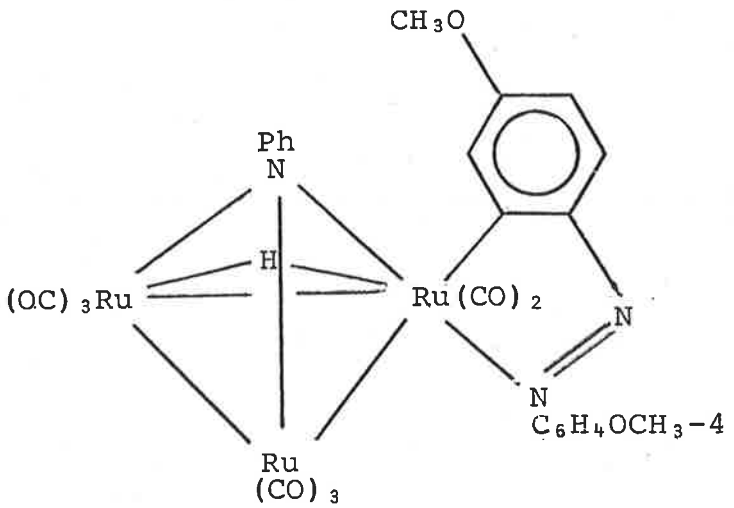
Azoarenes reacted with (14) and related aryl-substituted clusters under CO, to give $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}NAr')(CO)_9$.[35] Hydrogenation of these bis(imido) clusters afforded hydrido clusters; the structure of

$Ru_3(\mu_3-NC_6H_4Cl-4)_2(\mu-H)_2(CO)_8$ (29) was determined.



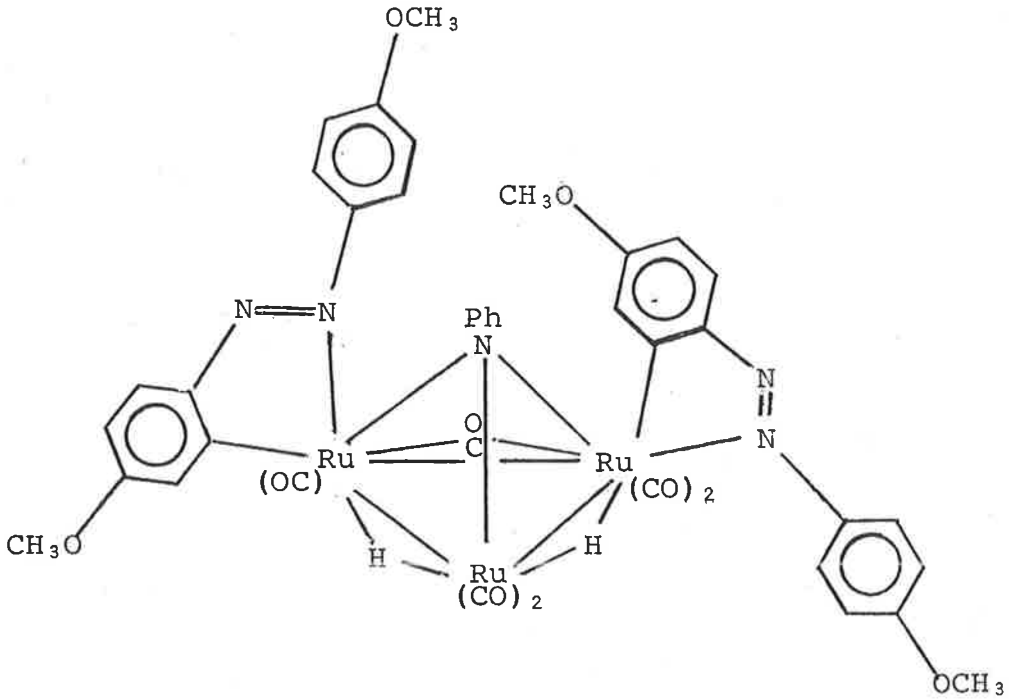
(29)

The reaction of (14) with 4,4´-dimethoxyazobenzene afforded $Ru_3(\mu_3-NPh)(\mu_3-NC_6H_4OCH_3-4)(CO)_9$ (30) and $Ru_3(\mu_3-NPh)(\mu-H)(CH_3OC_6H_3N=NC_6H_4OCH_3)(CO)_8$ (31), with the latter incorporating a cyclometallated azoarene.[36] Pyrolysis of (31) under a CO atmosphere gave (30) and $4-CH_3OC_6H_4NCO$. Reaction of (31) with excess 4,4´-dimethoxyazobenzene afforded (30) and (32).

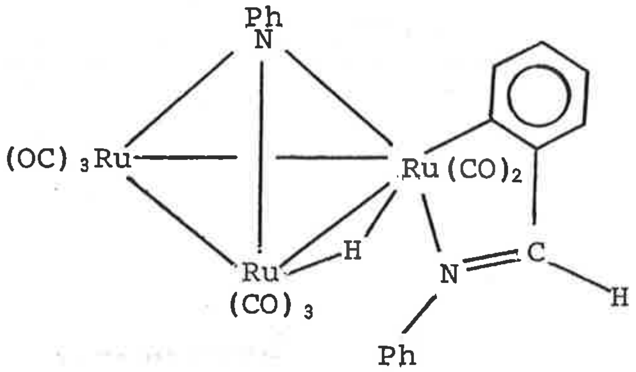


(31)

The formation of an cyclometallated cluster was dependent on the electronic character of the azoarene: with electron poor aromatic rings (e.g. 4,4´-dinitroazobenzene), cyclometallation was never observed, while with electron rich aromatic rings, N-N bond cleavage was preferred over cyclometallation only in the presence of CO. *N*-phenylbenzaldimine was cyclometallated by (14) under CO to give (33).



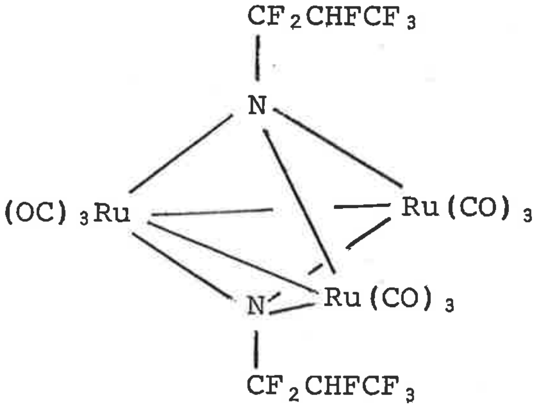
(32)



(<u>33</u>)

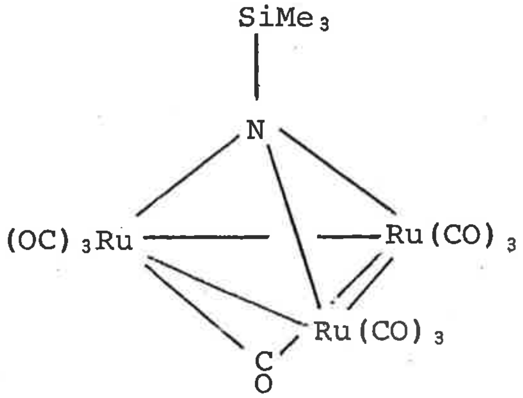
5. <u>Azides</u>

Reaction of $Ru_3(CO)_{12}$ with 2*H*-hexafluoropropyl azide



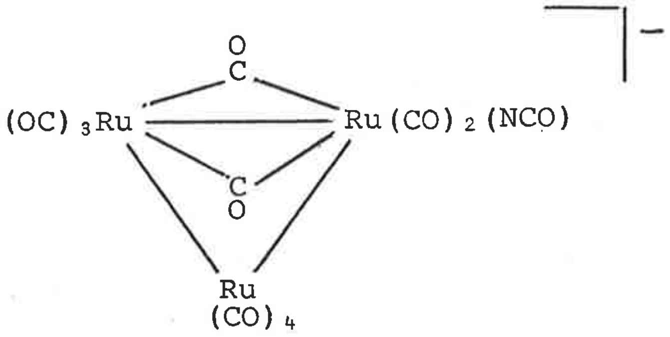
(<u>34</u>)

afforded $Ru_3(\mu_3\text{-}NCF_2CHFCF_3)_2(CO)_9$ (<u>34</u>);[37] the corresponding reaction with trimethylsilyl azide gave $Ru_3(\mu_3\text{-}NSiMe_3)\text{-}(\mu_3\text{-}CO)(CO)_9$ (<u>35</u>).[38]

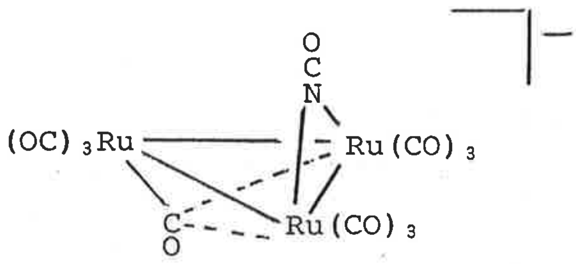


(<u>35</u>)

The reaction between $Ru_3(CO)_{12}$ and bis(triphenylphosphine)iminium (ppn) azide initially afforded $[Ru_3(\mu\text{-}CO)(CO)_{10}(NCO)]^-$ (36) which lost a CO to give $[Ru_3(\mu\text{-}NCO)(CO)_{10}]^-$ (37); over several days, (37) was slowly converted to $[Ru_4(\mu\text{-}CO)(\mu\text{-}NCO)(CO)_{12}]^-$ (38).[39] The postulated structures for (36), (37) and (38) are assigned on the basis of IR arguments.



(36)



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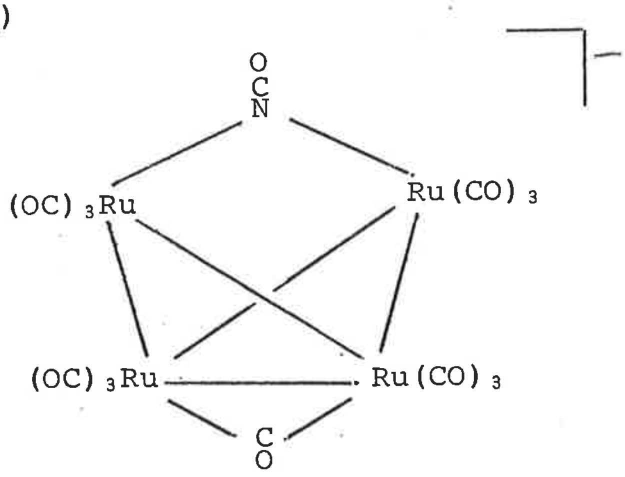
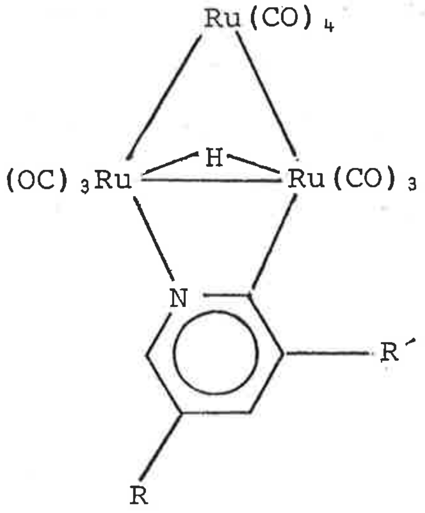


(38)

Refluxing a mixture of $Ru_3(CO)_{12}$ and $[ppn][N_3]$ in tetrahydofuran overnight gave $[ppn][Ru_6N(CO)_{16}]$ (39) in addition to (38);[40] formation of (39) involves the cleavage of a coordinated isocyanate into a coordinated nitrogen atom and carbon monoxide.

6. *N*-heterocycles

Pyridine reacted with $Ru_3(CO)_{12}$ to afford the cyclometallated complex $Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}$ (40);[41] the reaction is believed to occur *via* $Ru_3(CO)_{11}(C_5H_5N)$, but this intermediate was not detected either here or in the reaction with $Ru_3(CO)_{12-n}(NCMe)_n$ (n = 1 or 2).[4] The 2-,3- and 4- methyl substituted pyridines reacted with the latter to give analogous complexes; 3-methyl pyridine formed two isomers (41) and (42).[5] Diphenyl pyridylphosphine reacted with $Ru_3(CO)_{12}$ under catalytic substitution conditions to afford $Ru_3(CO)_{11}(PPh_2py)$ (43); this was metastable at ambient temperature, yielding $Ru_3\{\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N)\}\{\mu\text{-}\eta^2\text{-}C(O)(C_6H_5)\}(CO)_9$ (44).[42] The corresponding thermal reaction afforded $Ru_3(CO)_9(PPh_2py)_3$ along with monomeric species;[43] in both cases, initial coordination is through the P atom.

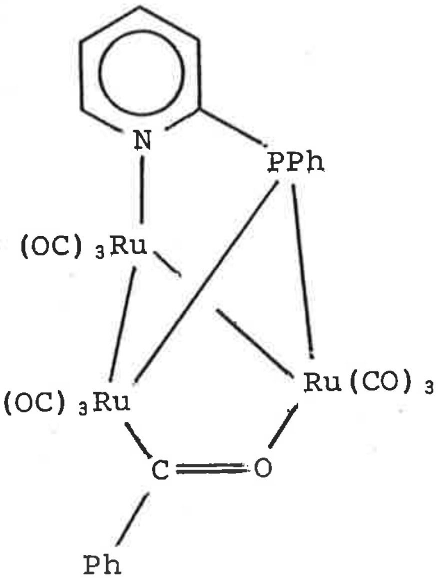


(40) R = R´ = H

(41) R = CH_3, R´ = H

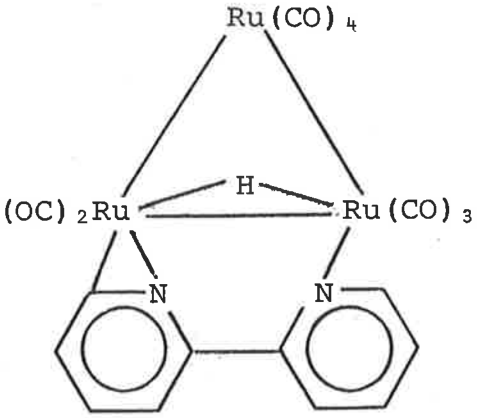
(42) R = H, R´ = CH_3

The reactions between $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCMe)_2$ and 2,2´-bipyridyl afforded a purple complex containing bridging CO groups, $Ru_3(bipy)(CO)_{10}$ (45);[5,44] a structure

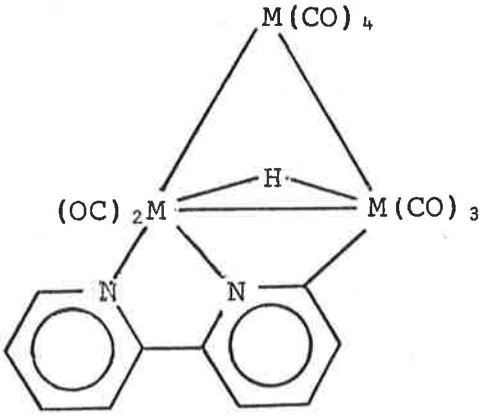


(44)

with the heterocycle bridging a metal-metal bond was postulated.[5] The pyrolysis of (45) in refluxing toluene afforded a cyclometallated complex for which the structure (46) was postulated.[5] However, the structure of the



(46)

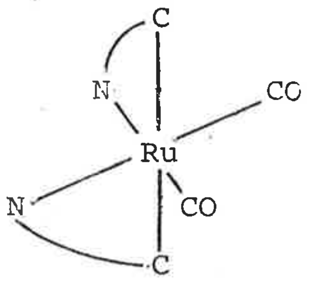


(47) M = Os

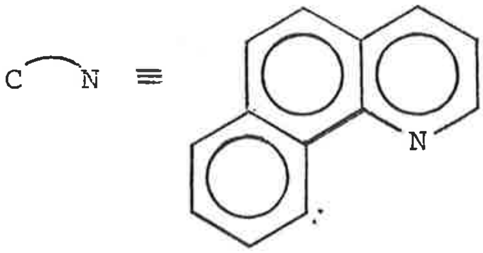
(48) M = Ru

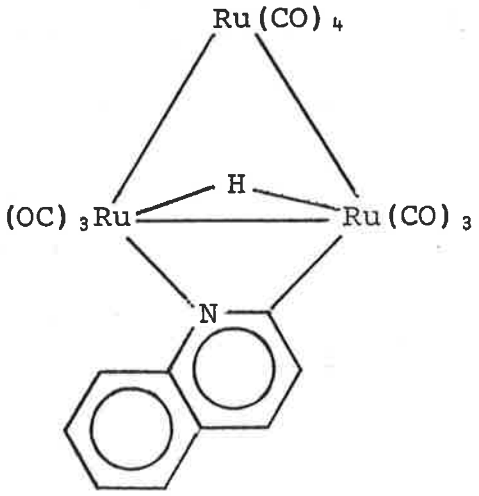
pyrolysis product from the reaction between $Os_3(CO)_{12}$ and 2,2′-bipyridyl has been determined, (47),[45] and structure (48) seems more likely. An $Ru_3(CO)_{12}$/2,2′-bipyridyl mixture has been reported to afford a high activity, low temperature catalyst for the water gas shift reaction.[46]

Reaction between $Ru_3(CO)_{12}$ and benzo[*h*]quinoline gave the mononuclear complex $Ru(CO)_2(bq)_2$ (49),[47,48] together with $Ru_4(\mu\text{-}H)_4(CO)_{12}$. The considerably more reactive cluster $Ru_3(CO)_{10}(NCMe)_2$ cyclometallated quinoline to afford the trinuclear complex (50); the corresponding reaction with isoquinoline afforded the two isomers (51) and (52).[5]

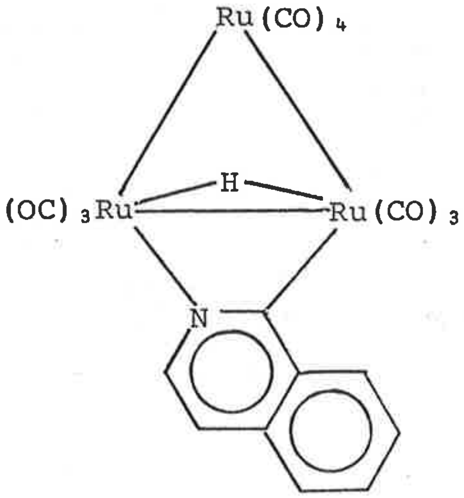


(49)

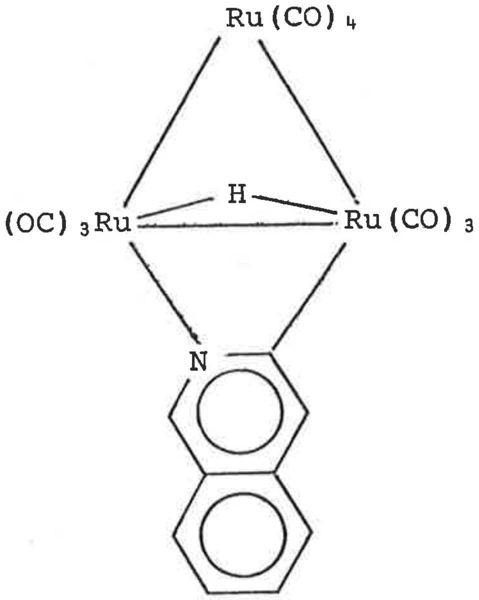



Ru(CO)4
H
(OC)3Ru
Ru(CO)3
N

(50)

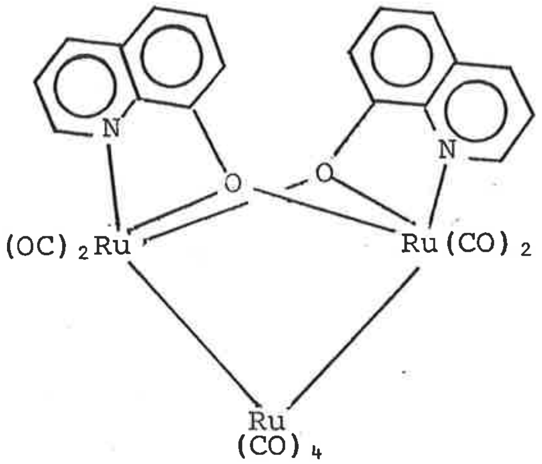

Ru(CO)4
H
(OC)3Ru
Ru(CO)3
N

(51)

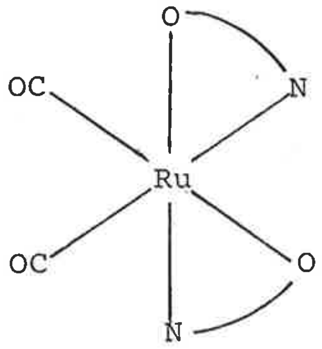

Ru(CO)4
H
(OC)3Ru
Ru(CO)3
N

(52)

8-Quinolinol reacted with $Ru_3(CO)_{12}$ to give (53) and (54); *O*-metallation is preferred to *C*-metallation.[49]



(53)



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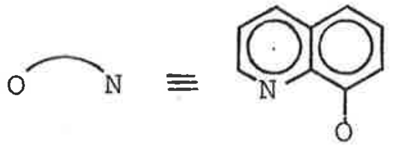
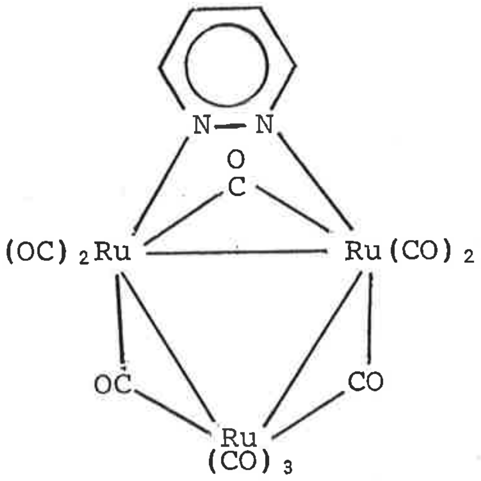
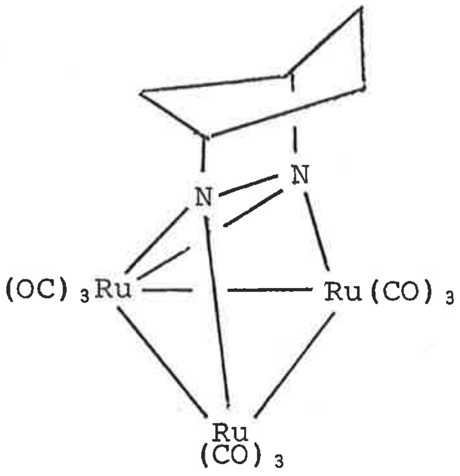


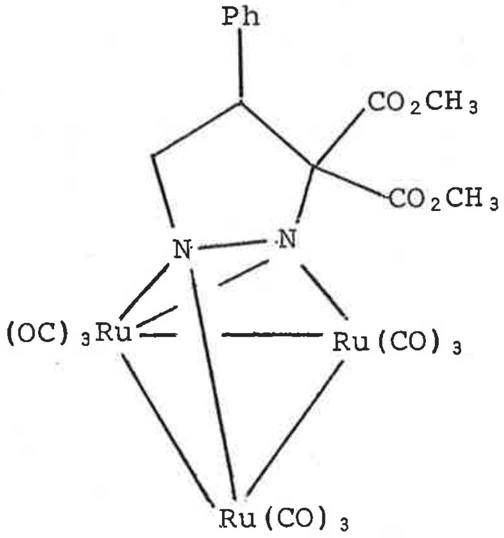
The reaction of 1,2-diazine with $Ru_3(CO)_{12}$ gave (55);[50,51] the analogous reactions of two other 1,2-diazines afforded (56) and (57).[52]



(55)



(56)

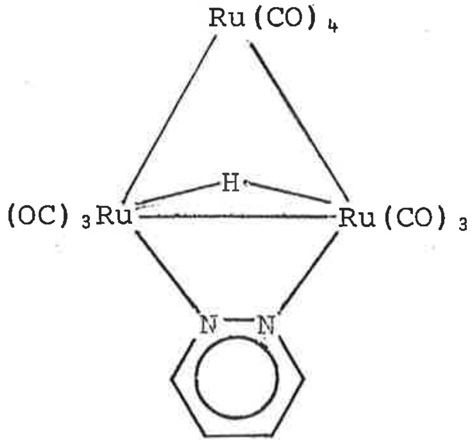


(57)

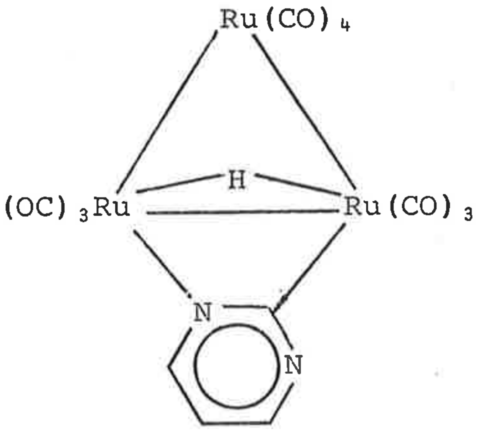
Complex (55) can be considered to be derived from the supposed μ-CO intermediate for scrambling CO groups on $Ru_3(CO)_{12}$. The NMR spectrum at -156°C is in agreement with the solid state structure. Between -156 and -86°C, the bridging and equatorial CO groups interchange by an exceptionally facile process (E_a = 25.5 kJmol^{-1}). Between -117 and -86°C the two axial CO groups on the unique ruthenium enter into the scrambling process, and all CO groups are equilibrated at 75°C (E_a = 58.1 kJmol^{-1}).

The ^{13}C NMR of (56) has also been studied in detail. A fast localised scrambling of the CO groups on the unique ruthenium atom occurs at -130°C; between -130 and -60°C, four resonances are present, three of which start broadening above -40°C and coalesce into one broad signal at room temperature. No internuclear scrambling is observed up to 40°C. The results indicate a significant difference in activation energies of localised CO scrambling with six- or seven- coordinated $M(CO)_3$ groups, and a large energy barrier to interchange of CO between groups of different coordination numbers. The results are explained by different sets of CO groups moving relative to each other, and not by rotation of the M_3 or M_3N_2 unit within a rigid ligand skeleton.

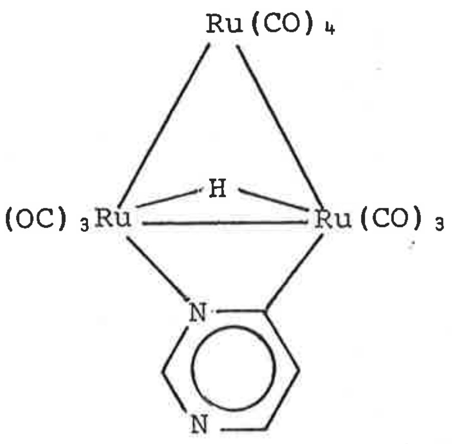
The complex $Ru_3(CO)_{10}(NCMe)_2$ reacted with 1,2-, 1,3- and 1,4-diazine to give (58), isomeric (59) and (60), and (61), respectively;[5] as with pyridine, when *N,N´*-coordination is not possible, cyclometallation occurs.



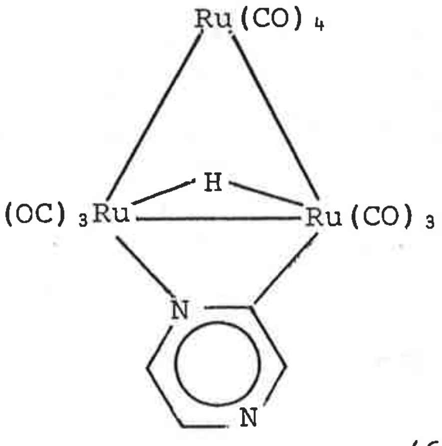
(58)



(59)

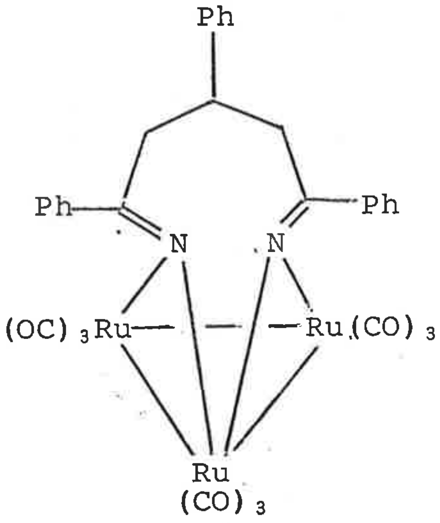


(60)



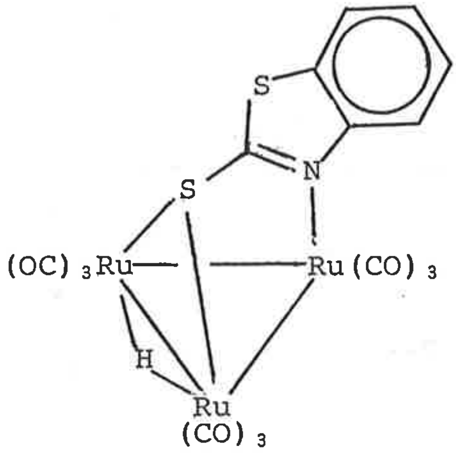
(61)

Even under very mild reaction conditions, $Ru_3(CO)_{12}$ and diazepines afforded mononuclear tricarbonyl complexes;[53,54] a small amount of (62) was isolated from the appropriate reaction.[54]



(62)

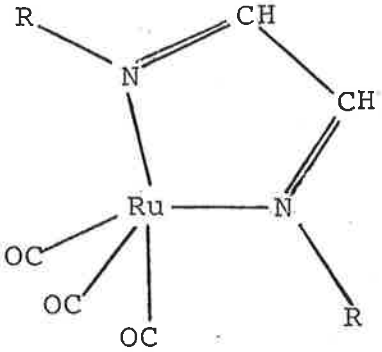
Coordination *via* the *N*-atom was favoured over *S*-coordination when $Ru_3(CO)_{12}$ reacted with mercaptobenzothiazole to give (63).[55]



(<u>63</u>)

7. <u>α-Diimines</u>

The reactions between $Ru_3(CO)_{12}$ and 1,4-diaza-1,3-butadienes (R-DAB, with nitrogen substituent R) have been investigated in some depth.[56] The initial product, $Ru(CO)_3(R\text{-}DAB)$, was isolated for R = 2,6-diisopropylmesityl (<u>64</u>), mesityl (<u>65</u>) and 2,6-xylyl (<u>66</u>).[56] For other R groups,

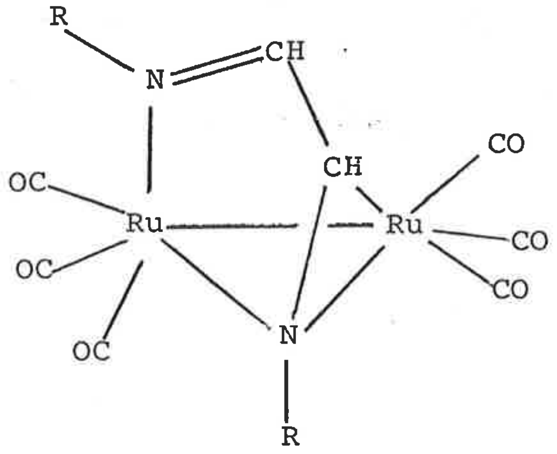


(<u>64</u>) R = 2,6-diisopropylmesityl

(<u>65</u>) R = mesityl

(<u>66</u>) R = 2,6-xylyl

the $Ru(CO)_3(R\text{-}DAB)$ intermediate reacted further with $Ru_3(CO)_{12}$ to give $Ru_2(CO)_6(R\text{-}DAB)$ [R = Pr^i (<u>67</u>), Bu^t (<u>68</u>), Cy (<u>69</u>)].[57] Reaction of (<u>67</u>) or (<u>69</u>) with Me_3NO or reaction between $Ru_3(CO)_{12}$ and R-DAB (R = CH_2Bu^t) afforded

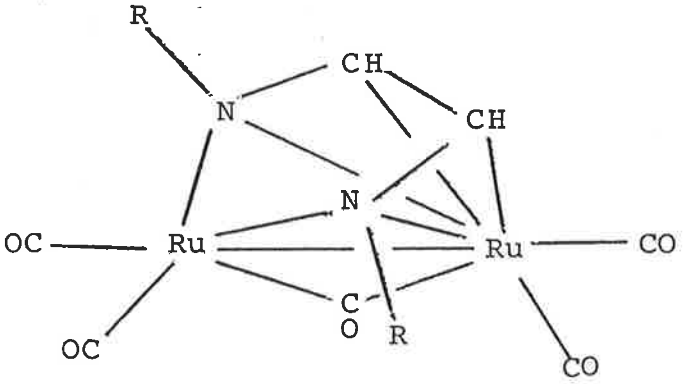


(67) R = Pr^i

(68) R = Bu^t

(69) R = Cy

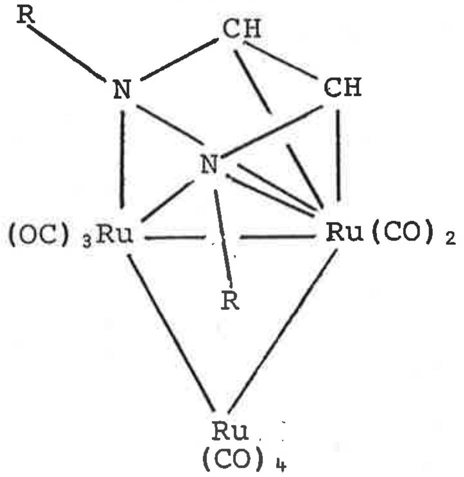
$Ru_2(CO)_5$(R-DAB) [R = Pr^i (70), Cy (71), CH_2Bu^t (72)].[58] When $Ru_2(CO)_5$(R-DAB) was heated with $Ru_3(CO)_{12}$, it gave (73) and (74).[59]



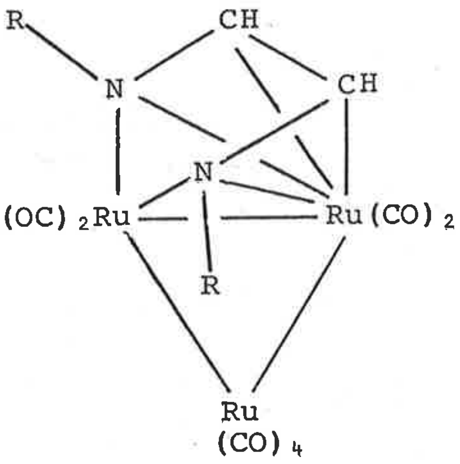
(70) R = Pr^i

(71) R = Cy

(72) R = CH_2Bu^t

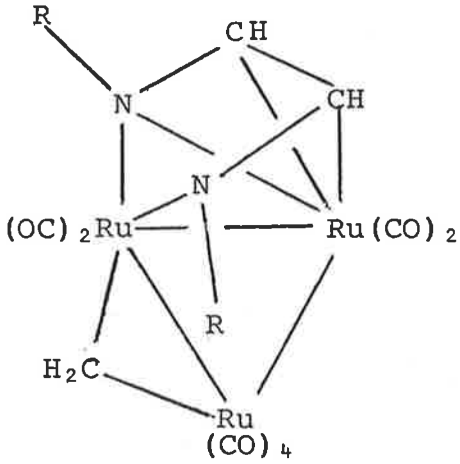


(73)



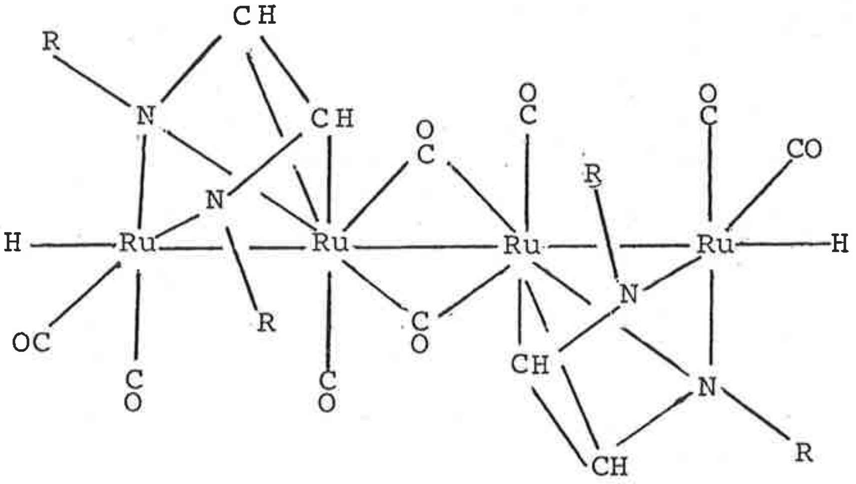
(74)

The latter reversibly added CO to give (73) and reacted with CH_2N_2 to afford (75) (R = CH_2Bu^t) and (76) (R = Bu^i).[60] Treating (74) with H_2 afforded (77).[61]



(75) R = CH_2Bu^t

(76) R = Bu^i

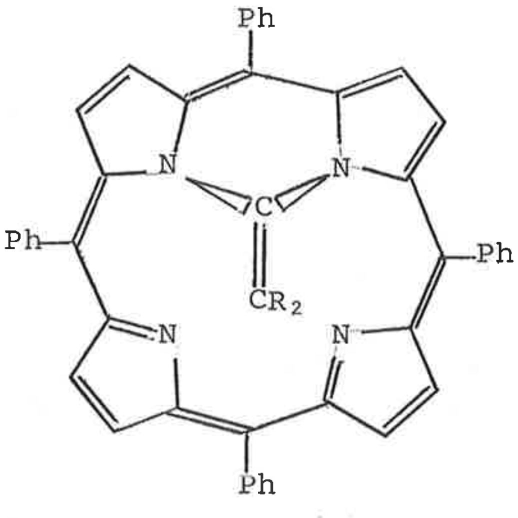


(77) R = CH_2Bu^t

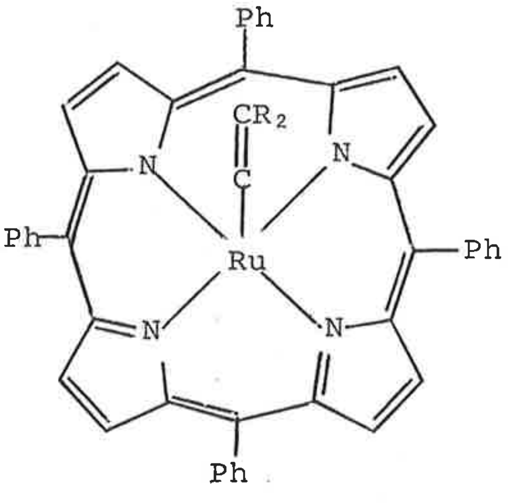
8. Other *N*-donor ligands

Porphyrins or phthalocyanines usually form mononuclear macrocyclic ligand complexes when reacted with $Ru_3(CO)_{12}$.

The product of the reaction between $Ru_3(CO)_{12}$ and tetraphenylporphyrin (tpp) when recrystallised from chloroform/ethanol was eventually shown to be Ru(CO)(EtOH)(tpp),[62] after an earlier X-ray study had erroneously formulated it as the dicarbonyl, $Ru(CO)_2(tpp)$;[63] the unidentate ligands occupy axial sites. The *N,N'*-bridged tetraphenylporphyrin (78) afforded (79) and (80) from reaction with

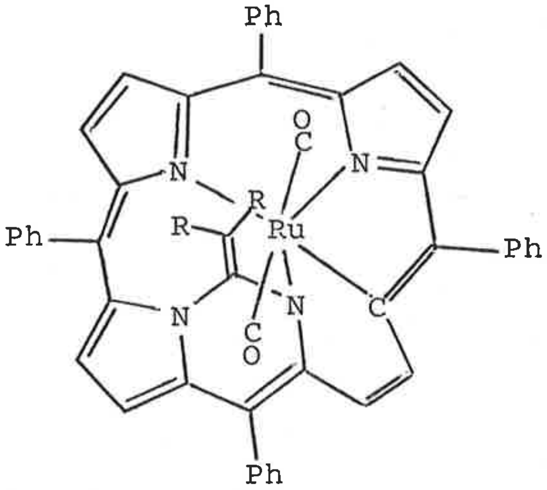


(78) R = C_6H_4Cl-4



(79) R = C_6H_4Cl-4

$Ru_3(CO)_{12}$, the former by insertion of the metal into the N-C(vinyl) bonds, the latter by insertion of the metal into a N-C(pyrrole) bond.[64,65]

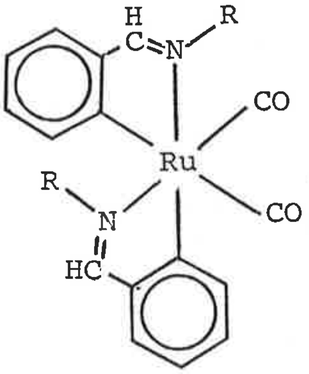


(80) R = C_6H_4Cl-4

Phthalocyanine (H_2Pc) reacted with $Ru_3(CO)_{12}$ in refluxing benzonitrile to give a dark blue solid, probably Ru(CO)(Pc); soxhlet extraction with pyridine afforded $Ru(py)_2(Pc)$.[66] The related complex Ru(CO)(py)(Pc) was obtained from the reaction between $Ru_3(CO)_{12}$ and phthalonitrile when followed by pyridine work-up.[67]

The reaction of $Ru_3(CO)_{12}$ with *N*-phenylsalicylidenimine afforded bis-(*N*-phenylsalicylideniminato)dicarbonylruthenium-(II); the corresponding reaction with *N*,*N*′-ethylenebis(salicylidenimine), salenH_2, gave a complex which analysed as Ru(CO)(salen) and was assigned a dimeric structure.[68] When this product was heated in pyridine, the monomer Ru(CO)(py)-(salen) was obtained.[69]

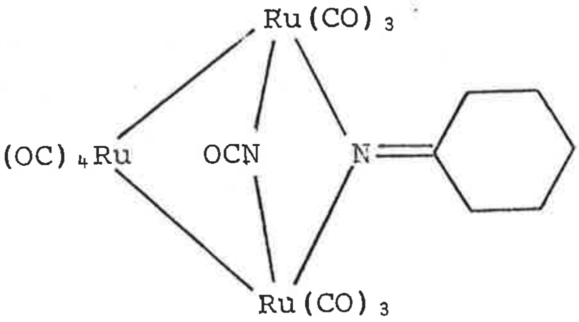
Other Schiff bases, PhCH=NR (R = Ph,Me), also afforded mononuclear complexes when reacted with $Ru_3(CO)_{12}$; yellow crystals of $\overbrace{Ru(CO)_2(C_6H_4CH=N}R)_2$ [R = Ph (81), Me (82)] were obtained.[70]



(81) R = Ph

(82) R = Me

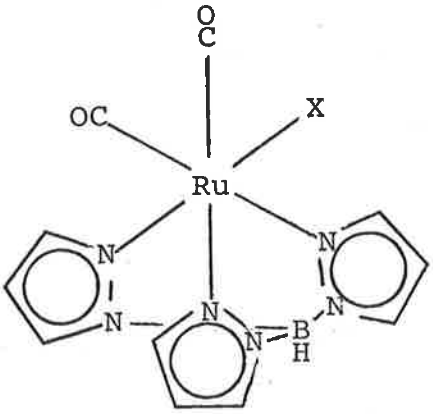
When pentamethylenediazine was reacted with $Ru_3(CO)_{12}$, the $\overline{CN=N}$ ring was cleaved to give the yellow complex (83), containing bridging ketimine and isocyanate ligands.[71]



(83)

The reaction between $Ru_3(CO)_{12}$ and potassium tris(pyrazolyl)borate, $KHB(pz)_3$, gave a deep red solution from which the compounds $RuX(CO)_2\{HB(pz)_3\}$ [X = Cl (84), Br (85), I (86)] were obtained on treatment with the appropriate halogen.[72]

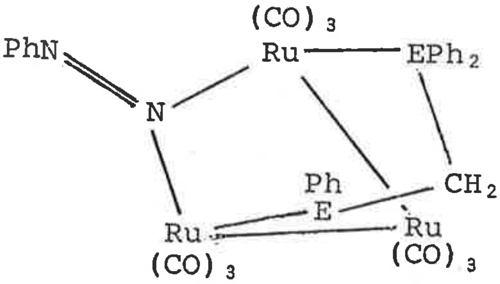
Given the large number of Ru_3 anions available, aryldiazonium cations have been little exploited. The reaction of $[Ru_3(\mu_3\text{-}PhECH_2EPh_2)(CO)_9]^-$ (E=P,As) with $[PhN_2]$-$[PF_6]$ gave (87) and (88), which cyclometallated on heating in cyclohexane to give (89) and (90).[73]



(84) X = Cl

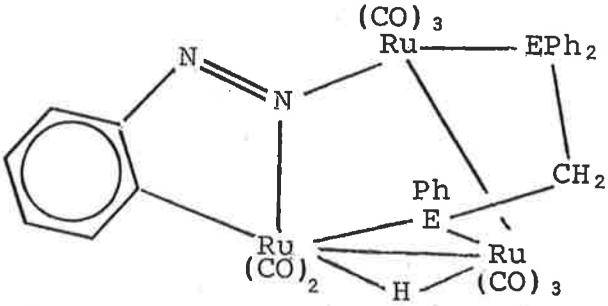
(85) X = Br

(86) X = I



(87) E = P

(88) E = As

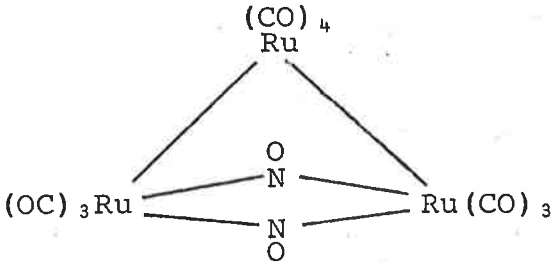


(89) E = P

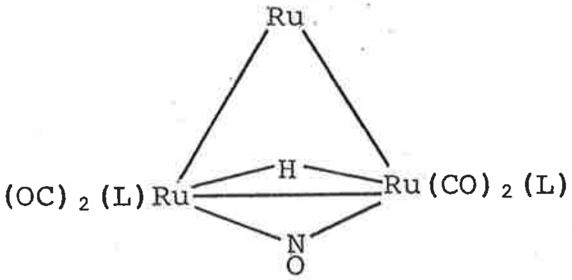
(90) E = As

9. Nitrosylating reagents

Nitric oxide, NO^+ and NO_2^- have all been used to prepare ruthenium cluster nitrosyls. The bis(nitrosyl)-bridged product $Ru_3(\mu\text{-}NO)_2(CO)_{10}$ (91) obtained from $Ru_3(CO)_{12}$ and NO gas degraded upon further reaction with NO to a brown insoluble polymeric material.[73] The cluster anion $[Ru_3(H)(CO)_{11}]^-$ reacted with $[NO][PF_6]$ to give $Ru_3(\mu\text{-}H)(\mu\text{-}NO)(CO)_{10}$ (92); carbonyl substitution of this complex with $P(OMe)_3$ afforded (93).[74] The reaction between $Ru_3(CO)_{12}$ and $[ppn][NO_2]$[75] gave $[ppn]\text{-}[Ru_3(\mu\text{-}NO)(CO)_{10}]$ (94), which afforded (92) upon protonation with CF_3CO_2H.[75,76].



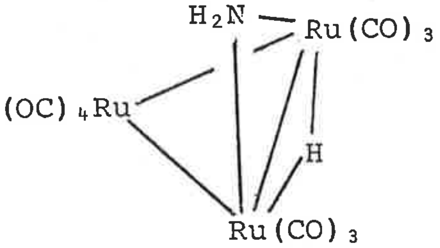
(91)



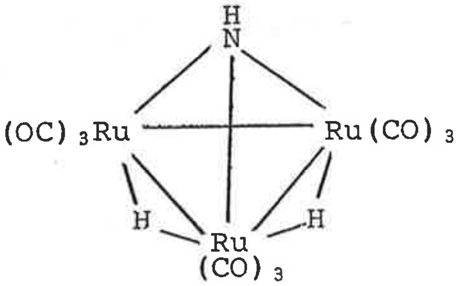
(92) L = CO

(93) L = $P(OMe)_3$

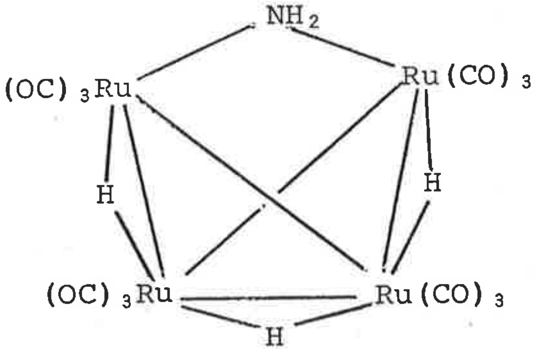
Hydrogenation of (<u>92</u>) gave $Ru_3(\mu\text{-}H)(\mu\text{-}NH_2)(CO)_{10}$ (<u>95</u>), $Ru_3(\mu_3\text{-}NH)(\mu\text{-}H)_2(CO)_9$ (<u>96</u>) and $Ru_4(\mu\text{-}H)_4(CO)_{12}$;[77] trace amounts of tetranuclear $Ru_4(\mu\text{-}H)_3(\mu\text{-}NH_2)(CO)_{12}$ (<u>97</u>) were also found.[78]



(<u>95</u>)

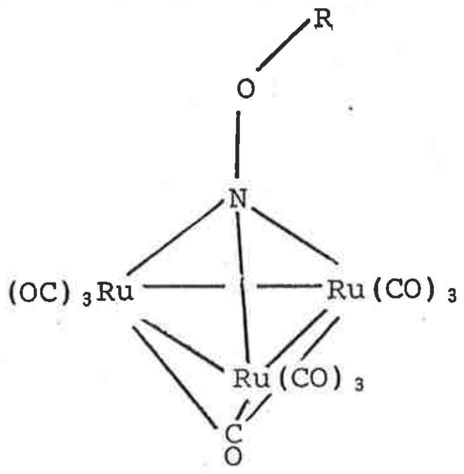


(<u>96</u>)



(<u>97</u>)

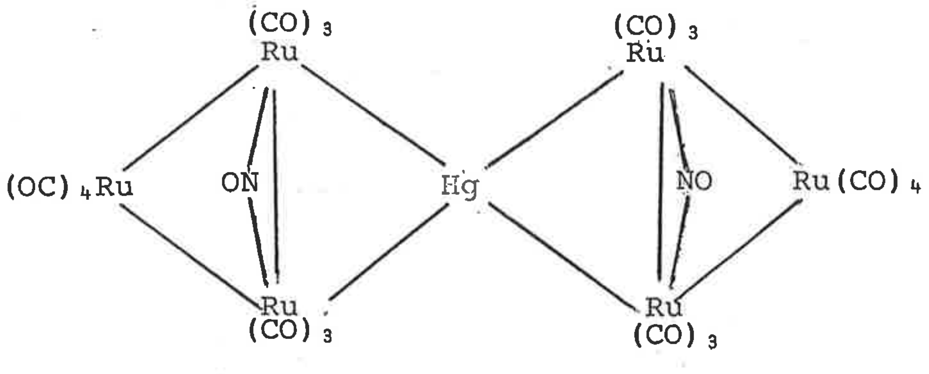
Protonation of (<u>94</u>) with CF_3SO_3H afforded (<u>98</u>);[79] addition of the proton to the nitrosyl oxygen and subsequent capping by the face bridging NOH and CO is in contrast to the addition across a metal-metal bond found when CF_3CO_2H is used.[75,76] Methylation with $CF_3SO_3CH_3$ gave the analogue (99).



(98) R = H

(99) R = Me

The reaction of (94) with $HgCl_2$ afforded (100), with the Hg bridging the same Ru-Ru bond in each Ru_3 triangular unit as the nitrosyl.[80]



(100)

In summary, the chemistry of triruthenium clusters with *N*-donor ligands has expanded since the last such survey, due in some part to the use of milder reaction conditions involving activated triruthenium precursors; in particular, the use of $Ru_3(CO)_{12-n}(NCMe)_n$ (n=1,2) has significantly increased the range of such clusters. A range of reaction types has been observed when the triruthenium clusters react with *N*-donor ligands, amongst which are oxidative addition across an Ru-Ru bond (benzonitriles, aromatic amines, *N*-heterocycles), reaction at a carbonyl ligand (aliphatic amines) and ligand fragmentation to give a μ_3-nitrene group (nitro- and nitroso-arenes, azoarenes, azides). However, there is considerable scope for further research; the only detailed study of the reactions of $Ru_3(CO)_{12}$ with a class of *N*-donor ligand is that of the α-diimines.

RESULTS AND DISCUSSION

This Chapter looks at the reactions between $Ru_3(CO)_{12}$ and some nitrogen heterocycles and examines the substitution chemistry of the bis(phenylimido) complex $Ru_3(\mu_3\text{-NPh})_2(CO)_9$.

In view of the uncertainty regarding the product formed when $Ru_3(CO)_{12}$ was reacted with 2,2′-bipyridyl (*vide supra*), it was decided to reinvestigate the reaction. The reactions between $Ru_3(CO)_{12}$ and pyrazoles had not been explored, although the comparable osmium chemistry had been investigated.[81] The reaction between $Ru_3(CO)_{12}$ and pyridine was known to afford $Ru_3(\mu\text{-H})(\mu\text{-NC}_5H_4)(CO)_{10}$; reaction of the reactive cluster $Ru_3(CO)_{10}(NCMe)_2$ with methyl-substituted pyridines gave analogous products, but $Ru_3(CO)_{12}$ had not been reacted with substituted pyridines. Related osmium chemistry has been developed with the activated clusters $Os_3(\mu\text{-H})_2(CO)_{10}$, $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{10}(C_8H_{14})_2$.[82-85]

The most tractable product from the reaction between $Ru_3(CO)_{12}$ and azobenzene was recently shown to be $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (<u>15</u>).[29] It was proposed to investigate the chemistry of the complex, but because of results by other workers in this field,[15,24-26,35,36] investigations were confined to its substitution chemistry.

1. Reactions between $Ru_3(CO)_{12}$ and some *N*-heterocycles

2,2′-Bipyridyl. The reaction between $Ru_3(CO)_{12}$ and 2,2′-bipyridyl (bipy) was carried out in refluxing cyclohexane and gave, in excellent yield, purple crystals of $Ru_3(\mu\text{-CO})_2(CO)_8(bipy)$ (<u>45</u>). The IR spectrum contains a weak band at 1740 cm^{-1} in addition to three terminal ν(CO) bands suggesting that the complex is a rare example of an Ru_3 cluster with μ-CO ligands. This was confirmed by an X-ray study.

Molecular structure of $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$

A molecule of (45) is shown in Figure 1. The three ruthenium atoms are joined by one short [2.757(1) Å] and two long [2.836(1), 2.855(1) Å] bonds. The two carbonyls C(1)-O(1) and C(2)-O(2) asymmetrically bridge the shortest Ru-Ru bond [Ru(1)-C(1) 1.963(5), Ru(3)-C(1) 2.217(6); Ru(1)-C(2) 2.029(6), Ru(3)-C(2) 2.089(5) Å]; the shorter metal-carbon bond distances are formed by the Ru atom chelated by the bipyridyl ligand as a result of the higher electron density at this metal atom and increased back-bonding to the CO ligand. The asymmetry is also reflected in the Ru-C-O angles [144.7(5), 133.0(4)° at C(1) and 139.6(5), 136.3(4)° at C(2). Of interest is the disparate asymmetry displayed by the bridging carbonyl groups. The difference in the Ru-C bond distances involving C(1) is 0.254 Å, whereas the difference is only 0.060 Å for those to C(2). The only apparent difference between these two carbonyls is found in the nature of their intermolecular contacts. Whereas the carbonyl C(1)-O(1) does not form any significant intermolecular contacts, a close O(2)...H(12´) [where H(12´) is related to O(2) by the symmetry operation $-1-x$, $1-y$, $-z$] contact of 2.469 Å is found for the other bridging CO ligand.

Complex (45) thus has the $Fe_3(CO)_{12}$-type structure previously found for derivatives of $Ru_3(CO)_{12}$ only in

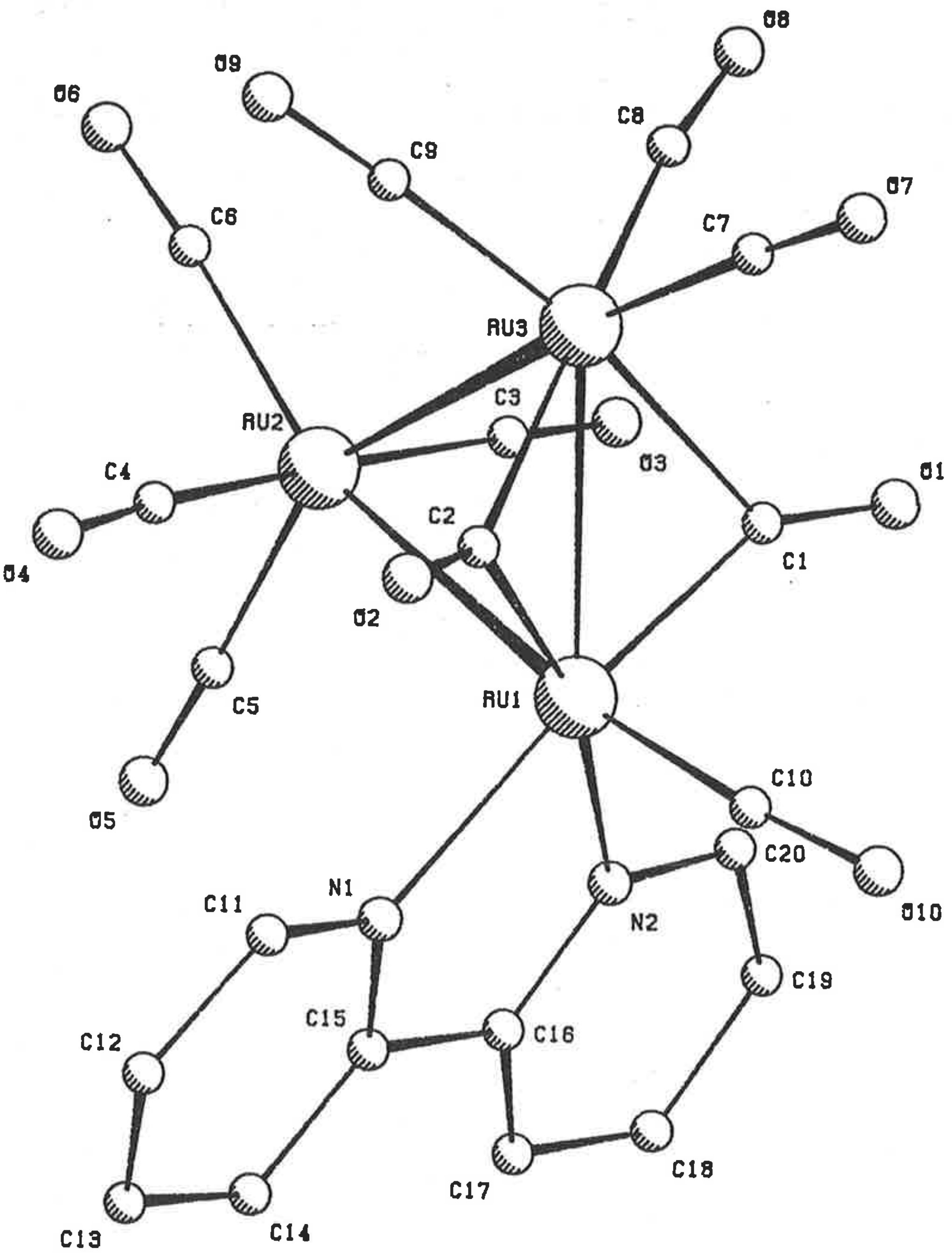


Figure 1: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_3(\mu-CO)_2(CO)_8(bipy)$ (45).

$Ru_3(\mu\text{-}CO)_2(CO)_6\{PPh(OMe)_2\}_4$.[86] In the phosphonite complex, the Ru-Ru separation bridged by the two CO groups (also asymmetrically) is 2.797(1) Å, similar to that found in (45). Structurally, (45) is also related to $Fe_2(\mu\text{-}CO)_2(CO)_5(bipy)$,[87] which similarly has two differing asymmetric μ-CO ligands. However, in this case, only one is approximately *trans* to one of the nitrogens of the chelating bipy ligand, whereas in (45), both μ-CO groups occupy coordination positions approximately *trans* to the nitrogens. In the iron complex, it is considered that the bipy-chelated iron atom donates electron density to the μ-CO π* orbitals, thus enabling some redistribution of the electron density. A similar mechanism probably operates in the case of (45), although the final solid-state structure is likely to be determined by intermolecular interactions.

The 2,2´-bipyridyl ligand does not bridge a metal-metal bond as proposed by others,[5] but chelates Ru(1) [Ru(1)-N(1) 2.188(4), Ru(1)-N(2) 2.191(5) Å]. The Ru_3 plane is almost perpendicular to that of the bipy ligand (dihedral angle 90.2°) and bisects this ligand. In the cyclometallated complex $Os_3(\mu\text{-}H)(\mu\text{-}N_2C_{10}H_7)(CO)_9$ (101), the two nitrogen atoms are bonded to one osmium, while the metallated ring is bonded via an Os-C bond to an adjacent osmium atom.[82]

The structure of a second crystal modification of this complex has been described briefly;[88] this study shows no significant differences between the chemically equivalent parameters in the two polymorphs.

Pyrazoles. The reaction between $Ru_3(CO)_{12}$ and pyrazole was carried out in refluxing cyclohexane for 2 h and gave a mixture of products which was separable with considerable difficulty. Extensive thin layer chromatography and crystallisation eventually gave a mixture of $Ru_3(CO)_{12}$ and $Ru_4(\mu\text{-}H)_4(CO)_{12}$, together with some orange $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3H_3)(CO)_{10}$ (102). This compound, which has formed by oxidative addition of the pyrazole to the cluster, to give (μ-H) and (μ-pyrazolide) ligands, with concomitant loss of two CO groups, does not show any bands assignable to μ-CO groups in its IR spectrum. The metal-bonded proton resonates at δ -13.44, while the symmetrical arrangement of the pyrazolide group is shown by the observation of the ring protons as two resonances at δ 6.26 and 7.50 of relative intensities 1/2, respectively.

The 3,5-dimethyl analogue (103) was similarly obtained, being characterised by resonances in its ^1H NMR spectrum at δ 2.04 (Me), 5.72 (CH) and -13.23 (RuH), with relative intensities 6/1/1. The corresponding 3,5-bis(trifluoromethyl) complex (104) was obtained in much higher yield (82%). All three complexes have similar IR ν(CO) spectra, and the ^1H NMR spectrum of (104) contains the two expected resonances at δ 6.78 (CH) and -13.16 (RuH). The mass spectra of all complexes contain molecular ions which fragment by successive loss of the ten CO groups; complex (103) gave particularly strong doubly-charged ions corresponding to the singly-charged ions.

Molecular structure of $Ru_3(\mu\text{-}H)\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$ (104)

Figure 2 shows a molecule of complex (104). The three metal atoms form an isosceles triangle [Ru(1)-Ru(2) 2.902(1), Ru(1)-Ru(3) 2.849(1), Ru(2)-Ru(3) 2.846(1) Å], the longer

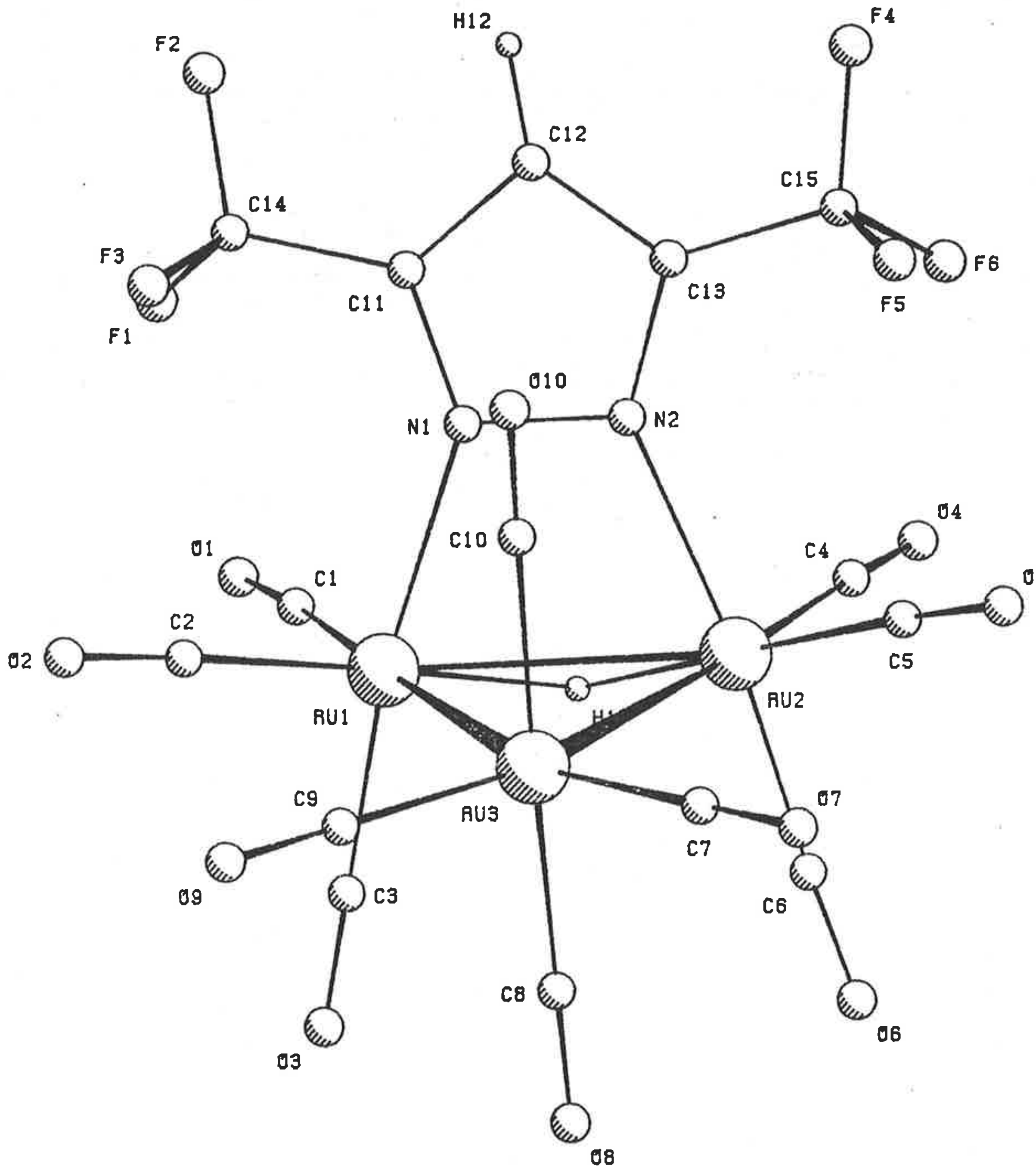
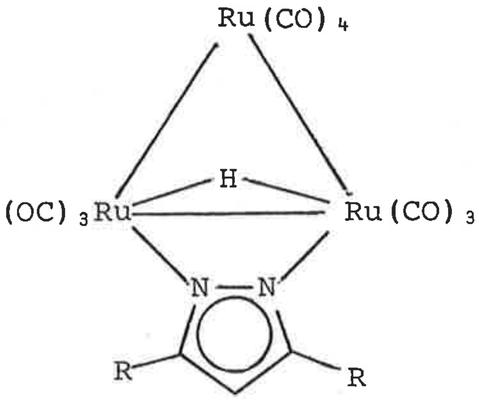


Figure 2: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_3(\mu\text{-}H)\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}\text{-}(CO)_{10}$ (104).

edge of which is bridged by the hydrogen atom (located during the refinement; Ru-H 1.78, 1.81Å) and the planar pyrazolide ligand [Ru(1)-N(1) 2.146(3), Ru(2)-N(2) 2.137(3) Å], which is inclined at an angle of 75.4° to the Ru_3 plane.



(<u>102</u>) R = H

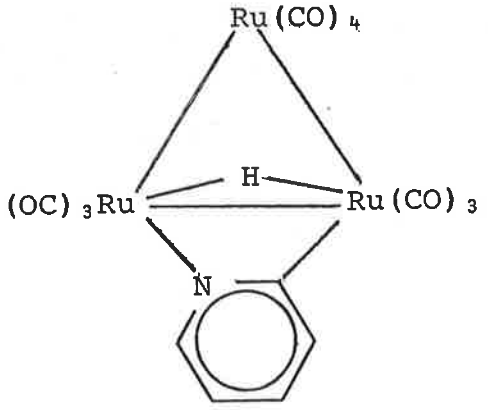
(<u>103</u>) R = CH_3

(<u>104</u>) R = CF_3

The structure is derived from that of $Ru_3(CO)_{12}$ by replacement of two axial CO groups on adjacent Ru atoms by the pyrazolide and H ligands.

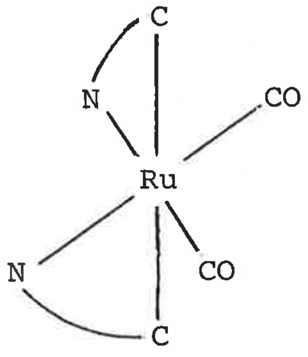
The ten CO groups are all terminal; the maximum deviation from linearity is found for Ru(3)-C(10)-O(10) [174.3(4)°] where C(10)-O(10) is the axial carbonyl group lying on the same side of the Ru_3 triangle as the pyrazolide ligand. The distortion of the Ru-C-O angle from the ideal 180° is such that the terminal O(10) atom is directed away from the planar pyrazolide ring thereby minimizing possible intramolecular interactions between these ligands. A similar distortion of the comparable carbonyl group is found in the structure of $Ru_3(\mu\text{-}N_2C_4H_4)(CO)_{10}$ in which the mean plane of the 1,2-diazine moiety forms a dihedral angle of 95.1° with the Ru_3 plane.[51]

Pyridines. The reaction between $Ru_3(CO)_{12}$ and pyridine gave the cyclometallated complex $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$ (40) (*vide supra*).[44]

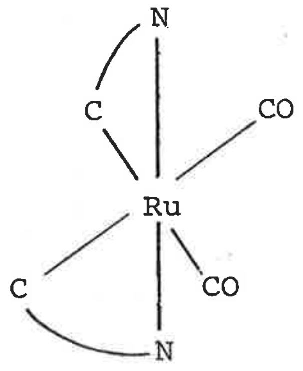


(40)

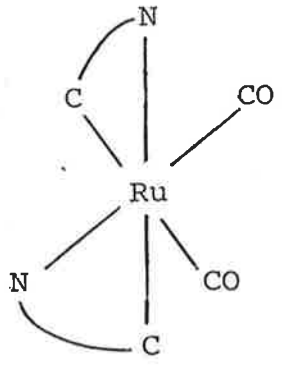
Reaction with some substituted pyridines did not preserve the integrity of the triruthenium cluster.



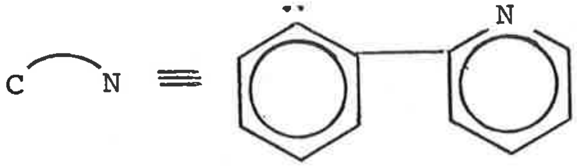
(105A)



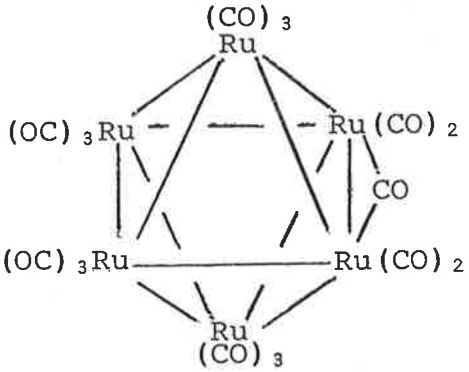
(105B)



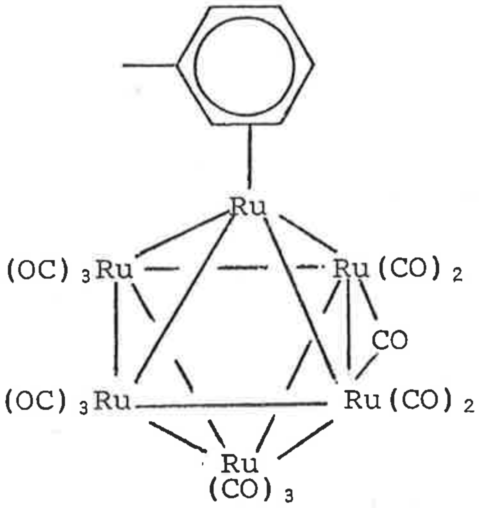
(105C)



When $Ru_3(CO)_{12}$ was reacted with 2-phenylpyridine, it afforded the mononuclear complex $Ru(CO)_2\{2\text{-}(2\text{-pyridyl})\text{-phenyl-}C^1,N^1\}_2$ (<u>105</u>); the mass spectrum contains a molecular ion and sequential loss of the two carbonyl groups. The ^1H NMR spectrum contains a multiplet from δ 6.8 - 8.6 assigned to the C_6H_4 and NC_5H_4 protons. The solution infrared spectrum contains four bands in the ν(CO) region, indicating the presence of isomers; two of the three possible *cis*-$Ru(CO)_2$ isomers (<u>105A</u>), (<u>105B</u>) and (<u>105C</u>) may be present.



(<u>106</u>)



(<u>107</u>)

The reaction between $Ru_3(CO)_{12}$ and 2,6-lutidine in refluxing octane gave, after chromatography, a small amount of the hexaruthenium carbido cluster $Ru_6C(\mu\text{-}CO)(CO)_{16}$ (<u>106</u>) while the reaction of $Ru_3(CO)_{12}$ and pentachloropyridine in refluxing toluene afforded (<u>106</u>)

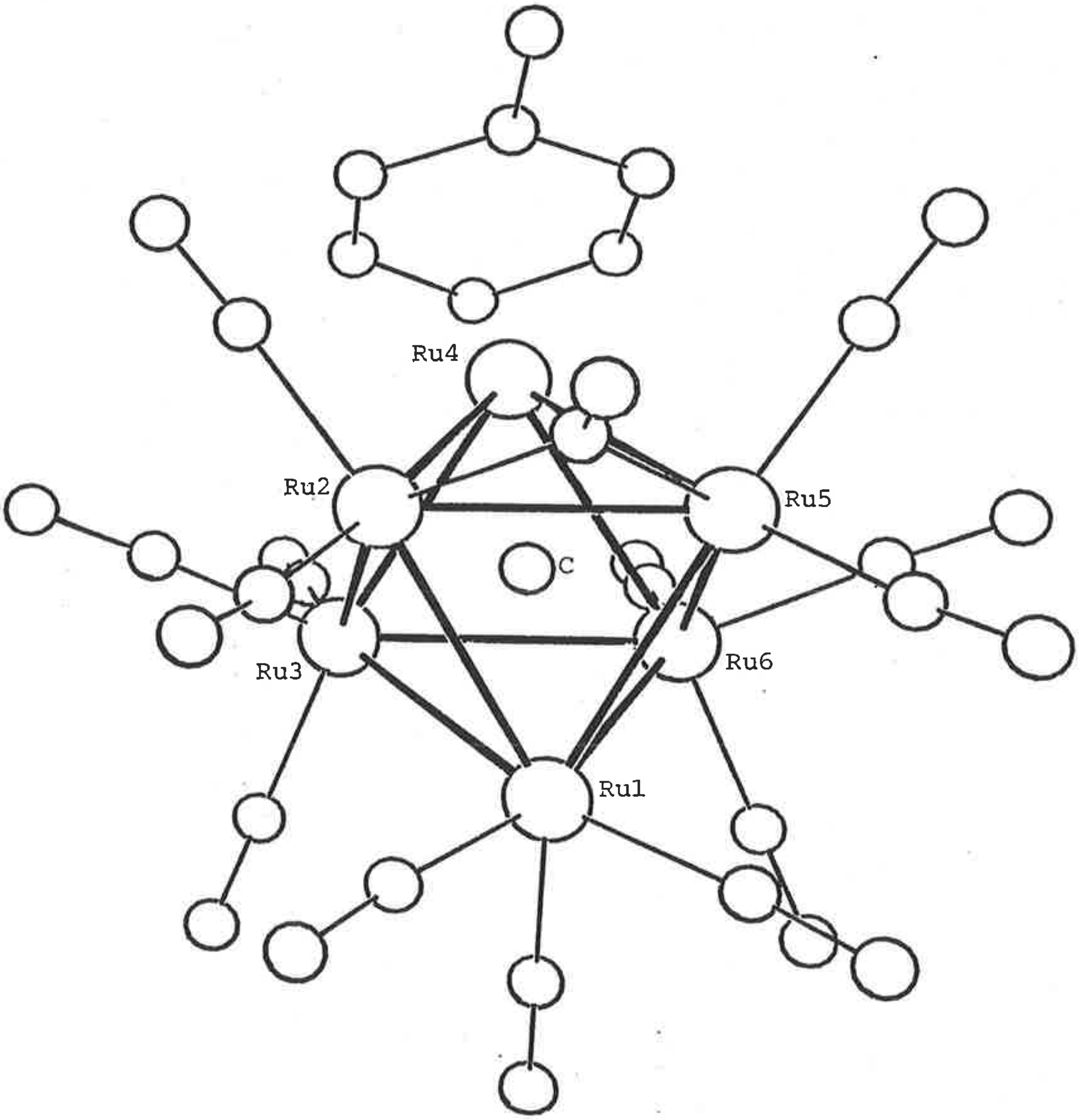


Figure 3: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_6C(\mu\text{-}CO)(CO)_{13}(\eta\text{-toluene})$ (107).

and $Ru_6C(\eta$-toluene$)(\mu$-$CO)(CO)_{13}$ (<u>107</u>). The crystal structure of (<u>107</u>) was determined and is shown in Figure 3.

An examination of Table 1 reveals no significant variations in Ru-Ru distances between those in (<u>107</u>) and those in the previously determined structures of (<u>106</u>)[89] and $Ru_6C(\eta^6$-mesitylene$)(\mu$-$CO)(CO)_{13}$ (<u>108</u>)[90]; comparing the respective metal-carbide and metal-arene distances for the three structures, it is apparent that they are experimentally indistinguishable.

<u>Comparison with osmium</u>. The reaction between $Os_3(CO)_{12}$ and pyridine is complex, four trinuclear and two isomeric binuclear derivatives being isolated from reactions carried out in refluxing octane or in sealed tubes at 184°C.[91] The trinuclear complexes included (<u>109</u>), two isomeric forms of $Os_3(\mu$-$H)(\mu$-$NC_5H_4)(CO)_9(py)$, and $Os_3(\mu$-$H)_2(\mu$-$NC_5H_4)_2(CO)_8$ (<u>110</u>). The simple pyridine-substituted complex $Os_3(CO)_{11}(py)$ was formed by rapid displacement of MeCN from $Os_3(CO)_{11}(NCMe)$.[6] On heating in refluxing octane for a short time, it was converted into (<u>109</u>) with loss of CO. The isolation of the simple substitution product contrasts with the formation of the metallated complex in the analogous ruthenium system, and indicates that once a route is found for the synthesis of the simple substitution product, further transformation of organic molecules is more facile when complexed to a ruthenium cluster than in the osmium analogue.

The reaction between 2,2′-bipyridyl and $Os_3(CO)_{12}$ gives the metallated complex (<u>111</u>); no compound analogous to (<u>45</u>) was obtained.[82] The related reaction of $Os_3(CO)_{10}$-

Table 1

Comparison of bond lengths in some hexaruthenium carbido clusters (distances in Ångstroms).

	Ru$_6$C(CO)$_{17}$[a]	Ru$_6$C(CO)$_{14}$-(mesitylene)[b]	Ru$_6$C(CO)$_{14}$-(toluene)[c]
Ru(1)-Ru(2)	2.885(6)	2.864	2.939(3)
Ru(1)-Ru(3)	2.951(6)	2.901	2.849(3)
Ru(1)-Ru(5)	2.827(5)		
Ru(1)-Ru(6)	2.927(5)		
Ru(2)-Ru(3)	2.897(5)	2.956	2.957(2)
Ru(2)-Ru(4)	2.909(5)	2.864	2.899(3)
Ru(2)-Ru(5)	2.855(6)	2.853	2.821(4)
Ru(3)-Ru(4)	2.917(6)	2.854	2.847(2)
Ru(3)-Ru(6)	2.840(6)	2.857	2.960(4)
Ru(4)-Ru(5)	2.858(6)		
Ru(4)-Ru(6)	2.872(7)		
Ru(5)-Ru(6)	3.034(5)		
Mean Ru-C-(carbide)	2.05(5)	2.04(4)	2.05(2)
max. dev. from mean	0.07	0.16	0.17
Mean Ru-C-(arene)	-	2.24	2.27(3)

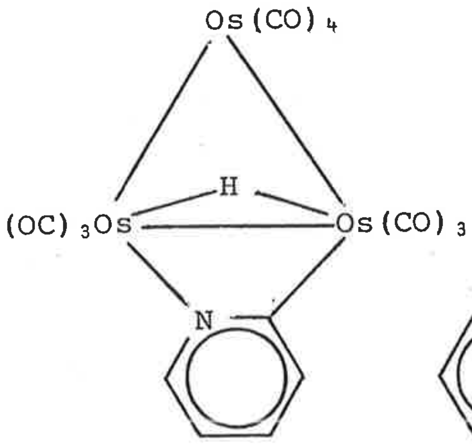
All structures contain a carbonyl group bridging Ru(2) and Ru(5). The arenes are bonded to Ru(4). The latter two structures were solved in a higher symmetry space group; hence, some atoms are equivalent. Both arene-containing structures have Ru(4)-C(carbide) of 1.88Å.

[a] Reference 89. [b] Reference 90. [c] Reference 105.

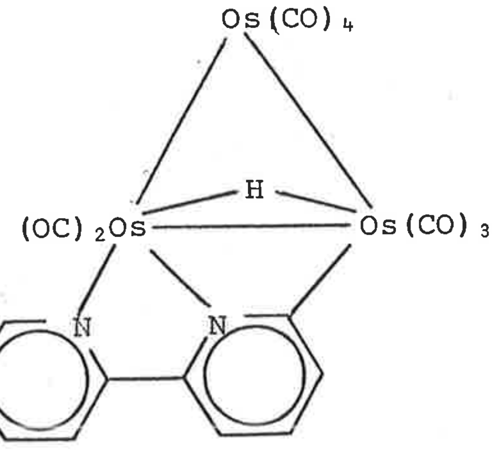
$(NCMe)_2$ does not appear to have been described, but might be expected to give the osmium analogue of (45). The facile conversion of (45) to (46) by heating in refluxing toluene has been referred to earlier; however, as was suggested above, the structure of the product is probably analogous to that of the osmium compound, which has been determined by an X-ray study.

Reactions between $Os_3(CO)_{12}$ and pyrazole afford initially a *C*-metallated complex which is converted to the osmium analogue of (102) on heating at 180°C.[81] With 3,5-disubstituted pyrazoles, the analogous *C*-metallated complexes cannot form. No evidence was obtained for the formation of any isomeric *C*-metallated derivative in the ruthenium system.

Substituted pyridines have been reacted with triosmium clusters to afford products in which the trinuclear framework is maintained, a function of the greater metal-metal bond strength for osmium *vis-à-vis* ruthenium.



(109)

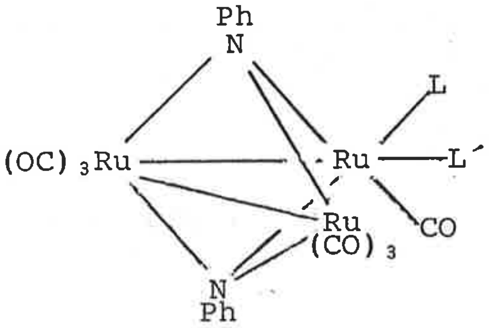


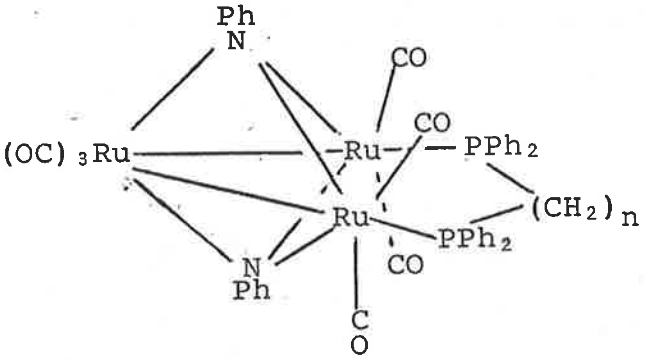
(111)

2. Substitution chemistry of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (15)

Ready substitution of CO [by isocyanide or tertiary phosphine ligands] occurred in reactions between RNC or PR_3 and $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ under electron-transfer (ET) catalysed conditions. Thus, with *m*-xylyl isocyanide, red-orange $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNxy)$ (112) was isolated in 40% yield. The IR spectrum contains a $\nu(CN)$ band at 2156 cm^{-1}, together with a complex $\nu(CO)$ pattern, the number of bands (11) suggesting the presence of isomers. However, the ^1H NMR spectrum shows the presence of only one environment for the Me groups. To determine the position of substitution, an X-ray study of (112) was undertaken, and this revealed that one of the axial CO groups on an outer ruthenium atom had been replaced by the isocyanide ligand. In other respects, the structure resembles that of the parent compound.

Similar reactions between $Ru_3(CO)_{12}$ and monodentate tertiary phosphines, such as PPh_3, or phosphites, such as $P(OMe)_3$, afforded monosubstituted complexes whose IR $\nu(CO)$ spectra differ from that of complex (112) in having only seven bands. The position of substitution was established as the equatorial site on one of the terminal ruthenium atoms by means of an X-ray study of the PPh_3 complex (113); the similarity of the IR $\nu(CO)$ spectra suggests that the $P(OMe)_3$ complex (114) has the same stereochemistry. The linear bis-tertiary phosphine, $C_2(PPh_2)_2$ (dppa), gave a red-orange complex with an IR $\nu(CO)$ spectrum similar to those of (113) and (114), and with an elemental micro-analysis and molecular weight (FAB MS) consistent with its being the 'binuclear' $\{Ru_3(\mu_3\text{-}NPh)_2(CO)_8\}_2(\mu\text{-}dppa)$ (115).





	L	L´
(<u>112</u>)	CNxy	CO
(<u>113</u>)	CO	PPh$_3$
(<u>114</u>)	CO	P(OMe)$_3$
(<u>115</u>)	CO	½(dppa)

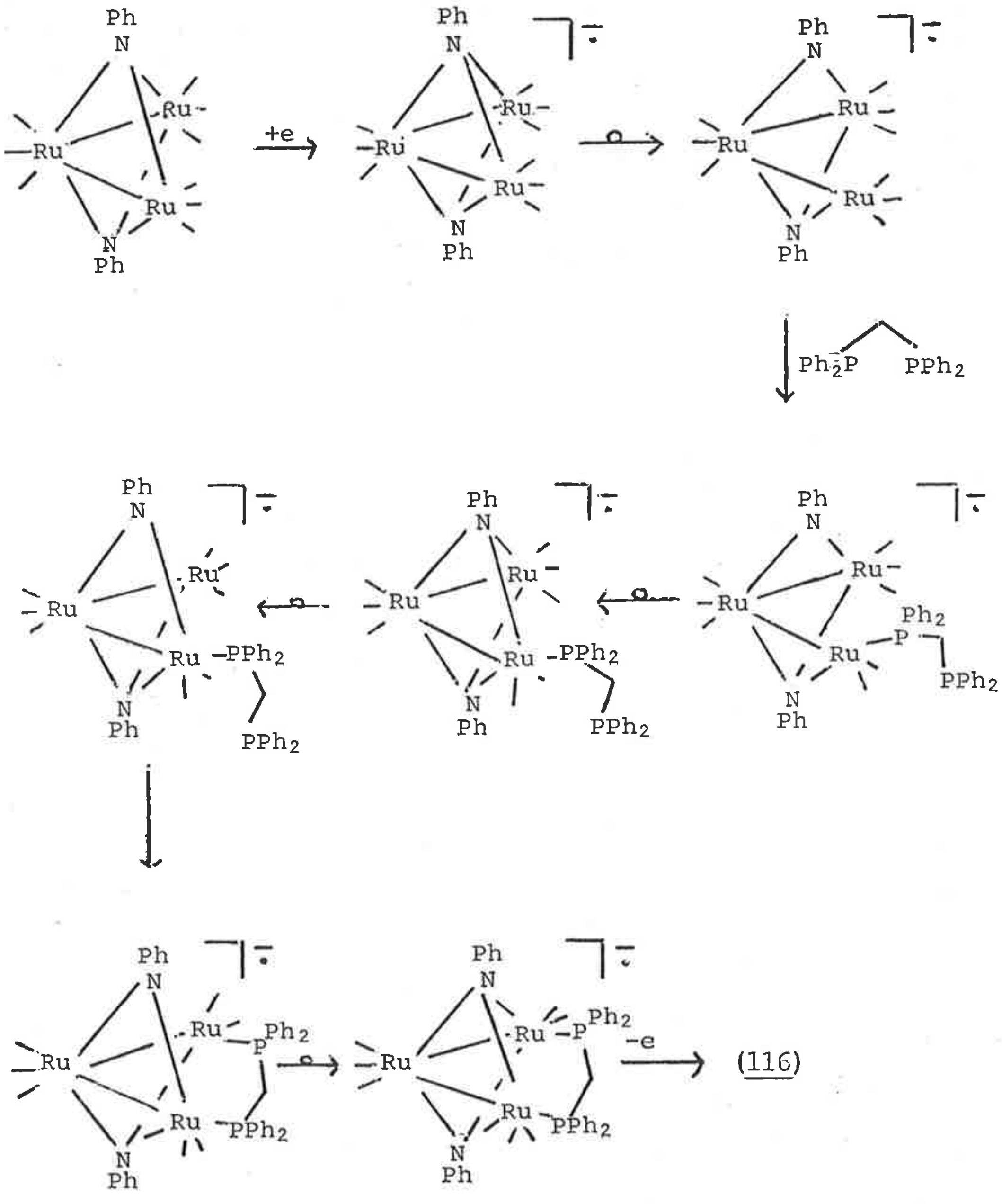
(<u>116</u>)	n = 1
(<u>117</u>)	n = 2

Reactions of (<u>15</u>) with the bidentate tertiary phosphines dppm and dppe afforded the complexes (<u>116</u>) and (<u>117</u>), respectively; the latter was obtained in only very low yield. Both complexes have similar IR ν(CO) spectra, and the X-ray study of (<u>116</u>) shows that the dppm ligand spans the non-bonded Ru...Ru vector, with the phosphorus atoms occupying the two equatorial sites.

Characterisation of these complexes was aided by their mass spectra. In the electron impact (EI) mass spectrum of (<u>116</u>), the strongest ion is [PPh$_3$]$^+$, indicating that thermal decomposition has occurred in the hot (150°C) source. Ions corresponding to [M-nCO]$^+$ (n = 0 - 8) are very weak. The fast atom bombardment (FAB) mass spectrum of (<u>15</u>) contains ions corresponding to $[M\text{-nCO}]^+$ (n = 0 - 9), together with $[Ru_3(CO)_{12-n}]^+$ (n = 0 - 5) or, possibly, $[Ru_3N_2(CO)_{11-n}]^+$ (n = 0 - 5). The FAB mass spectra of complexes (<u>112</u>) - (<u>117</u>) contain $[M]^+$ followed by sequential loss of all CO's; those of (<u>114</u>) - (<u>117</u>) also feature fragmentation of the ligand.

The substitution positions are the same as found for the parent carbonyl, $Ru_3(CO)_{12}$.[92] Isocyanides occupy axial positions in $Ru_3(CO)_{11}(CNBu^t)$ and $Ru_3(CO)_{10}(CNBu^t)_2$,[93] while tertiary phosphines and phosphites go into equatorial sites, as found in many such derivatives that have been studied. Bidentate phosphines also occupy equatorial sites on adjacent ruthenium atoms in complexes such as $Ru_3(CO)_{10}(dppm)$,[94] $Ru_3(CO)_8(dppm)_2$[95] and $Ru_3(CO)_{10}(dppe)$.[96,97]

In ETC reactions of $Ru_3(CO)_{12}$, the intermediate $[Ru_3(CO)_{12}]^{\bar{\cdot}}$ anion radical is assumed to have a 17e centre, and is readily substituted by Group 15 ligands.[102] The extra electron is accommodated in the LUMO which has metal-metal antibonding character.[98,99] Kochi and co-workers[100,101] have made a detailed study of $Fe_3(\mu_3\text{-PPh})_2(CO)_9$, a complex closely related to $Ru_3(\mu_3\text{-NPh})_2(CO)_9$, and of its reactions with a range of phosphorus-donor ligands, and have found that 'closed' and 'open' radical anions, the latter formed by 'slippage' of the PPh group, are formed. The consequent weakening or cleavage of the Fe-P bond generates a 17e metal centre which is substitution labile. Their studies offer an explanation for the dppe ligand bridging the non-bonded metal atoms in $Fe_3(\mu_3\text{-PPh})_2(\mu\text{-dppe})(CO)_7$, exactly paralleling the structure of $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$. It seems likely that similar intermediates are formed in the ETC-substitution reactions of the ruthenium complex. The suggested mechanism is shown in Scheme 2.



Scheme 2

The attempted substitution of (15) by $AsPh_3$ under ET-catalysed conditions was unsuccessful. Substitution of $Ru_3(CO)_{12}$ is also reported to be more difficult with arsines than with phosphines by ET catalysis.[102] Substitution of (15) with $P(OMe)_3$ using [ppn]acetate as a catalyst was also unsuccessful; thermally induced substitution afforded a much lower yield of (114) than the corresponding ET-catalysed reaction.

X-ray structures of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ and its substituted derivatives

As mentioned above, the X-ray structures of (112), (113) and (116) have been determined, and are compared below with that of the previously determined structure of (15).[22] Plots of each of the molecules (112), (113) and (116) are given in Figures 4 - 6, respectively: a commentary on significant structural features follows.

All four complexes contain an 'open' Ru_3 triangle capped on both sides by a μ_3-phenylimido ligand. The Ru_3N_2 core is thus based on a trigonal bipyramidal arrangement with the N atoms occupying axial positions. The carbonyl ligands in the complexes are terminal and any deviation from linearity arises either as a result of steric pressures within the complexes or significant intermolecular interactions as will be discussed below. Substitution of a carbonyl in (15) by CN(*m*-xylyl) in (112) and by PPh_3 in (113) occurs at one of the 'end' Ru atoms rather than at the middle Ru atom. The dppm ligand in (116) spans the non-bonded Ru...Ru vector.

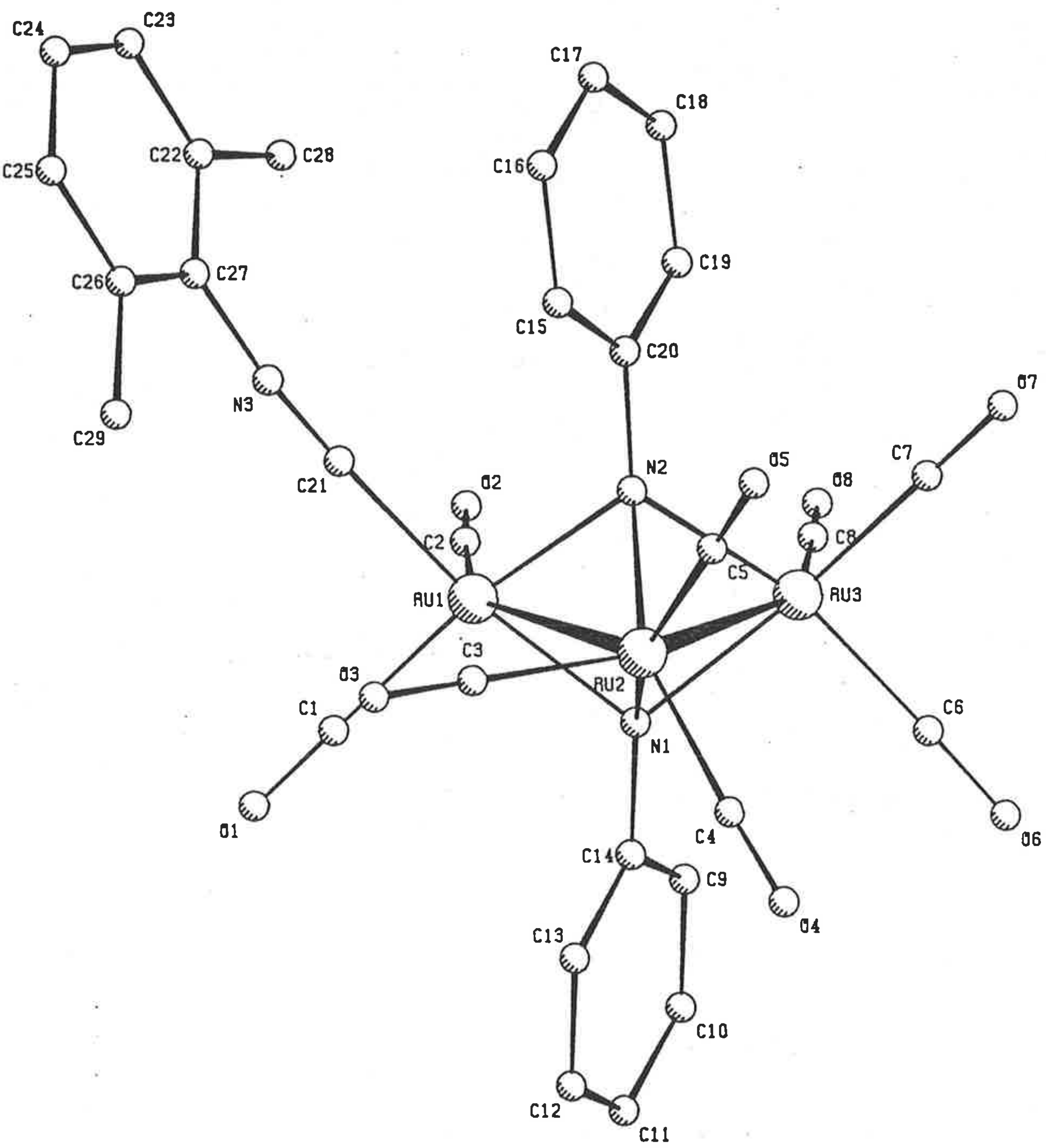


Figure 4: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_3(\mu_3\text{-}NPh)_2(CO)_8$-$(CNC_6H_3Me_2\text{-}2,6)$ (112).

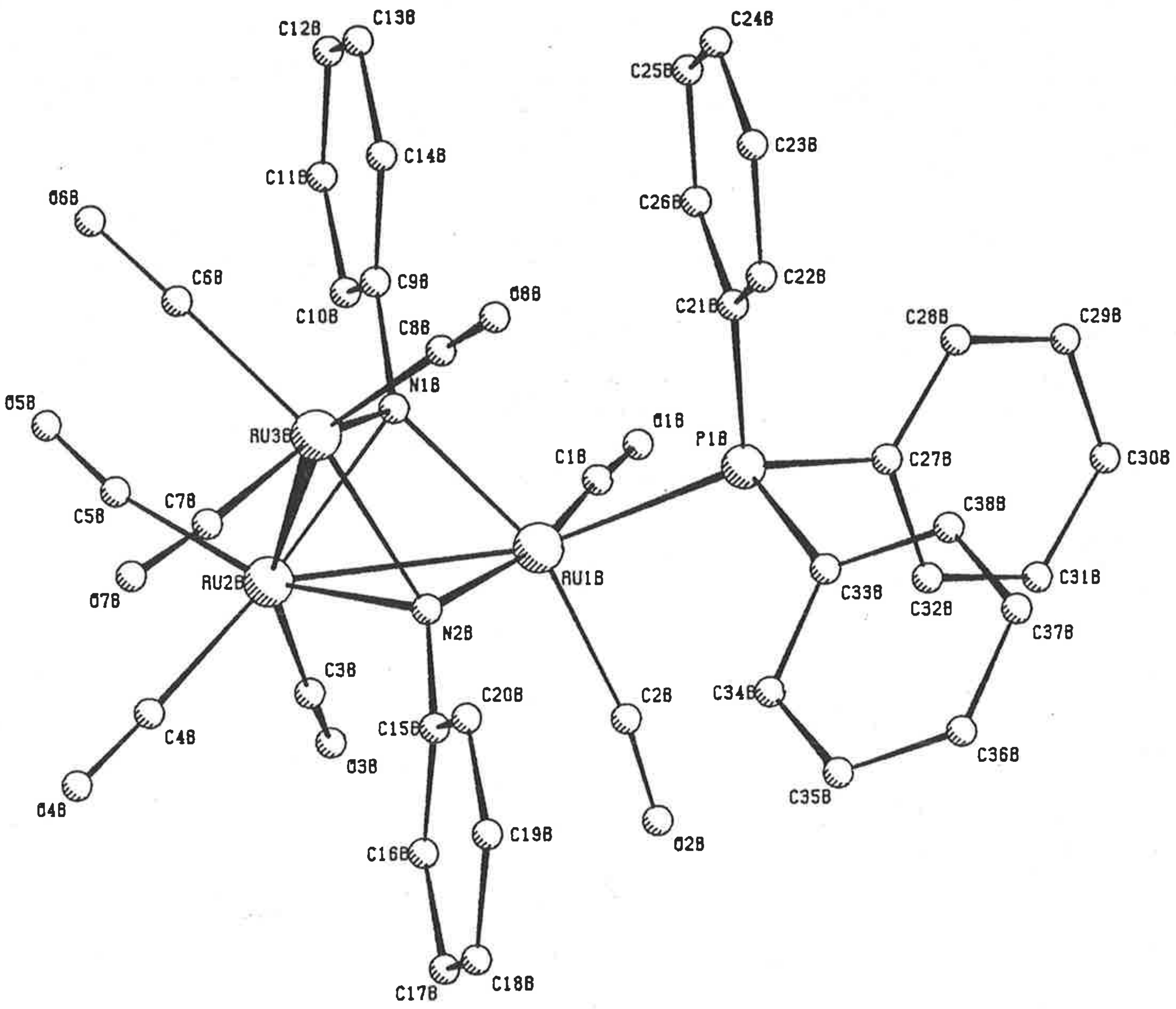


Figure 5: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(PPh_3)$ (113).

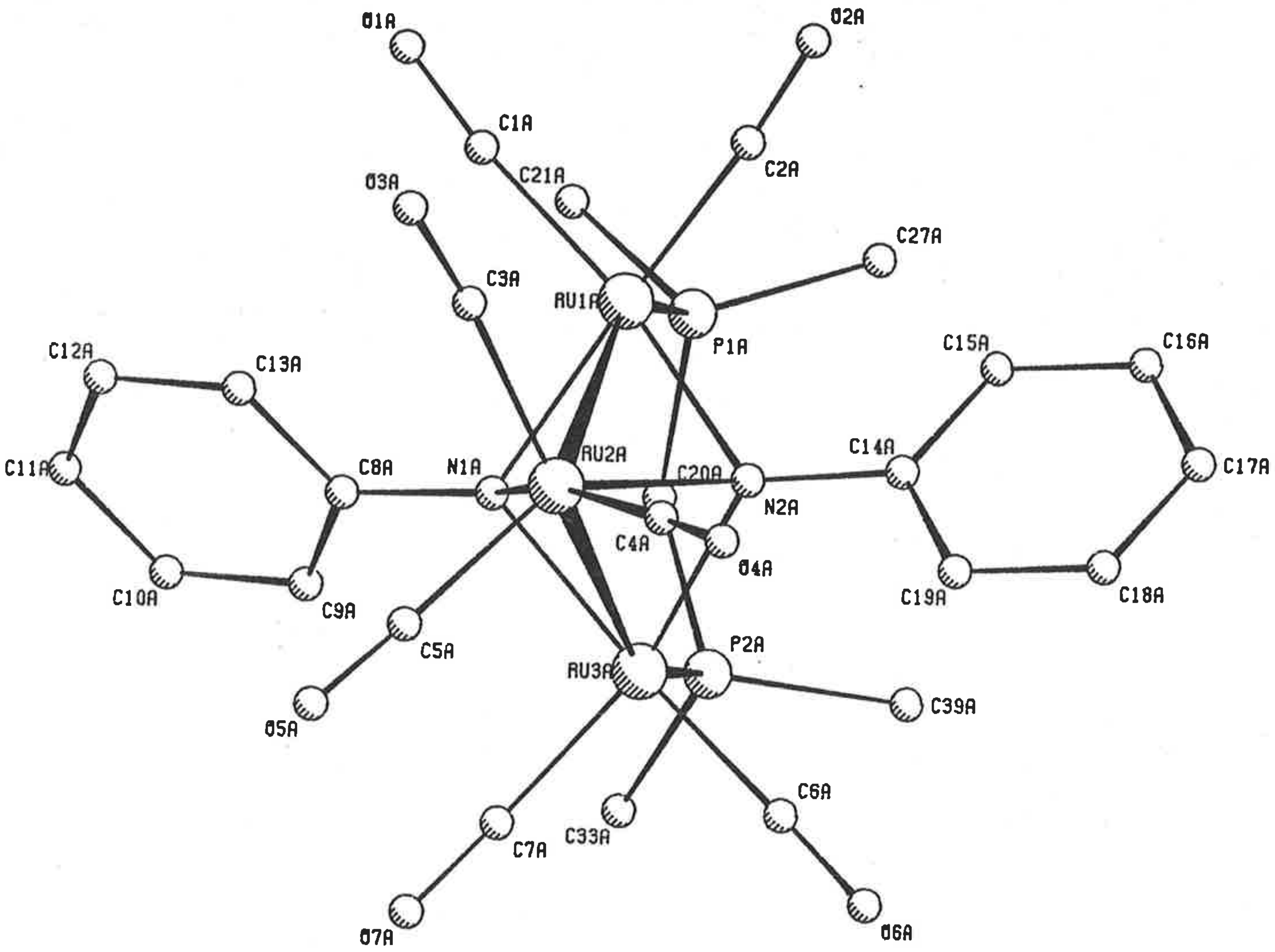


Figure 6: (by M.R. Snow and E.R.T. Tiekink). PLUTO plot of the molecular structure of $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}dppm)(CO)_7$ (116) (only the *ipso* carbons of the phenyl rings of dppm have been plotted, for reasons of clarity).

In complex (112), the isocyanide ligand replaces an 'axial' CO group on a terminal ruthenium atom (Figure 4). In these trigonal bipyramidal M_3N_2 complexes, the six CO groups that are not approximately coplanar with the Ru_3 core may be termed 'axial', although the Ru-C-N vector is inclined at 96.3° to the Ru_3 plane, with the N(1)-Ru(1)-C(21) angle 162.7(2)°. This may be compared with the corresponding N-Ru-P angle of approximately 109° found in (113) (below). However, the overall structure and disposition of the ligands is remarkably similar to those found in (15). The Ru-C-O angles range between 174.6(6) and 179.7(3) Å, while the Ru(1)-C(21)-N(3) angle is 175.9(5)°.

In (113) one of the carbonyl groups on an outside Ru atom of (15) has been substituted for a PPh_3 ligand (Figure 5). The PPh_3 molecule coordinates the Ru_3 triangle equatorially; for molecule A of the asymmetric unit, the P atom lies 0.11 Å above the Ru_3 plane (i.e. in the direction of the N(1A) atom) and in molecule B the P atom lies 0.03 Å below the Ru_3 plane. The asymmetry in the Ru-Ru bonds found in the structure of (15) persists in (113) in which the longer Ru-Ru bond involves the Ru atom coordinated by PPh_3. The presence of the bulky PPh_3 ligand is responsible for the deviation from linearity of the Ru(1)-C(2)-O(2) bond [167.1(9)°] as is shown in Figure 5. There are no major differences between chemically equivalent parameters defining the two molecules of (113) which comprise the asymmetric unit for this compound.

In complex (116), the dppm ligand spans the non-bonded Ru...Ru edge, the P atoms occupying approximately equatorial coordination sites, with the resulting C(20)P(1)-Ru(1)Ru(2)Ru(3)P(2) ring adopting a boat conformation. The Ru-P distance of 2.335(2)Å [2.304(2)Å for molecule B] is equal, within experimental error, to that found for the closely related compound (113).

A common feature of the bis-μ_3-phenylimido Ru_3 structures reported above, as well as the earlier examples, is the unequal distances of the Ru-Ru bonds in the Ru_3 triangles. It has been suggested[22] that it is the relative disposition of the ligands which is responsible for the disparate Ru-Ru distances. This point is now developed further. In each of the molecules there exists a weak intermolecular interaction, of *ca* 3.0 Å, between the terminal Ru atom and a carbonyl group bonded to the middle Ru atom. The geometry of this interaction is such that the 'semi-bridging' carbonyl is coplanar with the Ru_3 triangle and, further, it is noted that the greatest deviation from linearity of the Ru-C-O groups in these structures (except for that mentioned for (112) above) is found for the carbonyl groups involved in these intermolecular interactions. It is proposed that the presence of these additional, albeit weak, Ru...CO contacts is a major contributing factor to the minor asymmetry observed in the Ru-Ru bonds.

There is a systematic variation in the non-bonded Ru...Ru distances in these clusters which can be related to the substitution pattern of the coordination geometries.

For the compounds (15) and (112) the non-bonded Ru...Ru distances lie in the narrow range 3.284(1)-3.291(1) Å. An expansion of the Ru...Ru distance of *ca* 0.3 Å is found in (116) and of *ca* 0.7 Å in (113). The opening of the Ru_3 triangles in undoubtedly related to the presence of the sterically demanding phosphine substituents in equatorial positions in these structures.

The separation of the imido N atoms in the clusters lies in the range 2.41(1)-2.45(1) Å and it has been suggested by others that some direct interaction between these atoms is likely.[22]

CONCLUSION

Reactions between $Ru_3(CO)_{12}$ and the nitrogen heterocycles 2,2´-bipyridyl, pyrazole, 3,5-dimethylpyrazole and 3,5-bis(trifluoromethyl)pyrazole afforded triruthenium cluster complexes. 2,2´-Bipyridyl gave purple $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$, shown by an X-ray structure determination to have an $Fe_3(CO)_{12}$-type structure, with the bipy chelating one of the CO-bridged Ru atoms. The pyrazoles gave $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3HR_2)(CO)_{10}$ (R=H,Me or CF_3), in which the pyrazolide ligand spans an Ru-Ru bond also bridged by H, as shown by the X-ray structure of the CF_3 derivative.

Reactions between $Ru_3(CO)_{12}$ and azobenzene afforded $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ as the most tractable product. Electron transfer-catalysed substitution reactions with 2e donor ligands resulted in the formation of axially- (isocyanide) or equatorially- (tertiary phosphines and phosphites) substituted products; the latter reactions are analogous to those of $Fe_3(\mu_3\text{-}PPh)_2(CO)_9$,[100,101] and are assumed to proceed in a similar manner *via* opening of the Ru_2N triangle.

EXPERIMENTAL

All reactions were run under nitrogen; no special precautions were taken to exclude air during workup. Solvents were dried and distilled before use. Instruments used were as described in Chapter 1.

Starting materials

$Ru_3(CO)_{12}$ was prepared by a literature method.[103] The *N*-heterocycles, azobenzene and 2e donor ligands were commercial products and used as received.

Reactions of $Ru_3(CO)_{12}$ with nitrogen heterocycles

(a) 2,2´-Bipyridyl (with R.C. Wallis) - A mixture of $Ru_3(CO)_{12}$ (300 mg, 0.47 mmol) and 2,2´-bipyridyl (bipy) (73 mg, 0.47 mmol) was refluxed in cyclohexane (100 ml) for 20 min. The purple crystals that deposited were collected, washed with light petroleum and dried in air for a short period to give pure $Ru_3(CO)_{10}$(bipy) (45) (320 mg, 92%). (Found: C 31.9, H 1.4, N 4.0; $C_{20}H_8N_2O_{10}Ru_3$ requires C 32.5, H 1.1, N 3.8%). IR ($CHCl_3$): ν(CO) 2077m, 2034s, 1994s, and 1740vw cm^{-1}.

(b) Pyrazole - A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and pyrazole (24 mg, 0.358 mmol) was heated in refluxing cyclohexane (25 ml) for 2 h. The solvent was removed by rotary evaporation and a dichloromethane extract of the residue was chromatographed (silica TLC plates/light petroleum eluant), affording six bands. Multiple development of the chromatography plates was necessary to purify band 3, orange, which was crystallized (dichloromethane/methanol) and identified as $Ru_3(\mu\text{-}H)$-$(\mu\text{-}N_2C_3H_3)(CO)_{10}$ (103) (30 mg, 15%), m.p. 170-175°C (dec.).

(Found: C 24.01, H 0.43, N 4.10%, *M* (mass spectrometry) 653; $C_{13}H_4N_2O_{10}Ru_3$ requires C 23.97, H 0.62, N 4.30%; *M* 653). IR (cyclohexane): ν(CO) 2109m, 2072vs, 2066vs, 2030vs, 2016s, 1999(sh), 1997m, 1985w, 1974w, 1967w cm^{-1}. ^{1}H NMR: δ($CDCl_3$) -13.44, s, 1H, RuH; 6.20, t, *J*(HH) 2.2 Hz, 1H, H_4; 7.50, d, *J*(HH) 2.2 Hz, 2H, $H_3 + H_5$. About 40 mg of a mixture of $Ru_3(CO)_{12}$ and $Ru_4(\mu\text{-}H)_4(CO)_{12}$ was also recovered by chromatography.

(c) 3,5-Dimethylpyrazole - A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 3,5-dimethylpyrazole (31 mg, 0.32 mmol) was heated in refluxing cyclohexane for 16 h. The solvent was removed (rotary evaporator) and a dichloromethane extract of the residue was chromatographed (silica TLC plates/light petroleum eluant) affording five bands. As in (b), rechromatography proved necessary. Band 1, yellow, was identified as $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (5 mg, 9%). Band 2, orange, was crystallized (dichloromethane/methanol) and identified as $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3HMe_2\text{-}3,5)(CO)_{10}$ (103) (44 mg, 21%), m.p. 143-147°C. (Found: C 26.63, H 1.09, N 4.12%, *M* (mass spectrometry) 681; $C_{15}H_8N_2O_{10}Ru_3$ requires C 26.52, H 1.12, N 4.12%, *M* 681). IR (cyclohexane): ν(CO) 2108m, 2068vs, 2063vs, 2029vs, 2019m, 2010s, 1998m, 1994m, 1980w, 1971w, 1966w cm^{-1}. ^{1}H NMR: δ($CDCl_3$) -13.23, s, 1H, RuH; 2.04, s, 6H, Me; 5.72, s, 1H, H_4.

(d) 3,5-Bis(trifluoromethyl)pyrazole - A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 3,5-bis(trifluoromethyl)-pyrazole (142 mg, 0.70 mmol) was heated in refluxing cyclohexane (25 ml) for 3.5 h, after which time solvent was removed (rotary evaporator). Addition of methanol to a filtered dichloromethane extract of the residue, followed by concentration afforded orange crystals of $Ru_3(\mu\text{-}H)\text{-}\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$ (104) (202 mg, 82%), m.p. 127 - 131°C. (Found: C 22.78, H <0.2, N 3.20%, *M* (mass spectrometry) 789; $C_{15}H_2F_6N_2O_{10}Ru_3$ requires C 22.88, H 0.26, N 3.56%, *M* 789). IR (cyclohexane): ν(CO) 2116m, 2083vs, 2071vs, 2033vs, 2016m, 2006m, 1978w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ - 13.16, s, 1H, RuH; 6.78, s, 1H, H_4.

(e) 2-Phenylpyridine - A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 2-phenylpyridine (10 ml of a 0.23*M* solution in cyclohexane, 2.3 mmol) was heated in refluxing cyclohexane (30 ml) for 16 h, after which time solvent was removed (rotary evaporator). A light petroleum extract of the residue was concentrated, affording yellow crystals of $Ru(CO)_2\{2\text{-}(2\text{-pyridyl})\text{phenyl-}C^1,N^1\}_2$ (105) (116 mg, 80%), m.p. 240-245°C (dec.). *M* (mass spectrometry) 466; $C_{24}H_{16}N_2O_2Ru$ requires *M* (mass spectrometry) 466. IR (cyclohexane): ν(CO) 2085m, 2071s, 2025vs, 1964vs cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 6.8 - 8.6, m, C_6H_4 + NC_5H_4.

(f) 2,6-Lutidine - A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.313 mmol) and 2,6-lutidine (49 mg, 0.469 mmol) was heated in refluxing n-octane (20 ml) for 3 h, after which time solvent was removed. A dichloromethane extract of the residue was chromatographed on a silica column; 1:9 dichloromethane/light petroleum eluted an orange band which afforded purple crystals of $Ru_6C(CO)_{17}$ (106) (9 mg, 5%) after concentration. IR (cyclohexane): ν(CO) 2070s, 2050vs, 2004w, 1858w(br) cm^{-1} [lit[104] 2064s, 2049s, 2007w, 1993w, 1958w, 1854w(br) cm^{-1}]. *M* (mass) spectrometry), 1096 [lit[104] *M* (mass spectrometry) 1096].

(g) Pentachloropyridine - A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.782 mmol) and pentachloropyridine (200 mg, 0.796 mmol) was heated in refluxing toluene (80 ml) for 7.5h. After cooling to room temperature, the solution was filtered through Celite, and the solvent was removed (rotary evaporator). A dichloromethane extract of the residue was chromatographed on silica coated TLC plates, and eluted with 1:9 acetone/light petroleum, affording six bands. The fastest moving band, band 1, yellow, was identified as unreacted $Ru_3(CO)_{12}$ (276 mg, 55%). Band 4, orange, was identified as $Ru_6C(CO)_{17}$ (106) (5 mg, 1%), by its solution infrared spectrum. Band 6, red, was crystallised from ethanol/benzene and identified as $Ru_6C(\eta^6\text{-toluene})(CO)_{14}$ (107) (4 mg, 1%). IR (CH_2Cl_2):ν(CO) 2082s, 2032vs, 2003w, 1820w(br) cm^{-1} [lit[104] (cyclohexane): 2079s, 2035s(sh), 2028s, 2012w, 2001m, 1986m, 1974m, 1826w cm^{-1}]. *M* (mass spectrometry) 1104 [lit[104] *M* (mass spectrometry) 1104].

Preparation of $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (15) (with O.b. Shawkataly)

A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and azobenzene (285 mg, 1.56 mmol) was heated in refluxing n-octane (80 ml) until the reaction was judged to be complete [monitoring the disappearance of the 2061 cm^{-1} band of $Ru_3(CO)_{12}$ (*ca* 4h)]. Solvent was removed under reduced pressure and the residue was chromatographed (Florisil). Light petroleum eluted an orange band, which was recrystallised (n-pentane) to give $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (15) (115 mg, 20%), m.p. 157°C. (Found: C 34.18, H 1.43, N 3.79%, *M* 739; $C_{21}H_{10}N_2O_9Ru_3$ requires C 34.20, H 1.37, N 3.80%, *M* 739). IR (cyclohexane): ν(CO) 2098w, 2077vs, 2053vs, 2027vs, 2020vs, 2016vs, 1995s, 1984m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 6.7-7.3, m, Ph. ^{13}C NMR: δ ($CDCl_3$) 123.2, 124.2, 128.4, Ph; 191.7, m, CO. FAB mass spectrum: 739, $[M]^+$, 31; 711, $[M - CO]^+$, 93; 683, $[M - 2CO]^+$, 100; 655, $[M - 3CO]^+$, 17; 641, $[Ru_3(CO)_{12}]^+$ or $[Ru_3N_2(CO)_{11}]^+$ ($\equiv M'$), 14; 627, $[M - 4CO]^+$, 59; 613, $[M' - CO]^+$, 10; 599, $[M - 5CO]^+$, 21; 585, $[M' - 2CO]^+$, 10; 571, $[M - 6CO]^+$, 41; 557, $[M' - 3CO]^+$, 14; 543, $[M - 7CO]^+$, 48; 529, $[M' - 4CO]^+$, 21; 515, $[M - 8CO]^+$, 31; 501, $[M' - 5CO]^+$, 31; 487, $[M - 9CO]^+$, 31.

Reactions of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (15)

(a) With *m*-xylyl isocyanide - A solution of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and 2,6-dimethylphenyl isocyanide (9 mg, 0.068 mmol) in tetrahydrofuran (10 ml) was treated with six drops of sodium diphenylketyl solution (*ca* 0.025*M* $Na^+[Ph_2CO]^{\bar{}}$ in tetrahydrofuran). After stirring for 5 min, monitoring by TLC showed unreacted (15) remained. Addition of more initiator (six drops), was followed by stirring for 5 min longer, and evaporation *in vacuo*. A dichloromethane extract of the residue was chromatographed (preparative TLC on silica gel, 1:9 acetone/light petroleum eluant). The complex $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNxy)$ (112) (23 mg, 40%) was isolated from the second and major band (of six) ($R_f = 0.60$) as a red-orange powder, m.p. 125-128°C (dec.) (from $CHCl_3$/MeOH). (Found: C 40.89, H 2.51, N 4.83; $C_{29}H_{19}N_3O_8Ru_3$ requires C 41.43, H 2.28, N 5.00%). IR (cyclohexane): ν(CN) 2156m(br); ν(CO) 2086m, 2078s, 2061m, 2045vs, 2038s, 2018(sh), 2011vs, 1996s, 1984s, 1975m, 1969m

cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.15, s, 6H, CH_3; 6.86-7.10, m, 13H, Ph + $C_6\underline{H}_3Me_2$. FAB mass spectrum: 841, $[M]^+$, 12; 813, $[M - CO]^+$, 67; 785, $[M - 2CO]^+$, 100; 757, $[M - 3CO]^+$, 9; 745, ?, 9; 729, $[M - 4CO]^+$, 31; 701, $[M - 5CO]^+$, 16; 673, $[M - 6CO]^+$, 47; 645, $[M - 7CO]^+$, 34; 632, ?, 21; 616, $[M - 8CO - H]^+$, 37.

(b) With PPh_3 - As in (a) above, $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (50 mg, 0.068 mmol) and PPh_3 (18 mg, 0.069 mmol) afforded $Ru_3(\mu_3\text{-NPh})_2(CO)_8(PPh_3)$ (113) as an orange powder from dichloromethane/methanol (34 mg, 52%), m.p. 135-138°C (dec.). (Found: C 46.36, H 2.87, N 2.75 ; $C_{38}H_{25}N_2O_8PRu_3$ requires C 46.97, H 2.59, N 2.88%). IR (cyclohexane): ν(CO) 2075s, 2045vs, 2026vs, 2009vs, 1991m, 1981vs, 1973vs cm^{-1}. ^1H NMR: δ($CDCl_3$) 6.5-7.5, m, Ph. EI and FAB mass spectra (*m/z*, assignment, relative intensity values for FAB spectrum in brackets): 973, $[M]^+$, 26 (5); 945, $[M - CO]^+$, 76 (39); 917, $[M - 2CO]^+$, 13 (0); 889, $[M - 3CO]^+$, 21 (11); 861, $[M - 4CO]^+$, 100 (100); 833, $[M - 5CO]$, 21 (8); 821, ?, -(6); 805, $[M - 6CO]^+$, 82 (38); 777, $[M - 7CO]^+$, 47 (25); 763, ?, -(22); 749, $[M - 8CO]^+$, 87 (88); 262, $[PPh_3]^+$, 2630.

(c) With $P(OMe)_3$ - Similarly, $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (50 mg, 0.068 mmol) and $P(OMe)_3$ (1 ml of a 0.068*M* solution in tetrahydrofuran, 0.068 mmol), afforded $Ru_3(\mu_3\text{-NPh})_2(CO)_8\text{-}\{P(OMe)_3\}$ (114), isolated by TLC chromatography (silica; 1:9 acetone/light petroleum eluant) as the third of five bands eluted (R_f = 0.30), as red crystals from light petroleum (7 mg, 12%), m.p. 138-141°C (dec.). (Found: C 33.06, H 2.35, N 3.35; $C_{23}H_{19}N_2O_{11}PRu_3$ requires C 33.14, H 2.30, N 3.36%). IR (cyclohexane): 2078s, 2047vs, 2038m, 2032s, 2009vs, 1981s, 1973m cm^{-1}. ^1H NMR:

$\delta(CDCl_3)$ 3.49, d, *J*(HP) 12.2Hz, 9H, Me; 6.77-7.12, m, 10H, Ph. FAB mass spectrum: 835, $[M]^+$, 22; 807, $[M - CO]^+$, 100; 779, $[M - 2CO]^+$ 84; 751, $[M - 3CO]^+$, 16; 723, $[M - 4CO]^+$, 44; 695, $[M - 5CO]^+$, 25; 667, $[M - 6CO]^+$, 25; 636, $[M - 6CO - OMe]^+$, 22; 608, $[M - 7CO - OMe]^+$, 31; 578, $[M - 7CO - 2OMe]^+$, 22. Unreacted $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (11 mg, 22%) was recovered by chromatography as the fastest moving band (R_f = 0.80).

(d) With 1,2-bis(diphenylphosphino)acetylene (dppa) - The binuclear complex $\{Ru_3(\mu_3\text{-}NPh)_2(CO)_8\}_2(\mu\text{-}dppa)$ (116) (20 mg, 31%) was obtained similarly from $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and dppa (14 mg, 0.036 mmol). It was isolated by TLC (silica gel; 1:9 acetone/light petroleum eluant) in the fourth and major red-orange band of seven bands eluted (R_f = 0.25), which was rechromatographed as above and afforded three bands; the fastest moving and major component was identified as the product above after crystallisation from dichloromethane/methanol, m.p. 135-137°C (dec.). (Found: C 43.49, H 2.27, N 3.06; $C_{66}H_{40}N_4O_{16}P_2Ru_6$ requires C 43.71, H 3.09, N 2.22%). IR (cyclohexane): $\nu(CO)$ 2077s, 2059w, 2047vs, 2032s, 2012vs, 1995w, 1979s(br) cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 6.34-7.65, m, Ph. FAB mass spectrum: 1816, $[M]^+$, 8; 1732, $[M - 3CO]^+$, 10; 1648, $[M - 6CO]^+$, 17; 1620, $[M - 7CO]^+$, 8; 1592, $[M - 8CO]^+$, 12; 1564, $[M - 9CO]^+$, 15; 1536, $[M - 10CO]^+$, 11; 1508, $[M - 11CO]^+$, 10; 1480, $[M - 12CO]^+$, 5; 1452, $[M - 13CO]^+$, 9; 1424, $[M - 14CO]^+$, 11; 1396, $[M - 15CO]^+$, 8; 1368, $[M - 16CO]^+$, 8; 998, $[M - 16CO - 2PPh_2]^+$, 34; 937, ?, 100; 881, ?, 68.

(e) With bis(diphenylphosphino)methane (dppm) - A similar reaction between $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (50 mg, 0.068 mmol) and dppm (26 mg, 0.068 mmol) gave a product separated (preparative TLC, 1:9 acetone/light petroleum) into unreacted dppm, recovered $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (24 mg, 48%; R_f = 0.80) and a red-orange band (R_f = 0.20) crystallised (CH_2Cl_2/ethanol/hexane) as a red powder, and identified as $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$ (116) (27 mg, 37%), m.p. 190-193°C (dec.). (Found: C 49.55, H 3.21, N 2.56; $C_{44}H_{32}N_2O_7P_2Ru_3$ requires C 49.58, H 3.03, N 2.63%). IR (cyclohexane): ν(CO) 2057(sh), 2053vs, 2022vs, 2003s, 1994s, 1970s, 1950m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.33, t, *J*(HP) 11.4Hz, 2H, CH_2; 6.4-7.4, m, 30H, Ph. FAB mass spectrum: 1067, $[M]^+$, 21; 1039 $[M - CO]^+$, 38; 1011, $[M - 2CO]^+$, 67; 955, $[M - 4CO]^+$, 50; 927, $[M - 5CO]^+$, 13; 917, -, 13; 899, $[M - 6CO]^+$, 100; 871, $[M - 7CO]^+$, 42; 822, $[M - 6CO - Ph]^+$, 13; 794, $[M - 7CO - Ph]^+$, 33; 780, $[M - 7CO - NPh]^+$, 25.

(f) With 1,2-bis(diphenylphosphino)ethane (dppe) - The reaction between $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (50 mg, 0.068 mmol) and dppe (28 mg, 0.07 mmol) gave $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppe})(CO)_7.0.5CH_2Cl_2$ (117) (5 mg, 7%) from the second of three bands (silica gel, 1:4 acetone/light petroleum) as red crystals, m.p. 188-190°C (dec.) from CH_2Cl_2/MeOH. (Found: C 50.05, H 3.17, N 2.59; $C_{45}H_{34}N_2O_7P_2Ru_3.0.5CH_2Cl_2$ requires C 48.69, H 3.14, N 2.50%). IR (cyclohexane): ν(CO) 2056(sh), 2052vs, 2022vs, 2006s, 1991s, 1970s, 1950m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.79, m, 4H, PCH_2; 5.29, s, 1H, CH_2Cl_2; 7.59-7.63, m, 30H, Ph. FAB mass spectrum: 1080, $[M - H]^+$, 18; 1052, $[M - CO - H]^+$, 16; 1024, $[M - 2CO - H]^+$, 4; 984, ?, 4; 969, $[M - 4CO]^+$, 62; 941, $[M - 5CO]^+$, 6; 928,

$[M - PPh_2 + H]^+$, 18; 913, $[M - 6CO]^+$, 100; 885, $[M - 7CO]^+$, 10.

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APPENDIX

RECENT RESULTS RELEVANT TO WORK DESCRIBED IN THIS THESIS

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1. The monodentate dppm complex $RuCl(\eta^1\text{-dppm})(PPh_3)(\eta\text{-}C_5H_5)$ [complex (<u>5</u>) in Chapter 2] was reacted with $[Ru(EtOH)(1,10\text{-phen})(\eta\text{-}C_5H_5)]Cl$ (<u>1</u>) (1,10-phen = 1,10-phenanthroline), affording the bridged product $[(\eta\text{-}C_5H_5)(PPh_3)ClRu(\mu\text{-dppm})Ru(1,10\text{-phen})(\eta\text{-}C_5H_5)][PF_6]$ after anion exchange with NH_4PF_6.[1] The authors noted that the synthesis proceeded without the formation of by-products arising from PPh_3 transfer or chloride ligand replacement.[2] Similarly, the reaction of (<u>1</u>) with $[Ru(\eta^1\text{-dppm})(\eta^2\text{-dppm})(\eta\text{-}C_5H_5)][PF_6]$ [complex (<u>12</u>) in Chapter 2] afforded $[(\eta\text{-}C_5H_5)(dppm)Ru(\mu\text{-dppm})Ru(1,10\text{-phen})(\eta\text{-}C_5H_5)][PF_6]$.

2. The structure of the cyclopentadienylruthenium phosphine complex (*S*)-$[RuCl\{(S)\text{-dpompyr-}P,P'\}(\eta\text{-}C_5H_5)]$ (<u>2</u>) [dpompyr = *N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine] was reported,[3] and has similar metal-ligand bond lengths to those of another bidentate phosphine complex (*S*)-$[RuCl\{(R)\text{-}Ph_2PCH(Me)CH_2PPh_2\}(\eta\text{-}C_5H_5)]$ (<u>3</u>);[4] the only significant difference is in the Ru-P(2) parameter [shorter for (2) where P(2) is a phosphite P]. The structure of $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_8H_8)(\eta\text{-}C_5H_5)][PF_6]$ has also recently been determined.[5]

3. The reaction of $Ru_3(CO)_{12}$ and quinoline afforded $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ [complex (<u>50</u>) in Chapter 4].[6] Hydrogenation of this cluster afforded $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and quinoline, but no reaction was observed with the hydride reagents $LiAlH_4$ or $LiBEt_3H$. As the carbon-nitrogen double bond is not reduced in the complex, but

readily reduced in the free ligand, it seems the nitrogen ligand is not the site of reaction with H_2 or hydride reagents. Other heteroaromatic nitrogen compounds (1,2,3,4-tetrahydroquinoline,phenanthridine and 9,10-dihydrophenanthridine) also afforded oxidative addition products when reacted with $Ru_3(CO)_{12}$; the saturated nitrogen rings were dehydrogenated.

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