NEW ASPECTS OF ORGANOMETALLIC CHEMISTRY

by

Michael Lloyd Williams
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The Department of Physical and Inorganic Chemistry
The University of Adelaide

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SUMMARY

The rapid development of metal cluster chemistry has proven to be a source of new and interesting reactions. However, a continuing hindrance to this study, including reactions with simple donor ligands, is the severe reaction conditions required to bring about substitution of CO. These often result in cluster break-up, as found for $Fe_3(CO)_{12}$, or polysubstitution, as with $Ru_3(CO)_{12}$ or further transformations of the first-formed products, as with $Os_3(CO)_{12}$.

Recently it was shown that specific carbonyl substitution of bi- and tri-nuclear cobalt carbonyl derivatives could be achieved by electron-transfer-catalysed (ETC) reactions with phosphine donor ligands. The application of this reaction to the sequential incorporation of various ligands allows designed syntheses of $Ru_3(CO)_{12}$ derivatives by the addition of sodium diphenylketyl as the ETC catalyst. The first three Chapters of this Thesis discuss the syntheses and reactions of derivatives of $Ru_3(CO)_{12}$ containing functionally substituted phosphines.

Chapter One describes the synthesis of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ under mild conditions and its subsequent thermal rearrangement to $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$. The reactivity of the latter was also investigated. For instance, with CO under mild conditions two Ru-Ru bonds are broken within the Ru_5 framework, while hydrogenation proceeds stepwise with the absorption of three molecules of H_2 and successive formation of pentanuclear cluster complexes containing μ_5-vinylidene, -methylidyne and -carbide ligands.

The first isolated η^2-olefin complex of $Ru_3(CO)_{12}$ was prepared in an ETC reaction between the cluster and the olefinic tertiary phosphine $\underline{o}$-CH_2=$CHC_6H_4PPh_2$. The complex is rapidly converted to the hydrido-alkyne complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HCCC_6H_4PPh_2)(CO)_8$ and $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$, whilst at higher temperatures condensation to the tetranuclear cluster $Ru_4(\mu_4\text{-}\eta^2,\underline{P}\text{-}HCCC_6H_4PPh_2)(CO)_{11}$ occurs. Chapter Two discusses these reactions, and extends the work to some tri-osmium clusters.

The ready formation of $Ru_3(CO)_{10}(dppm)$ has allowed an investigation of its chemistry, including that of the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$, which was formed by the reaction of the former with $K[HBBu^s_3]$. The reaction of the anion with allyl chloride afforded an edge-bridging allyl complex, while with aryldiazonium salts aryldiazo complexes are formed which undergo facile cyclometallation reactions when heated. Of note is the formation of complexes $Ru_3M(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (M = Cu, Ag and Au) which has allowed the first structural comparison of Group IB metal-Ru bonds. Hydrogenation of $Ru_3(CO)_{10}(dppm)$ results in P-C bond cleavage with the elimination of benzene to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$. This chemistry and the scope of the P-C bond cleavage reaction is reported in Chapter Three.

The final Chapter of this Thesis describes the formation and properties of some of the chemistry of complexes containing the $[C_5(CO_2Me)_5]^-$ ligand. Complexes of predominantly ionic character have been obtained for alkali metals, alkaline earths, thallium(I) and first-row transition metals. Examples containing a covalently-bonded ligand were obtained for the derivatives of silver(I), gold(I) and ruthenium(II). In these cases, the ring carbon-metal bond is easily broken with the displacement of the stable $[C_5(CO_2Me)_5]^-$ anion on reaction with other donor ligands. For example, the reaction of the mixed metallocene $Ru(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CO_2Me)_5]$ with PPh_3 in CH_3CN affords $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$. This reaction forms the basis of a process for the oxidation of PPh_3 catalysed by the metallocene. Some related chemistry of $[C_5Me(CO_2Me)_4]^-$ is also 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.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

In general

Å	angstroms
atm	atmospheres
Bu^s	*sec*-butyl
Bu^t	*tert*-butyl
ca	circa
C_5H_5	cyclopentadienyl
cm	centimetres
cont.	continued
Cy	cyclohexyl
dec.	decomposed
dpam	bis(diphenylarsino)methane
dppa	1,2-bis(diphenylphosphino)ethyne
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	ethyl
g	grams
h	hours
H_B	bridging hydride
H_T	terminal hydride
Hz	hertz
i.r.	infrared
l	litres
lit.	literature
M	molecular ion
Me	methyl
mg	milligrams
MHz	megahertz

min	minutes
ml	millilitres
mm	millimetres
mmol	millimoles
m.p.	melting point
n.d.	none detected
n.m.r.	nuclear magnetic resonance
p.	page
Ph	phenyl
ppn	bis(triphenylphosphoranylidene)ammonium
Pr^i	_iso_-propyl
R	alkyl
ref.	reference
sec	seconds
sp	_ortho_-styryldiphenylphosphine
thf	tetrahydrofuran
tlc	thin layer chromatography
tppme	1,1,1-tris(diphenylphosphinomethyl)ethane
U.V.	ultraviolet

For Infrared Spectroscopy

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

For n.m.r. Spectroscopy

d	doublet
dd	doublet of doublets
dm	doublet of multiplets
dt	doublet of triplets
m	multiplets
s	singlets
t	triplet

CHAPTER ONE

SYNTHESIS AND REACTIVITY OF $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$

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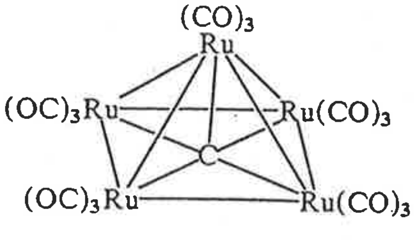
INTRODUCTION

PENTANUCLEAR RUTHENIUM CARBONYL COMPLEXES

While no binary pentanuclear ruthenium carbonyl complex is known, clusters containing additional bridging ligands such as carbide, nitride, phosphide, acetylide, or isocyanide have been reported. The following summary covers the synthesis of these clusters and the effect the heteronuclear ligand has on their stability and reactivity.

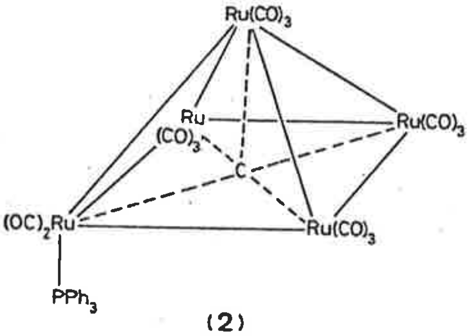
Pentanuclear carbido ruthenium complexes

The pentanuclear carbido cluster $Ru_5C(CO)_{15}$ (1) can be readily prepared in quantitative yield, together with $Ru(CO)_5$, from the reaction of $Ru_6C(CO)_{17}$ with carbon monoxide under precise conditions (80 atm, 70°C, 3 h).[1] This pentanuclear cluster, which was previously obtained in $\sim$1% yield by heating $Ru_4(\mu\text{-}H)_4(CO)_{12}$ with ethylene,[2] was shown by an X-ray diffraction study to contain a square-pyramidal structure and ligand arrangement similar to $Fe_5C(CO)_{15}$ [3] and $Os_5C(CO)_{15}$.[4]

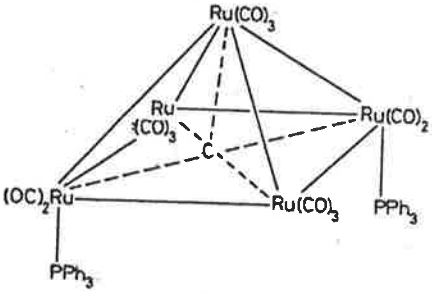


(1)

Substitution of CO by PPh_3 gives $Ru_5C(CO)_{14}(PPh_3)$ (2) and $Ru_5C(CO)_{13}(PPh_3)_2$ (3) is formed in the presence of excess PPh_3, while with $PMePh_2$ the three complexes $Ru_5C(CO)_{15-n}(PMePh_2)_n$ (n = 1-3) can be isolated. The molecular structures of the parent, of (2), and of (3) show that all contain a square-pyramidal Ru_5 core with an exposed carbido-atom which lies below the Ru_4 basal plane at a distance of 0.11(2), 0.19(1) and 0.23(1)Å respectively. Substitution has occurred at the basal ruthenium atoms with the PPh_3 ligands occupying axial sites. It is believed that steric interactions give rise to the *trans* arrangement of the phosphine ligands about the ruthenium square face in (3).[1] Complexes of the type $Ru_5C(CO)_{13}[PPh_2(CH_2)_nPPh_2]$ (n = 1-4) have also been reported.[5]



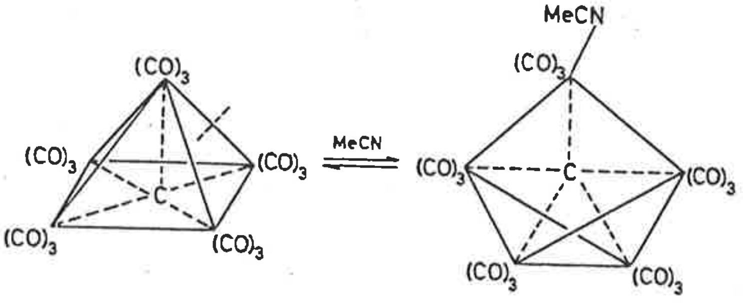
(2)



(3)

The main feature of the chemistry of (1) is its ability to undergo stereochemical rearrangement of the metal core due to addition of a nucleophile at one of the basal rutheniums with concomitant cleavage of the bond between this metal and the apical ruthenium.

Thus, (1) reacts reversibly with a variety of ligands (L) to afford 1:1 adducts of the type $Ru_5C(CO)_{15}(L)$ (L = MeOH, EtOH, MeCN, or CO) (Scheme 1).[1,6] The acetonitrile complex $Ru_5C(CO)_{15}(MeCN)$ (4), has been fully characterised by an X-ray diffraction study and adopts a bridged-butterfly arrangement of metal atoms i.e. the fifth metal atom spans the wing-tips of the butterfly. The MeCN group acts as a 2e-donor and occupies a terminal position on the bridging ruthenium atom.



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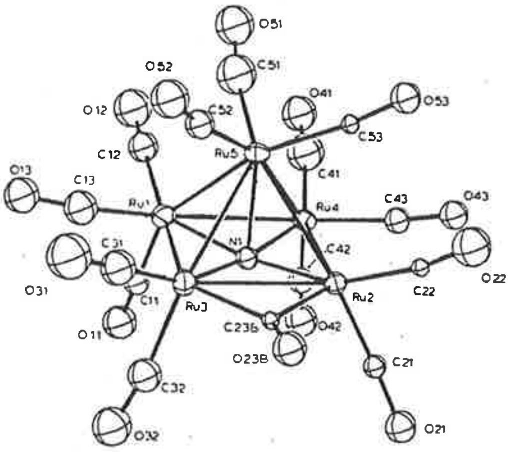
Scheme 1

The ease with which this rearrangement can be reversed demonstrates the ability of the carbide to 'hold' the metal cluster together whilst allowing considerable flexibility of the metal skeleton.

The oxidative addition of YX (Y = H, $AuPR_3$; X = Cl, Br, I), H_2S, H_2Se, HSR (R = Me, Et) or the nucleophilic attack of F^-, Cl^-, Br^-, I^-, or $C_5H_5^-$ to (1) also gives complexes containing the bridged-butterfly Ru_5 atom skeleton.[1,7-10]

Pentanuclear nitrido ruthenium complex

The pentanuclear ruthenium nitrido complex $[Ru_5N(CO)_{14}]^-$ (5) was formed in 5% yield by heating $[Ru_3(CO)_{10}(NO)]$ in refluxing thf.[11] Quantitative yields of (5) are formed within minutes from the reaction of $[Ru_6N(CO)_{16}]^-$ with carbon monoxide (1 atm). Structural details were provided by an X-ray diffraction study which revealed a square-pyramidal metal geometry with an interstitial nitrido atom located 0.21(2) Å below the basal ruthenium atoms.[12]



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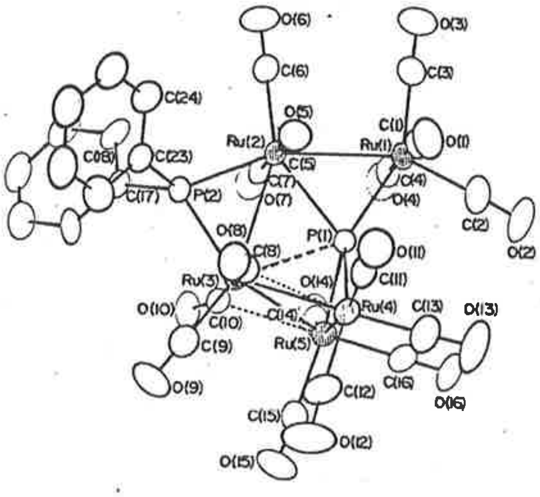
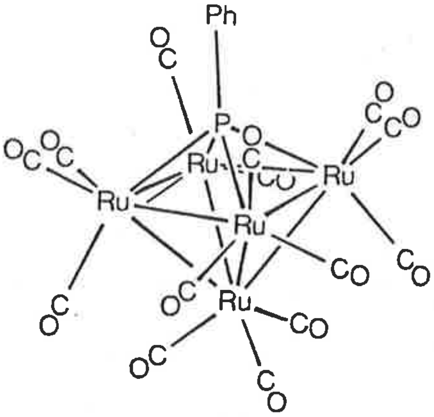
Pentanuclear phosphido ruthenium complexes

The complex $Ru_5(\mu_5\text{-}P)(\mu\text{-}PPh_2)(CO)_{16}$ (6), which contains a partially encapsulated phosphide group, was obtained as one of a number of complexes from the thermolysis of $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9$.[13] The molecular structure of (6) consists of five ruthenium atoms joined by five Ru-Ru bonds in an open array, three of these atoms forming a triangle to which is attached an Ru_2 side chain. The phosphide atom, which is a 5e-donor, is located 'inside' the core of the five metal atoms.



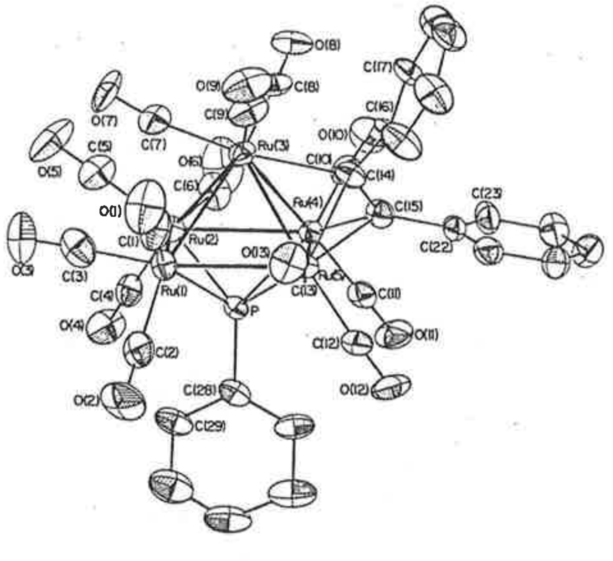
The reaction of $Ru_3(CO)_{12}$ with $Cp(CO)_2MnPRCl_2$ (R = Ph, Me, Et, or $C_6H_5CH_2$) in toluene at 100°C affords clusters of the type $Ru_5(\mu_4\text{-}PR)(CO)_{15}$ in low yield.[14] $Ru_5(\mu_4\text{-}PPh)(CO)_{15}$ is also obtained as one of a number of products by heating $Ru_3(CO)_{12}$ with $PPhH_2$ in refluxing toluene.[15] The molecular structures of $Ru_5(\mu_4\text{-}PR)(CO)_{15}$ [R = Ph (7), Et (8)] consist of five ruthenium atoms in a square-pyramidal arrangement with the phosphinidene capping the square face.



(**8**)

Pentanuclear ruthenium complexes containing RC≡N and RC≡C ligands

Thermolysis of $Ru_3(CO)_{11}(PPh_2C{\equiv}CPh)$ in heptane (70°, 8 h) results in fragmentation of the starting material to give $Ru_5(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{13}$ (9a) in 30% yield. This complex contains a C_2Ph ligand interacting with the four basal rutheniums of a square-pyramidal Ru_5 core; the PPh_2 bridges one of the edges of the square face.^{16,17} The analogous complex, $Ru_5(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}PPh_2)(CO)_{13}$ ($R = CHMe_2$) (9b), is prepared in a similar manner to that of (9a). Prolonged heating of (9a) results in conversion of the phosphido group to a phosphinidene, via phenyl group transfer to the acetylide ligand, to afford $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(CO)_{13}$ (10).^{18}



(10)

The reaction of $Ru_5(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}PPh_2)(CO)_{13}$ ($R = CHMe_2$) (9b) with PH_2Ph results in hydrogen transfer from the phosphine to the β-carbon of the acetylide ligand to give $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}CCH_2R)(\mu\text{-}PPh_2)(CO)_{12}$ (11). Further reduction of (11) by the addition of a two molar equivalents of PH_2Ph, afforded the alkane CH_3CH_2R, in which the C_2 unit present in the original acetylide is preserved, and $Ru_5(\mu\text{-}H)(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{10}$ (12). A plausible scheme for the stepwise conversion of (9b)-(12) is shown (Scheme 2); the unstable alkyl complex (13) was not isolated.[19]

$$\underset{(9b)}{Ru_5(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu\text{-}PPh_2)(CO)_{13}} \xrightarrow{PH_2Ph}$$

$$\underset{(11)}{Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}CCH_2R)(\mu\text{-}PPh_2)(CO)_{12}}$$

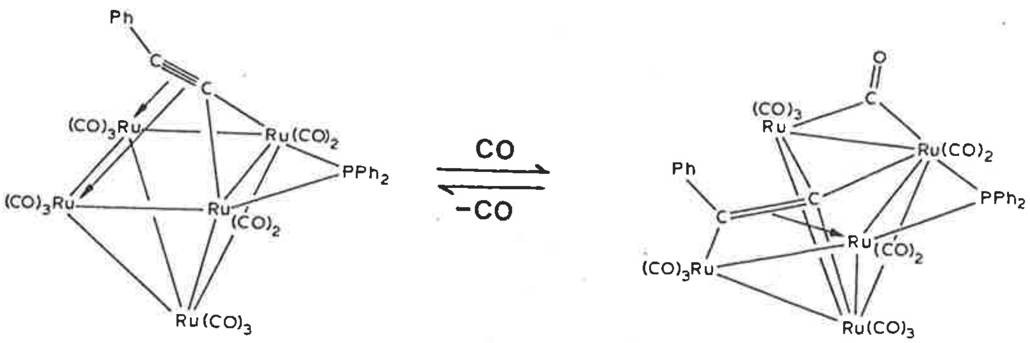
$$\Big\downarrow PH_2Ph$$

$$\xleftarrow{PH_2Ph} \underset{(13)}{Ru_5(CO)_{11}(CH_2CH_2R)(PPh_2)(PPh)_2}$$

$$\underset{(12)}{Ru_5(\mu\text{-}H)(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{10}} + CH_3CH_2R$$

(Scheme 2)

The addition of carbon monoxide to (9a) is accompanied by the cleavage of the basal Ru-Ru bond directly opposite the phosphido bridge to generate $Ru_5(\mu_5\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{14}$ (14) (Scheme 3).[17] The five metal atoms form an open array of three edge-fused triangles, bent at these edges to form a swallow-shaped cluster; the acetylide ligand now bonds to all five metal atoms in a $\mu_5\text{-}\eta^2$ $(4\sigma,\pi)$ mode [previously $\mu_4\text{-}\eta^2$ $(2\sigma,2\pi)$]. The adduct (14) is thermally rather unstable, reverting to (9a) on warming. The ease of this process has been related to the stability of the square-pyramidal Ru_5 cluster in (9a), compared with the open array in (14).



9a

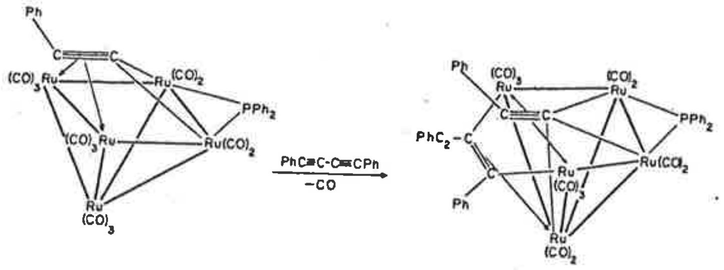
14

Scheme 3

Other ligands L, (L = MeCN, PhCN, NH_2Pr^1, NH_2Bu^s, or C_5H_5N), also add reversibly to (9a) to give the adducts $Ru_5(\mu_5-\eta^2-C_2Ph)(\mu-PPh_2)(CO)_{13}(L)$. These complexes have spectroscopic properties generally similar to those of (14) (L = CO), and undoubtedly have a similar structure.

The above results indicate that addition of ligands to (9a) occurs at basal sites; addition of ligands to the related complex (1) also occurs at basal sites.[1,6-10] However, basal-basal Ru-Ru bond cleavage occurs in the former case to give a swallow cluster, while in the latter apical-basal Ru-Ru bond cleavage occurs to give a bridged-butterfly cluster.

The reaction of (9a) with diphenylbutadiyne results in the loss of one molecule of CO and the cleavage of an Ru-Ru bond to give $Ru_5(\mu_5-\eta^2-C_2Ph)(\mu_3-\eta^2-PhC{\equiv}C-C{\equiv}CPh)(\mu-PPh_2)(CO)_{12}$ (15) (Scheme 4).[20] As in the reaction with carbon monoxide the basal Ru-Ru bond opposite the phosphido group was cleaved to give a swallow-shaped cluster. The alkyne PhC≡C-C≡CPh acts as a 4e-donor ligand and caps the 'opened' triangular face.



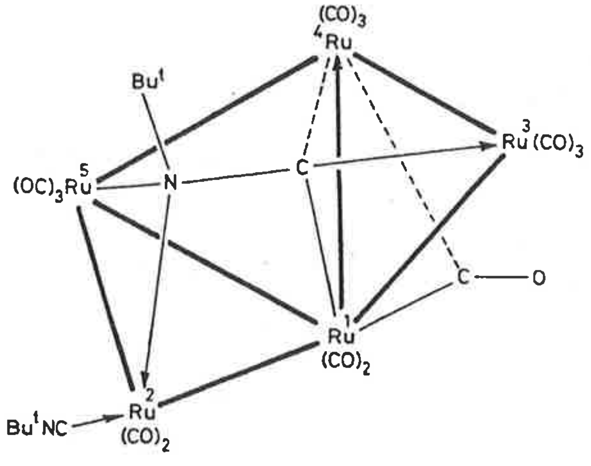
9a

15

Scheme 4

The first swallow-shaped cluster to be reported was Ru$_5$(μ_5-η^2-CNBu^t)(CO)$_{14}$(CNBu^t) (16), which has an isocyanide ligand acting as a 6e-donor, and was isolated in low yield from the pyrolysis of Ru$_3$(CO)$_{11}$(CNBu^t).^{21}

Continued heating of (16) in refluxing nonane (2 h) afforded Ru$_6$C(CO)$_{16}$(CNBu^t) (17) by cleavage of the C-N bond in the bridging isocyanide ligand.^{22}



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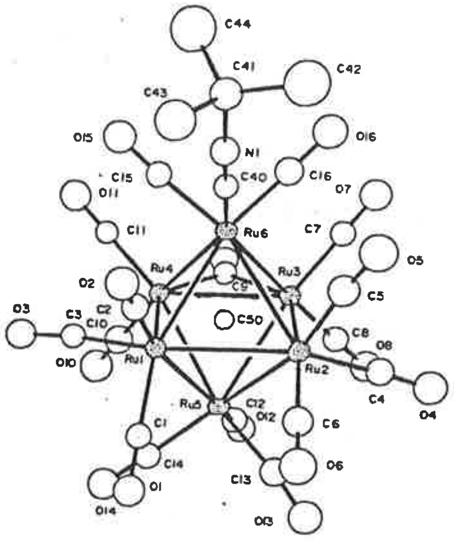

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The nature of the formation and rearrangement of unsaturated ligands on metal clusters is of interest as these reactions may be of relevance to the understanding of the behaviour of such molecules on metal surfaces.[23,24] The extended interactions that occur when multiply-bonded systems interact with 'open' Ru_5 clusters suggests that such complexes would be good models of metal surfaces. However, low yields of (16) and the instability of (14) have prevented investigations in this regard.

This chapter deals with the preparation and reactions of the open cluster $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ which can be prepared in high yield and therefore provided the opportunity to examine some of its reactions in detail.

RESULTS AND DISCUSSION

The facile substitution reactions of cluster carbonyls with tertiary phosphines, arsines, and related ligands, which are initiated by addition of small amounts of a radical ion such as sodium diphenylketyl, have afforded several reactive complexes, whose further reactions have given information concerning the transformation of functional groups on these clusters.[25] Particularly studied have been complexes derived from $Ru_3(CO)_{12}$. It was therefore of some interest to investigate the pyrolysis of a complex containing two $Ru_3(CO)_{11}$ units separated by the dppa ($PPh_2C{\equiv}CPPh_2$) ligand, anticipating that intramolecular condensation of the cluster units to larger metal aggregates would occur in reactions involving the C≡C triple bond, together with one or more P-C bond cleavage reactions.[18]

Preparation of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$

The reaction between $Ru_3(CO)_{12}$ and dppa in a 2/1 ratio in tetrahydrofuran was initiated by the dropwise addition of a sodium diphenylketyl solution, which resulted in rapid darkening of the solution with evolution of carbon monoxide. The presence of the C≡C triple bond in dppa results in a linear PCCP arrangement and ensures that this ligand cannot chelate one metal atom, or bridge two metal atoms which are bonded together, as found in $Ru_3(CO)_{10}(dppe)$.[26] The reaction proceeded readily, and good yields of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (18) were obtained. This orange complex was identified as the desired hexanuclear complex by elemental analysis, and by the similarity of its i.r. $\nu(CO)$ spectrum to those of other

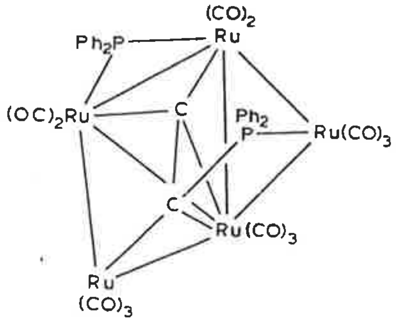
$Ru_3(CO)_{11}(PR_3)$ complexes.[25] The phospino-alkyne occupies an equatorial site on one ruthenium atom in each cluster, as found for other $Ru_3(CO)_{11}(PR_3)$ complexes [PR_3 = PPh_3 [27] or PCy_3 [28]].

Preparation of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$

Reactions between $Os_3(CO)_{12}$ and tertiary phosphines in the presence of sodium diphenylketyl result in polysubstition and generally lead to no improvement over thermal reactions.[29,30] Complexes of the type $Os_3(CO)_{11}(L)$ (L = CO, PPh_3, $CH_3C_6H_4SO_2$-CH_2NC-p) have been prepared in quantitative amounts from the reaction of $Os_3(CO)_{11}(NCMe)$ with the appropriate ligand L.[31] Treatment of $Os_3(CO)_{11}(NCMe)$ with dppa in a 2/1 ratio at ambient temperature similarly afforded $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (19) in 87% yield. This yellow complex was identified by usual methods [its spectroscopic properties were similar to those of (18)].

Pyrolysis of $[M_3(CO)_{11}]_2(\mu\text{-dppa})$ (M = Ru, Os)

The red solution of (18) in toluene rapidly darkens on heating, and after 1 h at 90°C it is black. Thin-layer chromatographic separation gave the pentanuclear complex $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) in 88% yield, together with small amounts of $Ru_3(CO)_{12}$. The black crystals of (20) are indefinitely stable in air, and readily soluble in benzene, chloroform, dichloromethane and acetone; they are only partially soluble in light petroleum, and insoluble in methanol. The solution i.r. spectrum shows only terminal $\nu(CO)$ bands, and the ^1H n.m.r. spectrum contains a multiplet at δ 7.40 assigned to the phenyl protons. Unambiguous identification of (20) was achieved by a single-crystal X-ray diffraction study.



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Similar heating of (19) in xylene (140°C, 2.5 h) gave the analogous complex $Os_5(\mu_5-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ (21) as a purple powder. This complex had generally similar spectral properties to those of (20) but so far the lack of suitable crystals has prevented X-ray confirmation of the molecular structure.

Molecular Structure of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ (20)

The molecular structure of (20) is shown in Figure 1 (see also Table 1). The five ruthenium atoms form an open array of three edge-fused triangles, resembling those found earlier in (14), (15) and (16). The seven Ru-Ru separations fall in the range 2.731(1)-2.932(1)Å. The shortest is between the phosphido-bridged atoms Ru(2) and Ru(3) [2.731(1)Å], while bonds from Ru(1), which bears the phosphine donor atom, to Ru(2) and Ru(5) are respectively, 2.932(1) and 2.921(1)Å, which are rather long for such interactions; the presence of the

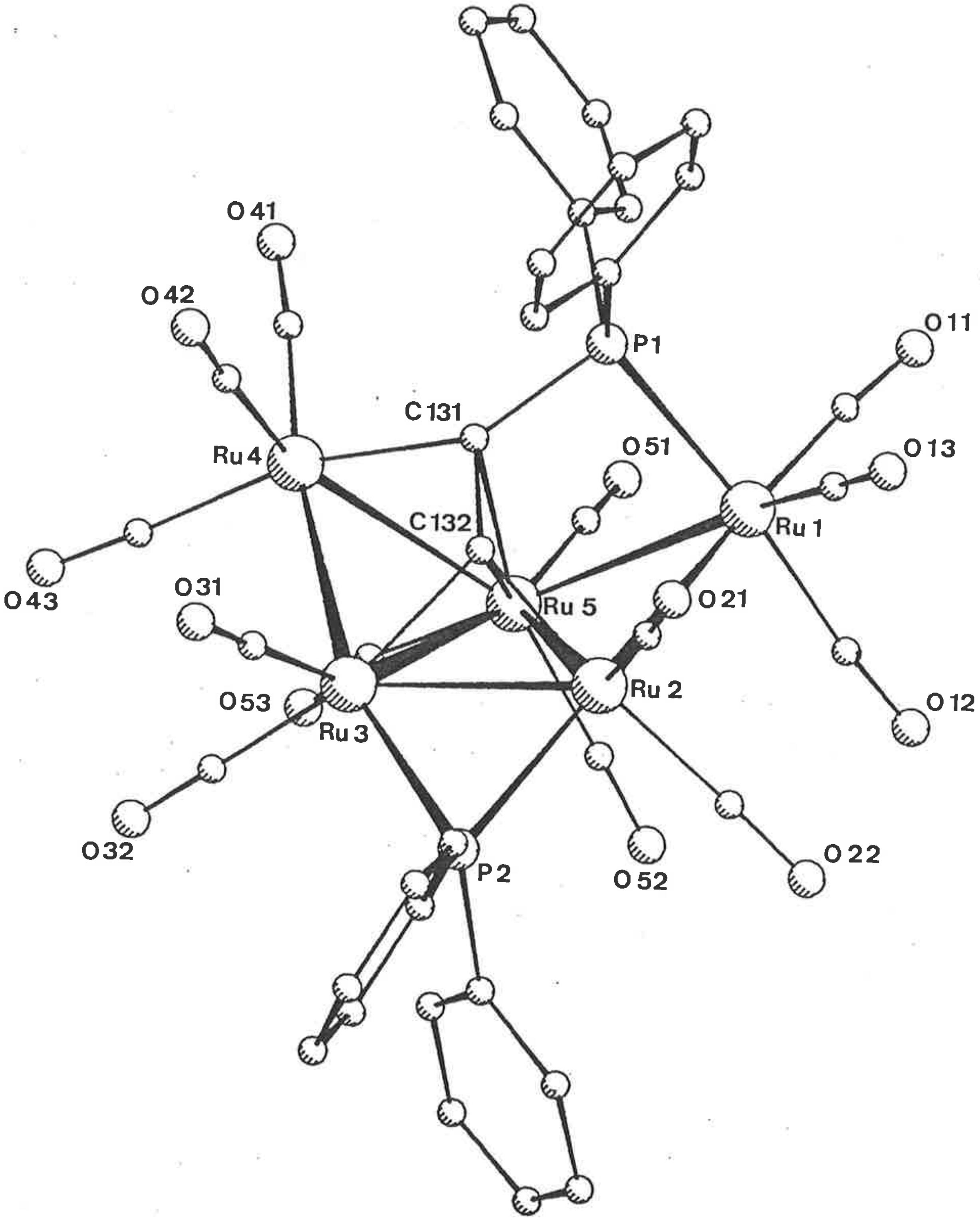


Figure 1: PLUTO plot of the molecular structure of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ (20), showing atom numbering scheme (by B.W. Skelton and A.H. White)

Table 1

Selected bond lengths and angles for $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)-(\mu-PPh_2)(CO)_{13}$ (20)

Bond lengths (Å)

Ru(1)-Ru(2)	2.932(2)	C(131)-C(132)	1.383(6)
Ru(1)-Ru(5)	2.921(2)	C(131)-Ru(4)	2.055(5)
Ru(1)-P(1)	2.373(2)	C(131)-Ru(5)	2.279(4)
Ru(2)-Ru(3)	2.731(2)	C(131)-P(1)	1.762(5)
Ru(2)-Ru(5)	2.890(1)	C(132)-Ru(2)	2.016(5)
Ru(2)-P(2)	2.353(2)	C(132)-Ru(3)	2.024(5)
Ru(3)-Ru(4)	2.854(2)	C(132)-Ru(4)	2.586(5)
Ru(3)-Ru(5)	2.909(1)	C(132)-Ru(5)	2.154(5)
Ru(3)-P(2)	2.279(2)	P(1)-C(111)	1.820(5)
P(2)-C(221)	1.813(5)	P(1)-C(121)	1.814(5)
Ru(4)-CO(53)	2.741(6)	P(2)-C(211)	1.815(5)
Ru(5)-CO(53)	1.915(6)		

Ru-CO range from 1.849(6)-1.947(6) (average 1.986)

C-O range from 1.124(8)-1.150(7) (average 1.139)

Angles (°)

Ru(1)-Ru(5)-Ru(2)	60.61(3)	Ru(3)-Ru(2)-P(2)	52.64(3)
Ru(1)-Ru(2)-Ru(5)	60.23(3)	Ru(2)-Ru(3)-P(2)	55.13(5)
Ru(2)-Ru(1)-Ru(5)	59.17(2)	Ru(3)-P(2)-Ru(2)	72.23(5)
Ru(2)-Ru(5)-Ru(3)	56.19(3)	C(131)-P(1)-Ru(2)	94.4(1)
Ru(2)-Ru(3)-Ru(5)	61.56(2)	C(131)-C(132)-Ru(2)	142.4(4)
Ru(3)-Ru(2)-Ru(5)	62.25(3)	C(131)-C(132)-Ru(3)	127.7(4)
Ru(3)-Ru(5)-Ru(4)	59.44(3)	C(131)-C(132)-Ru(5)	76.8(4)
Ru(3)-Ru(4)-Ru(5)	61.35(2)	C(132)-C(131)-Ru(4)	95.6(3)
Ru(4)-Ru(3)-Ru(5)	59.22(3)	C(132)-C(131)-P(1)	115.3(3)
Ru(1)-Ru(5)-Ru(4)	116.23(4)	Ru(4)-C(53)-Ru(5)	73.0(2)
Ru(1)-Ru(2)-Ru(3)	116.71(1)	Ru(5)-C(53)-O(53)	162.9(5)
Ru(4)-Ru(3)-Ru(2)	106.48(4)		

Ru-C-O range from 162.9(5)-178.8(7) (average 175.0)

Ru(1)-Ru(2)-Ru(5)/Ru(2)-Ru(3)-Ru(5) 152.1

Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) 134.2

teritary phosphine ligand simultaneously constrains Ru(1) and lengthens the bonds to the rest of the cluster.

The C_2PPh_2 group, formed by cleavage of PPh_2 from the original dppa ligand, interacts with all five metal atoms. The Ru(1)-P(1) bond [2.372(2)Å] is a conventional 2e-donor interaction of the tertiary phosphine with the metal atom. The acetylenic unit C(131)-C(132) interacts with the other four metal atoms, with C(131) being strongly σ-bonded [2.055(5)Å] to Ru(4), and the Ru(2)Ru(3)Ru(5) face being nearly symmetrically capped by C(132) [2.016(5), 2.024(5), and 2.154(4)Å, respectively]. There is also a much weaker interaction between C(131) and Ru(5) [2.279(4)Å], and the C_2 unit can be considered to have an asymmetric η^2 interaction with Ru(5). The situation in (14) is similar, with a further involvement of the C≡C function with the fifth ruthenium atom. The C≡C triple bond has lengthened to 1.383(6)Å in (20), and is comparable with that found in (14) [1.39(1)Å]; both are longer than that found in (9a) [1.342(11)Å], where the alkyne is attached to the square face of the square-pyramidal Ru(5) core.

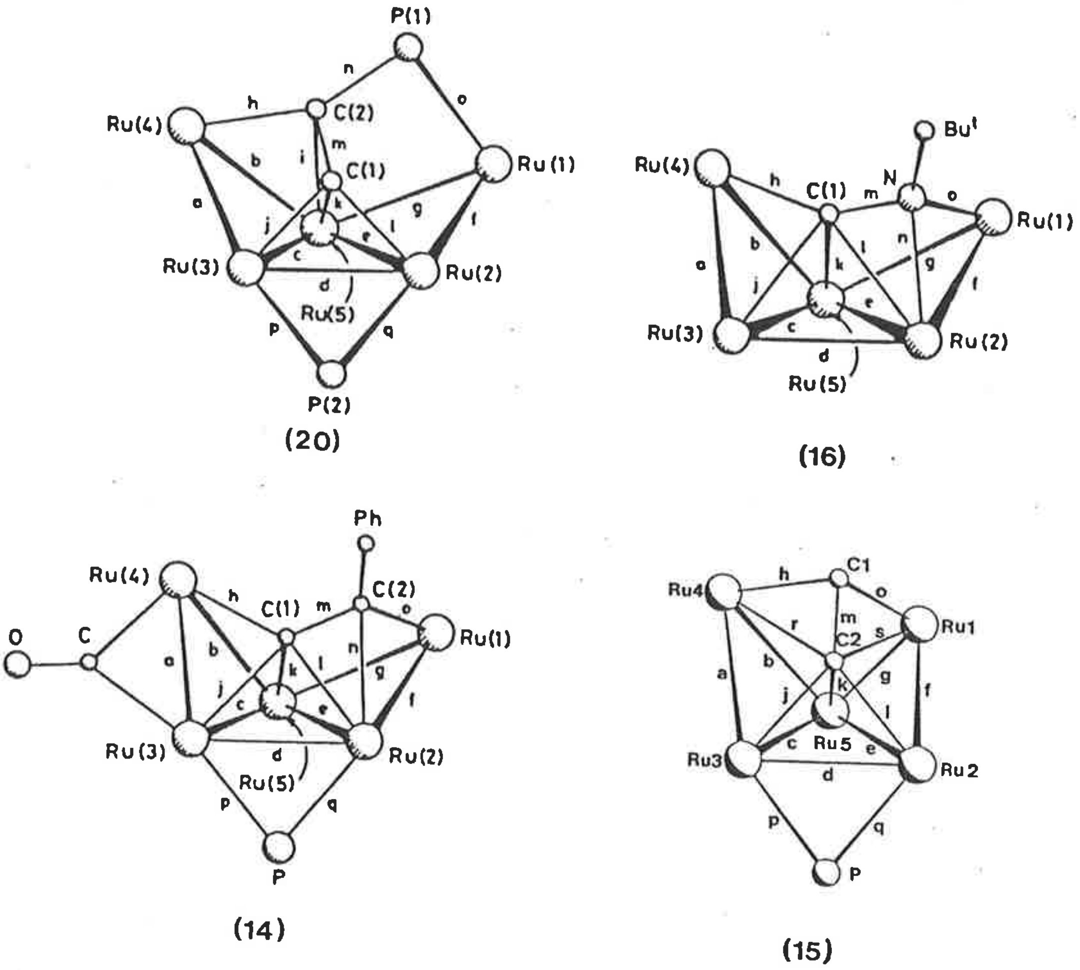
In (20), the CO groups are distributed two to each of the phosphido bridged Ru(2) and Ru(3) atoms, and three each to the other three metal atoms. The electron count shows that the C_2PPh_2 ligand functions as a 7e-donor to the cluster, which is electron-precise (76e). However, formal electron book-keeping at individual metal atoms shows that Ru(5) is electron-rich (20e), while Ru(4) and either Ru(2) or Ru(3) are electron deficient (depending on the direction of donation of electrons from the bridging phosphido ligand). This electron imbalance is partially compensated by the redistribution of electron density over the cluster via the semi-bridging CO(53) ligand

[Ru(5)-C(53), 1.915(6); Ru(4)-C(53), 2.741(6)Å].

The μ-PPh_2 group bridges the Ru(2)-Ru(3) edge in an asymmetric fashion [Ru(2)-P(2), 2.353(2)Å; Ru(3)-P(2) 2.279(2)Å].

There have now been described four Ru_5 clusters in which a C≡C or C≡N triple bond straddles an open arrangement of metal atoms. Complex (20) and (15) are apparently stable to further rearrangement, whereas the structurally closely related (14) readily loses CO to reform the nido-Ru_5 cluster (9a),[17] while (16) forms the closo-Ru_6C cluster (17) on heating.[22] No doubt the presence of the tertiary phosphine in (20), preserves the open nature of the cluster, since facile metal-metal bond formation is no longer possible even if CO were to be lost; the attachment of the alkyne PhC≡C-C≡CPh to the 'opened' face in (15) must have a similar stabilizing effect.

Figure 2 shows the heavy atom cores of complexes (20), (14), (15) and (16), together with the acetylide or isocyanide ligands, in a manner which details the interaction of the ligands with the Ru_5 skeletons, (see also Table 2). Atom numbering for (14), (15) and (16) in Figure 2 has been changed from that used in the original papers to simplify the following discussion; in (20), C(131) and C(132) are numbered C(2) and C(1) respectively. The closest similarities are found in (14) and (15), where the isoelectronic $Bu^tN{\equiv}C$ and $PhC{\equiv}C^-$ ligands are arranged so that the NC or C_2 moieties have an η^2 interaction with Ru(2), with a strong σ-bond from C(1) to Ru(4). This carbon is also bonded to Ru(5), and has much weaker interactions with Ru(2) and Ru(3). In (20), on the other hand, the presence of the tertiary phosphine attached to Ru(1)



(20)

(16)

(14)

(15)

Figure 2 Heavy-atom cores of complexes (20), (16), (14) and (15)

Table 2

Distance (A)	Complex (20)	(16)	(14)	(15)
a	2.854(2)	2.767(1)	2.826(1)	2.8884(7)
b	2.848(1)	2.833(1)	2.826(1)	2.8163(7)
c	2.909(1)	2.776(1)	2.789(1)	2.7660(6)
d	2.731(2)	2.864(1)	2.845(1)	2.7682(7)
e	2.890(1)	2.778(1)	2.885(1)	2.8878(7)
f	2.932(1)	2.745(1)	2.720(1)	2.9200(7)
g	2.921(2)	2.784(1)	2.927(1)	2.8127(7)
h	2.055(5)	1.923(7)	2.076(9)	2.212(6)
i	2.279(4)	-	-	-
j	2.024(5)	2.387(6)	2.326(8)	2.154(6)
k	2.154(4)	2.155(6)	2.135(8)	2.292(6)
l	2.016(5)	2.453(9)	2.225(8)	2.106(6)
m	1.383(6)	1.375(8)	1.398(13)	1.340(9)
n	1.762(5)	2.152(6)	2.265(8)	-
o	2.373(2)	2.128(4)	2.055(8)	2.204(6)
p	2.279(2)	-	2.333(2)	2.272(2)
q	2.353(2)	-	2.287(2)	2.275(2)
r	-	-	-	2.299(6)
s	-	-	-	2.336(6)

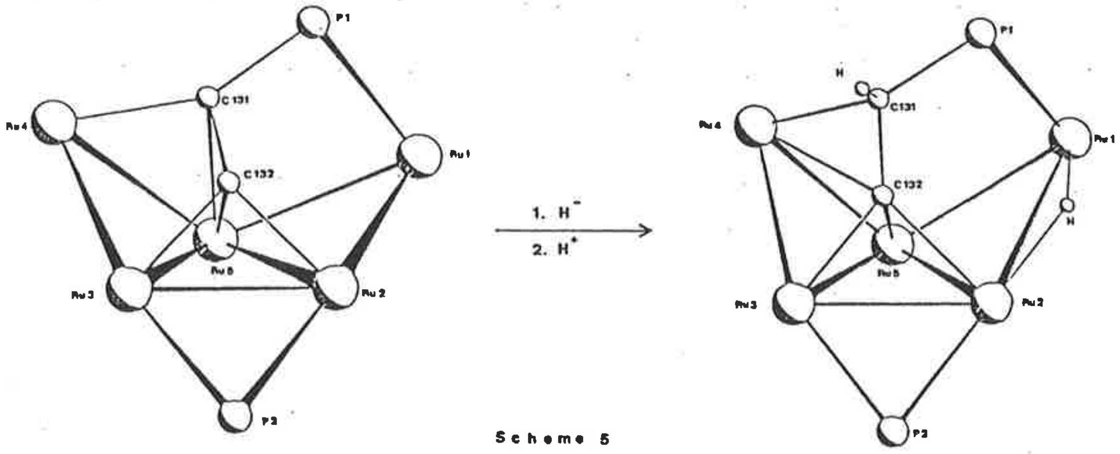
Dihedrals (°)				
Ru(1)-Ru(2)-Ru(5)/ Ru(2)-Ru(3)-Ru(5)	152.1	144.6	147.6	124.7
Ru(2)-Ru(3)-Ru(5)/ Ru(3)-Ru(4)-Ru(5)	134.2	119.4	115.9	121.0

removes the possibility of any interaction of C(1) with this metal atom, the acetylide portion of the ligand now being skewed so that it almost bisects the Ru(3)Ru(5)Ru(2) angle and interacts with Ru(5) in an η^2 manner. Carbon C(1) now interacts strongly with both Ru(2) and Ru(3), and this together with the μ-PPh_2 ligand results in the Ru(2)-Ru(3) separation being the shortest such distance of any of the four complexes. The mode of attachment of the phsophinoacetylide ligand in (20) also results in this complex having the most 'open' of the Ru_5 skeletons, with dihedrals Ru(1)-Ru(2)-Ru(5)/ Ru(2)-Ru(3)-Ru(5) and Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) of 152.1 and 134.2°; compared with 147.6, 115.9° for (14); 124.7, 121.0 for (15) and 144.6, 119.4° for (16) respectively. Collectively, these four complexes provide examples of a novel activation of the organic molecules by wrapping a metal cluster around one end of the molecule. Alternatively, the organic could be considered to 'burrow' into this fragment of a metal surface; in (20), the function of the $Ph_2P(1)$ group is to push the acetylide in somewhat deeper, with a closer association with the Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) faces.

The electron-deficient nature of the μ_4- or μ_5-C≡C or μ_5-C≡N moiety is clearly shown by the lengthening of these bonds when compared with the normal values found in the free ligands. This feature is further shown in the reactions of (20) with nucleophilic reagents.

Reaction of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) with $K(HBBu^s_3)$

Treatment of (20) in tetrahydrofuran solution with K-Selectride [$K(HBBu^s_3)$] as a source of H^-, followed by protonation (H_3PO_4) and subsequent work-up, afforded the vinylidine complex $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2,\underline{P}\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22) as black crystals. The ^1H n.m.r. spectrum contains three signals: that at δ 7.42 (m, 20H) was readily assigned to phenyl groups, and the resonance at δ -13.11 [dd, *J*(HP) 13.8 and 21.5 Hz, 1H] to a proton bridging two ruthenium atoms and coupled to two inequivalent phosphorus atoms. A single proton doublet at δ 5.86 [*J*(PH) 6 Hz] is consistent with a C*H* proton of a vinylidene unit coupled to phosphorus [*cf*. similar values in $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{=}CHPr^i)(\mu\text{-}PPh_2)(CO)_8$ at δ 5.10,[18] and $Ru_3Au_2(\mu_3\text{-}\eta^2\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ at δ 6.30 [32]]. These data suggest that formation of this complex occurs via hydride addition at the acetylide and protonation at the cluster core (Scheme 5). The precise stereochemistry of (22) was confirmed by an X-ray diffraction study and is shown in Figure 3 (see also Table 3).



Scheme 5

20

22

Comparison of (20) and (22) shows that little change has occurred in the heavy atom core and distribution of CO groups, two hydrogens have added to (20), one to bridge the Ru(1)-Ru(2) bond and the other to C(131), thus converting the 7e-donor

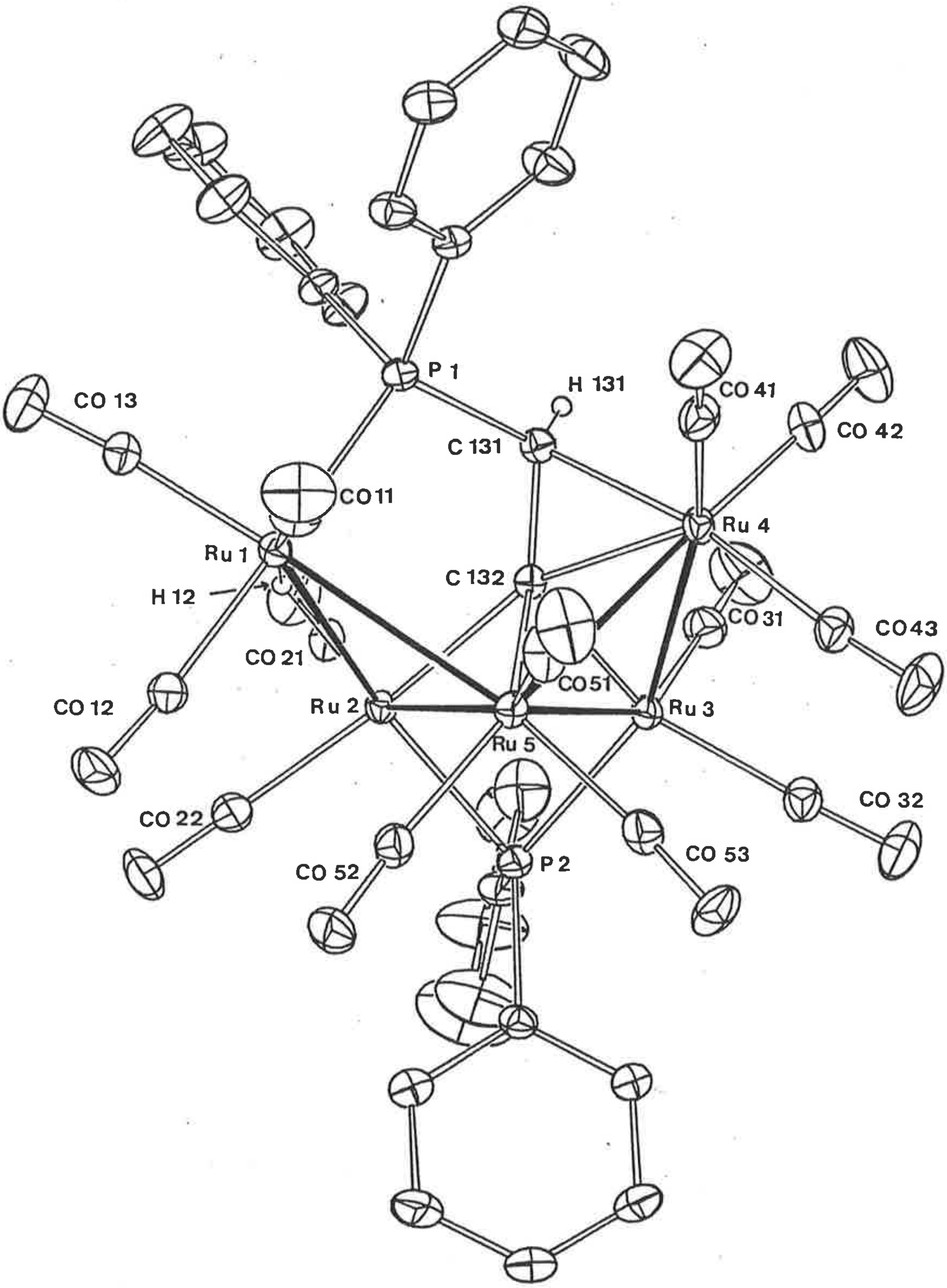


Figure 3. ORTEP plot of the molecular structure of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22), showing the atom numbering scheme (by B.W. Skelton and A.H. White).

Table 3

Selected bond lengths and angles for $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2,\underline{P}\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22)

Bond lengths (Å)

Ru(1)-Ru(2)	3.0729(7)	Ru(3)-P(2)	2.284(1)
Ru(1)-Ru(5)	2.9680(6)	Ru(2)-C(132)	2.175(4)
Ru(2)-Ru(3)	2.7805(7)	Ru(3)-C(132)	2.054(3)
Ru(2)-Ru(5)	2.7695(6)	Ru(4)-C(131)	2.175(4)
Ru(3)-Ru(4)	2.8139(6)	Ru(4)-C(132)	2.178(4)
Ru(3)-Ru(5)	2.8705(8)	Ru(5)-C(132)	2.162(4)
Ru(4)-Ru(5)	2.8397(7)	C(131)-C(132)	1.436(5)
Ru(1)-P(1)	2.388(1)	Ru(1)-H(12)	1.75(3)
Ru(2)-P(2)	2.326(1)	Ru(2)-H(12)	1.77(3)

Ru-CO range from 1.844(6)-1.929(5) (average 1.900)

C-O range from 1.120(6)-1.156(6) (average 1.378)

Angles (°)

Ru(2)-Ru(1)-Ru(5)	54.54(1)	Ru(3)-Ru(2)-P(2)	52.22(3)
Ru(1)-Ru(2)-Ru(3)	112.61(1)	Ru(2)-Ru(3)-P(2)	53.59(3)
Ru(1)-Ru(2)-Ru(5)	60.80(2)	Ru(3)-P(2)-Ru(2)	74.19(3)
Ru(3)-Ru(2)-Ru(5)	62.29(2)	Ru(4)-C(131)-P(1)	124.7(2)
Ru(2)-Ru(3)-Ru(4)	99.74(2)	C(131)-C(132)-Ru(2)	131.1(5)
Ru(2)-Ru(3)-Ru(5)	58.67(1)	C(131)-C(132)-Ru(3)	131.2(3)
Ru(4)-Ru(3)-Ru(5)	59.93(2)	C(131)-C(132)-Ru(4)	70.3(2)
Ru(3)-Ru(4)-Ru(5)	61.02(2)	C(131)-C(132)-Ru(5)	127.2(3)
Ru(1)-Ru(5)-Ru(2)	64.66(2)	C(132)-C(131)-Ru(4)	71.3(2)
Ru(2)-Ru(5)-Ru(3)	59.04(2)	C(132)-C(131)-P(1)	112.4(3)
Ru(3)-Ru(5)-Ru(4)	59.04(1)	Ru(1)-H(12)-Ru(2)	122(2)

Ru-C-O range from 170.6(5)-178.8(4) (average 175.8)

Ru(1)-Ru(2)-Ru(5)/Ru(2)-Ru(3)-Ru(5) 142.3(1)

Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) 125.6(1) acetylide ligand in (20) to the unusual 6e-donor diphenylphosphinovinylidene ligand in (22). The vinlyidene interacts in an η^2 fashion with Ru(4), while C(132) is within bonding distance of Ru(2), Ru(3) and Ru(5), a similar mode of bonding to that observed in the vinylidene complex $Ru_4(\mu_4-\eta^2-C{=}CHPr^i)(\mu_3-OH)(\mu-PPh_2)(CO)_{10}$.[33] The vinylidene C(131)-C(132) bond [1.436(5)Å] has lengthened appreciably from the corresponding value in (20) [1.383(6)Å], as a consequence of a reduction in C-C bond order. A further point of interest results from the change in bonding of the C_2 unit to the metal cores of (20) and (22) and relates to the marked decrease in the dihedral angles Ru(1)-Ru(2)-Ru(5)/Ru(2)-Ru(3)-Ru(4) (152.1° and 142.3° respectively) and Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) (134.2° and 125.6° respectively). The presence of the tertiary phosphine [P(1)], however, again prevents any interaction of the C_2 unit with Ru(1) and preserves the 'open' nature of the cluster since ready metal-metal bond formation is no longer possible.

Reaction of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ (20) with CO

Passage of CO into the black solutions of (20) in cyclohexane under mild conditions (25°C, 1 atm, 6 h) causes precipitation of a dark red complex (23) in 80-85% yield. More vigorous reaction conditions (70°C, 1 atm, 18 h) afforded a red solution, from which a second red complex (24) was isolated in 35% yield after chromatography. Conversion of (23) to (24) occurs under CO (70°C, 12 atm, 22 h). Single-crystal X-ray diffraction studies of (23) and (24) showed them to be isomers of composition $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{15}$.

The molecular structures of (23) and (24) are shown in Figures 4 and 5, while Figure 6 shows the heavy atom cores and salient bond distances (see also Table 4). It can be seen that both structures are closely related, differing only in the position of the μ-PPh_2 group [bridging Ru(2)-Ru(3) in (23), Ru(1)-Ru(2) in (24)], and the disposition of CO groups on Ru(1), Ru(2) and Ru(3).

Complex (23) is derived from (20), at least formally, by addition of one CO each to Ru(1) and Ru(2), with concomitant cleavage of the bonds from these metal atoms to Ru(5) (Scheme 6). At the same time coordination of the alkynyl group has altered so that its interaction with the Ru_3 triangle resembles that found in $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9$.[34,35] However, C(2) asymmetrically bridges the Ru(2)-Ru(3) vector [Ru(2)-C(2), 2.324(4); Ru(3)-C(2), 1.992(4)Å]. A similar situation was found in $Co_2FeRu(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)$.[36]

The most unusual feature of the structure of (23) is the coordination about Ru(1). This metal is approximately octahedrally coordinated by four CO ligands, P(1) and Ru(2). The P(1)-Ru(1) bond [2.406(1)Å] is a normal two-electron donor link and thus the metal atom achieves an $18e^-$ count from this tertiary phosphine and the four CO ligands. Consequently, the Ru(1)-Ru(2) bond [3.009(1)Å] must be considered to be another example of an unsupported donor bond, the first of which was observed in the complex $(OC)_5Os\rightarrow OsCl(GeCl_3)(CO)_3$.[37] In both instances, the metal atom separation is considerably longer than those found in the analogous $[M_3(CO)_{12}]$ (M = Ru or Os) complexes.

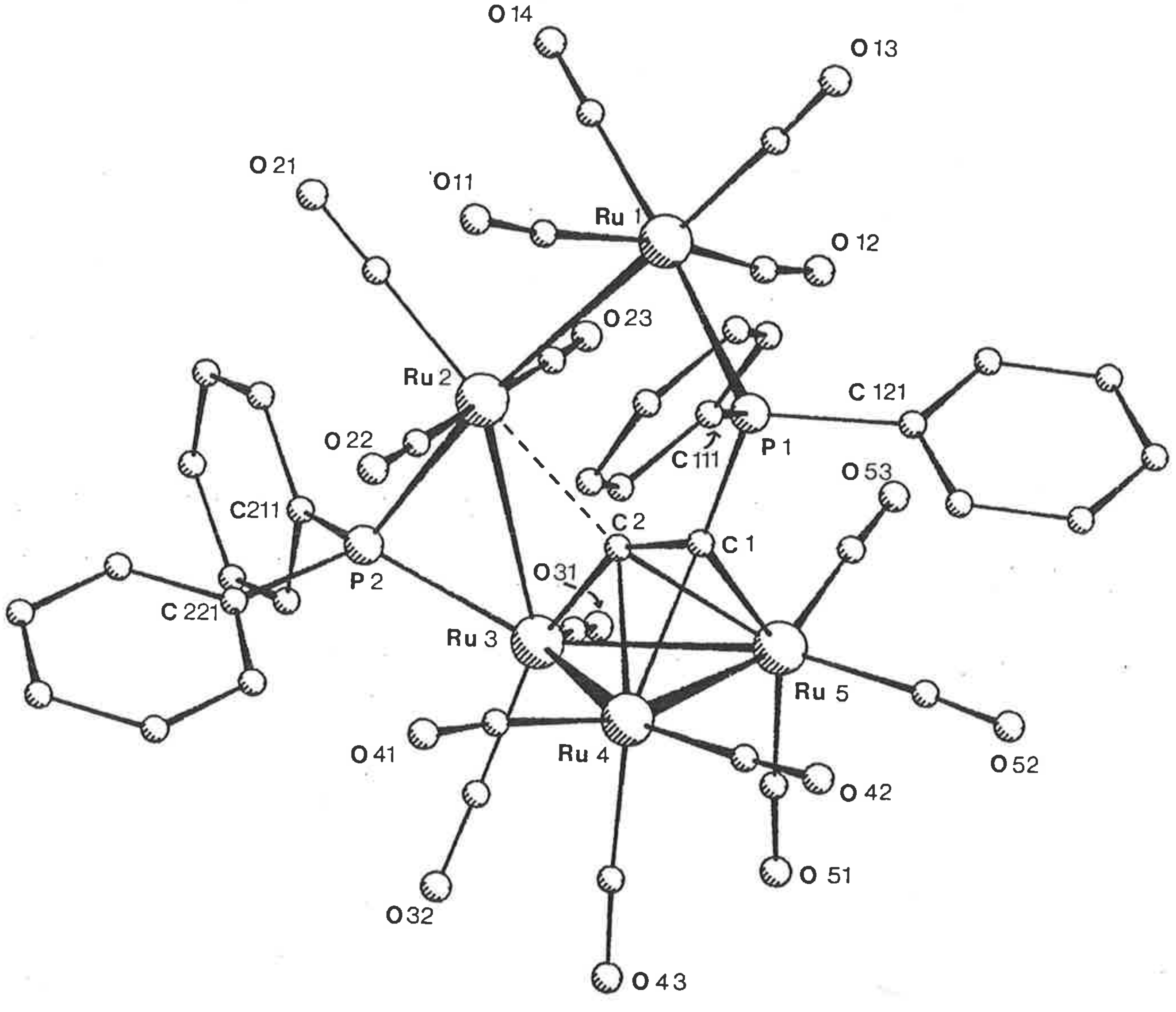


Figure 4: PLUTO plot of the molecular structure of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{15}$ (23), showing the atom-numbering scheme.

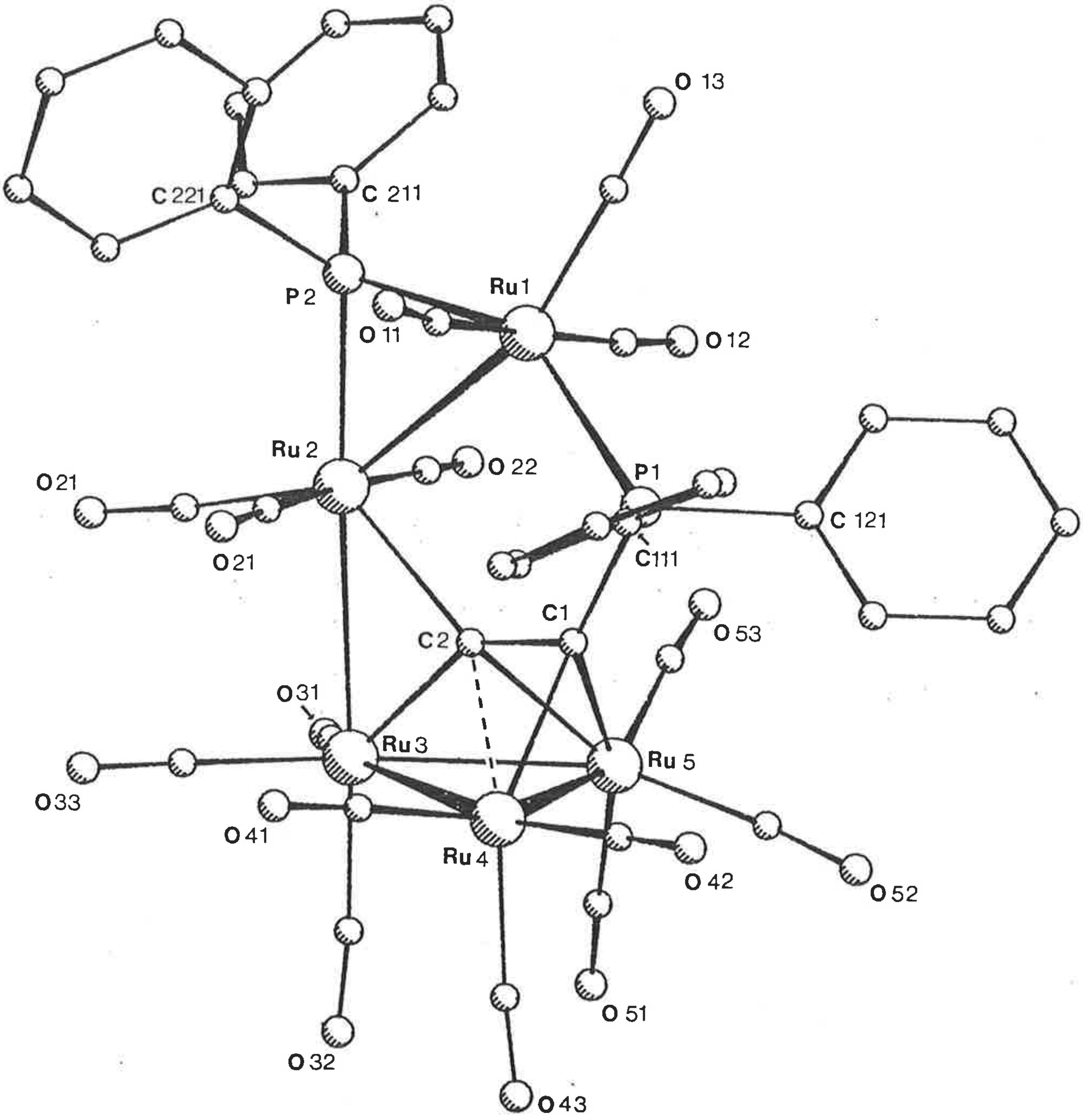


Figure 5: PLUTO plot of the molecular structure of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{15}$ (24) showing the atom-numbering scheme

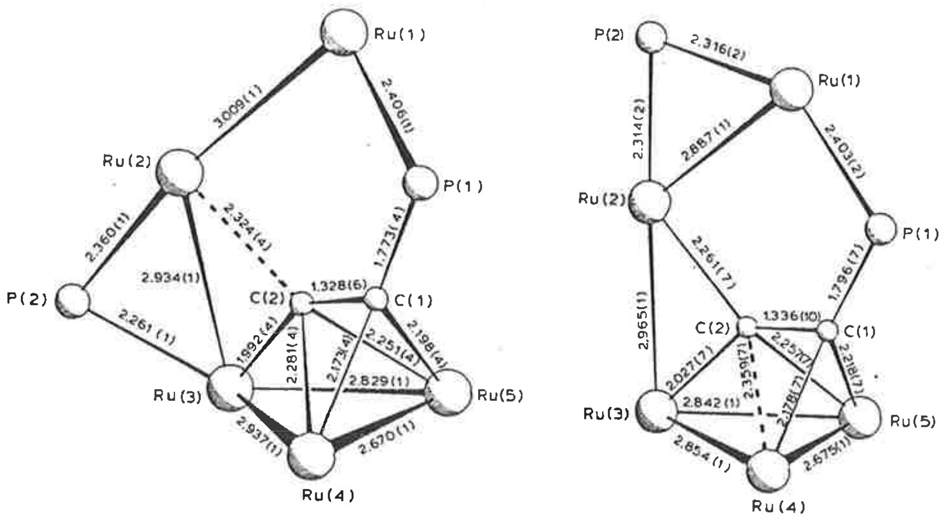


Figure 6 Heavy atom skeletons of (23) (left) and (24) (right), with important distances.

Table 4 Selected bond lengths and angles for (23) and (24)

Bond lengths (Å)	(23)	(24)
P(1)-C(111)	1.824(3)	1.815(6)
P(1)-C(121)	1.826(3)	1.820(5)
P(2)-C(211)	1.827(4)	1.826(6)
P(2)-C(221)	1.831(3)	1.813(6)
Ru-CO (average)	1.919	1.913
C-O (average)	1.132	1.134
Ru-CO range from	1.858(6)-1.969(5)	1.835(12)-1.954(10)
C-O range from	1.103(7)-1.154(7)	1.114(15)-1.153(15)
Angles (°)		
Ru(1)-Ru(2)-Ru(3)	121.8(-)	127.1(-)
Ru(2)-Ru(3)-Ru(4)	94.8(-)	99.0(-)
Ru(2)-Ru(3)-Ru(5)	98.5(-)	93.4(-)
Ru(4)-Ru(3)-Ru(5)	55.1(-)	56.0(-)
Ru(3)-Ru(4)-Ru(5)	60.4(-)	61.8(-)
Ru(3)-Ru(5)-Ru(4)	64.5(-)	62.2(-)
P(1)-Ru(1)-Ru(2)	86.6(-)	93.0(1)
P(2)-Ru(1)-Ru(2)	-	51.4(1)
P(2)-Ru(2)-Ru(1)	170.8(-)	51.5(1)
P(2)-Ru(2)-Ru(3)	49.1(-)	176.9(1)
P(2)-Ru(3)-Ru(2)	52.1(-)	-
P(2)-Ru(3)-Ru(4)	120.4(-)	-

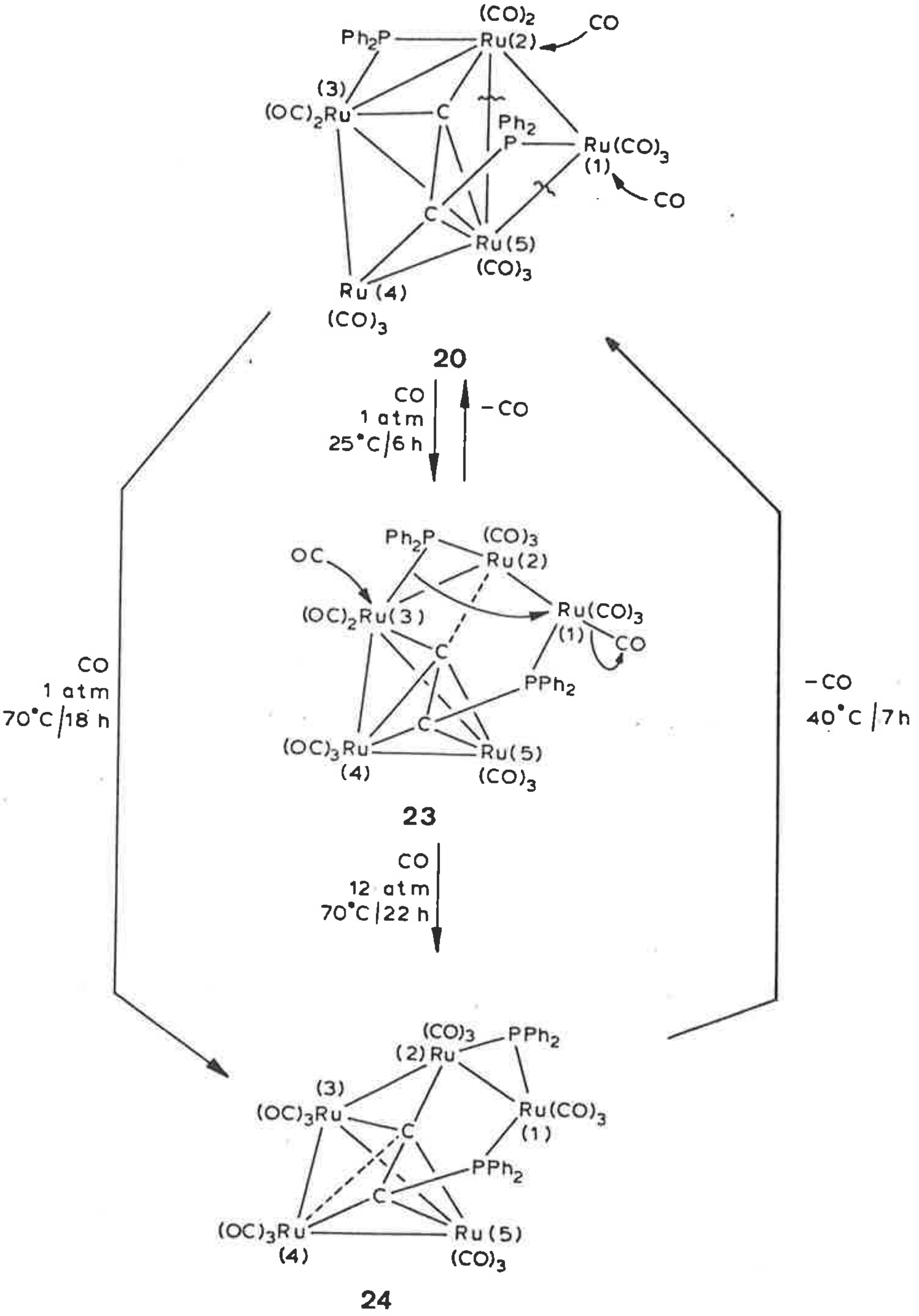
Table 4. (cont'd)

P(2)-Ru(3)-Ru(5)	150.6(-)	-
P(2)-Ru(1)-P(1)	-	144.0(1)
Ru(2)-P(2)-Ru(1)	-	77.2(1)
Ru(3)-P(2)-Ru(2)	78.8(-)	-
Ru(5)-C(1)-Ru(4)	75.3(1)	75.0(2)
Ru(5)-C(1)-P(1)	136.6(2)	136.3(4)
Ru(4)-C(1)-P(1)	145.4(2)	140.0(4)
Ru(2)-C(2)-Ru(3)	85.3(1)	87.3(3)
Ru(2)-C(2)-Ru(4)	139.5(2)	146.7(3)
Ru(2)-C(2)-Ru(5)	145.4(2)	138.6(3)
Ru(3)-C(2)-Ru(4)	86.6(1)	80.8(2)
Ru(3)-C(2)-Ru(5)	83.4(1)	82.9(2)
Ru(4)-C(2)-Ru(5)	72.2(1)	70.8(2)
C(1)-Ru(4)-Ru(3)	75.8(1)	77.5(2)
C(1)-Ru(4)-Ru(5)	52.8(1)	53.2(2)
C(1)-Ru(5)-Ru(3)	77.9(1)	77.1(2)
C(1)-Ru(5)-Ru(4)	51.9(1)	51.8(2)
C(1)-P(1)-Ru(1)	109.3(1)	106.3(2)
C(1)-C(2)-Ru(2)	126.8(3)	130.0(5)
C(1)-C(2)-Ru(3)	147.9(3)	142.5(5)
C(1)-C(2)-Ru(4)	68.3(2)	65.5(4)
C(1)-C(2)-Ru(5)	70.5(2)	71.0(4)
C(2)-Ru(2)-Ru(1)	82.8(1)	84.1(2)
C(2)-Ru(3)-Ru(2)	52.1(1)	49.6(2)
C(2)-Ru(3)-Ru(4)	50.8(1)	54.7(2)
C(2)-Ru(3)-Ru(5)	52.2(1)	52.0(2)
C(2)-Ru(4)-Ru(3)	42.6(1)	44.5(2)
C(2)-Ru(4)-Ru(5)	53.4(1)	52.8(2)
C(2)-Ru(5)-Ru(3)	44.4(1)	45.1(2)
C(2)-Ru(5)-Ru(4)	54.4(1)	56.4(2)
C(2)-Ru(4)-C(1)	34.6(1)	34.0(2)
C(2)-Ru(5)-C(1)	34.7(1)	34.7(3)
C(2)-C(1)-Ru(5)	74.8(2)	74.2(4)
C(2)-C(1)-Ru(4)	77.1(2)	80.5(4)
C(2)-C(1)-P(1)	125.9(3)	125.8(6)
C(1)-P(1)-C(111)	111.6(2)	107.5(3)
C(1)-P(1)-C(121)	106.8(2)	109.3(3)
C(111)-P(1)-C(121)	100.8(1)	101.4(3)
C(211)-P(2)-C(221)	101.1(2)	102.0(3)

Conversion of (23) into (24) can be formally achieved by attack of CO on Ru(3), displacing P(2) which pivots on Ru(2) to displace in turn a CO from Ru(1). This has the expected shortening effect on Ru(1)-Ru(2) [now 2.887(1)Å], although Ru(2)-Ru(3) is slightly longer, at 2.965(1)Å. The interaction of C(2) with Ru(2) is also strengthened [Ru(2)-C(2) 2.261(7), Ru(3)-C(2) 2.027(7)Å], while its interaction with Ru(4) is weakened [2.359(7) vs 2.281(4)Å in (23)]. The Ru_3 isosceles triangle in (24) has almost equal distances Ru(3)-Ru(4) and Ru(3)-Ru(5), whereas the former distance is ca 0.1Å longer in (23). In both complexes the Ru(4)-Ru(5) separation [2.670(1), 2.675(1)Å respectively] is, to the author's knowledge, the shortest such separation observed for neutral ruthenium carbonyl clusters and is probably the result of the interaction of the two π-bonds between these metals and the acetylenic C(1)-C(2) unit. A similar situation was found in $Fe_3(\mu\text{-}\eta^2\text{-}C{\equiv}NBu^t)(CO)_9$ where the Fe-Fe bond doubly-bridged by the C≡N moiety is appreciably shorter [2.482(1)Å]^{38} than the corresponding doubly-CO-bridged bond in $Fe_3(CO)_{12}$ [2.558(1)Å].^{39} None of the metal-metal bonds in (24) are of the type found between Ru(1) and Ru(2) in (23), and the net effect of the isomerisation is to give a more equable distribution of electron density over the cluster.

A further effect of the isomerisation has been to increase the thermal stability of (24); solutions of (23) readily lose CO to regenerate (20), while solutions of (24) require heating (42°C, 7 h) before CO is lost to give (20).

The conversion of (20) to (23), and subsequent isomerisation to (24) are depicted in Scheme 6, although the ready

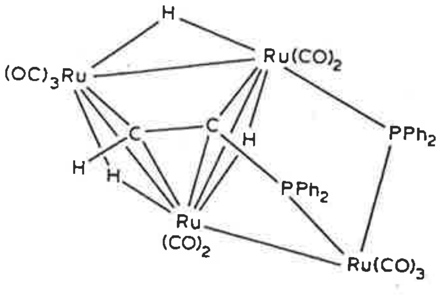

(CO)2
CO
Ph2P
Ru(2)
(3)
(OC)2Ru
C
Ph2
P
Ru(CO)3
(1)
CO
C
Ru(5)
(CO)3
Ru (4)
(CO)3
20
CO
1 atm
25°C/6 h
−CO
Ph2P
(CO)3
OC
Ru(2)
(OC)2Ru(3)
Ru(CO)3
(1)
CO
C
PPh2
C
(OC)3Ru
(4)
Ru(5)
(CO)3
23
CO
1 atm
70°C/18 h
−CO
40°C/7h
CO
12 atm
70°C/22 h
(CO)3
PPh2
(2) Ru
(3)
(OC)3Ru
C
Ru(CO)3
(1)
PPh2
C
(OC)3Ru
(4)
Ru (5)
(CO)3
24

Scheme 6

mobility of ligands such as CO on cluster complexes makes the detailed course of these novel reactions uncertain. The oft-expressed proposition[37] that bridging PR_2 groups may hold clusters intact during their reactions is again called into question[40,41] by the results depicted above: while the metal skeleton is essentially unaltered, the PPh_2 group migrates to a second site, remaining bonded to Ru(2) during this process. Such reactions, in which opening of the Ru_2P group generates a further coordination site, may have implications for the role of such groups in cluster-catalysed reactions.

Reaction of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) with H_2

Under 10 atm H_2 at 25°C complex (20) afforded the tetranuclear cluster $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,\underline{P}\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$ (25) in 61% yield; the fifth ruthenium is partially recovered as $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (15%). Complex (25), which was characterised by an X-ray diffraction study, exhibits a characteristic low-field signal at δ 9.10 (dd, $\underline{J}$(PH) 2.6 and 18.1 Hz, 1H) for the $C\underline{H}$ proton of the alkynyl unit coupled to two inequivalent phosphorus atoms, together with three equal intensity high-field resonances at δ -15.40m, -18.53dm and -19.00dm assigned to the hydride ligands which are not fluxional at room temperature.



25

Figure 7 shows an ORTEP plot of one molecule of (25), with the heavy atom core inset (see also Table 5). The complex consists of a triangular Ru_3 core, to which is attached the fourth ruthenium in an equatorial position. The four metal atoms are not coplanar, and all achieve individual 18e configurations. The C_2PPh_2 moiety in (20) has been converted to an ethynyldiphenylphosphine ligand, which is attached to all four metal atoms via a normal 2e-donor bond from P(4) to Ru(4), and the C_2 system interacting with the Ru_3 triangle in the common $(2\sigma + \pi)$, or μ_3-$2\eta^1,\eta^2$ mode. The μ-PPh_2 group, originally bridging an Ru-Ru bond in (20), now bridges Ru(2) and Ru(4), which are not within bonding distance of each other. The hydride ligands were located and refined in the X-ray analysis, and bridge the three edges of the Ru_3 triangle.

The Ru-Ru bonds range between 2.8370-3.0490(5)Å; the Ru_3 triangle contains two of medium length bonds at 2.8370(6) and 2.874(1)Å for Ru(1)-Ru(2) and Ru(1)-Ru(3), and a long bond at 3.0490(5)Å for Ru(2)-Ru(3). The latter is bridged by the alkyne (C_2) group, while the other two are bridged by only one carbon. The relatively long Ru(1)-Ru(4) bond [2.9178(5)Å] probably results from the steric problems in coordinating two PPh_2 groups in mutually cis positions [angle P(2)Ru(4)P(4) 83.56(3)°] while still remaining attached to the cluster.

The acetylenic C≡C bond undergoes the usual lengthening to 1.371(4)Å upon coordination to the Ru_3 core, but it is not as long as that found in $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}PPh_2)(CO)_9$ [1.415(11)Å].[20] The Ru-P distances [Ru(2)-P(2) 2.3799(7), Ru(4)-P(4) 2.3790(8), Ru(4)-P(2) 2.4665(8)Å] are consistent with 2e-donor bonds in the first two cases, and with a

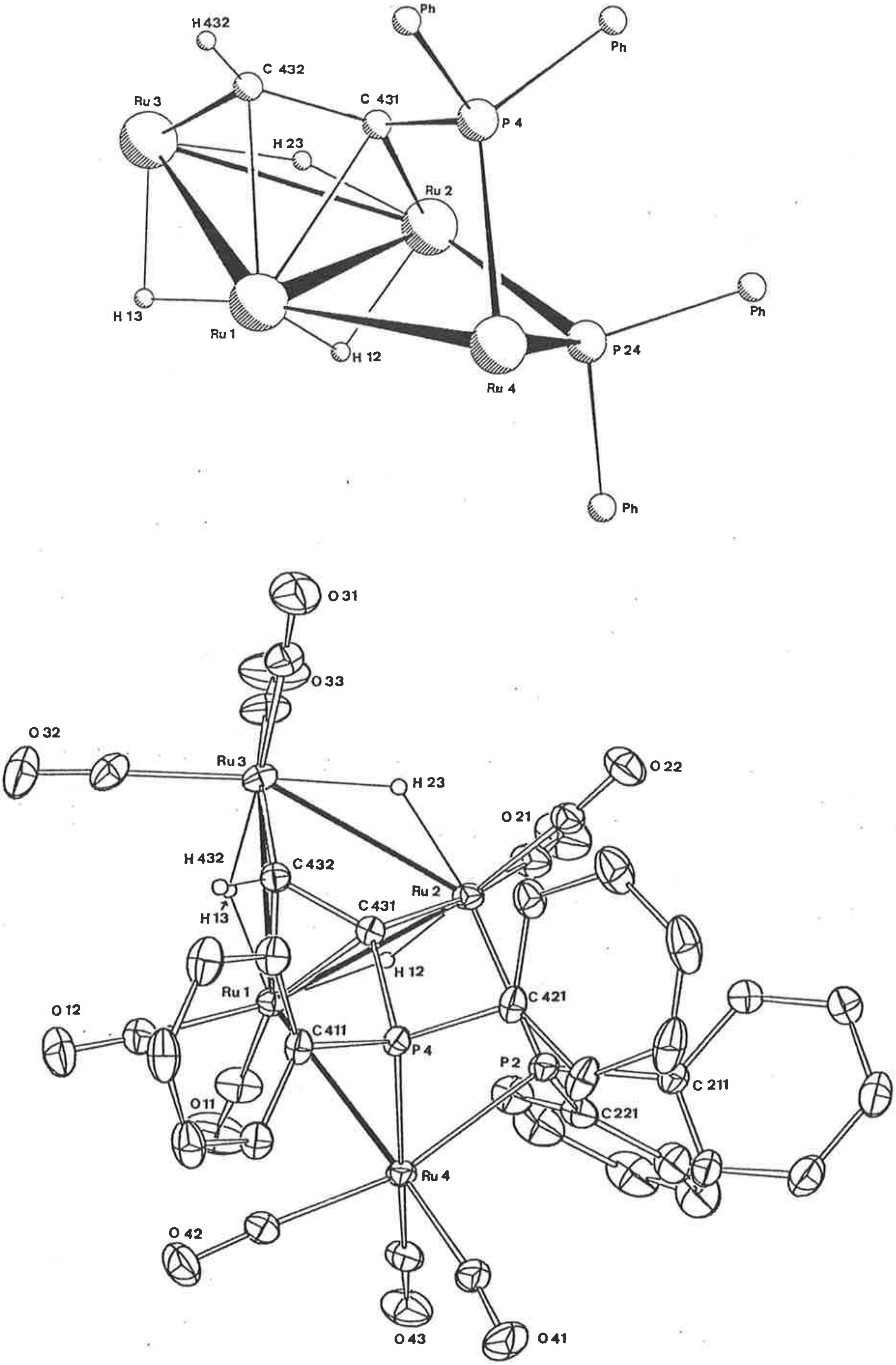


FIGURE 7: ORTEP plot of the molecular structure of $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,\underline{P}\text{-}HC_2PPh_2)(CO)_{10}$ (25), core geometry inset (by B.W. Skelton and A.H. White)

Table 5 Selected bond lengths and angles for $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2\text{-}\underline{P}\text{-}HC_2PPh_2)\text{-}(CO)_{10}$ (25)

Bond lengths (Å)

Ru(1)-Ru(2)	2.8370(6)	C(432)-Ru(1)	2.261(2)
Ru(1)-Ru(3)	2.8683(5)	C(432)-Ru(3)	2.071(2)
Ru(1)-Ru(4)	2.9178(5)	C(432)-C(431)	1.371(4)
Ru(2)-Ru(3)	3.0490(5)	Ru(1)-H(12)	1.86(3)
Ru(2)-P(2)	2.3799(7)	Ru(1)-H(13)	1.81(3)
Ru(4)-P(2)	2.4665(8)	Ru(2)-H(12)	1.68(2)
Ru(4)-P(4)	2.3790(8)	Ru(2)-H(23)	1.67(3)
C(431)-Ru(2)	2.112(3)	Ru(3)-H(23)	1.77(3)
C(431)-P(4)	1.791(2)	Ru(2)...Ru(4)	3.7931(6)

Ru-CO range from 1.887(4)-1.980(3) (average 1.919)

Angles (°)

Ru(1)-Ru(2)-Ru(3)	58.19(2)	Ru(2)-C(431)-Ru(1)	81.1(1)
Ru(1)-Ru(3)-Ru(2)	57.20(1)	Ru(3)-C(432)-Ru(1)	82.9(1)
Ru(3)-Ru(1)-Ru(2)	64.61(1)	Ru(1)-C(431)-P(4)	102.9(1)
Ru(3)-Ru(1)-Ru(4)	140.96(1)	Ru(2)-C(431)-P(4)	121.0(1)
Ru(2)-Ru(1)-Ru(4)	82.19(2)	Ru(1)-Ru(4)-P(4)	72.82(2)
Ru(1)-Ru(2)-P(2)	85.66(2)	P(2)-Ru(4)-P(4)	93.56(3)
Ru(1)-Ru(4)-P(2)	72.82(2)	C(431)-Ru(1)-C(432)	35.37(1)
Ru(3)-Ru(2)-P(2)	143.77(2)	C(431)-C(432)-P(4)	124.0(2)
Ru(1)-Ru(4)-P(4)	82.39(2)	Ru(1)-H(12)-Ru(2)	106(1)
Ru(2)-P(2)-Ru(4)	102.62(3)	Ru(1)-H(13)-Ru(3)	106(1)
Ru(2)-Ru(3)-C(432)	66.98(8)	Ru(2)-H(23)-Ru(3)	125(2)
Ru(3)-Ru(2)-C(431)	65.70(6)		

phosphido-metal bond from P(2) to Ru(4), as required by the 18e counts.

Tetrametal clusters usually have 60e (tetrahedral, six metal-metal bonds), 62e (butterfly, five metal-metal bonds) or 64e (planar rhomboidal, five metal-metal bonds) electron counts. Some lengthening (and weakening) of the metal-metal separations is usually evident in the latter, electron rich, clusters.[42,43] Complex (25) provides an example of a 64e cluster in which cleavage of a metal-metal bond, expected on addition of a 2e ligand to a 62e butterfly cluster, has occurred. The Ru(2)...Ru(4) separation is 3.7831(6)Å, while the average bonded Ru-Ru separation is 2.918Å. This value is considerably longer than found in $Ru_4(\mu_4\text{-}C{=}CHPr^i)(\mu_3\text{-}OR)(\mu\text{-}PPh_2)(CO)_{10}$ (R = H, Et), which also have 64e, where the hinge of the butterfly has cleaved; the average Ru-Ru distances in these complexes are 2.766 (R = H) and 2.758Å (R = Et).[33]

The mechanism of formation of (25) cannot be proposed with certainty at this stage. A reasonable site for initial attack is the Ru(3)-C(1) bond in (20); adddition of H_2 and cleavage of the PPh_2 bridge would allow elimination of an $HRu(CO)_3$ fragment [which appears as $Ru_4(\mu\text{-}H)_4(CO)_{12}$]. The final $\mu\text{-}2\eta^1,\eta^2$ geometry found for the alkyne must result from a rotation about the Ru_3 core, perhaps similar to that which relates the two isomers of $OsW_2\{\mu_3\text{-}\eta^2\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2$.[44-47] The net reaction is

$$4Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13} + 10\ H_2 \longrightarrow 4Ru_4(\mu_4\text{-}\eta^2,\underline{P}\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10} + Ru_4(\mu\text{-}H)_4(CO)_{12}$$

Thus addition of H_2 to the open Ru_5 cluster has resulted in conversion of the acetylide to the parent alkyne and excission of one of the ruthenium carbonyl groups. The alkyne-bonded PPh_2 group again prevents aggregation of the open Ru_4 cluster, so that the relatively rare metallo-ligated triangular core is found.

In contrast with the previous experiment passage of hydrogen into the black solution of (20) in refluxing cyclohexane resulted in a colour change to red. Preparative tlc enabled isolation of three major products in amounts which depend on the reaction time. They were identified as resulting from successive addition of one, two and three molecules of hydrogen to (20). Trace amounts of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and complex (25) were also separated from the reaction mixture.

Addition of 2H to (20) afforded (22) which was previously made by successive addition of H^- $[K(HBBu^s_3)]$ and H^+ (H_3PO_4) to (20) (see above) and was identified by comparison of its spectral properties with those of an authentic sample. Further addition of hydrogen gave dark red $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)\text{-}(\mu\text{-}PPh_2)(CO)_{13}$ (26) in 23-30% yield. The ^1H n.m.r. spectrum contains a two-proton multiplet at δ 5.04, which suggests that a second hydrogen has added to the β-carbon of the diphenylphosphinovinylidene in (22) to give a methylene group. The spectrum also contains a high-field doublet of doublets at δ -20.19 (J(PH) 6.9 and 12.0 Hz) consistent with two bridging metal hydrides that occupy similar positions on the cluster and couple to two inequivalent phosphorus atoms. Finally, prolonged reaction of hydrogen with (20) [and also with (22) and (26)] resulted in the formation of orange

$Ru_5C(\mu-H)_3(\mu-PPh_2)(CO)_{11}(PMePh_2)$ (27) in 30-54% yield. The ^1H n.m.r. spectrum exhibits a characteristic three-proton doublet at δ 1.88 (J(PH) 7.7 Hz) assigned to the methyl protons of a $PMePh_2$ group together with two high-field multiplets of relative intensity 2:1 at -19.97 and -22.50 assigned to three bridging metal hydrides. The structure of (27) was determined by an X-ray diffraction study, as is shown in Figure 8 (see also Table 6).

The metal skeleton in (27) forms a distorted square pyramid, which contains a carbido carbon, C(532), 0.06Å below the average plane of the square base. This carbon is the α-carbon of the acetylide ligand in (20). The β-carbon is found as the methyl group of the $PMePh_2$ ligand attached to Ru(5). Coordination about the five ruthenium atoms is completed by the $\mu-PPh_2$ group which bridges the Ru(2)-Ru(3) basal bond, the eleven CO ligands, and the three metal-bonded hydrogen atoms, H(15, 25, 45), which bridged three of the apical Ru-basal Ru bonds.

The overall geometry of the Ru_5C core is similar to that observed for the carbide clusters (1), (2) and (3). The atoms Ru(1), Ru(2), Ru(3) and Ru(4), which define the basal plane, deviate by less than ±0.07Å from the mean plane through these atoms. The eight Ru-Ru separations fall in the range 2.7705(6)-2.9014(7)Å. The shortest is between the phosphido-bridged basal atoms Ru(2)-Ru(3) [2.7705(6)Å], while the longest bond [Ru(1)-Ru(4) 2.9014(7)Å] is on the opposite side of the square face. The Ru-C (carbide) distances [mean 2.04(1)Å] are not significantly different from values observed for (1) [mean 2.02(2)Å] and (2) [mean 2.04(2)Å].

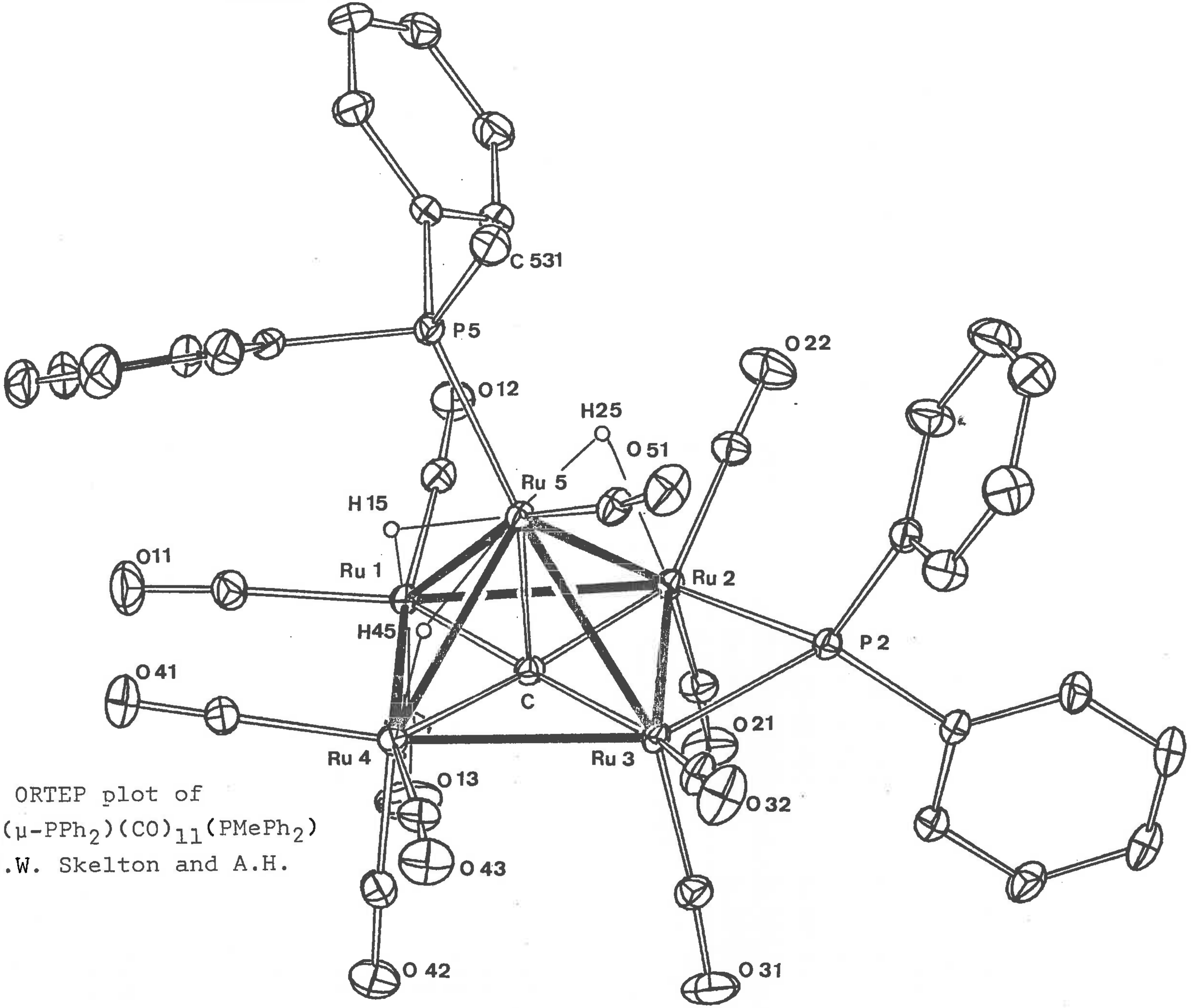


Figure 8: ORTEP plot of $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ (27) (by B.W. Skelton and A.H. White)

Table 6

Selected bond lengths and angles for $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ (27)

Bond lengths (Å)

Ru(1)-Ru(2)	2.9170(6)	Ru(1)-C	2.022(3)
Ru(1)-Ru(4)	2.9014(7)	Ru(2)-C	2.065(2)
Ru(1)-Ru(5)	2.8934(6)	Ru(3)-C	1.971(3)
Ru(2)-Ru(3)	2.7705(6)	Ru(4)-C	2.060(2)
Ru(2)-Ru(5)	2.8347(5)	Ru(5)-C	2.075(2)
Ru(3)-Ru(4)	2.8948(7)	Ru(1)-H(15)	1.79(3)
Ru(3)-Ru(5)	2.8820(6)	Ru(5)-H(15)	1.77(5)
Ru(4)-Ru(5)	2.8391(6)	Ru(2)-H(25)	1.88(3)
Ru(2)-P(2)	2.3094(10)	Ru(5)-H(25)	1.73(3)
Ru(3)-P(2)	2.3040(8)	Ru(4)-H(45)	1.92(3)
Ru(5)-P(5)	2.3408(8)	Ru(5)-H(45)	1.72(3)

Ru-CO range from 1.863(4)-1.947(4) (average 1.905)

C-O range from 1.123(5)-1.151(5) (average 1.132)

Angles (°)

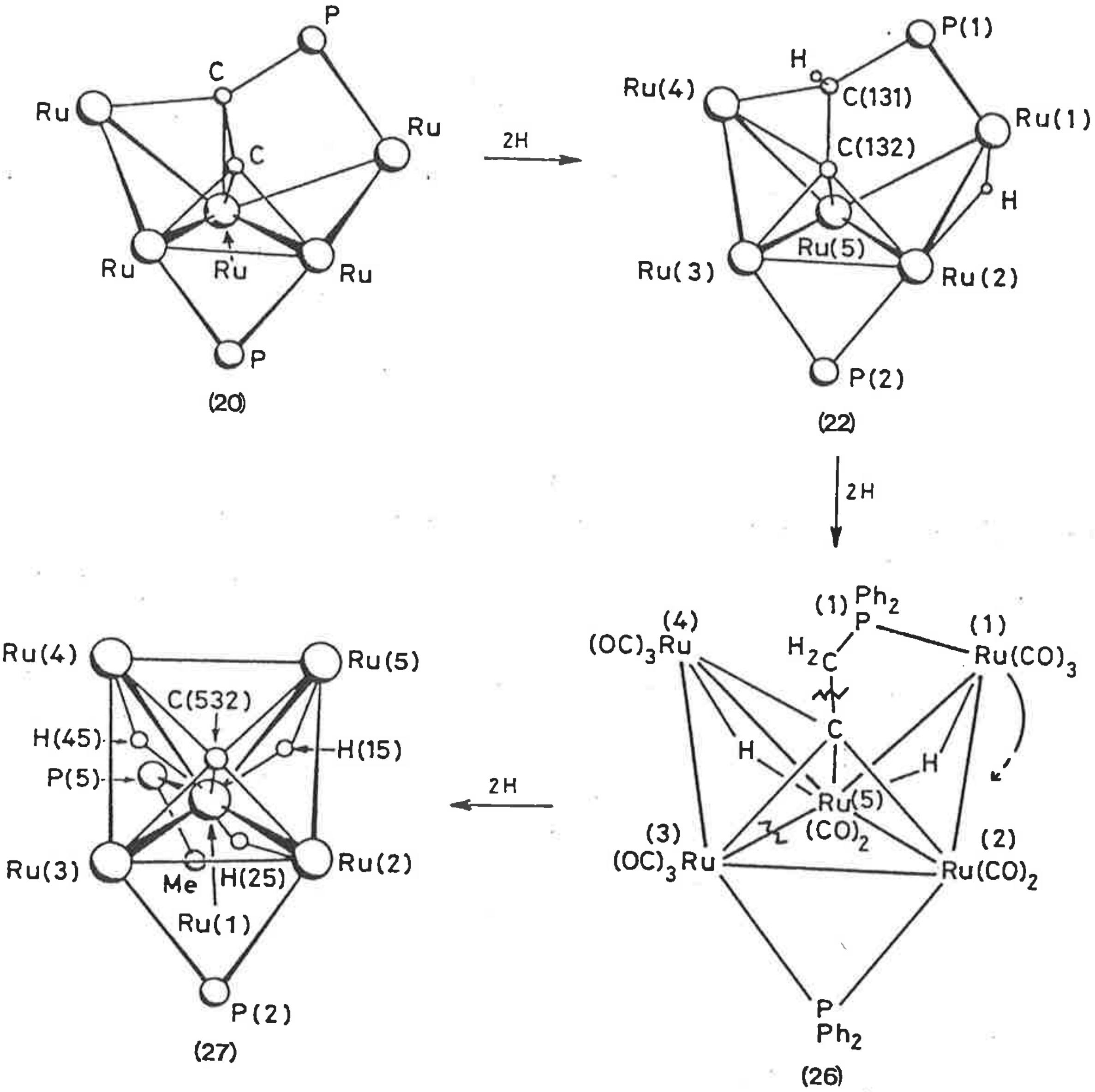
Ru(2)-Ru(1)-Ru(4)	90.09(1)	Ru(1)-C-Ru(2)	91.1(1)
Ru(2)-Ru(1)-Ru(5)	58.40(1)	Ru(1)-C-Ru(3)	177.6(1)
Ru(4)-Ru(1)-Ru(5)	58.67(1)	Ru(1)-C-Ru(4)	90.6(1)
Ru(1)-Ru(2)-Ru(3)	89.13(1)	Ru(1)-C-Ru(5)	89.9(1)
Ru(1)-Ru(2)-Ru(5)	60.38(2)	Ru(2)-C-Ru(3)	86.7(1)
Ru(3)-Ru(2)-Ru(5)	61.87(2)	Ru(2)-C-Ru(4)	173.0(1)
Ru(2)-Ru(3)-Ru(4)	93.20(2)	Ru(2)-C-Ru(5)	86.4(1)
Ru(2)-Ru(3)-Ru(5)	60.16(1)	Ru(3)-C-Ru(4)	91.8(1)
Ru(4)-Ru(3)-Ru(5)	58.87(2)	Ru(3)-C-Ru(5)	90.8(1)
Ru(1)-Ru(4)-Ru(5)	60.52(1)	Ru(4)-C-Ru(5)	86.7(1)
Ru(1)-Ru(4)-Ru(3)	87.07(1)	Ru(1)-Ru(2)-P(2)	141.94(2)
Ru(3)-Ru(4)-Ru(5)	60.34(2)	Ru(4)-Ru(3)-P(2)	145.25(3)
Ru(1)-Ru(5)-Ru(2)	61.22(2)	Ru(2)-Ru(3)-P(2)	53.18(2)
Ru(1)-Ru(5)-Ru(3)	87.46(1)	Ru(3)-Ru(2)-P(2)	53.00(2)
Ru(1)-Ru(5)-Ru(4)	60.80(2)	Ru(1)-Ru(5)-P(5)	105.91(2)
Ru(2)-Ru(5)-Ru(3)	57.97(1)	Ru(2)-P(2)-Ru(3)	73.81(3)
Ru(2)-Ru(5)-Ru(4)	93.05(2)	Ru(1)-H(15)-Ru(5)	109(2)
Ru(3)-Ru(5)-Ru(4)	60.79(1)	Ru(2)-H(25)-Ru(5)	103(2)
		Ru(4)-H(45)-Ru(5)	102(1)

Complex (27) is the first square pyramidal Ru_5 carbido cluster to contain a bridging phosphido group and also a phosphine donor ligand ($PMePh_2$) located on the apical metal; in the complexes (2) and (3) the phosphine ligands occupy axial sites on basal ruthenium atoms.

In light of the determined structures of (22) and (27), together with ^1H n.m.r. spectral evidence, it is now possible to propose a reasonable structure for (26). Consequently it is suggested that $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (26) has the illustrated structure (Scheme 7); the cluster contains a diphenylphosphinomethylmethylidyne ligand, and resembles to a degree the functionalised methylidyne ligands in tetranuclear iron clusters.[48] The positions of the hydride ligands are uncertain, however ^1H n.m.r. data suggest that they occupy similar positions on the cluster. Conversion of (26) to (27) (Scheme 7; the atom numbering of (27) has been changed to simplify the argument) requires the addition of two hydrogen atoms, one to the cluster core, and one to the β-carbon. The bond between the α-carbon and β-carbon is cleaved, thus allowing the ruthenium [Ru(1)] containing the newly formed $PMePh_2$ ligand to pivot on the Ru(2)-Ru(5) 'hinge' bond, the Ru(3)-Ru(5) bond breaks and new bonds between Ru(1) and Ru(3), Ru(4) and the α-carbon are formed.

A second possible mechanism for the transformation of (26) to (27) requires the breaking of the α-carbon - β-carbon bond with concomitant formation of a bond between Ru(1)-Ru(4); but it is apparent that migration of the $PMePh_2$ ligand to the apical ruthenium must occur in this case.

$$C{\equiv}CPPh_2 + 3H \longrightarrow C + H_3CPPh_2$$



(Scheme 7)

The successive transformation of (20) to (22), (26) to (27) are readily appreciated by reference to Scheme 7, which illustrates the C–C and heavy atom cores of the four complexes, and the pincer movement of the outer Ru atoms of the swallow Ru_5 clusters as they close and cleave the C–C unit of the μ-phosphinoacetylide ligand.

The normal course of hydrogenation of a C≡C triple bond is initial cis addition, with eventual formation of the corresponding alkane. To the author's knowledge, two examples of similar cluster-bound acetylides have been reported: addition of H_2 to $H_2Ru_3(\mu_3\text{-}\eta^2\text{-}C_2R)(CO)_9$ (R = Bu^t),[49] and the reaction of (9b) with PH_2Ph (Scheme 2, p 8),[19] both of which give complexes containing $\mu_3\text{-}CCH_2R$ ligands. Further reduction of the alkylidyne complexes afforded the corresponding alkane CH_3CH_2R.

The conversion of (26) to (27), which occurs with cleavage of the C–C bond, is therefore unprecedented. It results from concomitant formation of strong metal-metal bonds and a stable carbido cluster; a similar driving force occurs in the pyrolysis of (16) to (17)[22] and the conversion of (4) to (1) (Scheme 1, p. 4).[1]

EXPERIMENTAL

General Experimental Conditions

All reactions were carried out under a nitrogen atmosphere, unless stated otherwise. Common organic solvents were dried and distilled under a nitrogen atmosphere as described in Vogel.[50] Light petroleum refers to a fraction of b.p. 62-65°C. $Ru_3(CO)_{12}$,[51] $Os_3(CO)_{12}$,[52] $Os_3(CO)_{12-n}(MeCN)_n$ ($n = 1,2$)[31] and sodium diphenylketyl solutions[25] were prepared according to published procedures. Chemical reagents were commercial products and were used as received. High purity nitrogen and hydrogen were obtained from Commonwealth Industrial Gases (CIG) Limited and carbon monoxide from Matheson Gas Products; gases were used as received.

High pressure reactions were carried out in a Roth stainless steel autoclave, internal volume 100 ml, equipped with a removable glass liner.

Thin layer chromatography was carried out on preparative plates (20 x 20 cm) coated with Kielselgel 60 GF_{254}.

Elemental microanalyses were determined by the Canadian Microanalytical Service (Vancouver).

Infrared Spectra were recorded (using sodium chloride solution cells) on a Perkin Elmer 683 double beam infrared spectrophotometer calibrated with CO gas (2147.1 cm^{-1}).

N.m.r. spectra were recorded on Bruker WP-80DS (^1H, 80MHz; ^{13}C, 20.1MHz), or Bruker HX-90E (^{31}P, 36.43MHz; variable temperature ^1H, 90MHz) spectrometers. Deuterated solvents were required for the deuterium resonance lock and were used in 2.5, 5 or 10 mm tubes. Shifts were reported relative to internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P).

Mass spectra were recorded on an AEI-GEC MS 3074 spectrometer (70 eV ionizing energy).

Crystallography - General techniques and details given below apply to structures determined by the author.

Suitable crystals were mounted on a glass fiber and coated with cyanoacrylate super glue. Lattice parameters were determined from a least-squares fit to the setting angles of 25 high angle reflections on an Enraf-Nonius CAD4 four-circle diffractometer using monochromated Mo-*K*α 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 mins to check for crystal and electronic stability.

Data reduction and application of Lorentz and polarization corrections were performed by the programme SUSCAD.[53] Absorption corrections were applied using the programme ABSORB[54]; crystal dimensions were determined with a microscope equipped with callibration scales.

Computing for all solution and refinement work was performed using the SHELX[55] system of programmes. Reflections with intensities $I < 2.5\sigma(I)$ and systematically absent reflections were rejected, while equivalent reflections were averaged. Structures were solved by direct methods to give the metal atom positions, with all other non-hydrogen atoms being revealed in the Fourier difference maps of successive blockedmatrix least-squares refinements. Phenyl rings were included as rigid groups (C-C 1.395Å) with isotropic thermal parameters. Hydrogen atoms were generally placed in calculated positions (phenyl C-H 1.08Å, methylene C-H 0.97Å) with common group thermal parameters. In the final refinement cycles (with all non-hydrogen atoms and non-phenyl carbons anisotropic) the following weighting scheme was employed

$$\underline{\omega} = \underline{k}/(\sigma^2(\underline{F_o}) + |\underline{g}|F_o^2)$$

where the values of $\underline{k}$ and $\underline{g}$ were refined. The discrepancy factors $\underline{R}$ and $\underline{R_w}$ were determined as

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

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

Bond lengths, valence angles, non-bonded distances and their standard deviations were all calculated using SHELX. Least-squares planes and dihedral angles were calculated using the programme GEOM[56] and diagrams were plotted by PLUTO.[57] All programmes were implemented on the CYBER 173 computing system at the University of Adelaide.

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

Preparation of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (18)

A mixture of $Ru_3(CO)_{12}$ (150 mg, 0.235 mmol) and dppa (47 mg, 0.119 mmol) in thf (30 ml) at ambient temperature was treated dropwise from a syringe with a solution of $Na[Ph_2CO]$ (*ca* 0.025 mol dm^{-3}) in the same solvent until the reaction was complete (tlc). About 10 drops were required, when the solution rapidly darkened. Evaporation and recrystallisation from CH_2Cl_2/n-hexane afforded an orange powder of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (18) (135 mg, 71%), m.p. >150°C (dec). [Found: C, 35.56; H, 0.81; $C_{48}H_{20}O_{22}P_2Ru_6$ requires: C, 35.65; H, 1.25%]. Infrared (cyclohexane): ν(CO) 2102m, 2068(sh), 2052vs, 2034s, 2021vs, 2005(sh), 1997w, 1987(sh), 1970w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.50 (m, Ph).

Preparation of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (19)

A mixture of $Os_3(CO)_{11}(MeCN)$ (152 mg, 0.165 mmol), MeCN (5 ml) and dppa (33 mg, 0.083 mmol) in cyclohexane (100 ml) was stirred at 50°C for 30 min. Evaporation and recrystallization from CH_2Cl_2/MeOH afforded yellow crystals of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (19) (155 mg, 87%), m.p. 189-190°C. [Found: C, 26.81; H, 0.60; $C_{48}H_{20}O_{22}Os_6P_2$ requires: C, 26.79; H, 0.94%]. Infrared (cyclohexane): ν(CO) 2112s, 2062m, 2040w, 2026s, 2008w, 1999w, 1989w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.45 (m, Ph).

Pyrolysis of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (18)

A solution of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (18) (100 mg, 0.062 mmol) in toluene (15 ml) was heated at 90°C for 1 h, after which time the reaction was adjudged complete [the disappearance of the ν(CO) band of (18) at 2102 cm^{-1} was monitored]. Evaporation and preparative tlc (cyclohexane-acetone 90/10) gave two bands: Band 1, R_f 0.65, yellow, $Ru_3(CO)_{12}$ (6 mg, 15%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 2, R_f 0.35, black, recrystallised from CH_2Cl_2/MeOH to give black crystals of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) (69 mg, 88%), m.p. 200-210°C. [Found: C, 36.92; H, 1.01; $C_{39}H_{20}O_{13}P_2Ru_5$ requires: C, 37.06; H, 1.60%]. Infrared (cyclohexane): ν(CO) 2081w, 2061vs, 2021s, 1995w, 1985vw, 1972vw cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 7.40 (m, Ph).

Pyrolysis of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (19)

A solution of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (19) (65 mg, 0.030 mmol) in xylene (50 ml) was gently refluxed for 2.5 h, after which the reaction was adjudged complete (tlc). Evaporation and preparative tlc (petroleum spirit-acetone 80/20) gave one major purple band, R_f 0.30, recrystallisation from CH_2Cl_2/MeOH afforded a purple powder of $Os_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (21) (26 mg, 51%), m.p. >200°C. [Found: C, 27.27; H, 0.98; $C_{39}H_{20}O_{13}Os_5P_2$ requires: C, 27.40; H, 1.18%]. Infrared (cyclohexane): ν(CO) 2092m, 2070s, 2062s, 2040w, 2021vs, 2004w, 1994w, 1978w, 1968w, cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 7.42 (m, Ph).

Reaction of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) with $K[HBBu^s_3]$

A solution of (20) (50 mg, 0.04 mmol) in thf (5 ml) was treated with $[K(HBBu^s_3)]$ (0.10 ml of a 0.5 mol l^{-1} solution in thf, 0.05 mmol). After stirring at 25°C for 5 min H_3PO_4 (2 drops) was added and the solution was stirred for a further 5 min. The solvent was evaporated and the residue extracted with light petroleum (3 x 10 ml). The combined filtered extracts were evaporated and the residue recrystallized from CH_2Cl_2/MeOH to give black crystals of $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2,\underline{P}\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22) (12 mg, 24%), m.p. >200°C. [Found: C, 36.71; H, 1.43; $C_{39}H_{22}O_{13}P_2Ru_5$ requires C, 37.00, H, 1.75%]. Infrared (cyclohexane): ν(CO) 2084m, 2064s, 2029s, 2016s, 2002m, 1992vw, 1979m, 1965w, 1952w, cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 5.86 [d, _J_(PH) 6.0 Hz, 1H, CH], 7.42 (m, 20H, Ph), -13.11 [dd, _J_(PH) 13.8 and 21.5 Hz, 1H, RuH].

Reaction of $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (20) with CO

(A) At ambient temperature

(i) A solution of (20) (90 mg, 0.071 mmol) in cyclohexane (50 cm^3) was carbonylated in an autoclave (10 atm, 25°C, 36 h). The resulting red precipitate was collected by filtration, washed with cyclohexane (2 x 5 cm^3) and dried to give $Ru_5(\mu_5\text{-}\eta^2,\underline{P}\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}$ (23) (79 mg, 84%), m.p. 141-143°C (dec). [Found: C, 37.26; H, 1.26; $C_{41}H_{20}O_{15}P_2Ru_5$ requires C, 37.31; H, 1.53%]. Infrared (cyclohexane): ν(CO) 2112m, 2074m, 2060(sh), 2053s, 2044s, 2036(sh), 2018m, 2002s, 1987w, 1965w, 1954w cm^{-1}.

(ii) Carbon monoxide was passed through a solution of (20) (80 mg, 0.063 mmol) in cyclohexane (40 ml) for 6 h to give (23) as a red precipitate (66 mg, 79%). Identified by comparison of its i.r. ν(CO) spectrum with that of the sample prepared above.

(B) Under vigorous conditions Carbon monoxide was passed through a solution of (20) (150 mg, 0.119 mmol) in cyclohexane (70 ml) at 70°C for 18 h. Evaporation and preparative tlc (light petroleum-acetone 85/15) gave 2 bands: Band 1, R_f 0.40, black, recrystallised from CH_2Cl_2/MeOH to give black crystals of (20) (21 mg, 14%), identified by its infrared spectrum. Band 2, R_f 0.10, red, recrystallised from CH_2Cl_2/MeOH under a CO atmosphere to give red crystals of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{15}$ (24) (55 mg, 35%), m.p. 160-163°C (dec). [Found: C, 37.19; H, 1.56; $C_{41}H_{20}O_{15}P_2Ru_5$ requires C, 37.31; H, 1.53%]. Infrared (cyclohexane): ν(CO) 2100w, 2071m, 2067(sh), 2040s, 2037(sh), 2009w, 1999m, 1990w, 1983w, 1973w, 1966w, cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.15 (m, Ph).

Conversion of isomer (23) to isomer (24)

A solution of (23) (110 mg, 0.083 mmol) in benzene (50 ml) was carbonylated in an autoclave (12 atm, 70°C, 22 h). Evaporation of the red solution and recrystallisation of the residue from CH_2Cl_2/MeOH under a CO atmosphere gave red crystals of (24) (60 mg, 55%), identified by comparison of its i.r. ν(CO) spectrum with that of the sample prepared above.

CO loss from (23)

A solution of (23) (50 mg, 0.038 mmol) in CH_2Cl_2 (5 ml) was heated at reflux for 20 min. Addition of MeOH (5 ml) to the solution followed by concentration to _ca_ 5 ml and cooling to 0°C gave black crystals of (20) (43 mg, 90%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample.

Solutions of (23) readily revert to (20) within 2 h on standing at room temperature.

CO loss from (24)

A solution of (24) (50 mg, 0.038 mmol) in CH_2Cl_2 (10 ml) was heated at reflux for 7 h during which time the solution gradually darkened from red to black. Addition of MeOH (10 ml) and concentration to *ca* 10 ml and cooling to 0°C gave black crystals of (20) (30 mg, 63%), identified as above.

Reaction of $Ru_5(\mu_5-\eta^2,\underline{P}-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ with H_2

(A) Under 10 atm A solution of (20) (100 mg, 0.079 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (10 atm, 25°C, 18 h). The resulting burnt-yellow solution was evaporated to dryness and separated by preparative tlc (light petroleum-acetone 90/10) to give seven bands. Band 1, R_f 0.86 gave yellow $Ru_4(\mu-H_4)(CO)_{12}$ (9 mg, 16%) identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 3, R_f 0.48, yellow, recrystallised from CH_2Cl_2/MeOH to give yellow crystals of $Ru_4(\mu-H)_3(\mu_4-\eta^2,\underline{P}-HC_2PPh_2)$-$(\mu-PPh_2)(CO)_{10}$ (25) (52 mg, 63%), m.p. 161-164°C. [Found: C, 39.98; H, 2.23; $C_{36}H_{24}O_{10}P_2Ru_4$ requires C, 39.93; H, 2.23%]. Infrared (cyclohexane): ν(CO) 2097m, 2071s, 2038vs, 2024s, 2012m, 1987m, 1977m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.24 (m, 20H, Ph), 9.10 [dd, *J*(PH) 2.6 and 18.1 Hz, 1H, C_2H], -15.40 (m, 1H, RuH), -18.53 [dm, *J*(PH) 24.0 Hz, 1H, RuH], -19.00 [dm, *J*(PH) 18.9 Hz, 1H, RuH]. The remaining bands contained only trace amounts and were not identified.

(B) At normal pressure Hydrogen was passed through a solution of (20) (180 mg, 0.142 mmol) in refluxing cyclohexane (70 ml) for 5 h. Evaporation of the resulting red solution and preparative tlc (light petroleum-acetone 90/10) gave six bands. Band 1, R_f 0.81, yellow, $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (trace). Band 2, R_f 0.50, pink (trace), not identified. Band 3, R_f 0.45, yellow, recrystallised from CH_2Cl_2/MeOH to give yellow crystals of $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,\underline{P}\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$ (25) (2 mg, 1%). Band 4, R_f 0.40, brown $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2,\underline{P}\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22) (trace). Band 5, R_f 0.30, orange recrystallised from CH_2Cl_2/MeOH to give red crystals of $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}$(PMePh$_2$) (27) (93 mg, 54%), m.p. 155-157°C. [Found: C, 36.48; H, 1.86; $C_{37}H_{26}O_{11}P_2Ru_5$ requires C, 36.61; H, 2.16%]. Infrared (cyclohexane): ν(CO) 2085s, 2055vs, 2032vs, 2020vs, 2002m, 1994w, 1989w, 1979m, 1945w cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 1.88 [d, J(PH) 7.7 Hz, 3H, CH_3], 7.27 (m, 20H, Ph), -19.97 (m, 2H, RuH), -22.50 (dm, J(PH) 17.9 Hz, 1H, RuH). Band 6, R_f 0.22, orange, recrystallised from CH_2Cl_2/MeOH to give dark red crystals of $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (26) (41 mg, 23%), m.p. 165-169°C. [Found: C, 36.57; H, 1.59; $C_{39}H_{24}O_{13}P_2Ru_5$ requires: C, 36.97; H, 1.91%]. Infrared (cyclohexane) ν(CO) 2082m, 2058w, 2041m, 2028s, 2014(sh), 2004w, 1984m, 1977m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 5.04 (m, 2H, CH_2), 7.39 (m, 20H, Ph), -20.19 [dd, J(PH) 6.9 and 12.0 Hz, 2H, RuH]. Bands 1, 3 and 4 were identified by comparison of their i.r. ν(CO) spectra with those of authentic samples.

Shorter reaction times affords higher yields of (22) and (26) at the expense of (27).

Hydrogenation of $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2,\underline{P}\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (22)

In a similar reaction, hydrogenation of (22) in refluxing cyclohexane (45 min) afforded after preparative tlc $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (26) (53%) and $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)$-

$(CO)_{11}(PMePh_2)$ (27) (21%), identified by comparison of their i.r. ν(CO) spectra with those above.

Hydrogenation of $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (26)

In a similar reaction, hydrogenation of (23) in refluxing cyclohexane (2.5 h) afforded after crystallization $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ (27) in 53% yield, identified as above.

X-ray structure determinations of (23) and (24)

The general procedure has been outlined above. Suitable crystals of both complexes were obtained from CH_2Cl_2/MeOH under a CO atmosphere.

Crystal Data (23): $C_{41}H_{20}O_{15}P_2Ru_5$, M 1319.9, crystal size 0.65 x 0.33 x 0.29 mm, monoclinic, space group $P2_1/n$, a 11.661(2), b 17.312(4), c 22.377(2)Å, β 92.56(1)°, U 4512.8Å^3, D_m 1.92(2), D_c 1.94 g cm^{-3} for Z = 4, F(000) 2544, μ(Mo-Kα) 16.92 cm^{-1}, λ(Mo-Kα) 0.7107Å, scan type ω(1/3)θ, ω scan angle (2.0 + 0.35 tan θ)°, horizontal aperture (2.4 + 0.5 tan θ)mm; Data: 6002 unique reflections collected in the range $3<2\theta<46°$, with 5406 having $I>2.5\sigma(I)$ being used in the refinement. Absorption corrections were not applied. R = 0.029, R_w = 0.038, where $w = 1.00[\sigma^2(F_o) + 0.0009\,F_o{}^2]^{-1}$.

(24): $C_{41}H_{20}O_{15}P_2Ru_5$, M 1319.9, crystal size 0.40 x 0.28 x 0.16 mm, monoclinic, space group $P2_1/c$, a 11.496 (2), b 23.749(4), c 16.705(3)Å, β 93.44(2)°, U 4552.6Å^3, D_m 1.92(2), D_c 1.93 g cm^{-3} for Z = 4, F(000) 2544, μ(Mo-Kα) 16.92 cm^{-1}; λ(Mo-Kα) 0.7107Å, scan type ω(2/3)θ, ω scan angle (1.8 + 0.35 tan θ)°, horizontal aperture (2.4 + 0.5 tan θ)mm; Data: 4610 unique reflections collected in the range $2.6<2\theta<42°$, with 3879 having $\underline{I}>2.5\sigma(\underline{I})$ used in the refinement after correction for absorption. $\underline{R} = 0.029$, $\underline{R}_{\underline{w}} = 0.038$, where $\underline{w} = 1.95[\sigma^2(\underline{F}_o) + 0.0006\ \underline{F}_o{}^2]^{-1}$.

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CHAPTER TWO

SYNTHESIS AND REACTIVITY OF $M_3(CO)_{10}(sp)$ (M = Ru, Os)

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INTRODUCTION

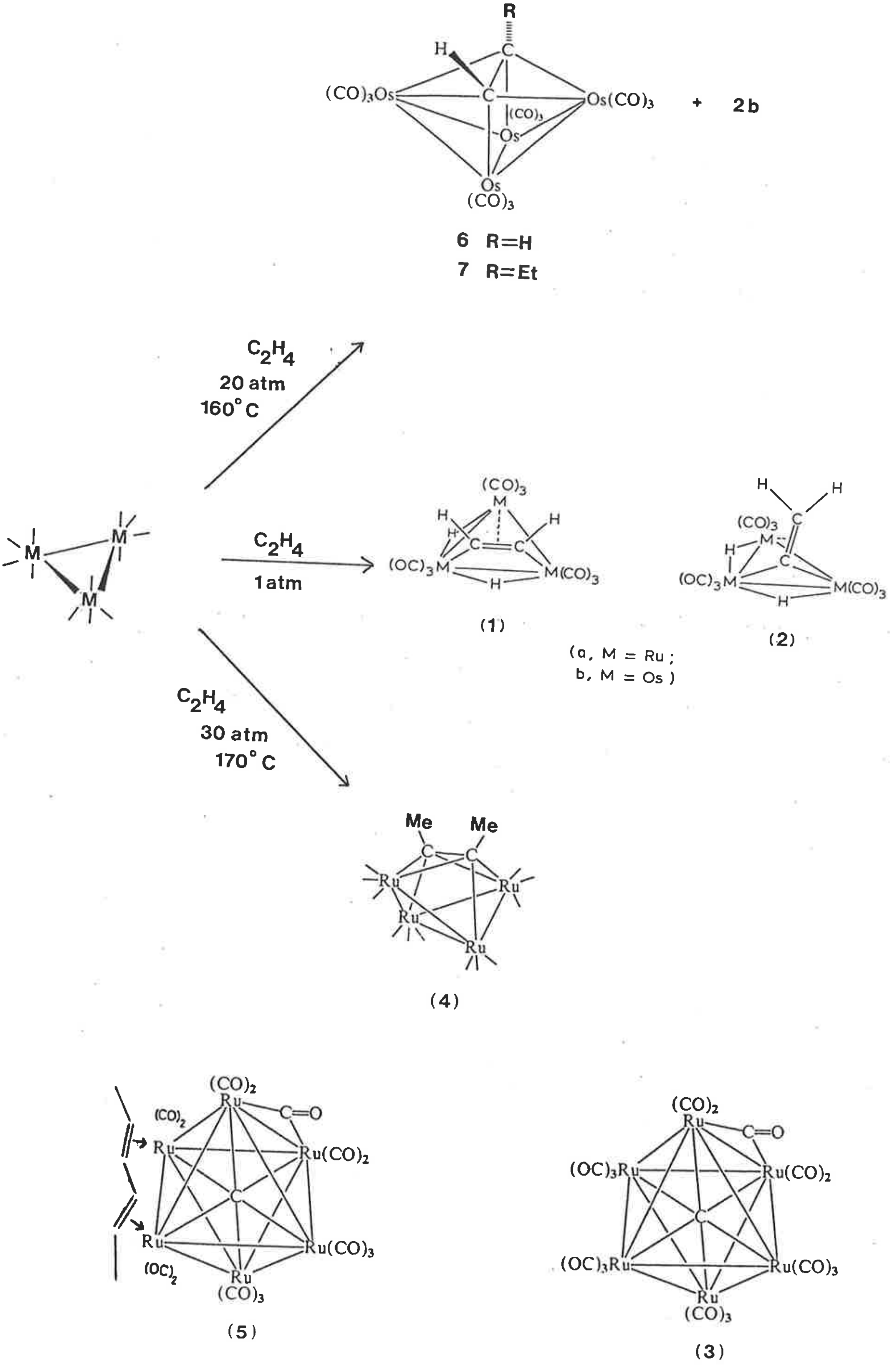
Dehydrogenation of ethylene by $Ru_3(CO)_{12}$ at atmospheric pressure has been reported to afford the isomeric complexes $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CH)(CO)_9$ (1a) and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(CO)_9$ (2a) (Scheme 1),[1] although a more recent paper[2] described the formation of (1a), together with the mononuclear complex $Ru_3(CO)_4(\eta\text{-}C_2H_4)$ and complexes containing oligomers of the olefin. The trinuclear osmium analogues (1b) and (2b) have been obtained from reactions between $Os_3(CO)_{12}$ and ethylene (1 atm).[3]

At higher temperatures and pressures ethylene reacts with $Ru_3(CO)_{12}$ to give $Ru_6C(CO)_{17}$ (3),[4] $Ru_4(\mu_4\text{-}\eta^2\text{-}MeC{\equiv}CMe)(CO)_{12}$ (4) and $Ru_6C(\mu\text{-}\eta^2,\eta^2\text{-}MeCH{=}CHCH{=}CHMe)(CO)_{15}$ (5),[5] while with $Os_3(CO)_{12}$ the complexes (2b), $Os_4(\mu_4\text{-}\eta^2\text{-}C_2H_2)(CO)_{12}$ (6) and $Os_4(\mu_4\text{-}\eta^2\text{-}C_2HEt)(CO)_{12}$ (7) are formed.[6]

The above products are believed to be formed via the intermediate complexes $M_3(CO)_{11}(\eta^2\text{-}C_2H_4)$ (M = Ru, Os) however these type of complexes have not been isolated from these reactions because of the vigorous conditions necessary to initiate them. The osmium analogue, $Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)$ (8), which is readily transformed to the μ_3-vinylidene complex (2b), can be obtained under relatively mild conditions from ethylene and $Os_3(CO)_{11}(NCMe)$[7] or by the action of Me_3NO on $Os_3(CO)_{12}$ in the presence of ethylene.[8]

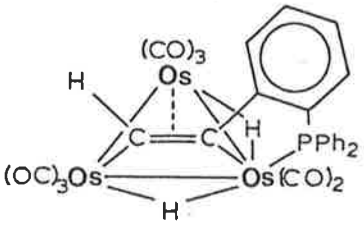
Several years ago it was reported that the olefinic tertiary phosphine 2-styryldiphenylphosphine ($2\text{-}Ph_2PC_6H_4CH{=}CH_2$, sp) reacted with $Ru_3(CO)_{12}$ to give the mononuclear complexes $Ru(CO)_3(sp)$ and $Ru(CO)_2(sp)_2$ (in refluxing octane) and $Ru(CO)(sp)_2$, $Ru(CO)_2[Ph_2PC_6H_4CH(CH_2)_2CHC_6H_4PPh_2]$ and

Scheme 1


R
H
C
(CO)3Os
Os(CO)3
(CO)3
Os
+ 2b
6 R=H
7 R=Et
C2H4
20 atm
160° C
M
C2H4
1 atm
(CO)3
H
C=C
(OC)3M
M(CO)3
(1)
(2)
(a, M = Ru ;
b, M = Os)
C2H4
30 atm
170° C
Me
Me
Ru
(4)
(CO)2
C=O
Ru(CO)2
Ru(CO)3
(OC)2
(5)
(OC)3Ru
(3)

$Ru(CO)(Ph_2PC_6H_4CH{=}CH{-}CH{=}CHC_6H_4PPh_2)$ (in refluxing nonane).[9] A transient deep reddish-purple colouration was reported before the colour lightened to orange or yellow. A later report[10] describes the isolation of the trinuclear complex $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (9) in low yield from the reaction of $Os_3(CO)_{12}$ and sp in refluxing octane.

With the advent of mild synthetic routes to the substitution products of $Ru_3(CO)_{12}$, initiated by the addition of small amounts of sodium diphenylketyl,[11] and of $Os_3(CO)_{12}$, via $Os_3(CO)_{12-n}(NCMe)_n$ (n = 1,2),[7] we decided to reinvestigate the reactions of these complexes with sp to establish the early course of the reactions leading to the mononuclear complexes or the hydrido triosmium complex (9).



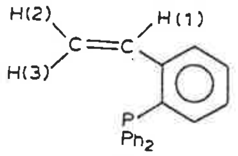
(9)

RESULTS AND DISCUSSION

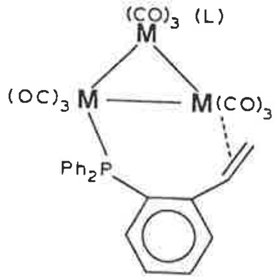
The reaction between $Ru_3(CO)_{12}$ and sp in tetrahydrofuran at room temperature was initiated by the dropwise addition of a solution of sodium diphenylketyl, and the solution rapidly darkened in colour to deep red. Crystallisation of the reaction mixture afforded red $Ru_3(CO)_{10}(sp)$ in 74% yield, readily identified as (10) by analytical and spectroscopic techniques, with the final stereochemical details being supplied by a single-crystal X-ray diffraction study. In the ^1H n.m.r. spectrum the presence of an η^2-complexed $CH_2{=}CH$ fragment was shown by three equal intensity resonances at δ 2.51d, 3.24d and 4.90dd assigned to H(2), H(3) and H(1) respectively (Table 1). These resonances have similar chemical shifts to those found in $Ru(CO)_3(sp)$ (δ 1.62, 2.45 and 3.96),[9] but are quite distinct from those of a non-complexed vinyl group, which appear at lower fields. There are no resonances from metal-bonded protons.

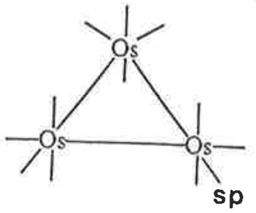
The molecular structure of (10) is shown in Figure 1 (see also Table 2) and consists of an Ru_3 cluster containing an unaltered sp ligand bridging the Ru(1)-Ru(2) bond, the P and C=C groups occupying adjacent equatorial sites. The $CH{=}CH_2$ group is displaced from the phenyl ring plane by 9.7°, and the plane C(42)-C(1)-C(2) is inclined at 72° to the Ru_3 plane. The C=C vector is nearly parallel to the Ru_3 plane and displaced by 0.2Å from it; the P atom lies in the Ru_3 plane. The Ru(2)-C(1) and Ru(2)-C(2) bond lengths are equal within the precision of the experiment, at 2.24Å (average), while the C(1)-C(2) bond [1.44(3)Å] is, as expected, intermediate in length between normal C-C single and C=C double bonds.

Table 1 ^{1}H n.m.r. data for the vinyl group of the sp ligand.

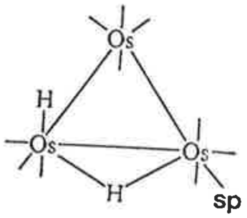


sp





(**12**)



(**13**)

(10) M=Ru L=CO
(14) M=Ru L=CNBu^t
(11) M=Os L=CO

Compound	Chemical shifts^a δH(1)	δH(2)*	δH(3)*	Coupling constants^b J(12)	J(13)	J(23)
sp	c	4.99dd	5.45dt	11.0	17.5	1.3
$RuBr_2(sp)_2$^{d}	3.30	2.08	3.11	9.0	12.5	<1
$Ru_3(CO)_{10}(sp)$ (10)	4.90dd	2.51d	3.24d	8.5	12.5	-
$Os_3(CO)_{10}(sp)$ (11)	4.71dd	2.21dd	2.87dd	8.0	19.5	2.5
$Os_3(CO)_{11}(sp)$ (12)	6.76dd	5.11d	5.68d	11.0	17.0	-
$Os_3(H)_2(CO)_{10}(sp)$ (13)	6.73dd	5.18d	5.67d	11.0	17.0	-
$Ru_3(CO)_9(sp)(CNBu^t)$ (14)	4.65dd	2.38d	3.07d	8.0	11.5	-

Measured in $CDCl_3$. a In ppm. b In Hz. c Obscured by aromatic resonances. d Ref 12.

*The assignment of H(2) and H(3) has been made on the basis of J(13) (trans-olefinic coupling) being greater than J(12) (cis-olefinic coupling).[12,13]

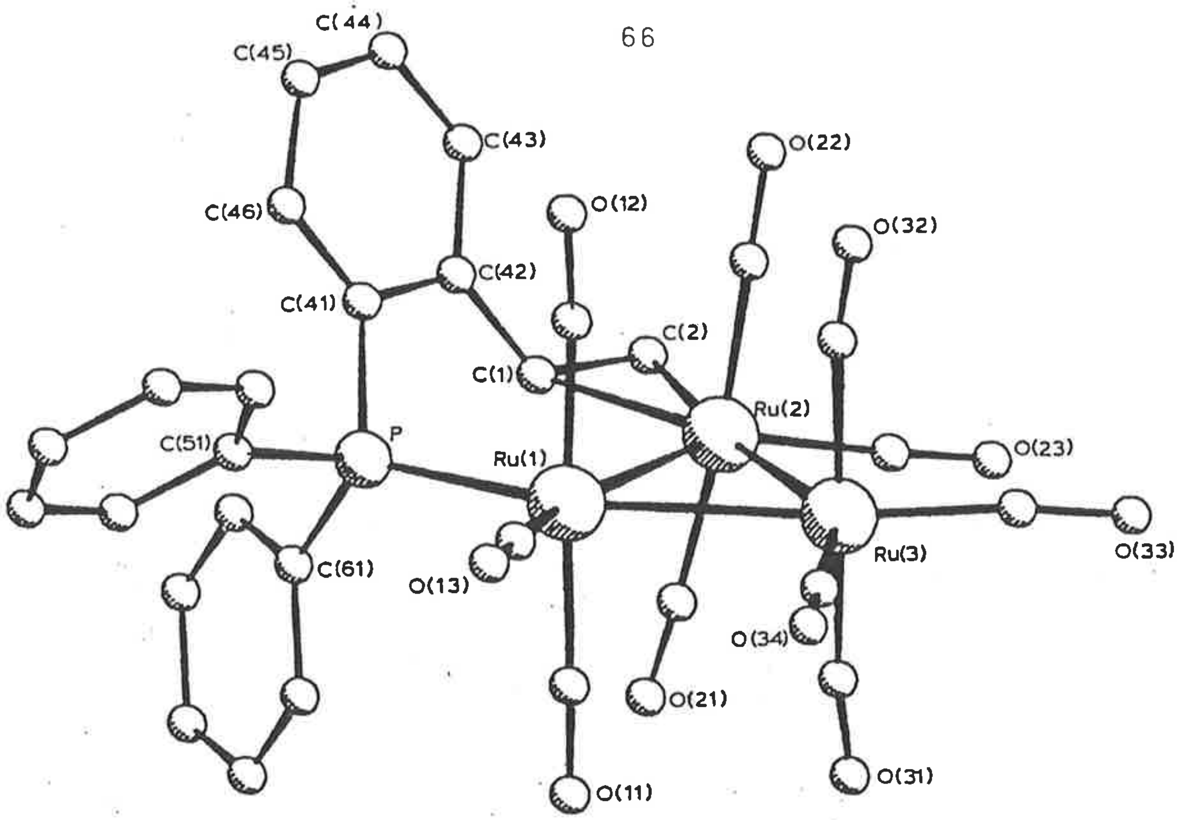


Figure 1: PLUTO plot of $Ru_3(CO)_{10}(sp)$ (10), showing the atom numbering scheme (by B.K. Nicholson)

Table 2: Selected bond lengths and angles for (10)

Bond lengths (Å)			
Ru(1)–Ru(2)	2.855(2)	C(1)–C(42)	1.44(2)
Ru(1)–Ru(3)	2.834(2)	C(41)–C(42)	1.46(3)
Ru(2)–Ru(3)	2.871(2)	C(42)–C(43)	1.44(2)
Ru(1)–P	2.348(5)	C(43)–C(44)	1.37(3)
Ru(2)–C(1)	2.25(2)	C(44)–C(45)	1.33(3)
Ru(2)–C(2)	2.23(2)	C(45)–C(46)	1.41(2)
C(1)–C(2)	1.44(3)	C(41)–C(46)	1.36(2)
P–C(41)	1.82(1)		
P–C(51)	1.84(1)		
P–C(61)	1.83(1)		
Ru–CO range from 1.86(2)–1.94(2) (average 1.91)			
C–O range from 1.10(2)–1.18(3) (average 1.15)			
Bond angles (°)			
Ru(1)–Ru(2)–Ru(3)	59.3(1)	C(1)–C(42)–C(41)	121.4(13)
Ru(2)–Ru(1)–Ru(3)	60.6(1)	C(42)–C(41)–P	118.3(11)
Ru(1)–Ru(3)–Ru(2)	60.1(1)	C(42)–C(41)–C(46)	118.9(13)
Ru(1)–Ru(2)–C(1)	88.7(4)	Ru(1)–P–C(41)	110.1(6)
Ru(1)–Ru(2)–C(2)	126.2(6)	Ru(1)–P–C(51)	113.9(3)
Ru(3)–Ru(2)–C(1)	147.6(4)	Ru(1)–P–C(61)	121.6(4)
Ru(3)–Ru(2)–C(2)	172.9(6)	Ru(2)–Ru(1)–P	97.4(1)
Ru(2)–C(1)–C(2)	70.3(10)	Ru(3)–Ru(1)–P	157.9(1)
Ru(2)–C(1)–C(42)	119.9(11)	C(2)–Ru(2)–C(1)	37.5(7)
Ru(2)–C(2)–C(1)	72.2(10)	C(42)–C(1)–C(2)	125.5(14)
		C(43)–C(42)–C(1)	123.3(16)
		C(41)–C(42)–C(43)	115.4(15)
Dihedral angles (°)			
Ru(1)–Ru(2)–Ru(3)/C(1)–C(2)–C(42)			72.0
Ru(1)–Ru(2)–Ru(3)/C(41)···C(46)			66.5
C(1)–C(2)–C(42)/C(41)···C(46)			9.7

No evidence was obtained for the formation of either the P-bonded or η^2-bonded isomers of a putative intermediate $Ru_3(CO)_{11}(sp)$.

The reaction between $Os_3(CO)_{10}(NCMe)_2$ with sp in heptane at 50°C afforded $Os_3(CO)_{10}(sp)$ (11) in moderate yield. This complex showed similar spectroscopic properties [i.r. ν(CO), ^1H n.m.r. (Table 1 and Experimental)] to those of (10) and undoubtedly has a similar structure.

Treatment of $Os_3(CO)_{11}(NCMe)$ with sp at room temperature afforded the P-bonded complex $Os_3(CO)_{11}(sp)$ (12) in 72% yield. This yellow complex was identified by elemental analysis and by the similarity of its i.r. ν(CO) spectrum to that of $Os_3(CO)_{11}(PPh_3)$.[7] The presence of the uncoordinated vinyl group was confirmed by the ^1H n.m.r. spectrum (Table 1); the olefinic protons appear at lower field than those found for the complexes (10) and (11).

The purple solution of the coordinatively unsaturated cluster $Os_3(\mu-H)_2(CO)_{10}$ in CH_2Cl_2 rapidly turns yellow upon addition of sp. Thin-layer chromatographic separation afforded yellow $Os_3(\mu-H)(H)(CO)_{10}(sp)$ (13) in 66% yield together with a small amount of a second yellow product which has not presently been identified. The i.r. ν(CO) spectrum of the major product closely resembles those found in other $Os_3(\mu-H)(H)(CO)_{10}L$ complexes [L = PPh_3,[14,15] PMe_2Ph,[14,15] and $P(OMe)_3$[16]]. The ^1H n.m.r. spectrum contains three characteristic signals at similar chemical shifts to those found in complex (12) (Table 1) for the uncoordinated vinyl group. The existence of the bridging and terminal hydride ligands, which are fluxional at room temperature, were revealed at 244 K at δ -19.76dd [J(H-H)

3.5 Hz, J(HP) 11.0 Hz] and δ -10.10d respectively. The precise stereochemistry of (13) was confirmed by an X-ray diffraction study.

The crystal of (13) consists of discrete molecules, and there are no intermolecular contacts shorter than Van der Waals separations. The molecular structure, which is similar to that found in $Os_3(\mu\text{-}H)(H)(CO)_{10}(PPh_3)$,[17] is shown in Figure 2 (see also Table 3). The three osmium atoms define a triangular cluster core with bond lengths Os(1)-Os(2) 3.018(1)Å, Os(1)-Os(3) 2.911(1)Å, and Os(2)-Os(3) 2.854(1)Å. The sp ligand is located in an equatorial site bonded to Os(1) [2.374(2)Å] as a monodentate phosphorus donor. The ten terminal CO groups are arranged such that Os(3) is associated with four, while Os(1) and Os(3) have three each. Although the hydride ligands were not located in the structural study, their positions may be deduced by the Os-Os separations and the geometry of the sp and CO ligands. Thus, the edge bridging hydride (H_B) is located in the equatorial plane displaced outward from the Os(1)-Os(2) bond for the following reasons: the Os(1)-Os(2) distance is significantly longer than the other two Os-Os distances, while the equatorial ligands P(1) and CO(21) are splayed out to form the usual cavity associated with bridging hydride ligands, the location of the terminal hydride (H_T) is the seemingly empty axial site on Os(2) trans to CO(23). The C(1)-C(2) bond [1.23(4)Å] is, within the precision of the experiment, consistent with a C=C double bond. The large e.s.d. associated with this bond length is in part the result of very high thermal motion associated with the terminal vinyl carbon C(2).

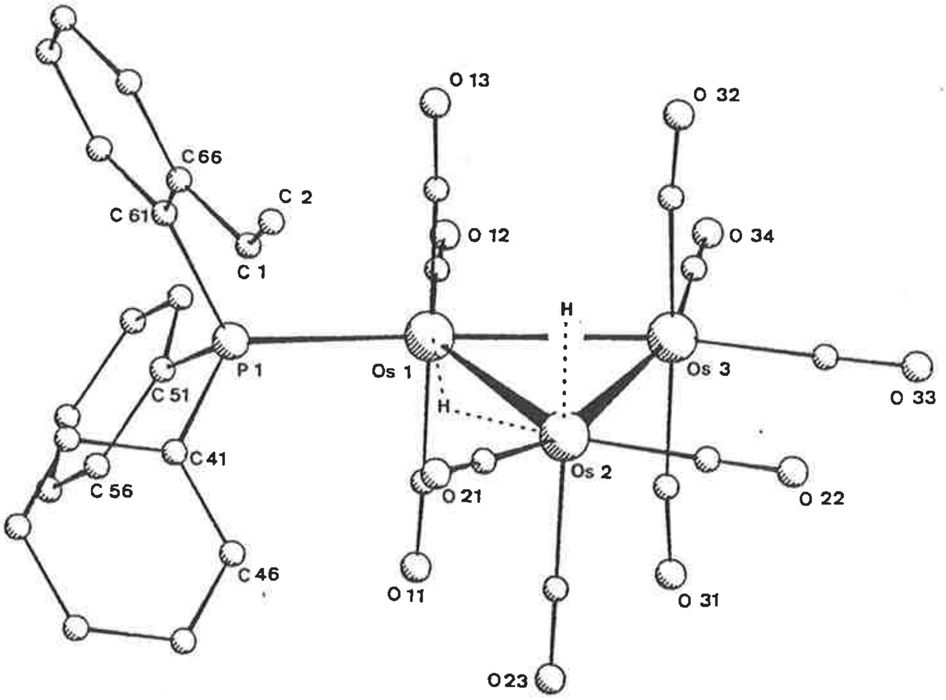


Figure 2. PLUTO plot of $Os_3(\mu\text{-}H)(H)(CO)_{10}(sp)$ (13), showing the atom numbering scheme.

Table 3 Selected bond lengths and angles for (13)

Bond lengths (Å)

Os(1)–Os(2)	3.018(1)	P(1)–C(41)	1.828(5)
Os(1)–Os(3)	2.911(1)	P(1)–C(51)	1.834(8)
Os(2)–Os(3)	2.854(1)	P(1)–C(61)	1.843(6)
Os(1)–P(1)	2.374(2)	C(1)–C(2)	1.23(4)
Os(2)...C(1)	4.01(1)	C(1)–C(66)	1.49(1)

Os–CO range from 1.88(1)–1.96(1) (average 1.92)

C–O range from 1.13(2)–1.17(2) (average 1.45)

Angles (°)

Os(1)–Os(2)–Os(3)	59.4(3)	Os(1)–P(1)–C(51)	110.7(2)
Os(2)–Os(1)–Os(3)	57.5(1)	Os(1)–P(1)–C(61)	116.3(2)
Os(1)–Os(3)–Os(2)	63.1(1)	C(66)–C(1)–C(2)	127.4(13)
Os(2)–Os(1)–P(1)	115.8(1)	C(66)–C(1)–C(2)	121.9(4)
Os(3)–Os(1)–P(1)	173.2(1)	C(61)–C(66)–C(1)	121.8(7)
Os(1)–P(1)–C(41)	117.2(2)		

Os–C–O range from 174.6(8)–178.7(13) (average 176.6)

Reactions of $Ru_3(CO)_{10}(sp)$ (10)

With $CNBu^t$: Attempts to prepare the more highly substituted derivatives $Ru_3(CO)_9(sp)_2$ or $Ru_3(CO)_8(sp)_2$ by the sodium diphenylketyl initiated reaction between $Ru_3(CO)_{10}(sp)$ (10) and sp met with no success. However, addition of the initiator to an equimolar mixture of $Ru_3(CO)_{11}(CNBu^t)$ and sp afforded, after chromatography, the mixed ligand complex $Ru_3(CO)_9(CNBu^t)(sp)$ (14) in 18% yield, together with (10) and unreacted $Ru_3(CO)_{11}(CNBu^t)$. Complex (14), which can also be prepared in low yield (*ca* 1-5%) from the addition of sodium diphenylketyl to a mixture of (10) and $CNBu^t$, was identified by the usual combination of analytical and spectroscopic techniques (see Table 1 and Experimental). The formation of (10) from the former reaction is not an unexpected result when we recall that $Ru_3(CO)_{11}(CNBu^t)$ reacts readily with donor ligands L by displacement of CO or $CNBu^t$ to give $Ru_3(CO)_{10}(CNBu^t)(L)$ and $Ru_3(CO)_{11}(L)$ respectively [L = $CNBu^t$, PPh_3, PCy_3, $AsPh_3$, and $P(C_6H_4Me\text{-}p)_3$].[18]

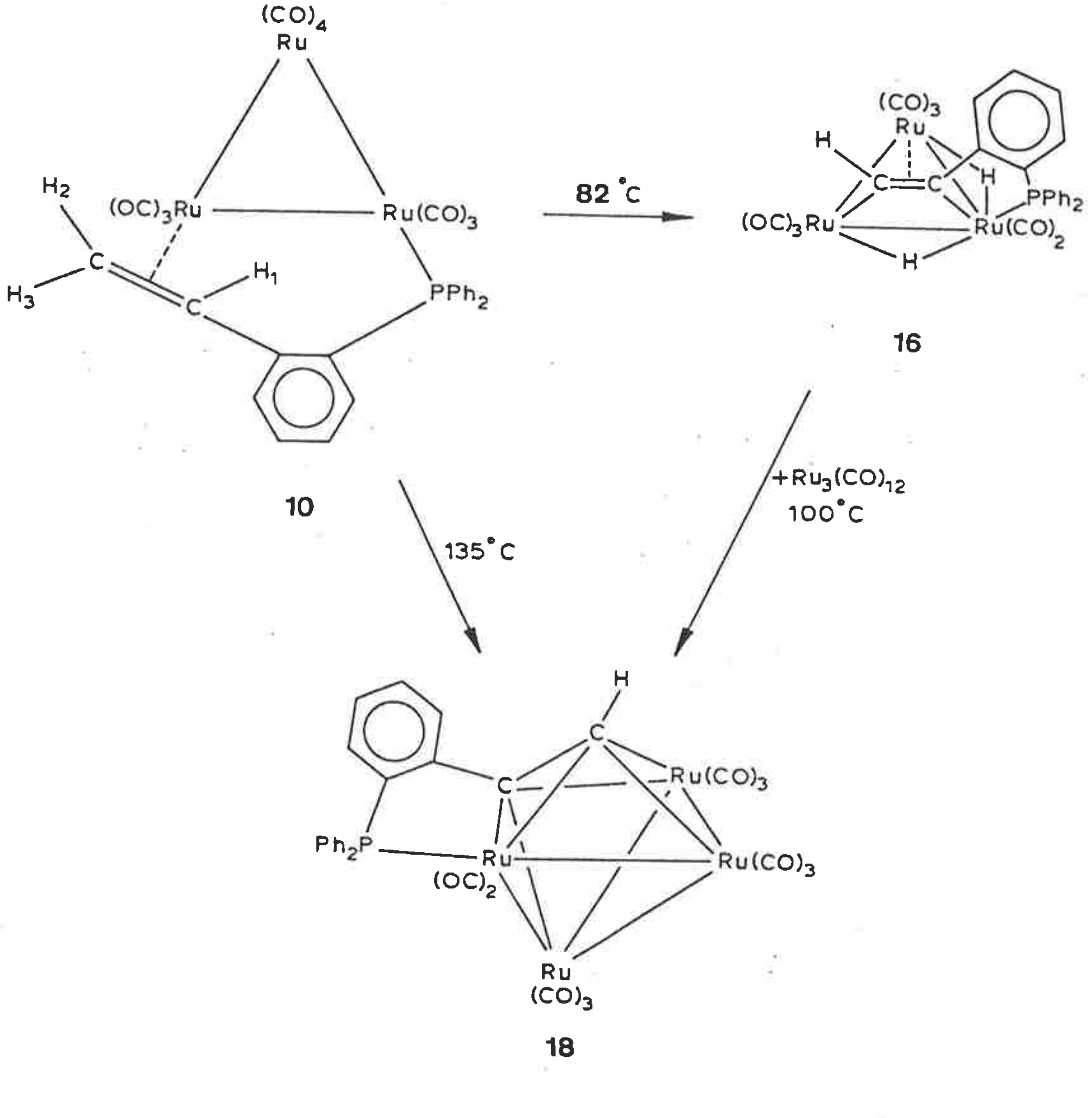
With hydrogen: The reaction of $Ru_3(CO)_{10}(sp)$ (10) with hydrogen (20 atm, 50°C, 2 h) proceeded readily to give $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and $Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_2C_6H_4Et\text{-}2)$ (15), together with a number of unidentified products. Characterisation of (15) rests on its spectroscopic properties, supported by elemental microanalysis. The i.r. spectrum of (15) contained the characteristic $\nu(CO)$ bands associated with other $Ru_4(\mu\text{-}H)_4(CO)_{11}(L)$ [L = PPh_3,[19,20] $PPh(OMe)_2$,[20] $P(OMe)_3$,[21,20] and $AsPh_3$ [20]] derivatives. In the ^1H n.m.r. spectrum, the presence of the *ortho*-Et fragment was shown by two resonances, a triplet at δ 0.98 and a multiplet at δ 2.51 of relative intensities 3/2. At high-field, a four proton doublet at δ -17.29 [J(PH) 4.5 Hz] was readily assigned to the bridging hydride ligands coupled to phosphorus.

The formation of (15) probably results from initial oxidative addition of hydrogen to the cluster followed by hydrogen transfer to the coordinated vinyl group to give the resultant ethyl fragment. Aggregation to give the hydrido Ru_4 core geometry will be discussed in greater detail in the following chapter.

Thermolysis of $Ru_3(CO)_{10}(sp)$ (10)

Short heating of $Ru_3(CO)_{10}(sp)$ (10) in refluxing cyclohexane gives the yellow complex (16) as the major product, together with small amounts of $Ru_3(CO)_{12}$, a second yellow complex (17) and three purple products which were not identified. The major product analyses for $Ru_3(CO)_8(sp)$, corresponding to a loss of two CO groups from (10). The ^1H n.m.r. spectrum contains a characteristic low-field signal at δ 10.14, assigned to a C≡CH group [cf. similar low-field resonances in $Os_3(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-}CO)(CO)_9$ at δ 9.67, and in $Os_3(\mu\text{-}H)_2(\mu_3\text{-}HCCMe)(CO)_9$ at δ 7.30[22]], together with a broad high-field singlet of relative intensity 2H at δ -17.7. These data suggest that the formation of this complex occurs by migration of two hydrogen atoms from the vinyl group to the Ru_3 cluster, with concomitant bridging of the three metal atoms by the alkyne unit so formed (Scheme 2). The structure thus corresponds to $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2\text{-}2)(CO)_8$ (16), and the precise stereochemistry was confirmed by an X-ray diffraction study.

Scheme 2


(CO)$_4$ Ru
(OC)$_3$Ru
Ru(CO)$_3$
H$_2$
H$_3$
C
C
H$_1$
PPh$_2$
10
82 °C
(CO)$_3$ Ru
H
C
C
H
PPh$_2$
(OC)$_3$Ru
Ru(CO)$_2$
H
16
135 °C
+Ru$_3$(CO)$_{12}$
100 °C
H
C
C
Ru(CO)$_3$
Ph$_2$P
Ru
(OC)$_2$
Ru(CO)$_3$
Ru (CO)$_3$
18

A PLUTO plot of (16) is shown in Figure 3 [see also Table 4]. In this complex the vinyl group of the sp ligand has been dehydrogenated to an ethynyl group which is now attached to all three metal atoms by means of σ-type interactions of C(1) and C(2) with Ru(3) and Ru(1), respectively, and a π-type interaction of C(1)-C(2) with Ru(2). The C_2 unit is thus attached in the familiar $(2\sigma + \pi)$, or μ_3-η^2, mode. The Ru-C σ-bonds are 2.085(6), 2.098(7)Å, while the distances of C(1) and C(2) from Ru(2) (2.262, 2.289(7)Å), are longer, and close to those of the η^2-vinyl-Ru group in (10). The phosphorus atom occupies an equatorial site, but is displaced by 0.80Å out of the Ru_3 plane. The C(1)-C(2) vector still lies effectively within the phenyl ring plane which is now inclined at 113° to the Ru_3 core; the displacements of C(1) and C(2) from the C_6 ring plane are 0.16 and 0.11Å, respectively. The C(1)-C(2) vector is almost parallel (5.1°) to the Ru(1)-Ru(3) edge. The Ru_3 cluster core contains one short Ru-Ru bond, at 2.731(1)Å, one of medium length, at 2.874(1)Å, and a long bond, at 3.021(1)Å. The latter is bridged by the alkyne (C_2) group, while the other two are bridged by only one carbon. The hydrogen atoms were not located in the structural study, but their chemical shift, and the Ru-Ru separations, suggest that they bridge Ru(1)-Ru(2) and Ru(1)-Ru(3). The single high-field resonance, considerably broadened, indicates that they equilibrate rapidly on the n.m.r. timescale. These locations are also consistent with the positions of the CO groups, which are splayed out to form the usual cavities which are occupied by the hydrogens. The Ru-P separation [2.303(2)Å] is a conventional 2e-donor interaction of a tertiary phosphine with

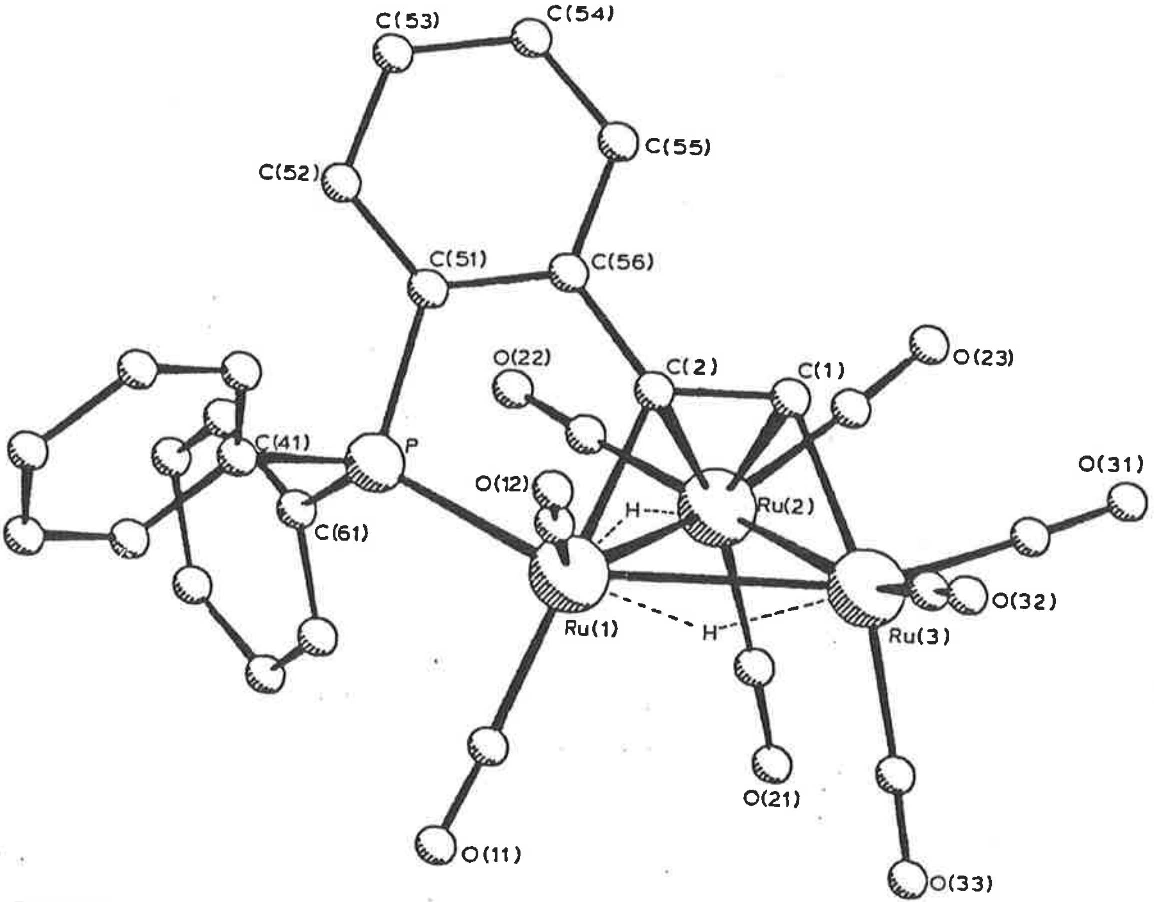


FIGURE 3: PLUTO plot of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}HC\equiv CC_6H_4PPh_2)(CO)_8$ (16) (by B.K. Nicholson)

Table 4: Selected bond lengths and angles for (16)

Bond lengths (Å)	Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.874(1)	2.871(1)
Ru(2)–Ru(3)	2.731(1)	2.736(1)
Ru(1)–Ru(3)	3.021(1)	3.016(1)
Ru(1)–C(2)	2.098(7)	2.104(9)
Ru(2)–C(2)	2.262(7)	2.278(6)
Ru(2)–C(1)	2.289(7)	2.293(6)
Ru(3)–C(1)	2.085(6)	2.083(7)
Ru(1)–P	2.303(2)	2.301(2)
C(2)–C(56)	1.478(8)	1.498(9)
P–C(41)	1.816(6)	1.816(6)
P–C(51)	1.826(7)	1.818(8)
P–C(61)	1.844(4)	1.825(3)
Bond angles (°)		
Ru(1)–Ru(2)–Ru(3)	65.2(1)	65.0(1)
Ru(1)–Ru(3)–Ru(2)	59.7(1)	59.6(1)
Ru(2)–Ru(1)–Ru(3)	55.1(1)	55.3(1)
Ru(1)–C(2)–Ru(2)	82.4(2)	81.8(2)
Ru(3)–C(1)–Ru(2)	77.1(2)	77.2(2)
Ru(3)–C(1)–C(2)	114.5(5)	113.5(6)
Ru(1)–C(2)–C(1)	111.4(4)	112.4(5)
Ru(1)–C(2)–C(56)	119.9(6)	118.7(6)
C(1)–C(2)–C(56)	128.2(7)	128.4(8)
Dihedral angles (°)		
Ru(1)–Ru(2)–Ru(3)/C(1)–C(2)–C(56)	115.1	115.9
Ru(1)–Ru(2)–Ru(3)/C(51) ··· C(56)	112.6	112.5
C(1)–C(2)–C(56)/C(51) ··· C(56)	4.5	4.1

the metal atom.

Complex (17), which was obtained as a minor product from the thermolysis of $Ru_3(CO)_{10}(sp)$ (10), is also formed, together with $Ru_3(CO)_{12}$, from the reaction of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) with CO (5 atm, 80°C). The relatively pale colour and simple i.r. ν(CO) spectrum suggested that (17) was a complex of low nuclearity. This was confirmed by the mass spectrum, which contained ions $[\underline{M}\text{-Me-}\underline{n}CO]^+$ (n = 0-6), where $\underline{M} = Ru_2(CO)_6(sp)$. However, the ^1H n.m.r. spectrum contained only two resonances, a doublet at δ 3.1 and a complex well-resolved multiplet between δ 6.4-8.0, of relative intensities 3/14. Considering the origin of the phosphine ligand, and the ready loss of a CH_3 group from the molecular ion, it was reasonable to assign the former signal to a CH_3 group coupled to the ^{31}P nucleus: evidently the original vinyl group had isomerised, probably to a CMe function. This was confirmed by an X-ray structural determination, which also enabled a rationalisation of the broad, finely-structured aromatic resonance.

The structure of $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17) is shown in Figure 4 (see also Table 5). The complex consists of two $Ru(CO)_3$ groups connected by a Ru-Ru bond (2.790Å) which is bridged by the rearranged sp ligand. This is coordinated to Ru(1) by the phosphorus atom, and to Ru(2) by an η^3-allylic interaction involving C(1), C(6) and C(7); C(7) is also η^1-bonded to Ru(1). Each ruthenium atom has approximately octahedral coordination, and has a formal 18 electron count, each of the metal atoms also being ligated by three CO groups. An alternative interpretation is in terms of C(7)

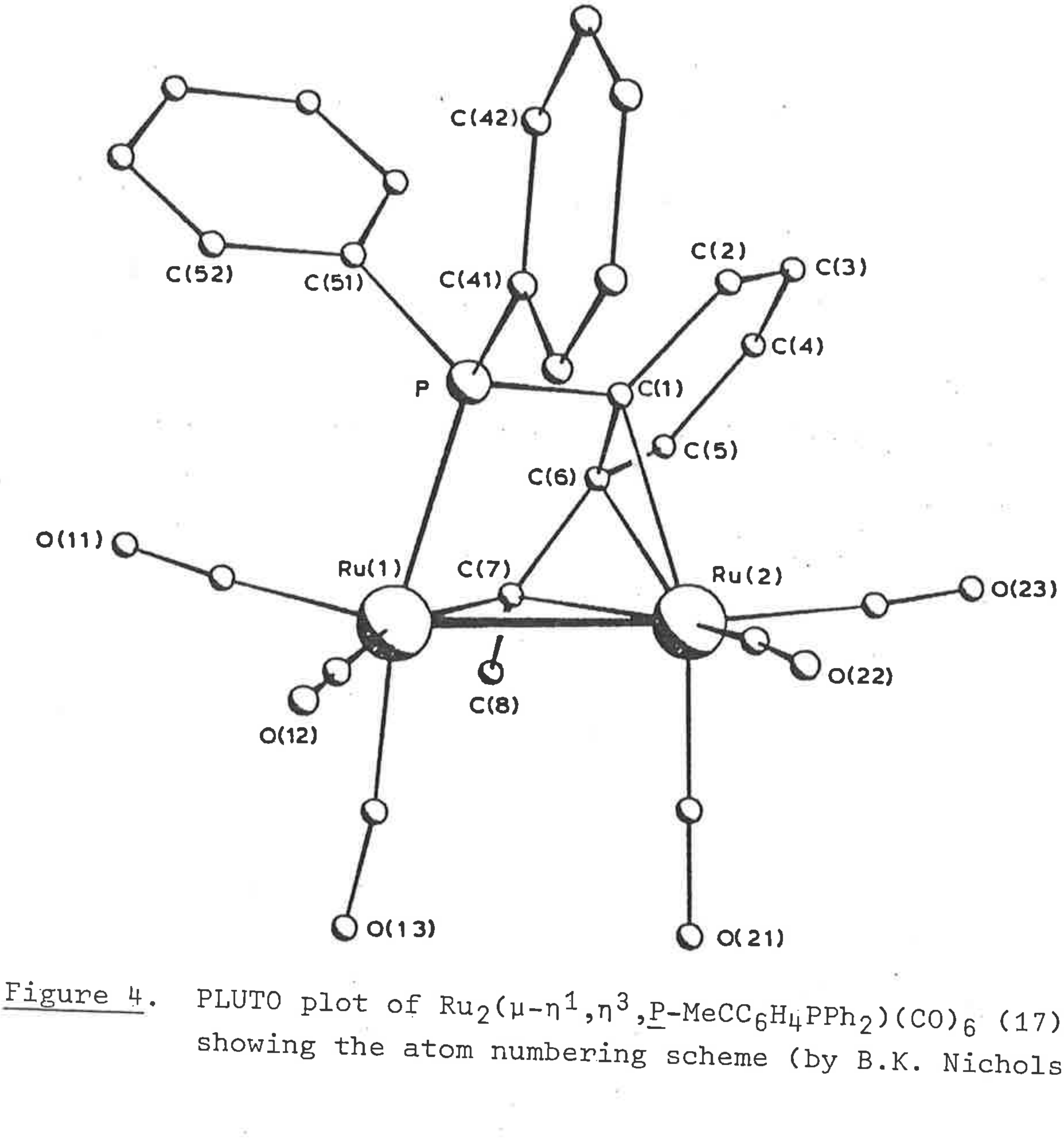


Figure 4. PLUTO plot of $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17), showing the atom numbering scheme (by B.K. Nicholson)

Table 5: Selected bond lengths and angles for $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17).

Bond lengths (Å)	Molecule 1	Molecule 2	Molecule 3
Ru(1)-Ru(2)	2.796(3)	2.786(3)	2.789(3)
Ru(1)-P	2.334(6)	2.336(7)	2.343(7)
Ru(1)-C(7)	2.17(2)	2.09(3)	2.12(2)
Ru(1)-C(1)	2.33(2)	2.29(2)	2.28(2)
Ru(2)-C(6)	2.23(2)	2.24(3)	2.22(3)
Ru(2)-C(7)	2.18(2)	2.20(3)	2.12(2)
P-C(1)	1.80(2)	1.84(3)	1.77(2)
C(1)-C(6)	1.43(3)	1.43(4)	1.39(3)
C(6)-C(7)	1.37(3)	1.44(4)	1.46(3)
C(7)-C(8)	1.48(3)	1.64(4)	1.52(4)

Angles (°)			
Ru(2)-Ru(1)-P	72.5(2)	73.5(2)	73.8(2)
Ru(2)-Ru(1)-C(7)	50.2(6)	51.1(7)	52.2(6)
P-Ru(1)-C(7)	80.4(6)	81.3(7)	82.2(6)
Ru(1)-Ru(2)-C(1)	76.7(6)	76.7(6)	75.0(6)
Ru(1)-Ru(2)-C(6)	73.8(7)	75.3(7)	73.6(7)
Ru(1)-Ru(2)-C(7)	49.8(6)	47.9(7)	48.3(6)
C(1)-Ru(2)-C(6)	36.6(9)	36.9(9)	36.0(8)
C(1)-Ru(2)-C(7)	65.3(6)	65.2(9)	65.6(8)
C(6)-Ru(2)-C(7)	36.1(9)	37.9(10)	38.0(9)
Ru(1)-P-C(1)	100.5(8)	98.2(8)	97.5(8)
P-C(1)-C(6)	110.3(18)	113.2(19)	113.4(17)
P-C(1)-Ru(2)	94.6(10)	96.1(10)	99.3(10)
C(1)-C(6)-C(7)	121(2)	115(2)	119(2)
C(5)-C(6)-C(7)	124(2)	130(2)	123(2)
C(6)-C(1)-Ru(2)	68.2(14)	69.6(14)	69.7(14)
C(1)-C(6)-Ru(2)	75.2(15)	73.5(15)	74.3(14)
C(6)-C(7)-C(8)	119(2)	114(2)	119(2)
C(6)-C(7)-Ru(1)	117.6(17)	121.4(19)	115.1(16)
C(6)-C(7)-Ru(2)	74.1(14)	72.6(15)	70.3(14)
Ru(1)-C(7)-Ru(2)	80.0(8)	81.0(9)	79.4(8)

acting as a bridging methylene carbon atom and the C(1)-C(6) bond coordinated via a two-electron π-donor interaction to Ru(2). The distances between Ru(2) and the three coordinated carbon atoms are more closely similar than in other η^3-benzyl complexes. Thus the difference between the Ru-C(1) and Ru-C(7) bonds is only 0.13Å, whereas the equivalent distances are 0.37Å in $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P(OMe)}_3]_3$,[23] 0.21Å in $(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_3)\text{-Mo(CO)}_2\text{Cp}$,[24] 0.36Å in $[\eta^3\text{-(CH}_3\text{C}_6\text{H}_4)_2\text{C]Mo}_2\text{(CO)}_4\text{Cp}_2$,[25] and 0.43Å in $[\text{PtW}(\eta^3\text{-CHC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_3)_2(\text{Cp})]^+$.[26] This indicates a strong interaction between Ru(2) and the ring carbon atoms. The phenyl ring is essentially planar (maximum deviation from the least-squares plane is 0.07Å); the exocyclic C(7) is twisted out of this plane by 0.18Å while the P atom is displaced by 0.8Å from the plane in the opposite sense. Averaged over all three independent molecules, the C(1)-C(6), C(2)-C(3) and C(4)-C(5) bonds are shorter than the other bonds in the ring suggesting that coordination of this group has localised the π-electron density in one of the valence-bond resonance forms of the benzene ring, although individual differences are not crystallographically significant.

The C(6)-C(7) bond (1.42Å) is indicative of a bond order less than one, consistent with the π-allyl bonding model. Similarly the C(6)-C(7)-C(8) angle of 117° is also consistent with the expected <u>sp</u>^{2} hydridisation at C(7).

The chelating mode of the phosphine ligand is apparently quite strained since the angles around the P atom differ markedly from tetrahedral values; the Ru(1)-P-C(1) value of 99° is particularly low while that to the free phenyl ring Ru(1)-P-C(41) at 124° is high.

The complex $Ru_3(CO)_{10}(sp)$ (10) is converted into the μ_4-alkyne derivative $Ru_4(\mu_4-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_{11}$ (18) (Scheme 2, p. 72) on heating for 4 h in an inert solvent. The latter complex is also formed on heating a mixture of $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) and $Ru_3(CO)_{12}$. Complex (18), which was characterised by an X-ray diffraction study, exhibits a characteristic singlet resonance at δ 9.57 for the C$\underline{H}$ proton of the alkynyl unit.

The unit cell of (18) contains two molecules of the complex, together with a disordered molecule of dichloromethane: there are no unusually short intermolecular contacts. A PLUTO plot of a molecule of (18) is shown in Figure 5. The structural study reveals few unusual features, apart from the anchoring of the alkyne unit to the Ru_4 butterfly via the $Ph_2PC_6H_4$ group. There are two other complexes containing the Ru_4C_2 core, namely $Ru_4(\mu_4-\eta^2-C_2R_2)(CO)_{12}$ [R = Me (4)[5] and Ph (19)[27]]; complexes of this type have long been known from the reactions between alkynes and ruthenium carbonyls.[28]

Selected bond lengths and angles for (18) are shown in Table 6, and where appropriate, corresponding values of the other Ru_4 complexes are also listed. As found previously, the Ru-Ru bonds of the Ru_4 butterfly embrace a set of four wing edges, ranging in lengths 2.722(1)-2.770(1)Å, and a longer 'hinge' bond of 2.823(1)Å, which is significantly shorter than that found in complex (4). The major difference between (18) and complexes (4) and (19) is the presence of the tertiary phosphine ligand attached to Ru(4), which significantly lengthens the Ru(1)-Ru(4) bond *trans* to P [to 2.770(1)Å], and to a lesser extent, the one *cis* to the phosphorus ligand

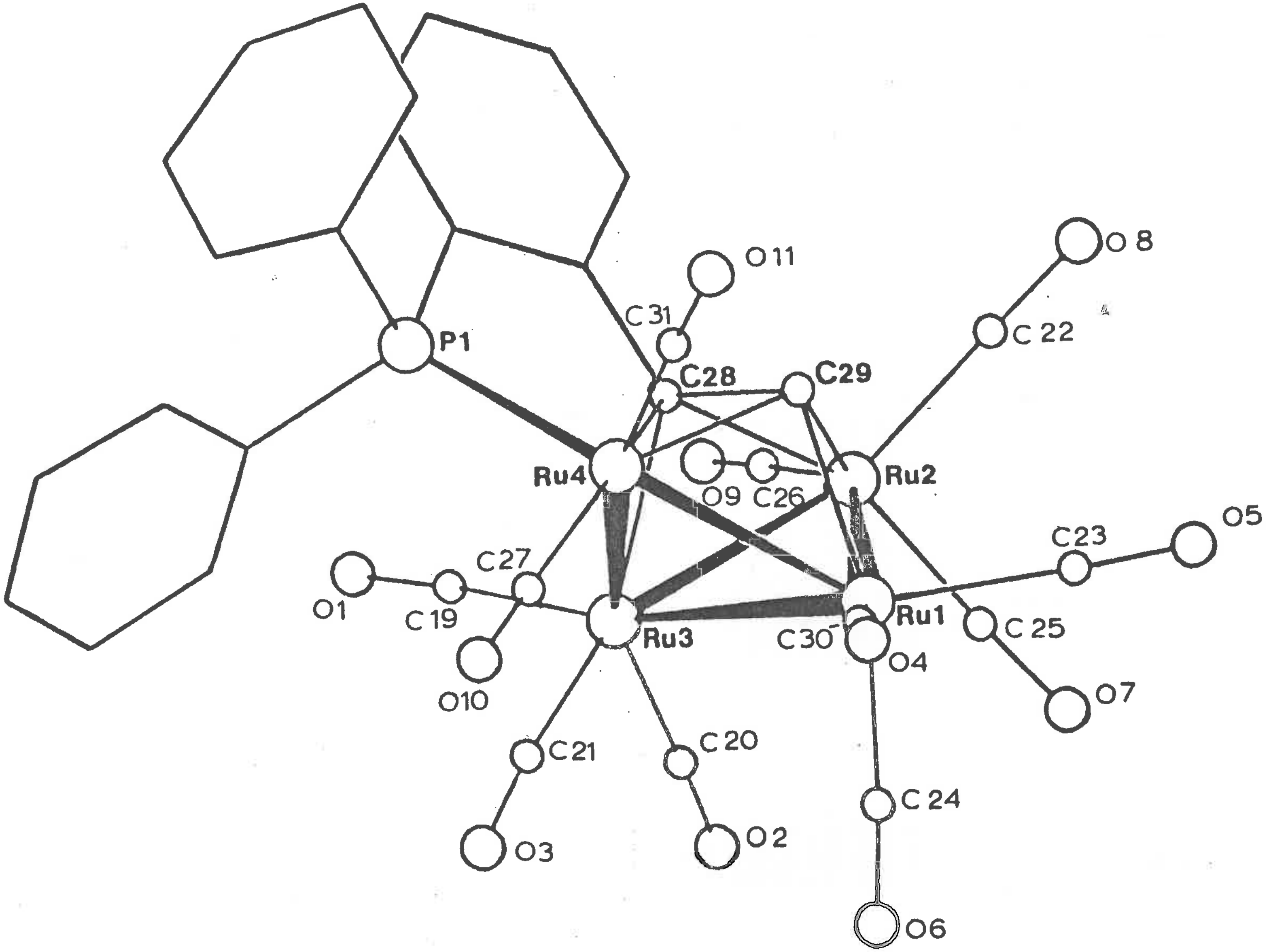


Figure 5. PLUTO plot of the molecular structure of $Ru_4(\mu_4\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_{11}$ (18) (by E. Horn and M.R. Snow)

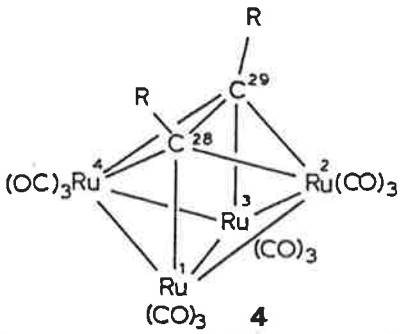


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Table 6: Selected bond lengths and angles for (18) and related complexes

Bond lengths (Å)	**18**	**4** (R = Me)	**19** (R = Ph)
Ru(1)–Ru(2)	2.735(1)	2.728(1)	2.74(1)
Ru(1)–Ru(3)	2.823(1)	2.880(1)	2.85(1)
Ru(1)–Ru(4)	2.770(1)	2.710(1)	2.71(1)
Ru(2)–Ru(3)	2.722(1)	2.710(1)	2.71(1)
Ru(3)–Ru(4)	2.749(1)	2.728(1)	2.74(1)
Ru(1)–C(29)	2.144(9)	2.16(1)	2.16(1)
Ru(2)–C(29)	2.235(8)	2.24(1)	2.25(1)
Ru(4)–C(29)	2.212(8)	2.27(1)	2.24(1)
Ru(2)–C(28)	2.266(8)	2.27(1)	2.26(1)
Ru(3)–C(28)	2.174(7)	2.16(1)	2.16(1)
Ru(4)–C(28)	2.190(7)	2.24(1)	2.24(1)
C(28)–C(29)	1.455(11)	1.45(1)	1.46(2)
Ru(4)–P(1)	2.297(3)		
P(1)–C(1)	1.805(8)		
P(1)–C(7)	1.787(10)		
P(1)–C(13)	1.826(7)		
C(2)–C(28)	1.508(13)		
Ru–CO (mean)	1.898 [range 1.860-1.942(11)]		
C–O (mean)	1.145 [range 1.115-1.189(12)]		

Bond angles (°)			**18**
Ru(1)–Ru(2)–Ru(3)	62.3	Ru(1)–Ru(3)–Ru(2)	59.1
Ru(1)–Ru(3)–Ru(4)	59.6	Ru(1)–Ru(4)–Ru(3)	61.5
Ru(2)–Ru(1)–Ru(3)	58.6	Ru(2)–Ru(1)–Ru(4)	91.1
Ru(3)–Ru(1)–Ru(4)	58.9		
Ru(1)–Ru(4)–P(1)	153.4(1)	Ru(3)–Ru(4)–P(1)	96.1(1)
Ru(1)–Ru(2)–C(28)	72.4(2)	Ru(1)–Ru(2)–C(29)	49.9(2)
Ru(1)–Ru(3)–C(28)	71.8(2)	Ru(1)–Ru(4)–C(28)	72.7(2)
Ru(1)–Ru(4)–C(29)	49.4(2)	Ru(2)–Ru(1)–C(29)	52.9(2)
Ru(2)–Ru(3)–C(28)	53.7(2)	Ru(3)–Ru(1)–C(29)	71.2(2)
Ru(3)–Ru(2)–C(29)	50.7(2)	Ru(3)–Ru(2)–C(29)	72.1(2)
Ru(3)–Ru(4)–C(28)	50.7(2)	Ru(3)–Ru(4)–C(29)	71.9(2)
Ru(4)–Ru(1)–C(29)	51.6(2)	Ru(4)–Ru(3)–C(28)	51.2(2)
Ru(1)–C(29)–Ru(2)	77.3(3)	Ru(1)–C(29)–Ru(2)	65.2(2)
Ru(1)–C(29)–Ru(4)	78.9(3)	Ru(2)–C(28)–Ru(3)	61.6(2)
Ru(2)–C(28)–Ru(4)	123.7(4)	Ru(2)–C(29)–Ru(4)	124.2(3)
Ru(3)–C(28)–Ru(4)	78.1(2)		
Ru(1)–C(29)–C(28)	110.2(5)	Ru(2)–C(28)–C(29)	70.0(5)
Ru(2)–C(29)–C(28)	72.3(4)	Ru(3)–C(28)–C(29)	114.7(5)
Ru(4)–C(28)–C(29)	71.5(4)	Ru(4)–C(29)–C(28)	69.9(4)
P(1)–Ru(4)–C(27)	93.0(3)	P(1)–Ru(4)–C(28)	82.0(2)
P(1)–Ru(4)–C(29)	112.5(2)	P(1)–Ru(4)–C(31)	93.8(3)
C(28)–Ru(2)–C(29)	37.7(3)	C(28)–Ru(4)–C(29)	38.6(3)
Ru–C–O (mean)	176.5 [range 174.1–178.5(7)]		

[Ru(3)-Ru(4), 2.749(1)Å]. The Ru(4)-P(1) separation [2.297(3)Å] is not significantly different from that found in $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC\equiv CC_6H_4PPh_2)(CO)_8$ (16) [2.302(2)Å]. The alkyne C(28)-C(29) bond [1.455(11)Å] has lengthened appreciably from the normal value associated with a C≡C triple bond, as a result of the interaction with the four metal atoms. The Ru(4)-P(1)-C(1)-C(2)-C(28) chelate ring is planar, and distorts the regular symmetry of the Ru_4C_2 cluster so that C(28) is slightly nearer to Ru_4, and further from Ru(2), than is C(29). The C(2)-C(28) separation [1.508(13)Å] is consistent with there being a normal single bond from the phenyl ring to the cluster (alkyne) carbon atom. The C(2)-C(28)-C(29) angle [123.1(10)°] may be compared with the similar Me-C-C angle of 123.8(2)° found in (4).

Thermolysis of $Os_3(CO)_{10}(sp)$ (11) and $Os_3(CO)_{11}(sp)$ (12)

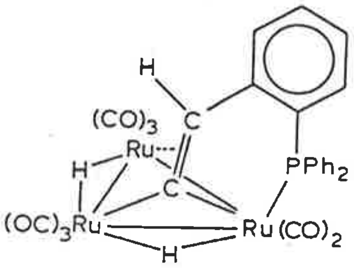
Thermolysis of either $Os_3(CO)_{10}(sp)$ (11) (111°C, 5 h) or $Os_3(CO)_{11}(sp)$ (12) (98°C, 18 h) affords yellow $Os_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC\equiv CC_6H_4PPh_2)(CO)_8$ (9) in moderate to high yield. This complex was readily identified by its spectral and microanalytical data, and by comparison with the analogous complex (16) and literature values.[10]

CONCLUSION

The radical-catalysed substitution of $Ru_3(CO)_{12}$ with sp occurs readily at room temperature within two minutes, two CO groups being displaced from cis equatorial positions on adjacent metal atoms by the chelate ligand to give

$Ru_3(CO)_{10}(sp)$ (10), the first η^2-olefinic derivative of $Ru_3(CO)_{12}$. The analogous osmium complex (11) is prepared by treating $Os_3(CO)_{10}(NCMe)_2$ with sp. The reactions of $Os_3(CO)_{11}(NCMe)$ or $Os_3(\mu\text{-}H)_2(CO)_{10}$ with sp give the P-bonded complexes $Os_3(CO)_{11}(sp)$ (12) and $Os_3(\mu\text{-}H)(H)(CO)_{10}(sp)$ (13) respectively which contain an uncoordinated vinyl group.

As expected on the basis of the results obtained earlier with simple olefins (Scheme 1),[1-3] (10) and (11) undergo ready migration of hydrogen from the η^2-olefin to the metal cluster, with concomitant loss of CO and structural rearrangement to give the μ_3-η^2-alkyne complexes $M_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ [M = Ru(16) and Os(9)]. These observations provide new evidence for the generally-held assumptions of the intermediacy of an (η^2-olefin)$M_3(CO)_{11}$ complex in the reactions between $M_3(CO)_{12}$ (M = Ru, Os) and ethylene.[7] The constraints imposed by the presence of the chelating phosphine in (10) and (11) evidently preclude the formation of vinylidene complexes such as (20).



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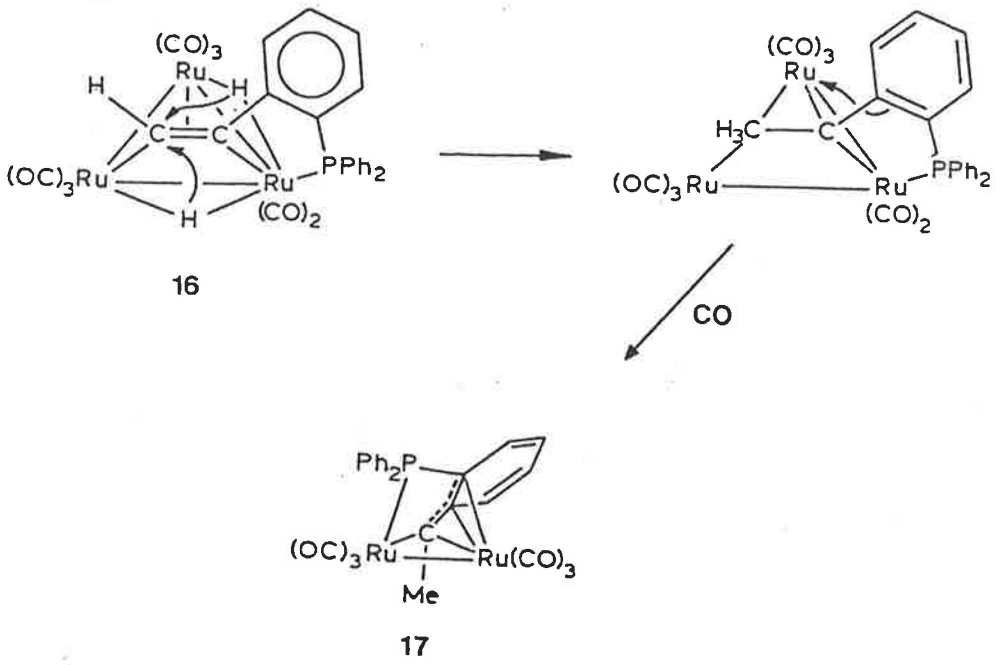
The complex $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17) may be an intermediate in the breakdown of the cluster complexes to the mononuclear products formed in the thermal reactions between $Ru_3(CO)_{12}$ and sp.[9] It is not possible to say how the isomerisation of the vinyl to the ethylidene ligand occurs, but a plausible route from $Ru_3(CO)_{10}(sp)$ (10) is via the hydrido complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) (Scheme 3). Transfer of both cluster-bound hydrogens to the terminal (β) carbon of the C_2 unit would afford the ligand found in (17); the C_6H_4 ring is then ideally located for the interaction of its π system with a Ru atom. Formation of (17) is completed by addition of CO and extrusion of an $Ru(CO)_4$ fragment; trimerisation of this would give $Ru_3(CO)_{12}$, which is isolated in yields comparable with that of (17). In a separate experiment it was shown that under CO pressure (16) is converted to the binuclear complex (17) in 25% yield, with $Ru_3(CO)_{12}$ as the other product. This strongly implicates the intermediacy of (16) in the overall thermolysis of $Ru_3(CO)_{10}(sp)$ (10) to (17).



(Scheme 3)

The formation of $Ru_4(\mu_4-\eta^2,\underline{P}-HC\equiv CC_6H_4PPh_2)(CO)_{11}$ (18) from $Ru_3(CO)_{10}(sp)$ (10) requires the formal addition of an $Ru(CO)_3$ group to generate the Ru_4 cluster, with concomitant loss of H_2. Significantly, simple heating of $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC\equiv CC_6H_4PPh_2)(CO)_8$ (16) alone at higher temperatures does not give any of (18), but this complex is formed on heating (16) and $Ru_3(CO)_{12}$ (Scheme 2, p. 72). It was noticed that $Ru_3(CO)_{12}$ was isolated from the reaction which afforded (18), and the intermediate yellow solution (see Experimental) contains both (16) and $Ru_3(CO)_{12}$. The $Ru_3(CO)_{12}$ required to produce (18) is probably generated by the initial break-down of (10) to (16) and (17).

A parallel can thus be drawn between the reaction of $Ru_3(CO)_{12}$ and sp to finally give (18) on the one hand, and the reaction with $PhCH=CH_2$ recently reported to give $Ru(\mu_4-\eta^2-HC\equiv CPh)(CO)_{12}$,[29] on the other; the intermediates (10) and (16) described above undoubtedly have their (undetected) counterparts in the latter reaction.

None of the mononuclear complexes prepared from the thermal reactions between $Ru_3(CO)_{12}$ and sp were detected among the reactions that have afforded (16), (17) or (18).

The thermolysis of either $Os_3(CO)_{10}(sp)$ (11) or $Os_3(CO)_{11}(sp)$ (12) gives the expected product $Os_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC\equiv CC_6H_4PPh_2)(CO)_8$ (9), which was previously prepared as one of a number of products from the reaction between $Os_3(CO)_{12}$ and sp. The former reactions offer both a greater specificity and a significant improvement in yield.

The variety of reactions discussed above further highlights the complexity of cluster chemistry and illustrates the use of a tertiary phosphine to anchor a reactive hydrocarbon to a metal cluster fragment in an attempt to isolate various intermediate complexes and to ultimately use these reactions to model changes that occur on metal surfaces.

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1. The sp ligand was kindly donated by Dr. M.A. Bennett (Australian National University).

Preparation of $Ru_3(CO)_{10}(sp)$ (10)

A mixture of $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and sp (120 mg, 0.42 mmol) in thf (40 ml) at ambient temperature was treated dropwise from a syringe with a solution of $Na[Ph_2CO]$ (ca 0.025 mol dm^{-3}, ∿30 drops) in the same solvent until the reaction was complete (tlc). The resulting deep red solution was evaporated to dryness and the residue recrystallised from Et_2O/MeOH to give red crystals of $Ru_3(CO)_{10}(sp)$ (10) (250 mg, 74%), m.p. 113-114°C. [Found: C, 42.21; H, 2.15; $C_{30}H_{17}O_{10}PRu_3$ requires C, 41.34; H, 1.97%]. Infrared (cyclohexane): ν(CO) 2094s, 2039s, 2026vs, 2015vs, 1999m, 1991w, 1976m, 1959w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 2.51 [d, J(12) 8.5 Hz, 1H, H(2)], 3.24 [d, J(13) 12.5 Hz, 1H, H(3)], 4.90 [dd, 1H, H(1)], 7.51 (m, 14H, Ph and C_6H_4).

Preparation of $Os_3(CO)_{10}(sp)$ (11)

A mixture of $Os_3(CO)_{10}(NCMe)_2$ (150 mg, 0.161 mmol) and sp (47 mg, 0.163 mmol) was stirred in cyclohexane (50 ml) at 50°C for 4 h. Evaporation and recrystallisation from CH_2Cl_2/MeOH afforded yellow crystals of $Os_3(CO)_{10}(sp)$ (11) (101 mg, 55%), m.p. 169-172°C. [Found: C, 31.95; H, 1.29; $C_{30}H_{17}O_{10}Os_3P$ requires C, 31.63; H, 1.50%]. Infrared (cyclohexane): ν(CO) 2104m, 2048m, 2032m, 2020vs, 2000w, 1987w, 1978m, 1969w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 2.21 [dd, *J*(12) 8.0 Hz, *J*(32) 2.5 Hz, 1H, H(2)], 2.87 [dd, *J*(13) 19.5 Hz, 1H, H(3)], 4.71 [dd, 1H, H(1)], 7.51 (m, 14H, Ph and C_6H_4).

Preparation of $Os_3(CO)_{11}(sp)$ (12)

A mixture of $Os_3(CO)_{11}(NCMe)$ (150 mg, 0.163 mmol) and sp (47 mg, 0.163 mmol) in dichloromethane (30 ml) was stirred at ambient temperature for 24 h. Evaporation and recrystallisation from CH_2Cl_2/MeOH afforded an orange yellow powder of $Os_3(CO)_{11}(sp)$ (12) (137 mg, 72%), m.p. 68-72°C. [Found: C, 32.17; H, 1.32; $C_{31}H_{17}O_{11}Os_3P$ requires C, 31.90; H, 1.47%]. Infrared (cyclohexane): ν(CO) 2112m, 2059s, 2038s, 2023vs, 2004w, 1997m, 1985m, 1972vw, 1963w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 5.11 [d, *J*(12) 11.0 Hz, 1H, H(2)], 5.68 [d, *J*(13) 17.0 Hz, 1H, H(3)], 6.76 [dd, 1H, H(1)], 7.50 (m, 14H, Ph and C_6H_4).

Preparation of $Os_3(\mu\text{-}H)(H)(CO)_{10}(sp)$ (13)

A mixture of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (100 mg, 0.117 mmol) and sp (35 mg, 0.121 mmol) in dichloromethane (5 ml) was stirred at ambient temperature for 15 min, during which time the colour changed from purple to yellow. Evaporation and preparative tlc (light petroleum-acetone 90/10) gave two bands: Band 1, *R*$_f$ 0.25, yellow, recrystallised from CH_2Cl_2/MeOH to give yellow crystals of $Os_3(\mu\text{-}H)(H)(CO)_{10}(sp)$ (13) (88 mg, 66%), m.p. 142-143°C. [Found: C, 31.88; H, 1.31; $C_{30}H_{19}O_{10}Os_3P$ requires C, 31.58; H, 1.66%]. Infrared (cyclohexane): ν(CO) 2109m, 2071m, 2056m, 2019vs, 2012(sh), 2004w, 1992(sh), 1989m, 1977m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$, 224 K) -19.76 [dd, *J*(H_BH_T) 3.5 Hz *J*(PH_B) 11.0 Hz, 1H, OsH_B], -10.10 [d, 1H, OsH_T], 5.18 [d, *J*(12) 11.0 Hz, 1H, H(2)], 5.67 [d, *J*(13) 17.0 Hz, 1H, H(3)], 6.73

[dd, 1H, H(1)], 7.49 (m, 14H, Ph and C_6H_4). Band 2, Rf 0.15, yellow, (trace), uncharacterised.

Reaction of $Ru_3(CO)_{11}(CNBu^t)$ with sp

A mixture of $Ru_3(CO)_{11}(CNBu^t)$ (150 mg, 0.216 mmol) and sp (69 mg, 0.239 mmol) in thf (10 ml) at ambient temperature was treated dropwise from a syringe with a solution of $Na[Ph_2CO]$ (ca 0.025 mol dm^{-3}, ∿ 1 ml) in the same solvent. Evaporation and preparative tlc (pentane-diethylether 90/10) gave four bands: Band 1, Rf 0.75, orange, $Ru_3(CO)_{11}(CNBu^t)$, (25 mg, 17%). Band 2, Rf 0.63, orange, $Ru_3(CO)_{10}(sp)$ (10), (21 mg, 11%). Band 3, Rf 0.50, red, recrystallised from warm hexane to give deep red crystals of $Ru_3(CO)_9(sp)(CNBu^t).C_6H_{14}$ (14) (36 mg, 18%). m.p. >200°C. [Found: C, 47.12; H, 3.86; N, 1.41; $C_{34}H_{26}NO_9PRu_3.C_6H_{14}$ requires C, 47.43; H, 3.98; N, 1.38%]. Infrared (cyclohexane): ν(CN) 2165w, ν(CO) 2074(sh), 2063m, 2051w, 2037w, 2024m, 2011vs, 1999vs, 1993m, 1985m, 1970s, 1961(sh) cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 1.43 (s, 9H, CMe_3), 2.38 [d, J(12) 8.0 Hz, 1H, H(2)], 3.07 [d, J(13) 11.5 Hz, 1H, H(3)], 4.65 [dd, 1H, H(1)], 7.46 (m, 14H, Ph and C_6H_4). Band 4, Rf 0.41 (trace), not identified. Bands 1 and 2 were identified by comparison of their i.r. ν(CO) spectra with those of authentic samples.

Hydrogenation of $Ru_3(CO)_{10}(sp)$ (10)

A solution of (10) (140 mg, 0.160 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (20 atm, 50°C, 2 h). The resulting red solution was evaporated to dryness and separated by preparative tlc (light petroleum-acetone 80/20) to give eight bands. Band 1, <u>R</u>$_f$ 0.87, yellow $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (7 mg, 6%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 2, <u>R</u>$_f$ 0.57, red, recrystallised from CH_2Cl_2/MeOH to give red crystals of $Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_2C_6H_4Et\text{-}2)$ (15) (33 mg, 20%). [Found: C, 38.01; H, 2.42; $C_{33}H_{25}O_{11}PRu_4$ requires C, 38.38; H, 2.44%]. Infrared (cyclohexane): ν(CO) 2099m, 2071m, 2061s, 2052s, 2030s, 2020vs, 2001(sh), 1994w, 1971w, 1964w cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) -17.29 [d, <u>J</u>(PH) 4.5 Hz, 4H, RuH], 0.98 (t, <u>J</u> 7.3 Hz, 3H, CH_3), 2.51 (m, 2H, CH_2), 17.45 (m, 14H, Ph and C_6H_4). Bands 3-8 were obtained in trace amounts and were not identified.

<u>Pyrolysis of $Ru_3(CO)_{10}(sp)$ (10) at 82°C</u>

A solution of $Ru_3(CO)_{10}(sp)$ (10) (100 mg, 0.12 mmol) in cyclohexane (20 ml) was heated at reflux point for 30 minutes, after which time the reaction was adjudged complete [the disappearance of the ν(CO) band of (10) at 2094 cm^{-1} was monitored]. Evaporation and preparative tlc (cyclohexane) gave three complexes: Band 1, <u>R</u>$_f$ 0.60, yellow, $Ru_3(CO)_{12}$ (4 mg, 5%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 2, <u>R</u>$_f$ 0.50, yellow, recrystallised from CH_2Cl_2/MeOH to give yellow crystals of $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17) (6 mg, 8%), m.p. 103-108°C. [Found: C, 48.18; H, 2.55; $C_{26}H_{19}O_6PRu_2$ requires C, 47.28; H, 2.90%]. Infrared (cyclohexane): ν(CO) 2069s, 2048(sh), 2037s, 2004s, 1991vs, 1982s cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 3.10 [d, <u>J</u>(PH) 1.5 Hz, 3H, CH_3], 6.44-8.02 (m, 14H, Ph and C_6H_4). Mass spectrum: (70 eV): [<u>M</u>-Me-nCO]$^+$ (n = 0-6) at <u>m/e</u> 647, 619, 591, 563, 535, 507, 479. Band 3, $\underline{R_f}$ 0.35, yellow, recrystallised from Et_2O/MeOH to give large yellow crystals of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) (61 mg, 65%), darkened >150°C, m.p. 184-188°C. [Found: C, 41.26; H, 1.90%, $\underline{M}$ (mass spectrum) 817; $C_{28}H_{17}O_8PRu_3$ requires C, 41.23; H, 2.10%; $\underline{M}$ 817]. Infrared (cyclohexane): ν(CO) 2099w, 2085s, 2062(sh), 2053vs, 2043s, 2029w, 2014vs, 2008s, 1999m, 1995w, 1989m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -17.72 [s(br), 2H, RuH], 7.31 (m, 14H, Ph and C_6H_4), 10.14 (s, 1H, C≡CH). Three purple products were present in trace amounts only and were not characterised.

Reaction of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) with CO

A solution of (20) (50 mg, 0.061 mmol) in cyclohexane was carbonylated in an autoclave (5 atm, 80°C, 2 h). Evaporation and preparative tlc (hexane) afforded three bands: Band 1, $\underline{R_f}$ 0.59, yellow, $Ru_3(CO)_{12}$ (22 mg, 56%). Band 2, $\underline{R_f}$ 0.48, yellow $Ru_2(\mu\text{-}\eta^1,\eta^3,\underline{P}\text{-}MeCC_6H_4PPh_2)(CO)_6$ (17) (10 mg, 25%). Band 3, $\underline{R_f}$ 0.35, unreacted starting material (6 mg, 12%). All were identified by comparison of their i.r. ν(CO) spectra with those of authentic samples.

Pyrolysis of $Ru_3(CO)_{10}(sp)$ (10) at 135°C

A solution of $Ru_3(CO)_{10}(sp)$ (10) (100 mg, 0.115 mmol) in petroleum spirit (boiling range 120-160°C, 35 ml) was stirred at 135°C (bath temperature) for 4 h. The red solution first lightened to yellow, and then the colour deepened to black-purple. After cooling, and filtering to remove some ruthenium metal, the solvent was removed under reduced pressure. The residue was chromatographed by preparative tlc (cyclohexanediethylether 95/5) to give five bands: Band 1, Rf 0.57, yellow $Ru_2(\mu-\eta^1,\eta^3,\underline{P}-MeCC_6H_4PPh_2)(CO)_6$ (17) (trace). Band 2, $\underline{R_f}$ 0.43, yellow, $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) (trace). Band 3, $\underline{R_f}$ 0.34, (trace), uncharacterised. Band 4, $\underline{R_f}$ 0.26, purple, recrystallised from CH_2Cl_2/isopentane to give purple crystals of $Ru_4(\mu_4-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_{11}\cdot 0.5CH_2Cl_2$ (18) (20 mg, 17%) [Found: C, 35.76; H, 1.22; $C_{35}H_{15}O_{11}PRu_4\cdot 0.5CH_2Cl_2$ requires C, 36.34; H, 1.55%]. Infrared (cyclohexane): ν(CO) 2078m, 2060(sh), 2040s, 2026vs, 2004w, 1993m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.40 (m, 14H, Ph and C_6H_4), 9.57 (s, 1H, C≡CH). Band 5, $\underline{R_f}$ 0.10, (trace), uncharacterised. Bands 1 and 2 were identified by comparison of their i.r. ν(CO) spectra with those of authentic samples.

Analysis [tlc, i.r. ν(CO)] of the intermediate yellow solution showed the presence of $Ru_3(CO)_{12}$, (16) and (17).

Reaction of $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) with $Ru_3(CO)_{12}$

A mixture of $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) (100 mg, 0.123 mmol) and $Ru_3(CO)_{12}$ (70 mg, 0.123 mmol) in n-heptane (30 ml) was heated at 100°C for 48 h. During this time the solution became turbid, and the colour changed from orange to purple. Evaporation and preparative tlc (light petroleum) afforded five bands. Band 1, $\underline{R_f}$ 0.86, yellow, $Ru_3(CO)_{12}$ (45 mg, 58%). Band 2, $\underline{R_f}$ 0.34, yellow $Ru_3(\mu-H)_2(\mu_3-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (16) (60 mg, 60%). Band 3, $\underline{R_f}$ 0.10, purple, $Ru_4(\mu_4-\eta^2,\underline{P}-HC{\equiv}CC_6H_4PPh_2)(CO)_{11}$ (18) (20 mg, 16%). The above complexes were identified by comparison of their i.r. ν(CO) spectrum with those of authentic samples. Two other products were present in trace amounts only and were not characterised.

Heating complex (16) in the absents of $Ru_3(CO)_{12}$ at temperatures >100°C does not give any of complex (18).

Pyrolysis of $Os_3(CO)_{10}(sp)$ (11)

A solution of $Os_3(CO)_{10}(sp)$ (11) (100 mg, 0.088 mmol) in toluene (25 ml) was heated at reflux point for 5 h after which time the reaction was adjudged complete (tlc). Evaporation and preparative tlc (light petroleum-acetone 85/15) afforded one major pale yellow product, $\underline{R_f}$ 0.31, recrystallisation from CH_2Cl_2/MeOH gave yellow rosettes of $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ (9) (69 mg, 73%), m.p. 225-230°C (lit.[10] 230-235°C). [Found: C, 30.93; H, 1.43; $C_{28}H_{17}O_8Os_3P$ requires C, 31.05, H, 1.58%]. Infrared (cyclohexane): ν(CO) 2099w, 2086s, 2053vs, 2037vs, 2022w, 2008vs, 1999m, 1991vs, 1987w, 1981w, 1964w cm^{-1} (lit[10] 2090w, 2082vs, 2065(sh), 2050vs, 2031s, 2017w, 2007s, 1997w, 1983m, 1970w cm^{-1}). ^1H n.m.r.: δ ($CDCl_3$) -20.52 [d, $\underline{J}$(PH) 27.5 Hz, 1H, OsH], -18.04 [s(br), 1H, OsH], 7.51 (m, 14H, Ph and C_6H_4), 10.78 (s, 1H, C≡CH). Three yellow products were present in trace amounts only and were not characterised.

Pyrolysis of $Os_3(CO)_{11}(sp)$ (12)

A solution of $Os_3(CO)_{11}(sp)$ (12) (30 mg, 0.026 mmol) in n-heptane (10 ml) was heated at reflux point for 18 h after which time the reaction was adjudged complete [the disappearance of the i.r. ν(CO) band of (12) at 2112 cm^{-1} was monitored]. Evaporation and recrystallisation from CH_2Cl_2/MeOH gave pale yellow crystals of $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\underline{P}\text{-}HC{\equiv}CC_6H_4PPh_2)\text{-}(CO)_8$ (9) (19 mg, 67%), identified by comparison of its i.r. ν(CO) spectrum with the above.

X-ray structure determination of $Os_3(\mu\text{-}H)(H)(CO)_{10}(sp)$ (13)

The general procedure has been outlined in chapter 1. Suitable crystals of (13) were obtained from CH_2Cl_2/MeOH. Crystal data: $C_{30}H_{19}O_{10}Os_3P$, M 1141.0, crystal size 0.10 x 0.14 x 0.45 mm, triclinic, spacegroup P$\bar{1}$, $\underline{a}$ 10.546(4), $\underline{b}$ 11.272(2), $\underline{c}$ 15.214(4)Å, α 67.63(2), β 73.82(2), γ 74.04(2)°, $\underline{U}$ = 1576.9Å^3, $\underline{D}_{\underline{m}}$ 2.40, $\underline{D}_{\underline{c}}$ 2.40 g cm^{-3} for $\underline{Z}$ = 2, F(000) 1042, λ(Mo-$\underline{K}$α) 0.7107Å, μ(Mo-$\underline{K}$α) 121.47 cm^{-1}. Scan type ω-(1/3)θ, ω scan angle (1.8 + 0.35tanθ)°, horizontal aperture (2.4 + 0.5tanθ)mm. Data: 3731 unique reflections were collected in range $2.4 < 2\theta < 44°$ with 3383 having $\underline{I} > 2.5\sigma(\underline{I})$ being used in the refinement after correction for absorption. $\underline{R}$ = 0.032, $\underline{R}_{\underline{w}}$ = 0.032 where $\underline{w} = 12.3742[\sigma^2(\underline{F}) + 0.000046\underline{F}^2]^{-1}$. Abnormal features: six peaks of ca 2 eÅ^{-3} near the metal atoms were observed in the final difference map.

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CHAPTER THREE

ELEMENT-CARBON BOND CLEAVAGE REACTIONS OF TRI- AND TETRA-NUCLEAR dppm, dpam AND dppe COMPLEXES. SOME REACTIONS OF $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ (E = P, As).

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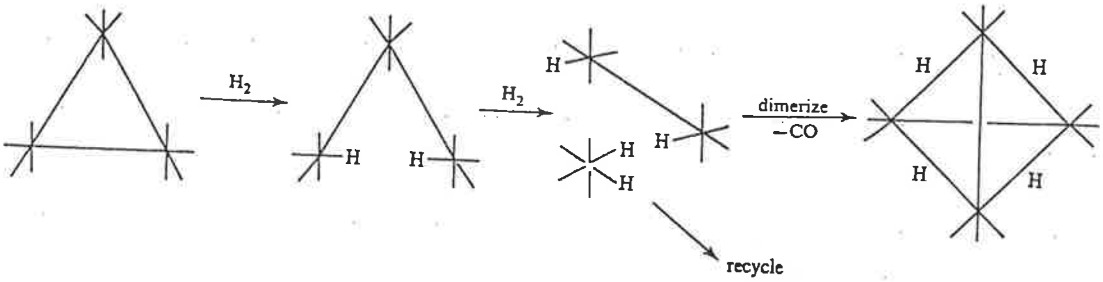
INTRODUCTION

The potential utility of transition metal cluster complexes in homogeneous catalysis has often been considered in recent years.[1-5] However, such complexes often undergo cluster fragmentation reactions under conditions where catalytic activity may occur, e.g. under hydrogen, $Ru_3(CO)_{12}$ readily gives $Ru_4(\mu\text{-}H)_4(CO)_{12}$;[6] the conversion is assumed to proceed by addition of H_2 to the trinuclear cluster, resulting in cleavage of Ru-Ru bonds to produce dinuclear and mononuclear fragments which on aggregation give the tetranuclear hydrido cluster (Scheme 1). It would therefore be difficult unambiguously to assign any catalytic activity to the presence of the initial cluster species.



(Scheme 1)

In the previous Chapter it was shown that the reaction of $Ru_3(CO)_{10}(sp)$ with hydrogen (50°C, 20 atm) (p 70) results both in addition of hydrogen to the coordinated vinyl group and loss of cluster integrity to give $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and $Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_2C_6H_4Et\text{-}2)$. Under slightly more vigorous conditions (H_2, 20 atm, 80°C, 2 h), the trinuclear complexes $Ru_3(CO)_{12-n}L_n$ (L = tertiary phosphine, arsine or phosphite; n = 1-3) give mixtures of the tetranuclear hydrido clusters $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(L)_n$ (n = 0-4); Table 1 summarises the

TABLE 1 Complexes formed from $Ru_3(CO)_{12-n}L_n$ and H_2

Precursor, $Ru_3(CO)_{12-n}L_n$		Product, $H_4Ru_4(CO)_{12-n}(L)_n$				
L	n	n=0	n=1	n=2	n=3	n=4
PPh_3	1	4.9	67.0	7.8	n.d.	n.d.
	2	1.7	62.8	10.8	n.d.	n.d.
	3	n.d.	n.d.	64.3	n.d.	n.d.
$PPh(OMe)_2$	1	4.4	69.9	5.2	1.2	n.d.
	2	n.d.	34.2	43.9	10.4	n.d.
	3	n.d.	2.2	28.1	21.5	n.d.
$P(OMe)_3$	1	7.2	57.8	3.9	n.d.	n.d.
	2	0.6	16.9	57.1	3.0	n.d.
	3	n.d.	n.d.	15.0	14.0	3.3

results obtained for L = PPh_3, $PPh(OMe)_2$ and $P(OMe)_3$;[7] complexes containing other tertiary phosphines, arsines and phosphites behaved similarly.[8] The reactions are characterised by the ready formation of polysubstituted complexes, even when the precursor is monosubstituted, together with an apparent reluctance to form the tetrasubstituted derivatives, $Ru_4(\mu\text{-}H)_4(CO)_8(L)_4$, even when the trinuclear complex contained one ligand on each metal atom [cf. the X-ray structure of $Ru_3(CO)_9(PMe_3)_3$ [9]].

Consideration of the results presented in Table 1 indicates that these apparently simple reactions are in reality quite complex, and that even a qualitative rationalisation of the reaction products requires that

(i) facile rearrangement/redistribution reactions occur between these complexes (this has been confirmed by separate experiments);[8]

(ii) ligands L can be readily displaced by CO (and perhaps H_2), and *vice versa*;

(iii) the final product ratios may be affected by the size of the ligand L (no tri- or tetra-substituted cluster hydride was obtained for L = PPh_3);

(iv) the Ru-Ru bonds are cleaved by oxidative addition of H_2 (no products formed by degradation of the tertiary phosphine or phosphite ligands were identified in any reaction).

Hydrogenation of $Ru_3(CO)_{11}(CNBu^t)$ affords $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(CNBu^t)_n$ (n = 0-2) together with $Ru_3(\mu\text{-}H)(\mu_3\text{-}HC{=}NBu^t)(CO)_9$, the latter being formed by the addition of hydrogen to the isocyanide ligand and the cluster core.[10] Thus, the presence of the potential μ_3-bridging ligand has prevented to some extent the fragmentation of the cluster.

A solution to the fragmentation problem was sought by the design of clusters containing bridging or potential μ_3-bridging ligands capable of allowing metal-metal bond cleavage and reformation. We therefore decided to investigate the hydrogenation reactions of complexes containing bidentate tertiary phosphines and arsines as these might be expected to give different results if fragmentation of the cluster was prevented by the bidentate ligands.

RESULTS AND DISCUSSION

With the advent of mild synthetic routes to derivatives of $Ru_3(CO)_{12}$ containing tertiary phosphine, phosphite and arsine ligands,[11] considerable interest in their chemistry has ensued. Extension of these studies to complexes containing bidentate ligands, in the hope that cluster degradation under more severe reaction conditions might be prevented, has uncovered an interesting microcosm of cluster chemistry. The thermal reaction between bis(diphenylphosphino)methane (dppm) and $Ru_3(CO)_{12}$ in tetrahydrofuran was first described in 1977,[12] when the fluxional properties of the resulting $Ru_3(CO)_{10}(dppm)$ (1) were also examined. A structural study of this molecule did not appear until seven years later, when the complex was obtained as one of the products of the reaction between $Fe_2(CO)_9$ and $\{RuCl_2(\underline{p}\text{-cymene})\}_2(dppm)$ in refluxing benzene.[13] Meanwhile, the reaction between dppm and $Ru_3(CO)_{12}$ in xylene at 80-85°C had been found to give $Ru_3(CO)_8(dppm)_2$ (2);[14] under more vigorous conditions, the complex $Ru_3(\mu_3\text{-}PPh)(\mu_3\text{-}CHPPh)(CO)_7(dppm)$ (3) is formed, and this complex may also be obtained by heating (2) in xylene at 100°C. This Chapter describes the improved synthesis of (1), some of its reactions including its conversion to the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$, together with some reactions of the latter: some related studies of the arsine analogues are also included.

The reaction between $Ru_3(CO)_{12}$ and dppm in warm thf was initiated by the dropwise addition of a sodium diphenylketyl solution. Crystallisation of the reaction mixture afforded $Ru_3(CO)_{10}(dppm)$ (1) in 90-95% yield. A similar reaction catalysed by [ppn][OAc] has been recently reported.[15] An analogous reaction employing dpam gave the new complex $Ru_3(CO)_{10}(dpam)$ (4) in 92% yield. Details of the reactions and characterisation of (1) and (4) are in the Experimental section.

The reaction between $Os_3(CO)_{10}(NCMe)_2$ and dppm in cyclohexane at 40°C afforded orange $Os_3(CO)_{10}(dppm)$ (5) in 54% yield. The complex was readily identified by elemental microanalysis and spectroscopic data. The i.r. $\nu(CO)$ spectrum closely resembles that of (1). In a recent report[16] it has been shown that (5) can be obtained in comparable yields to the above by the treatment of a benzene solution of an equimolar mixture of $Os_3(CO)_{12}$ and dppm with $Me_3NO.2H_2O$ (2 equiv.) in methanol at 60°C.

The addition of the initiator solution to a stoicheiometric mixture of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and (L_2) (L_2 = dppm, dpam) afforded the new complexes $Ru_4(\mu\text{-}H)_4(CO)_{10}(L_2)$ [L_2 = dppm (6), dpam (7)] after crystallisation. These complexes were identified by the usual methods. The ^1H n.m.r. spectra of (6) and (7) each contained a high-field resonance (of relative intensity 4), at δ -16.72 and δ -17.00 respectively, assigned to metal bridging hydrides, and a broad multiplet (of relative intensity 20) at δ 7.20 and δ 7.31 respectively assigned to phenyl groups. The methylene (CH_2) protons were shown to be magnetically inequivalent; for (6) a complex signal at δ 3.80 was the AB portion of an ABX_2 system (where X_2 are the two phosphorus nuclei) while for (7) an AB quartet at δ 3.37 [$\underline{J}$(AB) 12 Hz] was observed.

It has been shown that there are two isomers of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)$;[17-19] complex (8) in which the tertiary phosphine chelates one of the ruthenium atoms, and complex (9) in which the dppe ligand bridges the Ru(1)-Ru(2) vector. Similar alternatives can be proposed for complexes (6) and (7), therefore an X-ray diffraction study was performed on complex (6).

The crystal is composed of discrete molecules with no unusually short intermolecular contacts shorter than Van der Waals separations. The molecular structure of (6), which is shown in Figure 1 (see also Table 2), is based upon a distorted tetrahedral Ru_4 core with the dppm ligand spanning the hydride-bridged Ru(1)-Ru(2) vector [2.987(-)Å] in a similar manner to (9).[19] Each of the phosphorus atoms is attached to the cluster via normal 2e-donor bonds [Ru(1)-P(1) 2.360(1), Ru(2)-P(2) 2.337(1)Å]. The ten CO ligands are all in terminal positions and are distributed two to each of the dppm-bridged Ru atoms and three each to the other two metal atoms. The Ru-Ru distances fall into two groups, four long hydride-bridged vectors [mean 2.960(1)Å] and two shorter unbridged Ru-Ru bonds [mean 2.777(1)Å]. The four hydride ligands, which were located and refined in the X-ray study, are arranged such that the $Ru_4(\mu\text{-}H)_4$ core has configuration (10a) with idealized $\underline{C_s}$ symmetry. This arrangement is similar to that observed for complexes (8) and (9) but is unlike the $\underline{D_{2d}}$ core symmetry (10b) observed for $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (11),[20] $Ru_4(\mu\text{-}H)_4(CO)_{11}[P(OMe)_3]$ (12),[21] and $Ru_4(\mu\text{-}H)_4(CO)_{10}(PPh_3)_2$ (13).[20,22]

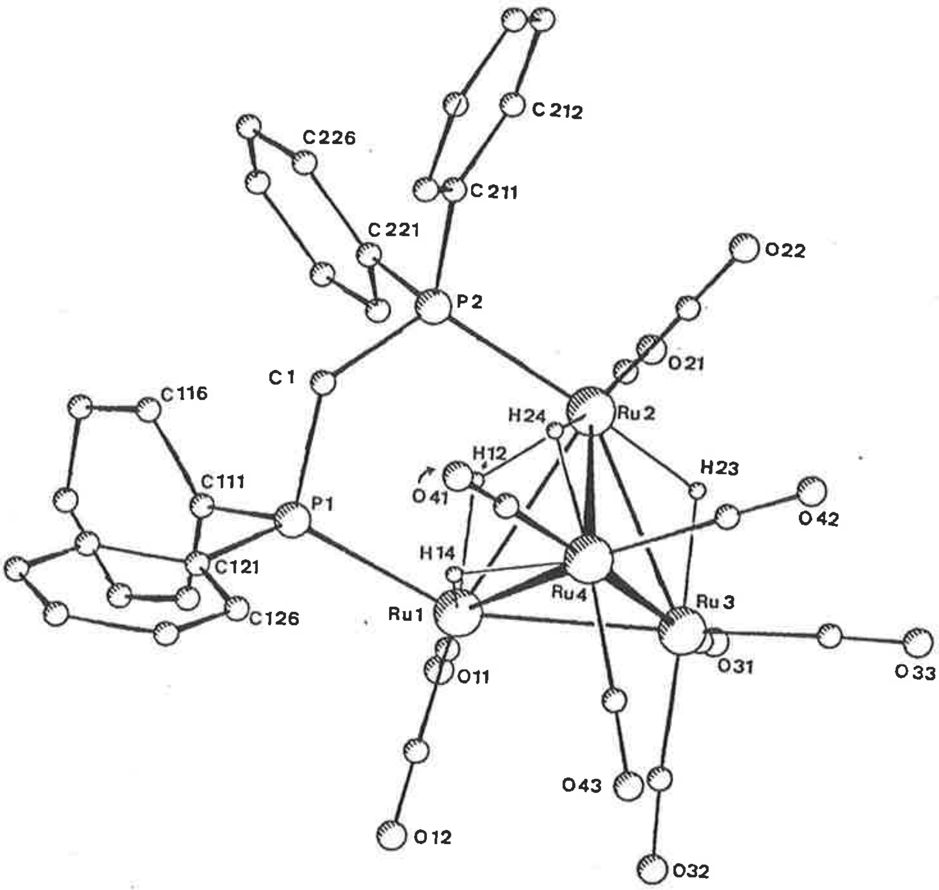


Figure 1 PLUTO plot of the molecular sturcture of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppm)$ (6) showing the atom numbering scheme.

Table 2 Selected bond lengths and angles for (6)

Bond lengths (A)

Ru(1)-Ru(2)	2.987(-)	Ru(3)-H(23)	1.75(2)
Ru(1)-Ru(3)	2.777(-)	Ru(1)-H(14)	1.79(2)
Ru(1)-Ru(4)	2.935(-)	Ru(4)-H(14)	1.79(2)
Ru(2)-Ru(3)	2.937(-)	Ru(2)-H(24)	1.81(3)
Ru(2)-Ru(4)	2.981(-)	Ru(4)-H(24)	1.76(4)
Ru(3)-Ru(4)	2.776(-)	P(1)-C(111)	1.820(4)
Ru(1)-P(1)	2.360(1)	P(1)-C(121)	1.847(3)
Ru(2)-P(2)	2.337(1)	P(2)-C(211)	1.823(2)
Ru(1)-H(12)	1.72(4)	P(2)-C(221)	1.818(2)
Ru(2)-H(12)	1.72(5)	P(1)-C(1)	1.851(3)
Ru(2)-H(23)	1.64(3)	P(2)-C(1)	1.840(3)

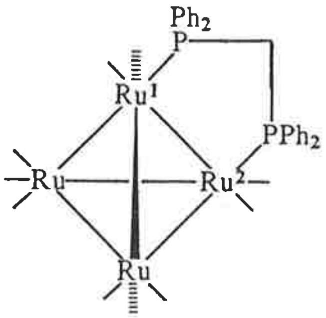
Ru-CO range from 1.867(5)-1.937(4) (average 1.895)

C-O range from 1.129(5)-1.152(6) (average 1.139).

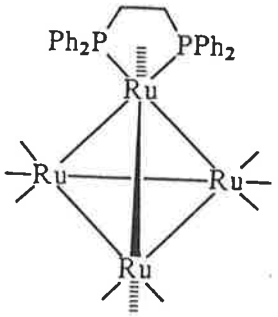
Angles (°)

Ru(2)-Ru(1)-Ru(3)	61.1(-)	Ru(1)-Ru(2)-P(2)	90.3(-)
Ru(2)-Ru(1)-Ru(4)	60.4(-)	Ru(2)-Ru(1)-P(1)	93.8(-)
Ru(3)-Ru(1)-Ru(4)	58.1(-)	Ru(1)-P(1)-C(1)	108.7(1)
Ru(1)-Ru(2)-Ru(3)	55.9(-)	Ru(2)-P(2)-C(1)	111.3(1)
Ru(1)-Ru(2)-Ru(4)	58.9(-)	Ru(1)-P(1)-C(111)	117.1(1)
Ru(3)-Ru(2)-Ru(4)	55.9(-)	Ru(1)-P(1)-C(121)	120.7(1)
Ru(1)-Ru(3)-Ru(2)	63.0(-)	Ru(2)-P(2)-C(211)	111.6(1)
Ru(1)-Ru(3)-Ru(4)	63.8(-)	Ru(2)-P(2)-C(221)	119.2(1)
Ru(2)-Ru(3)-Ru(4)	62.8(-)	Ru(2)-Ru(4)-Ru(3)	61.2(-)
Ru(1)-Ru(4)-Ru(2)	60.7(-)	P(1)-C(1)-P(2)	117.8(2)
Ru(1)-Ru(4)-Ru(3)	58.1(-)		

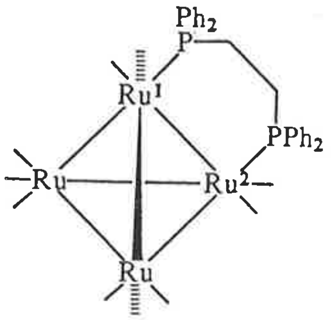
Ru-C-O range from 176.0-179.4 (average 178.0)



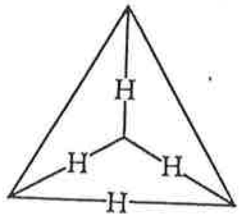
(6)



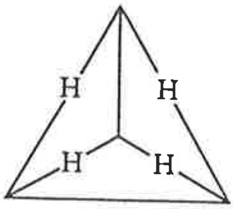
(8)



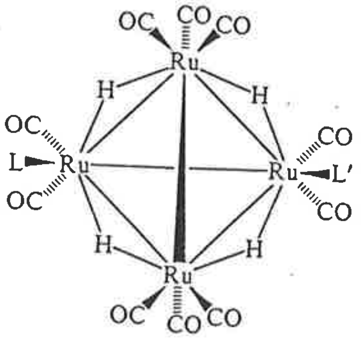
(9)



(10a) C_s



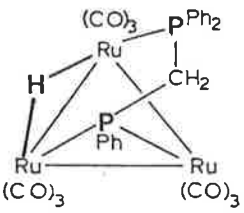
(10b) D_{2d}



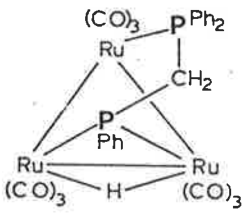
11 L = L' = CO
12 L = CO, L' = P(OMe)$_3$
13 L = L' = PPh$_3$

Element-Carbon Bond Cleavage Reactions

Hydrogenation (80°C, 20 atm, 2 h) of Ru$_3$(CO)$_{10}$(dppm) (1) proceeds readily to afford a monohydrido cluster which was readily identified as Ru$_3$(μ-H)(μ_3-PPhCH$_2$PPh$_2$)(CO)$_9$ (14) by elemental microanalysis and from its spectroscopic properties. Thus, the ^{1}H n.m.r. spectrum contained a high-field triplet (of relative intensity 1) at δ -16.65, assigned to a proton bridging a metal-metal bond, and a broad singlet (relative intensity 2) at δ 3.93 assigned to the CH_2 group. The aromatic multiplet at δ 7.44 had relative intensity 15H, showing that one of the Ph groups of the dppm ligand originally present had been eliminated, probably as benzene, with concomitant formation of a μ-phosphido group. It has recently been shown[23] by ^1H and $^{31}P\{^1H\}$ n.m.r. studies that complex (14) exists as a mixture of two isomers (14a) and (14b), that differ in the position of the hydride ligand on the Ru_3 triangle. At room temperature these two isomers interconvert rapidly on the n.m.r. time scale, while at 253 K (14a) is the preferred isomer. It has also been shown that in the solid state only isomer (14a) is observed.



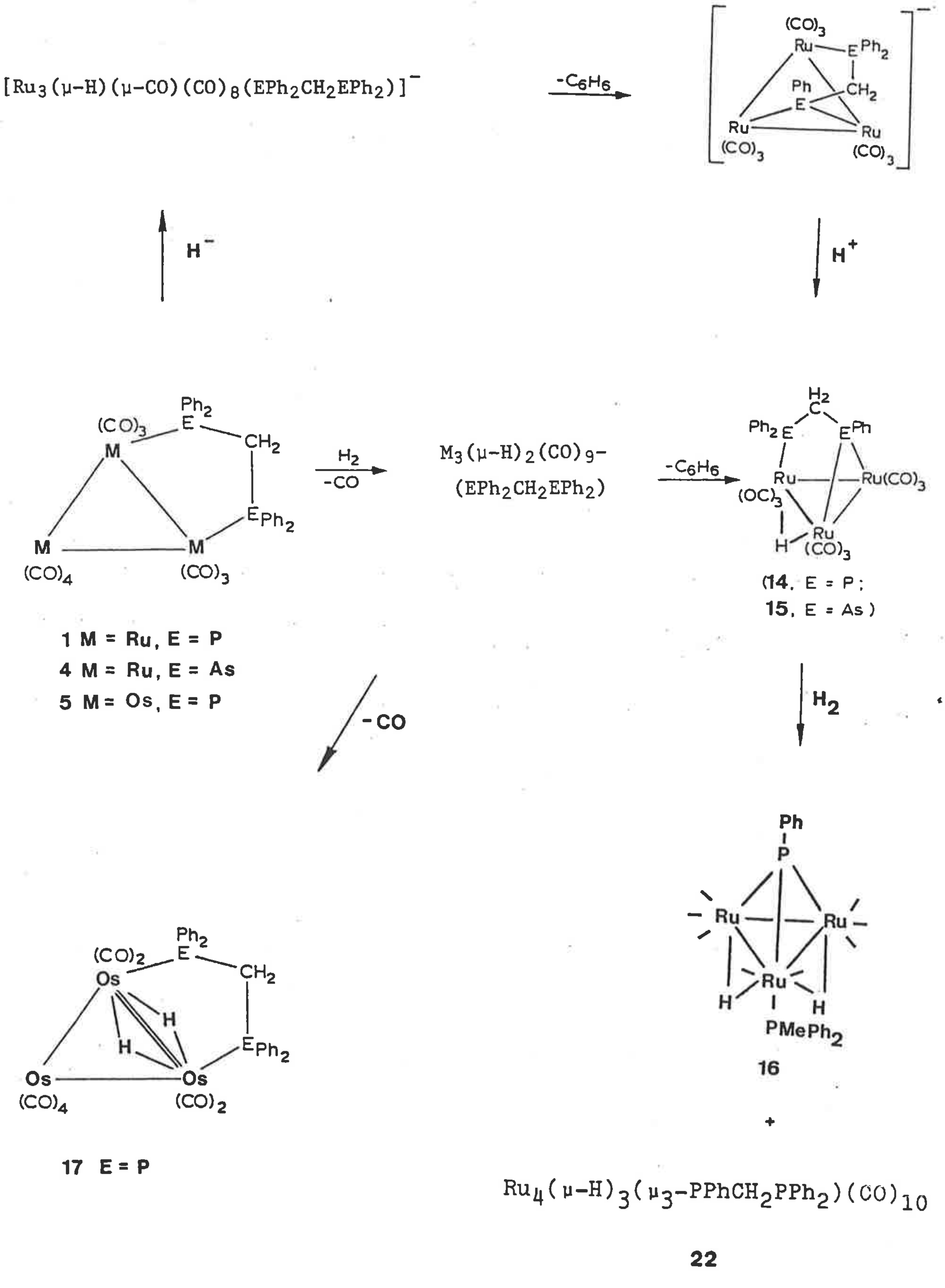
(14a)



(14b)

The arsenic analogue (15) was obtained similarly by hydrogenation of $Ru_3(CO)_{10}(dpam)$ (4) (see Experimental).

Prolonged hydrogenation of (1) (85°C, 20 atm, 20 h) or (14) (85°C, 20 atm, 21 h) leads to the cleavage of a second P-C bond, thus giving $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (16), and aggregation to give $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (22) (Scheme 2). The former complex was identified by comparison with an authentic sample,[24] while the latter was compared with a sample prepared from the pyrolysis of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppm)$ (6) (see below).

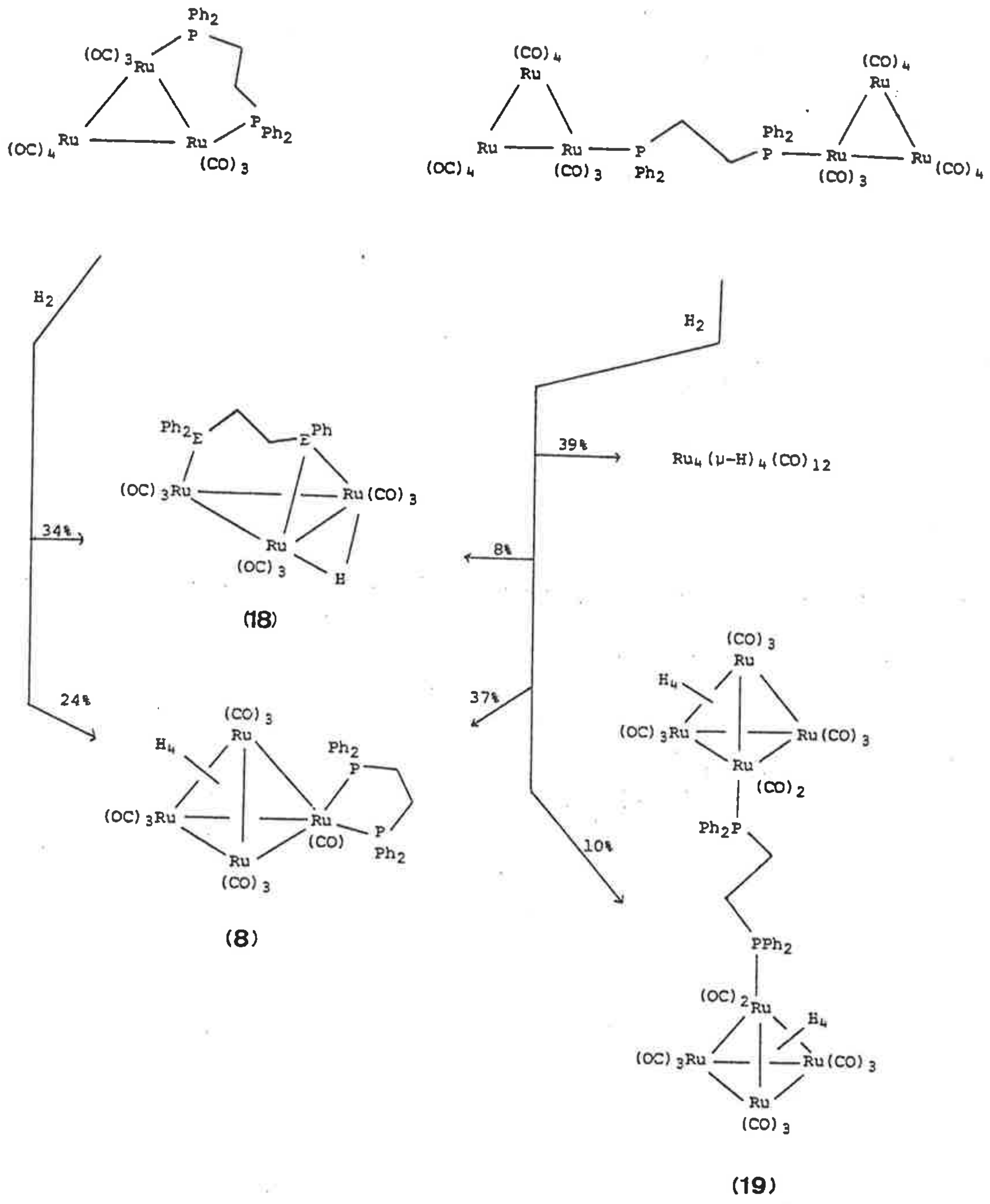

[Ru3(μ-H)(μ-CO)(CO)8(EPh2CH2EPh2)]⁻
-C6H6
(CO)3 Ru EPh2 Ph E CH2 Ru (CO)3 Ru (CO)3
H⁻
H⁺
(CO)3 M EPh2 CH2 EPh2 M (CO)4 M (CO)3
1 M = Ru, E = P
4 M = Ru, E = As
5 M = Os, E = P
H2
-CO
M3(μ-H)2(CO)9-(EPh2CH2EPh2)
-C6H6
H2 C Ph2E EPh Ru (OC)3 Ru(CO)3 H Ru (CO)3
(14, E = P;
15, E = As)
H2
-CO
(CO)2 Os EPh2 CH2 EPh2 H H Os (CO)4 Os (CO)2
17 E = P
Ph P Ru Ru Ru H H PMePh2
16
+
Ru4(μ-H)3(μ3-PPhCH2PPh2)(CO)10
22

(Scheme 2)

The unusual formation of (16) is a net conversion of the dppm ligand to benzene, coordinated phenylphosphinidene and $PMePh_2$ mediated by the cluster. More significantly however, is the formation of the tetranuclear cluster (22), thus indicating that cluster integrity can still be lost even in the presence of a potential or μ_3-bridging ligand under the above reaction conditions.

In contrast to the above reactions, hydrogenation (85°C, 25 atm, 2 h) of $Os_3(CO)_{10}(dppm)$ (5) results not in P-C bond cleavage but in oxidative addition of H_2 to the cluster followed by elimination of two CO groups to give the coordinatively unsaturated complex $Os_3(\mu\text{-}H)_2(CO)_8(dppm)$ (17) in moderate yield. The above formulation is consistent with the intense red colour of (17), its elemental microanalysis and its mass spectrum which contained a molecular ion centred on m/z 1182, together with a fragmentation pattern due to the successive stepwise loss of eight CO ligands. The ^1H n.m.r. spectrum contained an aromatic multiplet (relative intensity 20) at δ 7.30, and a triplet (relative intensity 2) at δ 4.15 [J(PH) 10.5Hz] assigned to the CH_2 group. At high-field, a two-proton triplet resonates at δ -10.31 [J(PH) 10.5Hz], and these data suggests that the hydride and dppm ligands bridge the Os=Os double bond as illustrated (Scheme 2).

In contrast again, the complexes $Ru_3(CO)_{10}(dppe)$ and $[Ru_3(CO)_{11}]_2(\mu\text{-}dppe)$ undergo both P-C bond cleavage to give the trinuclear complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ (18), and aggregation to give $Ru_4(\mu\text{-}H)_4(CO)_{12}$, $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)$ (8) and $[Ru_4(\mu\text{-}H)_4(CO)_{11}]_2(\mu\text{-}dppe)$ (19) (Scheme 3). The above complexes were readily identified by the usual methods [the



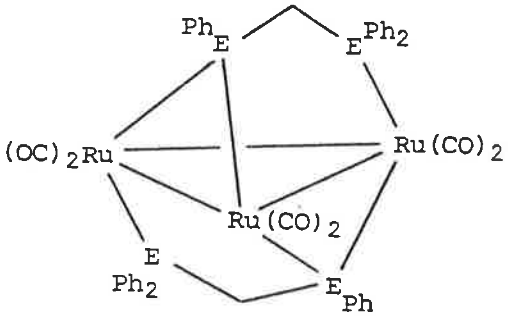
(Scheme 3)

i.r. ν(CO) spectrum of complex (18) was similar to that of (14)] (see Experimental). A route to the tetranuclear complex (8) could involve conversion of the precursor to an intermediate containing an η^1-dppe ligand, which would be expected to react is a similar way to the other complexes containing monodentate ligands described above, and also observed with $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$.

Mechanism of element-carbon bond cleavage

The element-carbon bond cleavage reactions observed for complexes (1), (4) and to some extent $Ru_3(CO)_{10}(dppe)$ and $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$, probably proceed via initial oxidative addition of H_2 to the Ru_3 core followed by hydrogen transfer and cleavage of the element-carbon bond with elimination of benzene (Scheme 2), the μ-bridging ligands preventing both break-up and condensation of the clusters as expected.

While this work was in progress, a report appeared describing the formation of $Ru_3(\mu\text{-H})_2(\mu_3\text{-EPhCH}_2\text{EPh}_2)_2(CO)_6$ [E = P (20), As (21)], which are closely akin to (14) and (15), by the hydrogenation of $Ru_3(CO)_8(L_2)_2$ (L_2 = dppm or dpam respectively).[25] This provides further examples of element-carbon bond cleavage reactions to give μ_3-phosphido-phosphine and μ_3-arsenido-arsine ligands.



(20) E = P

(21) E = As

This type of reaction is also exhibited by Group 6 donor ligands. The reaction between $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ and hydrogen afforded $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$,[7] a not-unexpected result since cleavage of the C-S bond by heating $Ru_3(\mu\text{-}H)(\mu\text{-}SEt)(CO)_{10}$ in concentrated sulphuric acid has been described previously.[26] Hydrogenation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_7(dppm)$ also results in C-S, but not C-P, bond cleavage, giving the complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(dppm)$ as the sole product.[7] Others have also remarked that such reactions are common with sulphur-containing ligands,[27] although they are apparently not well documented.

Pyrolysis of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppm)$ (6)

The facile loss of small molecules formed by element-carbon bond cleavage and combination of the resulting fragment with a hydrogen atom on the metal cluster is also demonstrated by pyrolysis of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppm)$ (6). Thus, short heating in refluxing cyclohexane smoothly converted (6) to the dephenylated complex $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (22). Characterisation of this complex rests on its spectroscopic properties and elemental microanalysis. The i.r. spectrum contains ν(CO) bands consistent with the presence of both terminal and bridging carbonyl ligands. The ^1H n.m.r. spectrum contains two broad high-field singlets at δ -17.95 (relative intensity 1) and δ -19.74 (relative intensity 2), assigned to three protons bridging Ru-Ru bonds. The methylene protons appear as a broad triplet at δ 3.22 (relative intensity 2). The aromatic multiplet at δ 7.55 had relative intensity 15H, showing that one of the Ph groups of the dppm ligand had been eliminated, probably with one of the hydride ligands as benzene. The mass spectrum contains a parent ion centred on m/z 996, corresponding to the above formulation, and fragment ions formed by stepwise loss of the ten CO ligands. The above requirements are met by formular (22) which contains a tetrahedral Ru_4 core, one face of which has been capped by the μ_3-$PPhCH_2PPh_2$ ligand. The exact arrangement of the CO and hydride ligands cannot be proposed with certainty; the lack of suitable crystals has prevented full stereochemical characterisation.

A noteworthy feature is that complex (6) readily undergoes P-C bond cleavage to give (22) and benzene, while the dppe analogue complex (9) undergoes rearrangement to give the isomeric complex (8).[19]

Pyrolysis of $Ru_3(CO)_{10}(dppm)$ (1)

Pyrolysis of (1) in refluxing cyclohexane (10 h) results in a darkening of the solution to deep red; subsequent chromatographic separation and crystallisation afforded red crystals of $Ru_3[\mu_3\text{-}PPhCH_2PPh(C_6H_4)](CO)_9$ (23) (Scheme 4) in 57% yield. The solution i.r. spectrum shows no detectable absorption in the bridging carbonyl region. The ^1H n.m.r. spectrum contains two resonances, a multiplet at δ 4.19 and a complex multiplet between δ 6.18-8.03, of relative intensities 2/14. Considering the origin of the phosphine ligand and the relative intensities of the n.m.r. signals, it is reasonable to assign the former signal to an AB(XY) pattern for the methylene protons (where X and Y are two inequivalent ^{31}P nuclei), while the latter signal is consistent with three phenyl groups, one of which has undergone cyclometallation to the cluster core. Full structural details were supplied by a single-crystal X-ray diffraction study [during the writing of this thesis, J-J. Bonnet also reported[23] the preparation and crystal structure of (23)].

The complex (Figure 2, see also Table 3) consists of a triangular Ru_3 core capped by a six-electron-donor orthometallated $PPhCH_2PPh(C_6H_4)$ ligand. The coordination of each ruthenium atom is completed by three CO groups. The Ru-Ru bonds range between 2.8250(7)-2.9862(7)Å, the longest bond [Ru(1)-Ru(3)] being bridged by the phosphido fragment and semi-bridged by C(10)-O(10) [Ru(1)-C(10) 1.963(5)Å, Ru(3)-C(10) 2.543(5)Å, Ru(1)-C(10)-O(10) 159.1(4)°].

The mode of attachment of the $PPhCH_2PPh(C_6H_4)$ ligand resembles to some extent the dephenylated $PPhCH_2PPh_2$ ligands found earlier in (14)[23] and (20)[25]. Further attachment to the cluster is achieved by cyclometallation of one of the phenyl rings on P(2) to give a conventional Ru-C σ-bond [Ru(1)-C(212) 2.170(4)Å] trans to the semi-bridging CO group.

The mechanism of the formation of (23) cannot be established with any certainty at this stage. Plausible intermediate steps involve oxidative addition of one of the aryl C-H bonds to give the (unobserved) complex (24) (Scheme 4) and concomitant loss of CO. This process might occur in an analogous fashion to the displacement of CO by a P-C bond of a μ-PPh_2 ligand found in $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}$,[28a] except that to form (24), initial "coordination" of the aryl C$\overset{\cdots}{=}$C bond

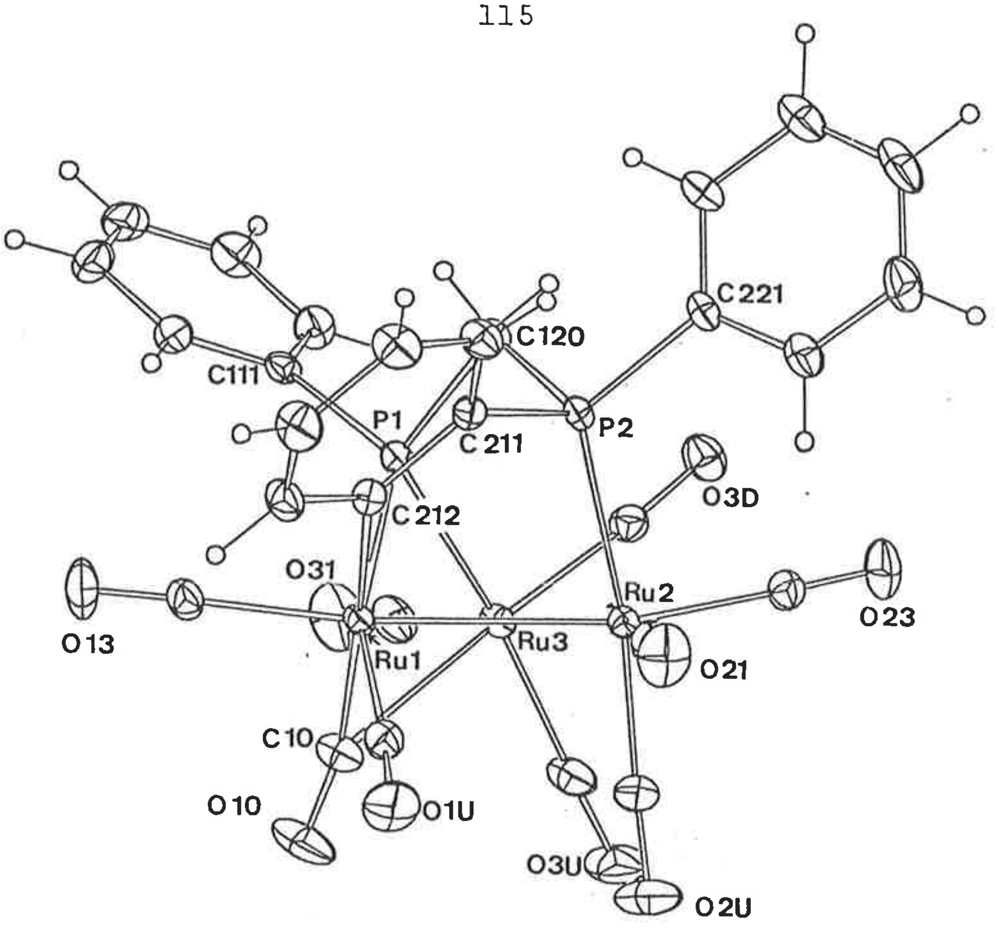


Figure 2. ORTEP plot of the molecular structure of $Ru_3[\mu_3\text{-}PPhCH_2PPh(C_6H_4)](CO)_9$ (23), showing the atom numbering scheme (by B.W. Skelton and A.H. White).

Table 3 Selected bond lengths and angles for (23)

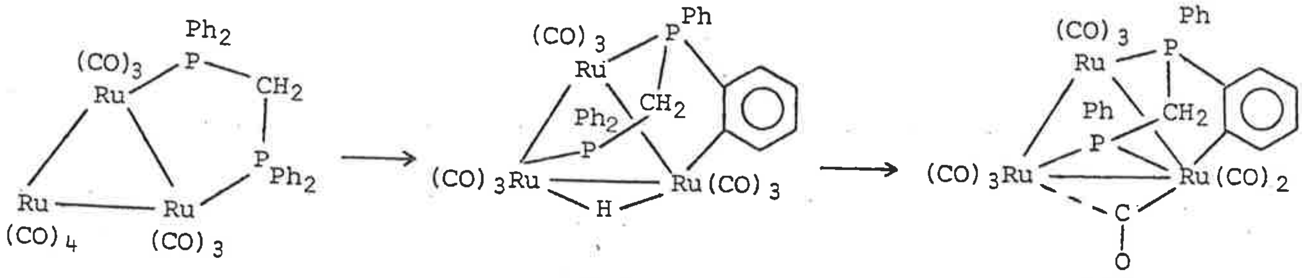
Bond lengths (Å)

Ru(1)-Ru(2)	2.8618(7)	Ru(1)-C(212)	2.170(4)
Ru(1)-Ru(3)	2.8962(7)	Ru(1)-C(10)	1.963(5)
Ru(2)-Ru(3)	2.8250(7)	Ru(3)-C(10)	2.543(5)
Ru(1)-P(1)	2.349(1)	P(2)-C(211)	1.804(4)
Ru(3)-P(1)	2.303(1)	C(10)-O(10)	1.144(6)
Ru(2)-P(2)	2.359(1)		

Angles (°)

Ru(1)-Ru(2)-Ru(3)	61.23(2)	Ru(3)-Ru(1)-C(212)	130.1(1)
Ru(2)-Ru(3)-Ru(1)	60.01(2)	Ru(1)-C(10)-O(10)	159.1(4)
Ru(3)-Ru(1)-Ru(3)	58.76(1)	Ru(3)-C(10)-O(10)	122.1(4)
Ru(1)-P(1)-Ru(3)	77.00(4)	Ru(1)-C(10)-Ru(3)	78.8(2)
Ru(2)-P(2)-C(211)	118.7(1)	P(1)-C(120)-P(2)	102.5(2)

must occur. Formation of (23) is completed by elimination of C_6H_6, formed by combination of the cluster-bound hydrogen with one of the phenyl groups on P(2). Of some interest is the recently reported thermolysis of the osmium analogue of (1), which also appears to proceed through an intermediate such as (24); loss of CO rather than C_6H_6 then occurs, to give the unsaturated hydrido cluster $Os_3(\mu\text{-}H)[\mu_3\text{-}PPh_2CH_2PPh(C_6H_4)]\text{-}(CO)_8$. It is noteworthy to remember that hydrogenation of the tri-osmium complex (5) also results in the isolation of a coordinatively-unsaturated hydrido cluster via the loss of CO and not C_6H_6.



(Scheme 4)

Reaction between $Ru_3(CO)_{10}(dppm)$ (1) and $K[HBBu^s_3]$

The dephenylated complex (14) can also be obtained by the sequential addition of H^- and H^+ to (1). Thus, treatment of (1) in tetrahydrofuran solution with K-Selectride ($K[HBBu^s_3]$) at ambient temperature resulted in an immediate darkening, followed by a slow (hours) change in the colour of the solution from deep red to orange-yellow. The infrared spectrum of this solution contained ν(CO) bands at 2033 and 2019 cm^{-1}. Protonation (H_3PO_4) and subsequent work-up afforded (14) in high yield. The arsenic analogue (15), was obtained by a similar sequence, although the elimination of benzene occurs at a much slower rate than found for (1). Addition of $K[HBBu^{s}_{3}]$ to $Ru_3(CO)_{10}$(dppe), heating the mixture at reflux point overnight and subsequent protonation, afforded the related complex (18) in low yield.

These unusual reactions probably proceed by initial formation of an anionic hydrido cluster, such as $[HRu_3(CO)_9(dppm)]^-$ (Scheme 2). In support of this, the i.r. spectrum of the initial deep red solution contains a broad medium intensity absorption at 1665 cm^{-1}, which is similar to that assigned to a ν(μ-CO) vibration in $[HRu_3(CO)_{11}]^-$.[28b] The subsequent elimination of benzene resembles well-established reactions of other cluster hydrides containing tertiary phophines or arsines, or thiolate ligands discussed above. In most cases, however, cleavage of the element-carbon bond occurs on heating, and we believe that this is the first occasion on which such a process has been accomplished by addition of hydride ion. However, the formation of $MnRu(\mu\text{-}PPh_2)(CO)_8(PPh_3)_2$ in the reaction between $RuCl_2(PPh_3)_3$ and $[Mn(CO)_5]^-$ is assumed to proceed via an intermediate anionic hydrido complex.[29]

It is interesting to note that deprotonation of the methylene protons of the bidentate ligands did not take place, probably because the approach of the bulky borohydride derivative to the methylene carbon is prevented by the phenyl groups.

Reactions of the anions $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ $(E = P$ or $As)$.

The anions generated from (1) or (4) by addition of $K[HBBu^s_3]$ proved to be useful synthetic intermediates. The anions react readily with sources of $[M(PPh_3)]^+$ fragments (M = Cu, Ag, Au) to give complexes in which the bridging hydride ligand in (14) or (15) has been replaced by the $M(PPh_3)$ group, a not unexpected result in view of the well-established isolobal relationship between H and $Au(PPh_3)$.

Thus, when solutions of the anions reacted with $[CuCl(PPh_3)]_4$, $[Ag\{C_5(CO_2Me)_5\}(PPh_3)]$ or $AuCl(PPh_3)$, the colour changes slightly, and the orange to red crystalline complexes $[MRu_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9(PPh_3)]$ [E = P, M = Cu (25), Ag (26), Au(27); E = As, M = Au (28)] were obtained in good yield. They were identified by elemental microanalyses and from their spectral characteristics. Their infrared spectra contained well-resolved $\nu(CO)$ patterns which resembled those of (14) or (15), while the ^1H n.m.r. spectra contained resonances from the bridging ligand and PPh_3, but no high-field signals as found in the parent hydrides. The methylene protons for complexes (25)-(27) appeared as doublets of doublets between δ 4.38-4.62, the A_2 part of an A_2XY system (where X and Y are two inequivalent phosphorus nuclei), while for (28) they appeared as a singlet at δ 4.46. The ^{13}C n.m.r. spectrum of (27) at room temperature contained a broad singlet at δ 199.8, assigned to the carbonyl groups (which are fluxional), a multiplet between δ 127.8-145.5 for the aromatic carbons and a doublet of doublets at δ 45.3 [*J*(PC) 19.1Hz and

26.5Hz] assigned to the methylene carbon which is coupled to two inequivalent phosphorus nuclei. The $^{31}P\{^1H\}$ n.m.r. spectrum exhibited three signals: a singlet at δ 68.7 assigned to the PPh_3 group, and two doublets for the $\underline{P}PhCH_2\underline{P}Ph_2$ ligand at δ 11.5 for the terminal phosphorus atom [*J*(PP) 117Hz], and δ 128.8 assigned to the μ-bridging phosphorus atom [cf. $\underline{P}PhCH_2\underline{P}Ph_2$ ligand in isomer (14b) at δ 18.9 (d, terminal P atom, *J*(PP) 100Hz) and δ 122.4 (d, μ-bridging P atom)[23]. Unambiguous identification of all three complexes (25)-(27) was achieved by single-crystal X-ray diffraction studies, well-formed crystals of which have afforded the first opportunity to compare this series of Group IB derivatives.

A similar reaction between the anion, generated by reaction of $K[HBBu^s_3]$ with $Ru_3(CO)_{10}(dppe)$, and $AuCl(PPh_3)$ gave the analogous complex $[AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)]$ (29) as red crystals. This complex had generally similar infrared ν(CO) spectra and ^1H n.m.r. spectra (except for the CH_2 resonances) to those of (27), and undoubtedly has a similar structure.

Crystal structures of $MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (M = Cu, Ag and Au)

Crystals of $MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ [M = Cu (25), Ag (26), and Au (27)] are isomorphous and contain discrete molecular units. The three derivatives are also isostructural, but this does not extend to include the resolved or unresolved disorder of some of the peripheral phenyl rings. The molecular structure of the Ag derivative is shown in Figure 3, while Table 4 shows selected bond lengths and angles. The complexes contain an MRu_3 'butterfly' cluster, the Ru_3 face of which is bridged by the μ_3-$PPhCH_2PPh_2$ ligand in a fashion similar to that found earlier in $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPhCH_2PPh_2)_2(CO)_6$ (20)[25] and $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2\text{-}PPh_2)(CO)_9$ (14)[23]; the bond parameters between these complexes do not differ significantly. The $M(PPh_3)$ moiety bridges the Ru(1)-Ru(3) edge on the opposite side to the phosphido group P(1). The coordination about each of the Ru atoms is completed by three CO groups. The symmetry of the MRu_3 core is a reasonable approximation to m; Ru(2)-Ru(1,3) are generally similar, but not equivalent Ru(2)-Ru(1) range from 2.891(2)-2.896(1)Å, while Ru(2)-Ru(3) are slightly less [2.867(2)-2.873(1)Å]. In (25) the Ru(1)-Ru(3) distance [2.885(1)Å] is similar to Ru(2)-Ru(1,3), while in (26) and (27) they are appreciably longer [2.944(1), 2.942(1)Å respectively]. The slight asymmetry in Ru(2)-Ru(1,3) is reflected in a similar and opposite asymmetry where M-Ru(1) is generally shorter than M-Ru(3) by 0.015-0.025Å; this is also true of P(1)-Ru(1,3). The deviation of P(1) from the Ru_3 plane is essentially constant (Table 4) as is the dihedral angle of the associated $P(1)Ru_2$ plane; by contrast, the deviation of Cu from the Ru_3 plane is rather less than those of Ag and Au which are almost identical. However, caution must be exercised when comparing 'butterfly' angles from solid state measurements as these deviations may be an effect of crystal packing[30] and not an effect of changing the coinage metal. The $MOs_3(\mu\text{-}H)(CO)_{10}(PPh_3)$ (M = Cu, Au)[31] complexes are

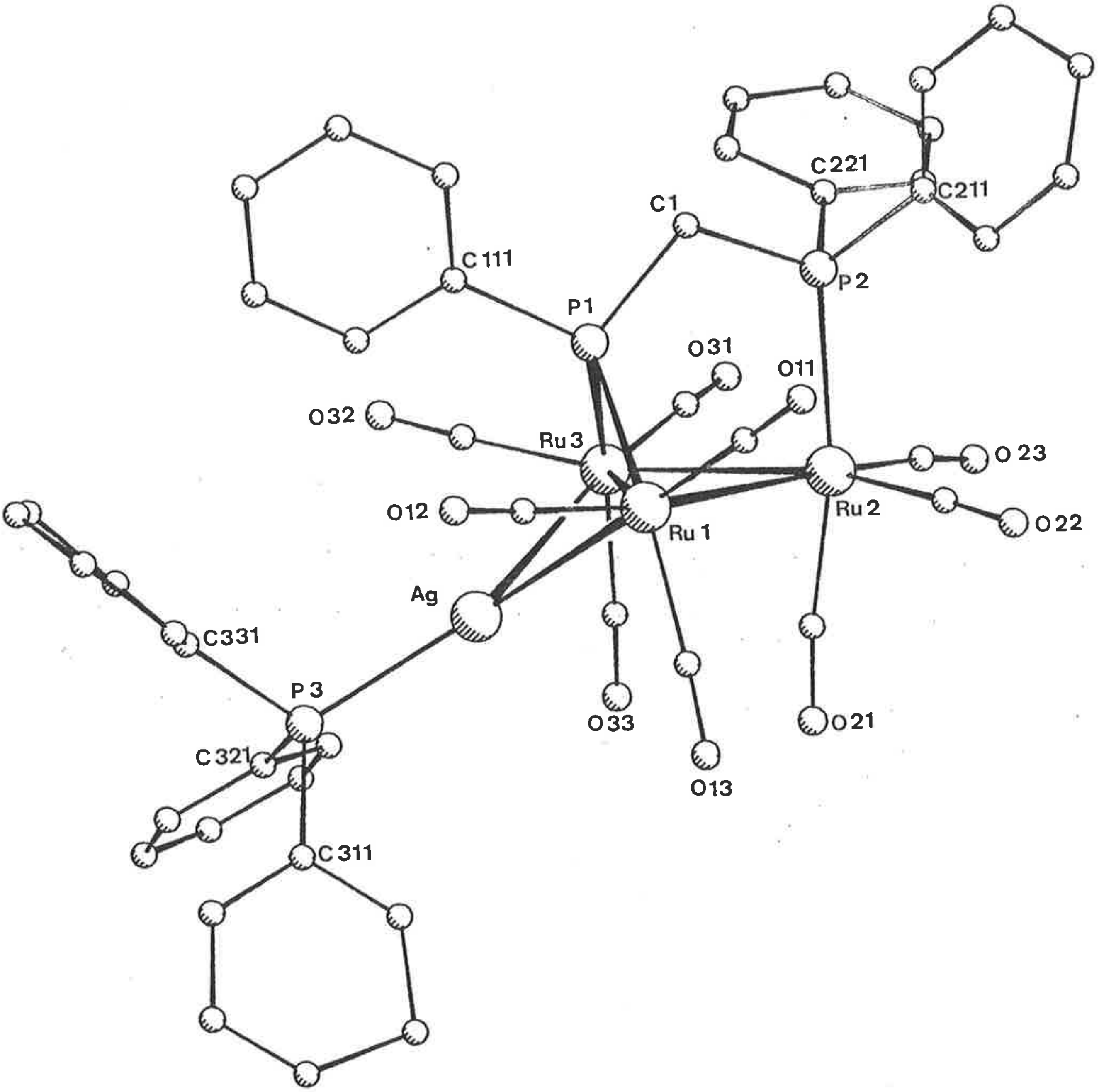
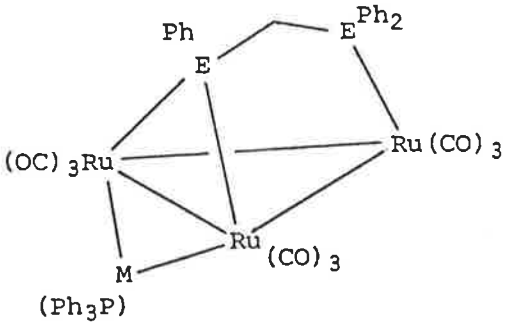
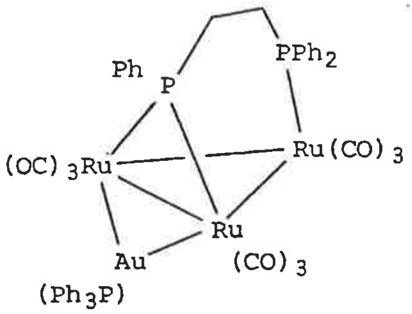


Figure 3: PLUTO plot of the molecular structure of $AgRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (29), showing the atom numbering scheme (by B.W. Skelton and A.H. White).

Table 4: Selected bond lengths and angles for $MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ [M = Cu (25), Ag (26), and Au (27)]

Bond lengths (Å)	(25)	(26)	(27)
Ru(1)-Ru(2)	2.896(1)	2.894(1)	2.891(1)
Ru(1)-Ru(3)	2.885(1)	2.944(1)	2.942(1)
Ru(3)-Ru(2)	2.873(1)	2.873(1)	2.867(1)
Ru(1)-M	2.607(1)	2.767(1)	2.751(1)
Ru(3)-M	2.622(1)	2.806(1)	2.786(1)
Ru(1)-P(1)	2.316(2)	2.328(2)	2.320(2)
Ru(3)-P(1)	2.336(2)	2.349(2)	2.348(2)
Ru(2)-P(2)	2.415(2)	2.432(2)	2.419(2)
P(3)-M	2.228(2)	2.422(3)	2.297(2)
Angles (°)			
Ru(1)-Ru(2)-Ru(3)	60.00(1)	61.39(2)	61.42(2)
Ru(2)-Ru(3)-Ru(1)	60.39(3)	59.67(4)	59.89(4)
Ru(3)-Ru(1)-Ru(2)	59.61(3)	58.95(3)	58.86(4)
Ru(1)-M-Ru(3)	66.95(3)	63.76(3)	64.18(3)
Ru(1)-P(1)-Ru(3)	76.6(1)	76.2(1)	78.1(1)
Ru(1)-Ru(2)-Ru(3)/ Ru(1)-M-Ru(3)	158.0(1)	146.0(1)	144.2(1)
Ru(1)-Ru(2)-Ru(3)/ Ru(1)-P(1)-Ru(3)	80.8(1)	81.5(1)	79.4(1)





(29)

	E	M
(25)	P	Cu
(26)	P	Ag
(27)	P	Au
(28)	As	Au

the only other examples in which a comparative structural study of the effect of the coinage metal has been made. In the former case the Os-Cu distances [2.695(5), 2.726(5)Å] are appreciably longer than in (25) [Ru(1,3)-Cu 2.607(1), 2.622(1)Å respectively]; the Cu-P distance [2.213(8)Å] is not significantly different from the present value [2.228(2)Å]. In the $AuOs_3$ cluster, the Os-Au distances [2.772(2), 2.738(1)Å] are similar to those in the present Au derivative (27) [Ru(1,3)-Au 2.751(1), 2.786(1)Å respectively]; the Au-P separation [2.320(7)Å] is slightly longer than found in (27) [2.297(2)Å]. Unfortunately, no comparable study exists for a silver derivative as one of the most unusual and as yet unexplained results is the long Ag-P distance [2.422(3)Å] cf. the Cu-P and Au-P values [2.228(2), 2.297(2)Å respectively].

Recent theoretical discussions have stressed that $Au(PR_3)$ is isolobal with H, in that it provides one orbital and one electron for cluster bonding.[33,34] This theoretical parallel has been supported by a number of structural studies which have shown that in mono-gold phosphine clusters, the $Au(PR_3)$ groups are located in the same site occupied by the H in the hydride analogues.[32,34-37] It has been suggested that gold derivatives of clusters may be used to predict H bonding sites when the corresponding hydride can not be located.[35] The results described above show that this approach is not valid as the $Au(PPh_3)$ moiety in (27) bridges the phosphido bridge Ru-Ru edge, while the solid state structure of (14) shows that the hydride bridges one of the Ru-Ru edges bridged by the phosphine and phosphido groups.[23] Similar discrepancies have been noted for the $(\mu\text{-}X)Fe_3(\mu_3\text{-}\eta^2\text{-}HC{=}NBu^t)$-

$(CO)_9$ [30] and $(\mu_3\text{-}X)CoRu_3(CO)_{13}$ [38] pairs [X = H, $Au(PPh_3)$]. Further to the above discussions, Evans and Mingos[39a] have predicted that bonding for the $Cu(PPh_3)$ group would be different to that observed for $Au(PPh_3)$ because in the former case the $\underline{p_x}$ and $\underline{p_y}$ orbitals are lower lying and may therefore make contributions to skeletal bonding. In contrast, recent calculations have shown that the $\underline{p_x}$ and $\underline{p_y}$ levels for $Cu(PPh_3)$ are not significantly lower in energy than for $Au(PPh_3)$.[39b] The latter theoretical study is in agreement with our experimental observations as we find no significant difference in the bonding of the $Cu(PPh_3)$ and $Au(PPh_3)$ fragments in (25) and (27). No theoretical studies for $Ag(PPh_3)$ have been reported.

Reaction with organic halides

The reaction between the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ and CHI_3 occurred readily to give one product, $Ru_3(\mu\text{-}I)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (30), which forms yellow crystals. The composition was indicated by elemental microanalysis and spectral data. The i.r. spectrum contained well-resolved ν(CO) bands which resembled those of (14) and (15), thus suggesting a similar structure. As with (14),[23] the ^1H n.m.r. spectrum contained resonances that can be assigned to the presence of two isomers, (30a) and (30b) [cf. (14a) and (14b) respectively], that differ in the position of the μ-I group on the Ru_3 triangle; at room temperature the isomers are observed in a 2:1 ratio respectively. The position of the μ-I group induces magnetic inequivalence of the proton nuclei within the methylene group; thus the complex multiplet at δ 5.00 is assigned to the AB portion of an AB(XY) system for (30a) (where X and Y are the two inequivalent phosphorus nuclei). In (30b), where the protons within the methylene group are magnetically equivalent, a doublet of doublets at δ 4.41 [*J*(PH) 10.0 and 11.5 Hz] was readily assigned to the A_2 portion of an A_2(XY) system [cf. the similar resonance in (27) 4.62, dd, *J*(PH) 10.0 and 12.4 Hz]. The aromatic multiplet is observed at δ 7.56 (relative intensity 15). The spectroscopic data that have been obtained are not sufficient to distinguish between a 1e- or 3e-donor I group and therefore full stereochemical characterisation is not possible at this stage.

Addition of $CH_2=CHCH_2Cl$ to the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ resulted in an immediate reaction (tlc); evaporation and crystallisation gave golden-yellow crystals of $Ru_3(C_3H_5)(PPhCH_2PPh_2)(CO)_8$ (31). The i.r. spectrum contains ν(CO) bands consistent with the presence of both terminal and bridging carbonyl ligands. Complex (31) is relatively insoluble, and informative ^1H n.m.r. spectra were not obtained.

An X-ray diffraction study of (31) was performed to determine the mode of attachment of the allylic group to the cluster.

A molecule of (31) is shown in Figure 4 (see also Table 5). The three ruthenium atoms define an isosceles triangle with the Ru(1)-Ru(2) and Ru(1)-Ru(3) edges being of equal length [2.853(1)Å], while Ru(2)-Ru(3) is slightly longer at 2.887(1)Å. The Ru_3 core is capped by the dephenylated $PPhCH_2PPh_2$ ligand in the same fashion as found earlier in

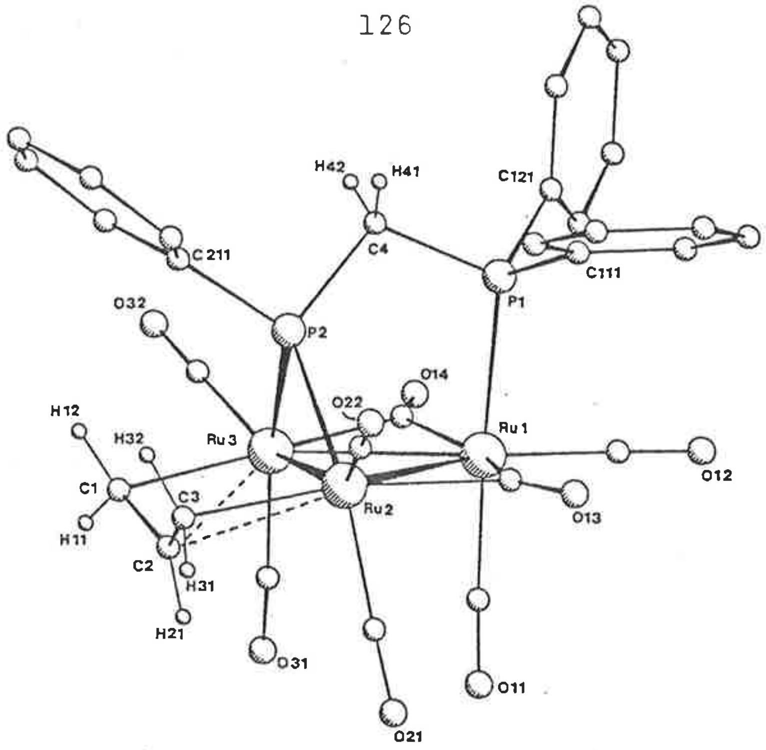


Figure 4 PLUTO plot of the molecular structure of $Ru_3(\mu\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (31), showing the atom numbering scheme.

Table 5 Selected bond lengths and angles for (31)

Bond lengths (Å)

Ru(1)-Ru(2)	2.853(1)	Ru(1)-C(41)	2.114(4)
Ru(1)-Ru(3)	2.853(1)	Ru(3)-C(41)	2.159(5)
Ru(2)-Ru(3)	2.887(1)	Ru(2)-C(3)	2.196(6)
Ru(1)-P(1)	2.411(1)	Ru(2)-C(2)	2.596(6)
Ru(2)-P(2)	2.359(1)	Ru(3)-C(2)	2.565(4)
Ru(3)-P(2)	2.344(1)	Ru(3)-C(1)	2.197(6)
Ru(1)-C(13)	2.079(4)	C(1)-C(2)	1.390(7)
Ru(2)-C(13)	2.185(5)	C(2)-C(3)	1.421(7)

Angles (°)

Ru(1)-Ru(2)-Ru(3)	59.6(1)	Ru(2)-Ru(3)-C(1)	85.5(1)
Ru(2)-Ru(3)-Ru(1)	59.6(1)	Ru(2)-C(3)-C(2)	88.9(3)
Ru(3)-Ru(1)-Ru(2)	60.8(1)	Ru(3)-C(1)-C(2)	88.3(4)
Ru(2)-P(2)-Ru(1)	75.7(1)	Ru(3)-C(2)-Ru(2)	68.1(1)
Ru(3)-Ru(2)-C(3)	84.7(1)	C(1)-C(2)-C(3)	126.4(4)
Ru(3)-Ru(2)-Ru(1)/C(1)-C(2)-C(3)		69.9(1)	

$MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ [M = Cu (25), Ag (26) and Au (27)]; the bond parameters between these complexes do not differ significantly. Each ruthenium is bonded to two terminal CO ligands, the remaining two μ-CO groups asymmetrically bridging the Ru(1)-Ru(2) [Ru(1)-C(13) 2.079(4), Ru(2)-C(13) 2.185(5)Å] and Ru(1)-Ru(3) [Ru(1)-C(14) 2.114(4), Ru(3)-C(14) 2.159(5)Å] edges. The third edge Ru(2)-Ru(3) is bridged by the phosphido atom [P(2)] and the allylic group C(1)-C(2)-C(3). The C(1)-C(2) and C(2)-C(3) bonds [1.390(7) and 1.421(7)Å, respectively] make an angle of 126.4(4)°; the angle between the C_3 and Ru_3 planes is 69.9(1)°. Atoms C(2), P(2), P(1) and Ru(1) define an approximate mirror plane that bisects the cluster normal to the Ru_3 triangle.

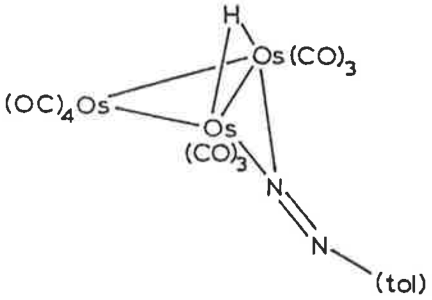
The terminal carbons of the allylic group C(1) and C(3) interact strongly with Ru(3) [2.197(6)Å] and Ru(2) [2.196(6)Å], respectively, while the central carbon atom is almost equidistant from these two metal atoms at a significantly greater separation [Ru(2)-C(2) 2.592(6), Ru(3)-C(2) 2.565(4)Å]. A similar mode of attachment has been described in the complexes $Pd_2(\mu\text{-}I)(\mu\text{-}C_3H_5)(PPh_3)_2$ [40] and $Pd_2(\mu\text{-}MeC_3H_4\text{-}2)(L)_2(\mu\text{-}C_5H_5)$ [L = PPh_3, $P(OC_6H_4CH_3\text{-}2)_3$][41] where the Pd-terminal carbon distances range from 2.10-2.20Å, while the Pd-central carbon distances range from 2.50-2.56Å.

Normally these central carbon-metal distances would be considered as too long for a bonding interaction, however, formal electron counting requires that the $\mu\text{-}C_3H_5$ group is acting as a three-electron donor, indicating a weak π-interaction exists between the allyl group and the metal edge. M.O. calculations have shown that binuclear Pd complexes possess two acceptor orbitals ($\underline{a}_1$ and $\underline{b}_1$) which can overlap with the 1π and $2\pi_a$ orbitals of a μ-η^3-C_5H_5 ligand which coordinates to the metals in an analogous manner to (31).[42]

To my knowledge, no example of a μ-η^3-C_3H_5 group symmetrically attached to a metal cluster has been crystallographically characterised. Other cluster complexes containing allylic groups include $[PPh_4][Rh_6(\eta^3\text{-}C_3H_5)(CO)_{14}]$,[43] in which the C_3H_5 ligand is bonded to one metal atom only, and the well-known systems containing $2\eta^1,\eta^3$-C_3 ligands, such as $Ru_3(\mu\text{-}H)(\mu_3\text{-}2\eta^1,\eta^3\text{-}CMeCHCEt)(CO)_9$ [44] or $Ru_3(\mu\text{-}H)(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_9$ [45,46]. The trinuclear complexes $(\eta\text{-}C_5H_5)MM'Pt(\mu\text{-}CH_2CMeCH_2)(CO)_3(PPr^i_3)_2$ (M = Cr, Mo, W; M' = Pd, Pt) and $CoPd(\mu\text{-}CH_2CMeCH_2)(CO)_4(PPr^i_3)_2$ [47,48] also contain μ-allyl groups; however these have not yet been crystallographically characterised, so no structural comparison with (31) is possible.

Reactions with aryldiazonium salts

Although extensive studies of mononuclear complexes containing nitrosyl (NO) or aryldiazo (ArN_2) ligands have shown the complementary nature of these two ligands,[49,50] there are only two structurally characterised cluster complexes, $Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}N{=}NC_6H_4Me\text{-}p)(CO)_{10}$ (32)[51] and $Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}N{=}NPh)(CO)_{10}$ (33),[52] containing the ArN_2 ligands. Recently a reversible photochemical/thermal interconversion of the η^1- and η^2-ArN_2 ligands in these two types of complexes has been described.



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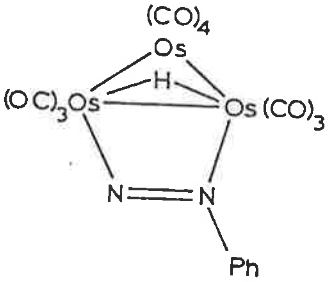


(33)

The reactions between $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ and $[PhN_2][PF_6]$ or $[2,4\text{-}Cl_2C_6H_3N_2][BF_4]$ in thf proceeded readily at room temperature to give yellow-orange complexes $Ru_3(\mu\text{-}\eta^1\text{-}N_2R)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9$ [R = Ph, E = P (34), As (35); R = $C_6H_3Cl_2$-2,4, E = P (36)] (Scheme 5), together with small amounts of the corresponding hydrido complexes (14) and (15). The formation of the latter complexes are likely to have resulted from protonation of the cluster anions by small amounts of HF which is present as a minor impurity in the aryldiazonium salts. Complexes (34)-(36) were identified by elemental microanalysis and from their spectral properties. Their i.r. spectra contained ν(CO) patterns and ν(NN) absorptions, while the ^1H n.m.r. spectra contained resonances from the bridging dephenylated ligands and the aryldiazo groups (see Experimental). Full stereochemical details of complex (36) were supplied by an X-ray diffraction study.

Complexes (34) and (35) undergo facile cyclometallation of the aryldiazo ligand on heating in refluxing cyclohexane (1 h) to give orange $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_8$ [E = P (37), As (38)] in high yields (Scheme 5). The ^1H

n.m.r. spectra confirm the presence of the metal-bonded hydrogen at δ -11.45 [dd, _J_(PH) 2.5 and 15.5Hz] for (35) and δ -11.65(s) for (37), together with the extended aromatic proton resonances between δ 7.10-8.25. An AB(XY) pattern at δ 2.45 for (37), which is similar to that observed for complex (23), and an AB quartet at δ 2.66 [_J_(AB) 12.9Hz] for (38) can be assigned to the magnetically inequivalent methylene protons. The above formulations were confirmed by an X-ray diffraction study of (38), which also enabled a rationalisation of the magnetic inequivalence of the methylene protons.

Molecular structures of (36) and (38)

The molecular structures of complexes (36) and (38) are shown in Figures 5 and 6 respectively, (see also Table 6). The μ_3-$EPhCH_2EPh_2$ ligands [E = P (36), As (38)], which are similar to those observed above, sit on one side of a somewhat enlarged Ru_3 triangle, two edges of which are bonding [Ru(1)-Ru(2) 2.875(2), Ru(1)-Ru(3) 2.893(2)Å for (36); Ru(1)-Ru(2) 2.903(1), Ru(2)-Ru(3) 3.055(1)Å for (38); the latter bond in (38) is bridged by both the hydride, and arsenido ligands]. The third edge, [Ru(2)-Ru(3) 3.321(2)Å for (36); Ru(1)-Ru(3) 3.547(1)Å for (38)] is lengthened by the presence of the 3e-donor aryldiazo ligands; in (36) the Ru(2)-Ru(3) vector is also bridged on the opposite side of the Ru_3 plane by the phosphido group. These separations, which are essentially non-bonding interactions, may be compared with that found in $[Ru_3(\mu\text{-}NO)_2(CO)_{10}]$ (3.15Å)[53] and contrast with that found in (32), in which the ArN_2 ligand has added to the Os=Os double bond in $Os_3(\mu\text{-}H)_2(CO)_{10}$, and which thus contains an Os-Os

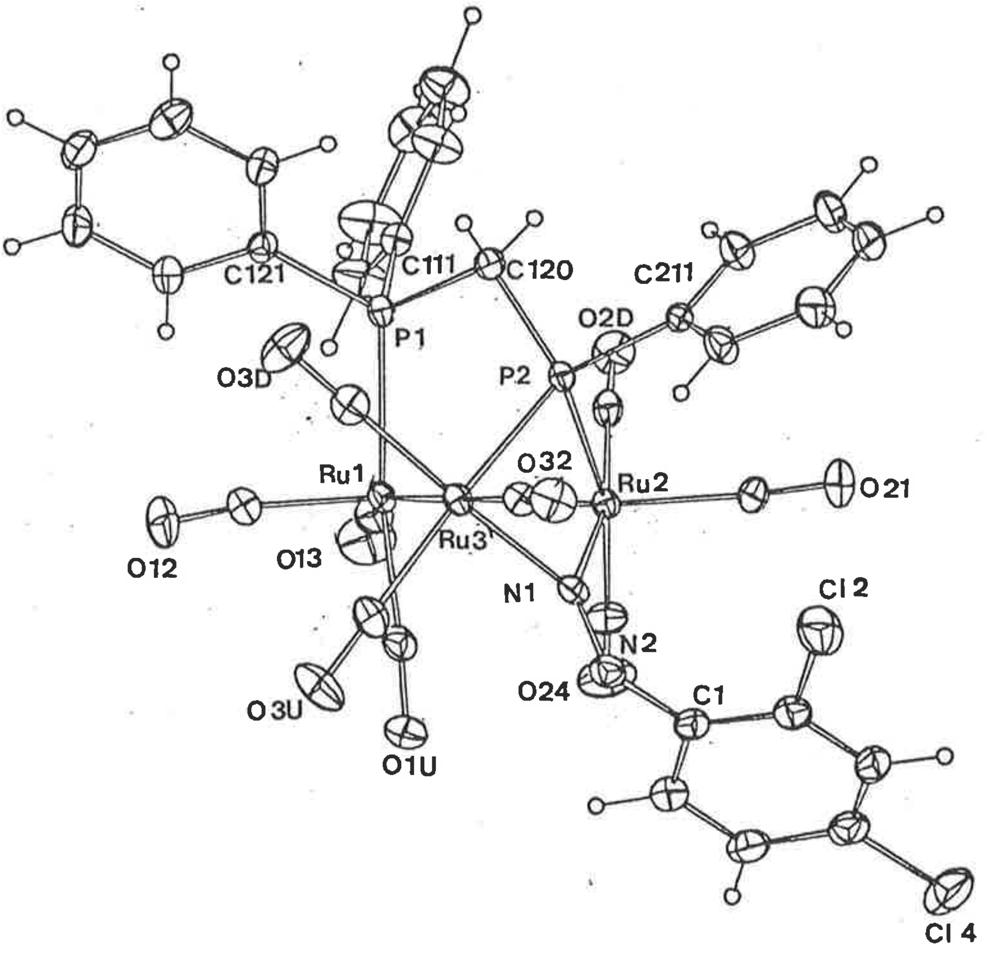


Figure 5: ORTEP plot of the molecular structure of $Ru_3(\mu\text{-}\eta^1\text{-}N_2C_6H_3Cl_2\text{-}2,4)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (36) showing the atom numbering scheme (by B.W. Skelton and A.H. White).

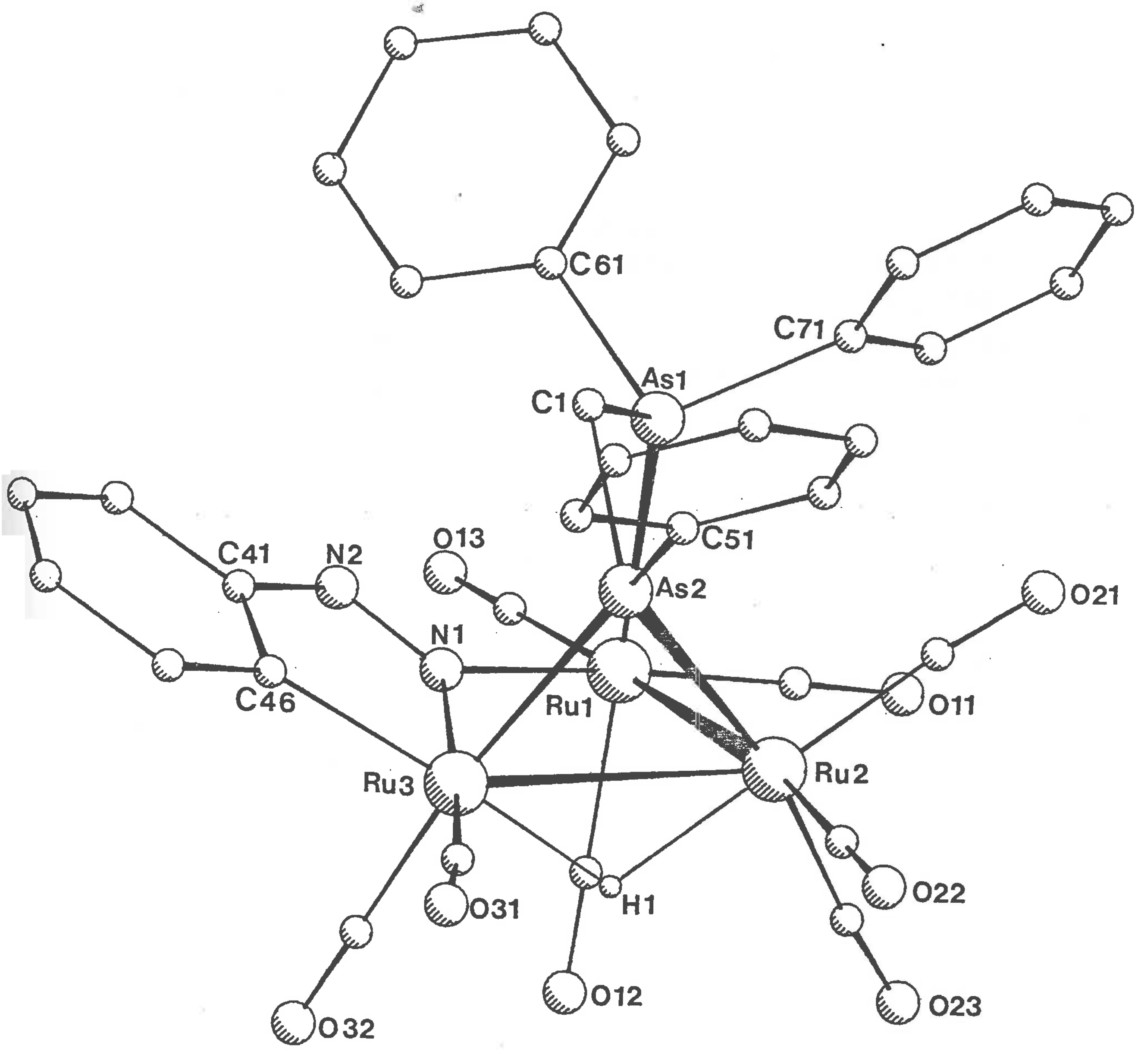


Figure 6. PLUTO plot of the molecular structure of $Ru_3(\mu-H)(\mu-\eta^1,\eta^1-N_2C_6H_4)(\mu_3-AsPhCH_2AsPh_2)(CO)_8$ (38), showing the atom numbering scheme.

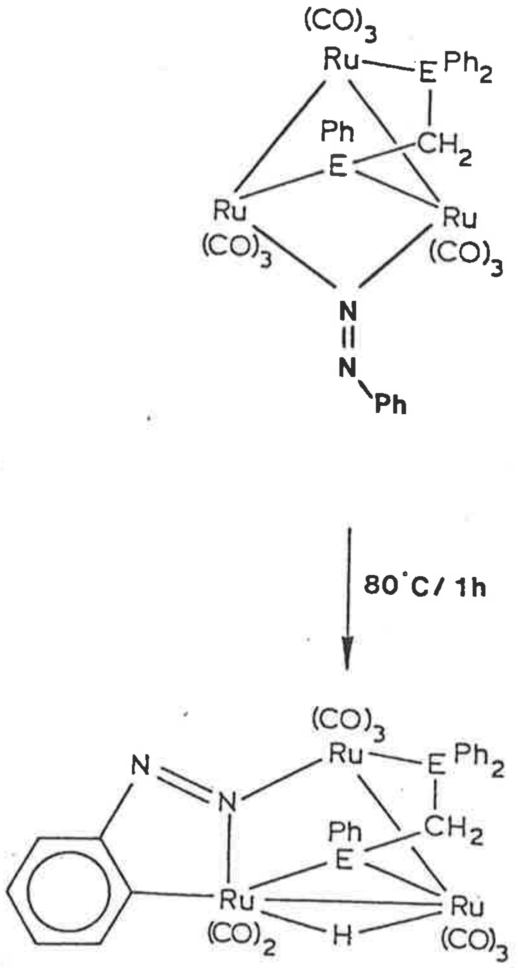
Table 6. Selected bond lengths and angles for $Ru_3(\mu-\eta^1-N_2C_6H_3Cl_2-2,4)(\mu_3-PPhCH_2PPh_2)(CO)_9$ (36) and $Ru_3(\mu-H)(\mu-\eta^1,\eta^1-N_2C_6H_4)(\mu_3-AsPhCH_2AsPh_2)(CO)_8$ (38).

Bond lengths (Å)	(36) E=P	(38) E=As
Ru(1)-Ru(2)	2.875(2)	2.903(1)
Ru(2)-Ru(3)	3.321(2)	3.055(1)
Ru(1)-Ru(3)	2.893(2)	3.547(1)
Ru(1)-E(1)	2.415(2)	2.498(1)
Ru(2)-E(2)	2.367(2)	2.456(1)
Ru(3)-E(2)	2.374(2)	2.437(1)
Ru(2)-N(1)	2.137(4)	-
Ru(3)-N(1)	2.098(4)	2.065(7)
Ru(1)-N(1)	-	2.092(5)
Ru(3)-C(46)	-	2.083(4)
Ru(2)-H(1)	-	1.89(3)
Ru(3)-H(1)	-	1.79(2)
N(1)-N(2)	1.230(5)	1.267(8)
N(2)-C(41)	-	1.392(7)
N(2)-C(1)	1.460(7)	-

Angles (°)		
Ru(1)-Ru(2)-Ru(3)	55.1(1)	73.7(1)
Ru(2)-Ru(3)-Ru(1)	54.6(1)	51.2(1)
Ru(3)-Ru(1)-Ru(2)	70.3(1)	55.1(1)
Ru(3)-E(2)-Ru(2)	88.9(1)	77.3(1)
Ru(1)-N(1)-Ru(3)	-	118.6(3)
Ru(2)-N(1)-Ru(3)	103.3(1)	-
Ru(2)-N(1)-N(2)	134.7(4)	-
Ru(3)-N(1)-N(2)	121.9(3)	119.7(5)
Ru(1)-N(1)-N(2)	-	121.2(5)
N(1)-N(2)-C(41)	-	112.6(7)
N(1)-N(2)-C(1)	116.8(4)	-
N(1)-Ru(3)-C(46)	-	77.4(2)
N(2)-C(41)-C(46)	-	120.0(5)
C(41)-C(46)-Ru(3)	-	109.6(3)

single bond [2.823(1)Å].[52] The N(1)-N(2) separations [1.230(5)Å for (36); 1.267(8)Å for (38)] are consistent with the presence of N=N double bonds, and are similar to that found in (32) [2.238(18)Å]. The two atoms Ru(1) and Ru(3) in (36) are bridged by N(1) [Ru(2)-N(1) 2.137(4), Ru(3)-N(1) 2.098(4)Å] while in (38) Ru(1) and Ru(3) are bridged by N(1) [Ru(1)-N(1) 2.092(5), Ru(3)-N(1) 2.065(7)Å; cf. Os-N distances of 2.036(11), 2.056(11)Å in (32)]. Coordination about the Ru_3 triangle in (36) is completed by the nine CO groups which are distributed three to each of the metal atoms. In (38) there are eight CO groups, three on each of Ru(1) and Ru(2) and two on Ru(3). The structure determination of (38) confirms that the ArN_2 ligand is cyclometallated, the phenyl ring on N(2) also being attached to Ru(3) by a conventional Ru-C σ-bond [Ru(3)-C(46) 2.083(4)Å]; there is no interaction of the C_6H_4 group with either of the other two metal atoms. The $C_6H_4N_2$ and Ru_3 planes make an angle of 170.4°, thus resulting in the magnetic inequivalence of the proton nuclei within the CH_2 C(1) group that is observed in the ^1H n.m.r. spectrum.

Cyclometallation of the aryldiazo ligand has occurred by oxidative addition of the ortho-C-H bond to Ru(3), the hydrogen (which was located and refined in the X-ray study) taking up a bridging position between Ru(3) and Ru(2). As can be seen by reference to Scheme 5, the cyclometallation reaction is accompanied by either a shift in the aryldiazo ligand with concomitant Ru-Ru bond cleavage and closure or a migration of the dephenylated μ_3-phosphido-phosphine and μ_3-arsenido-arsine ligands.



37 E = P
38 E = As

(Scheme 5)

This reaction contrasts with the η^1- and η^2-ArN_2 interconversions observed in complexes such as (32) and (33),[52] and is characteristic of phenylazo ligands (such as azobenzene) on mononuclear complexes.[54,55] Indeed azobenzenes react with some ruthenium cluster complexes to give mononuclear cyclometallated derivatives;[56] in the present instance the μ_3-$EPhCH_2EPh_2$ ligand prevents cluster degradation.

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1. The complexes $Ru_3(CO)_{10}(dppe)$ and $[Ru_3(CO)_{11}]_2$-(μ-dppe) were prepared by published procedures,[57] while the diazonium salts were prepared by diazotisation of the appropriately substituted aniline with $NaNO_2/HBF_4$.

Preparation of $Ru_3(CO)_{10}(dppm)$ (1)

A mixture of $Ru_3(CO)_{12}$ (1.0 g, 1.56 mmol) and dppm (0.62 g, 1.61 mmol) in thf (100 ml) was warmed to 40°C to dissolve all of the carbonyl. A solution of $Na[Ph_2CO]$ in thf [*ca* 0.025 mol l^{-1}] was added dropwise from a syringe until the solution darkened and the 2061 cm^{-1} band of $Ru_3(CO)_{12}$ was absent (1-5 drops). The solution volume was reduced to *ca* 5 ml (rotary evaporator). Addition of MeOH (40 ml) and cooling gave orange-red crystals of $Ru_3(CO)_{10}(dppm)$ (1) (1.37 g, 91%) m.p. 180-181°C [Found: C, 43.76; H, 2.05; $C_{35}H_{22}O_{10}P_2Ru_3$ requires C, 43.44; H, 2.29%]. Infrared (cyclohexane): ν(CO) 2086m, 2024(sh), 2018s, 2005s, 1991w, 1968m, 1965m, 1947w cm^{-1} [lit.[12] ν(CO) (CH_2Cl_2) 2080m, 2040w, 2010s, 1988(sh), 1960m cm^{-1}]. ^1H n.m.r.: δ ($CDCl_3$) 4.29 [t, *J*(PH), 10.5Hz, 2H, CH_2], 7.37 (m, 20H, Ph).

Preparation of $[Ru_3(CO)_{10}(dpam)]$ (4)

This complex was obtained in 91% yield by the $Na[Ph_2CO]$-catalysed reaction between $Ru_3(CO)_{12}$ and dpam, carried out as described above for the dppm complex, m.p. 170-174°C [Found: C, 39.81; H, 1.96; $C_{35}H_{22}As_2O_{10}Ru_3$ requires C, 39.82; H, 2.10%]. Infrared: ν(CO) at 2087m, 2028w, 2014vs, 2010(sh), 1993w, 1968m, 1962m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 4.15 (s, 2H, CH_2), 7.38 (m, 20H, Ph).

Preparation of $Os_3(CO)_{10}$(dppm) (5)

A mixture of $Os_3(CO)_{10}(CNMe)_2$ (317 mg, 0.34 mmol), MeCN (20 ml) and dppm (130 mg, 0.34 mmol) in cyclohexane (100 ml) was stirred at 40°C for 4 h. Evaporation and preparative tlc [light petroleum-acetone 90/10] afforded one major band. $\underline{R_f}$ 0.30, yellow, recrystallised from CH_2Cl_2/MeOH to give large yellow-orange crystals of $Os_3(CO)_{10}$(dppm) (5) (225 mg, 54%), m.p. >165°C (dec). [Found: C, 34.12; H, 1.65; $C_{35}H_{22}O_{10}Os_3P_2$ requires C, 34.04; H, 1.78%]. Infrared (cyclohexane): ν(CO) 2098m, 2033m, 2019s, 2010vs, 1986m, 1968m, 1958s, 1947w, 1922vw cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 5.05 [t, $\underline{J}$(PH) 10.5 Hz, 2H, CH_2], 7.38 (m, 20H, Ph).

Preparation of $Ru_4(\mu\text{-}H)_4(CO)_{10}$(dppm) (6)

A mixture of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (200 mg, 0.269 mmol) and dppm (110 mg, 0.286 mmol) in thf (40 ml) was warmed to ca 40°C to dissolve all of the cluster. A solution of Na[Ph_2CO] in thf [ca. 0.025 mol l^{-1}] was added dropwise from a syringe until the solution darkened and the 2084 cm^{-1} band of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ was absent (0.5 ml). Evaporation and recrystallisation from CH_2Cl_2/MeOH gave red crystals of $Ru_4(\mu\text{-}H)_4(CO)_{10}$(dppm) (6) (249 mg, 86%), m.p. 150-153°C. [Found: C, 39.01; H, 2.30; $C_{35}H_{26}O_{10}P_2Ru_4$ requires C, 39.19, H, 2.44%]. Infrared (cyclohexane): ν(CO) 2088w, 2076m, 2054s, 2037vs, 2026w, 2015s, 1999w, 1985w, 1976m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -16.72 (s, 4H, RuH), 3.80 (m, 2H, CH_2), 7.20 (m, 20H, Ph).

Preparation of $Ru_4(\mu-H)_4(CO)_{10}$(dpam) (7)

This complex m.p. >150°C (dec) was obtained in 58% yield by the Na[Ph_2CO]-catalysed reaction between $Ru_4(\mu-H)_4(CO)_{12}$ and dpam, carried out as described above for the dppm complex. [Found: C, 36.47; H, 2.42; $C_{35}H_{26}As_2O_{10}Ru_4$ requires C, 36.22; H, 2.26%]. Infrared (cyclohexane): ν(CO) 2077m, 2054s, 2038vs, 1998w, 1987w, 1977m, 1973(sh), 1975w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -17.00 (s, 4H, RuH), 3.37 [AB quartet, *J*(AB) 12Hz, 2H, CH_2], 7.31 (m, 20H, Ph).

Hydrogenation of $Ru_3(CO)_{10}$(dppm) (1)

A solution of $Ru_3(CO)_{10}$(dppm) (1) (200 mg, 0.206 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (80°C, 20 atm, 2 h). The resulting yellow solution was filtered and evaporated to dryness. Recrystallisation of the residue from Et_2O/MeOH gave yellow crystals of $Ru_3(\mu-H)(\mu_3-PPhCH_2PPh_2)(CO)_9$ (14) (134 mg, 75%), identified by comparison of its i.r. ν(CO) spectrum with that of a sample prepared as described below (p. 142).

Hydrogenation of $Ru_3(CO)_{10}$(dpam) (4)

A similar reaction of $Ru_3(CO)_{10}$(dpam) (4) afforded orange-yellow crystals of $Ru_3(\mu-H)(\mu_3-AsPhCH_2AsPh_2)(CO)_9$ (15) (117 mg, 65%), identified by comparison of its i.r. ν(CO) spectrum with that of a sample prepared as described below (p. 143).

Prolonged hydrogenation of $Ru_3(CO)_{10}(dppm)$ (1)

A solution of $Ru_3(CO)_{10}(dppm)$ (1) (200 mg, 0.206 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (85°C, 20 atm, 20 h). The resulting yellow solution was taken to dryness and separated by preparative tlc [light petroleum-acetone 85/15] to give four bands. Band 1 $\underline{R_f}$ 0.45, yellow, recrystallised from CH_2Cl_2/MeOH to give yellow crystals of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (16) (18 mg, 10%), identified by comparison of its i.r. $\nu(CO)$ spectrum with that of an authentic sample.[24] Band 2, $\underline{R_f}$ 0.40 yellow, recrystallised from CH_2Cl_2/MeOH to give a yellow powder of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14) (75 mg, 42%). Band 3, $\underline{R_f}$ 0.30, yellow (trace), not identified. Band 4, $\underline{R_f}$ 0.17, orange, recrystallised from CH_2Cl_2/MeOH to give $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (22) (19 mg, 10%). Bands 2 and 4 were identified by comparison of their i.r. $\nu(CO)$ spectra with those authentic samples prepared as described below.

Hydrogenation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14)

A similar reaction of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14) (85°C, 20 atm, 21 h) afforded $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (16) (5%), $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14) (50%) and $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (22) (13%). All were identified as above.

Longer reaction times (40 h) afforded complexes (16) and (22) in 45% and 13% yields, respectively.[24]

Hydrogenation of $Os_3(CO)_{10}(dppm)$ (5)

A solution of $Os_3(CO)_{10}(dppm)$ (5) (90 mg, 0.073 mmol) in toluene (30 ml) was hydrogenated in an autoclave (85°C, 25 atm, 12 h). The resulting red solution was taken to dryness and the residue recrystallised from CH_2Cl_2/MeOH to give red plate-like crystals of $Os_3(\mu\text{-}H)_2(CO)_8(dppm)$ (17) (58 mg, 67%), m.p. 235-238°C. [Found: C, 33.44; H, 1.84; *M* (mass spectrum), 1181. $C_{33}H_{24}O_8Os_3P_2$ requires C, 33.55; H, 2.05%, *M*, 1181]. Infrared (cyclohexane): ν(CO) 2076m, 2013s, 1995vs, 1974m, 1959m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -10.31 [t, *J*(PH) 10.5 Hz, 2H, OsH], 4.15 [t, *J*(PH) 10.5 Hz, 2H, CH_2], 7.30 (m, 20H, Ph).

Hydrogenation of $Ru_3(CO)_{10}(dppe)$

A solution of $Ru_3(CO)_{10}(dppe)$ (200 mg, 0.204 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (80°C, 20 atm, 5 h). The resulting yellow solution was taken to dryness and chromatographed by preparative tlc [light petroleum-acetone 90/10] to give 4 bands. Band 1, *R_f* 0.36, yellow, recrystallised from CH_2Cl_2/MeOH to give an orange powder of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ (18) (60 mg, 34%), m.p. 110-115°C [Found: C, 39.83; H, 2.30; *M* (mass spectrum), 879. $C_{29}H_{20}O_9P_2Ru_3$ requires C, 39.69; H, 2.30%, *M*, 879]. Infrared (cyclohexane): ν(CO) 2087m, 2043s, 2016vs, 2007w, 1995w, 1990w, 1979m, 1968w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 7.45 (m, 15H, Ph), 4.46 [s(br), 4H, CH_2], -16.36 [s(br), 1H, RuH]. Band 4 *R_f* 0.13, yellow, recrystallised from CH_2Cl_2/MeOH to give orange crystals of $Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)$ (8) (52 mg, 23%)

identified by comparison of infrared and ^1H n.m.r. data with literature values.[18,19] Bands 2 and 3 were obtained in trace amounts and were not identified.

Hydrogenation of $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$

A solution of $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$ (250 mg, 0.154 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (80°C, 20 atm, 10 h). The resulting yellow solution was taken to dryness and chromatographed by preparative tlc (light petroleum-acetone 90/10) to give ten bands. Band 1, $\underline{R_f}$ 0.80, yellow, $Ru_4(\mu\text{-H})_4(CO)_{12}$ (45 mg, 39%). Band 2, $\underline{R_f}$ 0.37, yellow recrystallised from CH_2Cl_2/MeOH to give an orange powder of $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2CH_2PPh_2)(CO)_9$ (18) (11 mg, 8%). Band 3, $\underline{R_f}$ 0.32, orange, recrystallised from CH_2Cl_2/MeOH to give red crystals of $[Ru_4(\mu\text{-H})_4(CO)_{11}]_2(\mu\text{-dppe})$ (19) (27 mg, 10%), m.p. 190-195°C (dec). [Found: C, 31.85; H, 1.77; $C_{48}H_{32}O_{22}P_2Ru_8$ requires C, 31.48; H, 1.76%]. Infrared (cyclohexane): ν(CO) 2098m, 2072vs, 2062vs, 2029vs, 2014s, 1996w, 1978w, 1966m cm^{-1}. Band 8, $\underline{R_f}$ 0.13, orange, recrystallised from CH_2Cl_2/MeOH to give red crystals of $Ru_4(\mu\text{-H})_4(CO)_{10}$(dppe) (8) (62 mg, 37%). Bands 1, 2 and 8 were identified by comparison of their i.r. ν(CO) spectra with those of authentic samples. Bands 4-7, 9 and 10 were obtained in trace amounts and were not identified.

Thermolysis of $Ru_4(\mu\text{-H})_4(CO)_{10}$(dppm) (6)

A solution of $Ru_4(\mu\text{-H})_4(CO)_{10}$(dppm) (6) (100 mg, 0.093 mmol) was heated in refluxing cyclohexane (10 ml) for 1 h, after which time the reaction was adjudged complete [the disappearance of the ν(CO) band at 2015 cm^{-1} was monitored]. Filtration, addition of n-heptane (5 ml), reduction in volume to ca 5 ml (rotary evaporator) and cooling gave fine orange crystals of $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (22) (70 mg, 76%), m.p. 180-185°C (dec). [Found: C, 35.00; H, 2.00; M (mass spectrum), 996. $C_{29}H_{20}O_{10}P_2Ru_4$ requires C, 35.12; H 2.03%; M, 996]. Infrared (cyclohexane): ν(CO) 2075m, 2056s, 2024vs, 1996m, 1981m, 1898w, 1843m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) -17.95 [s(br), 1H, RuH], -19.74 [s(br), 2H, RuH], 3.22 [t, J(PH) 10.5Hz, 2H, CH_2], 7.55 [m, 15H, Ph].

Thermolysis of $Ru_3(CO)_{10}(dppm)$ (1)

A solution of $Ru_3(CO)_{10}(dppm)$ (1) (100 mg, 0.103 mmol) was heated in refluxing cyclohexane (15 ml) for 10 h, after which time the reaction was adjudged complete (tlc). Evaporation and preparative tlc [light petroleum-acetone 90/10] afforded one major band. R_f 0.31, red, recrystallised from CH_2Cl_2/MeOH to give red crystals of $Ru_3[\mu_3\text{-}PPhCH_2PPh\text{-}(C_6H_4)](CO)_9$ (23) (51 mg, 57%) m.p. 145-148°C. [Found: C, 39.64; H 1.62; $C_{28}H_{16}O_9P_2Ru_3$ requires C, 39.03; H, 1.87%]. Infrared (cyclohexane): ν(CO) 2078s, 2040vs, 2033vs, 2010m, 1995m, 1988w, 1971w, 1942m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 4.19 [AB(XY) pattern, 2H, CH_2], 6.18-8.03 (m, 14H, Ph and C_6H_4).

Preparation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14)

A solution of $Ru_3(CO)_{10}(dppm)$ (1) (150 mg, 0.155 mmol) in thf (10 ml) was treated with $K[HBBu^s_3]$ (0.31 ml of a 0.5 mol

l^{-1} solution in thf, 0.155 mmol). An immediate darkening in colour to deep red occurred initially, followed by a gradual lightening to orange after stirring at 25°C for 5 h. Addition of H_3PO_4 (0.25 ml) to the reaction mixture resulted in a further lightening in colour to yellow. The solvent was evaporated and the residue extracted with light petroleum (3 x 10 ml). The combined filtered extracts were taken to dryness, recrystallisation from Et_2O/MeOH afforded yellow crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14) (92 mg, 69%) m.p. 135-140°C (dec). [Found: C, 38.85; H, 1.67; M(mass spectrum), 865. $C_{28}H_{18}O_9P_2Ru_3$ requires C, 38.94; H, 2.10%; M, 865]. Infrared (cyclohexane): ν(CO) 2084s, 2053vs, 2031vs, 2014m, 2001m, 1996m, 1990m, 1984m, 1964w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -16.65 [t (br), J(PH) 10.8Hz, 1H, RuH], 3.93 [s(br), 2H, CH_2], 7.44 (m, 15H, Ph).

Attempts to isolate the first-formed deep red anion, for example, by crystallisation with [ppn]Cl, were not successful. The infrared spectrum contains a ν(CO) band at 1665m cm^{-1}, which is characteristic of a μ-CO ligand in anionic hydrido clusters.

Preparation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (15)

A solution of $Ru_3(CO)_{10}$(dpam) (4) (100 mg, 0.095 mmol) in thf (10 ml) was treated with $K[HBBu^s_3]$ (0.2 ml of a 0.5 mol l^{-1} solution in thf, 0.10 mmol). After stirring at 25°C for 20 h H_3PO_4 (0.25 ml) was added. The solution was then taken to dryness and the residue extracted with light petroleum (3 x 10 ml). The combined filtered extracts were taken to dryness, recrystallisation from Et_2O/MeOH afforded orange yellow crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (15) (48 mg, 53%). m.p. 157-159°C (dec) [Found: C, 35.76; H, 1.67; $C_{28}H_{18}As_2O_9Ru_3$ requires C, 35.35; H, 1.91%]. Infrared (cyclohexane): ν(CO) 2081s, 2052vs, 2029vs, 2009s, 1992s, 1979w, 1968m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -16.35 [s(br), 1H, Ru$\underline{H}$], 4.47 [s(br), 2H, CH_2], 7.45 (m, 15H, aromatic). ^{13}C n.m.r.: δ ($CDCl_3$) 41.93 [s(br), $\underline{C}H_2$], 128.93-142.98 (m, aromatic); 196.46 [s(br), $\underline{C}O$].

Preparation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ (18)

A solution of $Ru_3(CO)_{10}$(dppe) (100 mg, 0.102 mmol) in thf (10 ml) was treated with K[$HBBu^s_3$] (0.22 cm^3 of a 0.5 mol l^{-1} solution in thf, 0.11 mmol). After stirring at reflux for 18 h H_3PO_4 (0.25 ml) was added. The solution was taken to dryness and the residue extracted with light petroleum (3x10 ml). The combined yellow filtered extracts were taken to dryness; recrystallisation from CH_2Cl_2/MeOH gave an orange yellow powder of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ (18) (22 mg, 25%).

This complex was identified by comparison of its ν(CO) spectrum with that of an authentic sample.

Only $Ru_3(CO)_{10}$(dppe) was recovered (70%) after stirring with K[$HBBu^s_3$] at room temperature for 5 h, followed by addition of H_3PO_4.

Preparation of Group IB derivatives

(a) $CuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (25) A solution of $Ru_3(CO)_{10}$(dppm) (1) (300 mg, 0.309 mmol) in thf (10 ml) was treated with K[HBBu$^s_3$] (0.63 ml of a 0.5 mol l^{-1} solution in thf, 0.315 mmol). After stirring at 25°C for 5 h, the initial deep red solution had lightened to orange. Solid $[CuCl(PPh_3)]_4$ (114 mg, 0.315 mmol) was added to the anionic solution resulting in a further change in colour to a deeper orange. After stirring at ambient temperature for 30 min solvent was removed and the residue extracted with diethyl ether (3 x 20 ml). Filtration through celite, addition of methanol (10 ml) to the filtrate and reduction of the solution volume to _ca_ 10 ml gave $CuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (25) as an orange powder (297 mg, 81%), m.p. 179-184°C (dec). [Found: C, 46.25; H, 2.86; $C_{46}H_{32}CuO_9P_3Ru_3$ requires C, 46.49; H, 2.71%]. Infrared (cyclohexane): ν(CO) 2057m, 2013vs, 2007(sh), 1996m, 1984w, 1965m, 1947m cm^{-1}. ^1H n.m.r. δ ($CDCl_3$): 4.38 [dd, _J_(PH) 10.0 and 12.2Hz, 2H, CH_2], 7.39 (m, 30H, Ph).

(b) <u>$AgRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (26)</u> The cluster anion was prepared by the above method using $Ru_3(CO)_{10}(dppm)$ (1) (100 mg, 0.103 mmol), thf (10 ml) and K[HBBu$^s_3$] (0.21 ml of a 0.5 mol l^{-1} solution in thf, 0.105 mmol). A solution of $Ag\{C_5(CO_2Me)_5\}(PPh_3)$ (75 mg, 0.103 mmol) in thf (50 ml) was added dropwise (0.5 h) to the anionic solution, resulting in a darkening from orange to red. After removal of the solvent, the residue was extracted with CH_2Cl_2 (2x10 ml) and filtered through celite. Addition of MeOH (20 ml) to the filtrate followed by concentration to _ca_ 20 ml (rotary evaporator) and cooling to 0°C gave well-formed deep red crystals of $AgRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)$ (26) (104 mg, 82%), m.p. 198-201°C.

[Found: C, 44.36; H, 2.27; $C_{46}H_{32}AgO_9P_3Ru_3$ requires C, 44.82; H, 2.62%]. Infrared (cyclohexane): ν(CO) 2054m, 2014vs, 2000s(sh), 1985m, 1961w, 1950m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 4.54 [dd, *J*(PH) 9.5 and 11.7Hz, 2H, CH_2], 7.45 (m, 30H, Ph).

(c) $AuRu_3(\mu_3$-$PPhCH_2PPh_2)(CO)_9(PPh)_3$ (27) A solution of $Ru_3(CO)_{10}$(dppm) (1) (100 mg, 0.103 mmol) in dry thf (10 ml) was treated with $K[HBBu^{s}_{3}]$ (0.21 ml of a 0.5 mol l^{-1} solution in thf, 0.105 mmol). After stirring at 25°C for 5 h, the initial deep red solution lightened to orange. Solid $[AuCl(PPh_3)]$ (52 mg, 0.105 mmol) was added and the mixture stirred for 30 min. The solution was taken to dryness, extracted with diethyl ether (3x25 ml) and filtered through celite. Evaporation and recrystallisation from CH_2Cl_2/MeOH afforded orange-red crystals of $AuRu_3(\mu_3$-$PPhCH_2PPh_2)(CO)_9$-(PPh_3) (27) (100 mg, 74%), m.p. 224-226°C (dec). [Found: C, 41.56; H, 2.09; $C_{46}H_{32}AuO_9P_3Ru_3$ requires C, 41.80; H, 2.44%]. Infrared (cyclohexane): ν(CO) 2058m, 2023vs, 2011s, 1992m, 1977w, 1963m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 4.62 [dd, *J*(PH) 10.0 and 12.4Hz, 2H, CH_2], 7.43 (m, 30H, Ph). ^{13}C n.m.r.: δ ($CDCl_3$) 45.33 [dd, *J*(PC) 19.1 and 26.5Hz, CH_2], 127.8-146.6 (m, C_6H_5), 198.7-199.9 (m, CO). ^{31}P n.m.r.: δ ($CDCl_3$) 11.46 [d, *J*(PP) 117Hz, PPh_2], 68.68 (s, PPh_3), 128.81 (d, *J*(PP) 117Hz, PPh).

(d) $AuRu_3(\mu_3$-$AsPhCH_2AsPh_2)(CO)_9(PPh_3)$ (28) A reaction similar to (a), using $Ru_3(CO)_{10}$(dpam) (4) (100 mg, 0.095 mmol) gave large well formed crystals of $AuRu_3(\mu_3$-$AsPhCH_2AsPh_2)$-$(CO)_9(PPh_3)$ (101 mg, 75%), m.p. 191-195°C. [Found: C, 39.10;

H, 2.00; $C_{46}H_{32}As_2AuPRu_3$ requires C, 39.19; H, 2.29%]. Infrared (cyclohexane): ν(CO) 2070vw, 2056m, 2040vw, 2022vs, 2009s, 1989m, 1974w, 1965m, 1960w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.46 (s, 2H, CH_2), 7.43 (m, 30H, Ph).

(e) $AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)$ (29) A solution of $Ru_3(CO)_{10}$(dppe) (50 mg, 0.051 mmol) in dry thf (10 ml) was treated with K[$HBBu^s_3$] (0.15 ml of a 0.5 mol l^{-1} solution in thf, 0.08 mmol). After stirring at 40°C for 5 h, solid [AuCl(PPh_3)] (28 mg, 0.057 mmol) was added and the mixture stirred for 2 h. The solution was extracted with diethyl ether (3x10 ml) and filtered. Evaporation and recrystallisation from CH_2Cl_2/isopentane afforded red crystals of $AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)$ (29) (18 mg, 26%), m.p. 206-209°C. [Found: C, 42.13; H, 2.47; $C_{47}H_{34}AuO_9P_3Ru_3$ requires C, 42.26; H, 2.57%]. Infrared (cyclohexane): ν(CO) 2073m, 2021s, 2009m, 1997vs, 1991w, 1969w, 1950m, 1936w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.45 [s(br), 4H, CH_2], 7.45 (m, 30H, Ph).

Reaction of $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ with CHI_3

A solution of $Ru_3(CO)_{10}$(dppm) (1) (200 mg, 0.207 mmol) in thf (30 ml) was treated with K[$HBBu^s_3$] (0.42 ml of a 0.5 mol l^{-1} solution in thf, 0.21 mmol). After stirring at 25°C for 5 h, solid CHI_3 (81 mg, 0.207 mmol) was added and the mixture stirred for 1 h. The solution was taken to dryness, extracted with Et_2O (3x10 ml) and filtered through celite. Evaporation and recrystallisation from CH_2Cl_2/MeOH afforded large yellow crystals of $Ru_3(\mu\text{-}I)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (30) (107 mg, 52%), m.p. >150°C (dec). [Found: C, 33.97; H, 1.62; $C_{28}H_{17}IO_9P_2Ru_3$ requires C, 33.99; H, 1.73%]. Infrared (cyclohexane): $\nu(CO)$ 2082s, 2057vs, 2030vs, 2018w, 2003m, 1993w, 1988m, 1978w, 1965m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.41 [dd, *J*(PH) 10.0 and 11.5 Hz, CH_2, isomer (30b)], 5.00 [m, CH_2 isomer (30a)], 7.56 (m, 15H, Ph).

Preparation of $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (31)

A solution of $Ru_3(CO)_{10}(dppm)$ (1) (300 mg, 0.31 mmol) in thf (30 ml) was treated with $K[HBBu^{\underline{s}}_3]$ (0.62 ml of a 0.5 mol l^{-1} solution in thf, 0.31 mmol). After stirring at 25°C for 5 h the solvent was evaporated to dryness. Excess allyl chloride (2 ml) was added to the residue and the resulting mixture stirred for 10 min. The allyl chloride was removed under vacuum and the residue extracted with CH_2Cl_2 (*ca* 5 ml). Filtration and addition of MeOH (*ca* 5 ml) to the filtrate afforded golden yellow crystals of $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (31) (88 mg, 32%), m.p. 169-171°C. [Found: C, 41.42; H, 2.21; $C_{30}H_{22}O_8P_2Ru_3$ requires C, 41.15; H, 2.53%]. Infrared (CH_2Cl_2): $\nu(CO)$ 2057s, 2018vs, 1983m, 1966m, 1857(br)m, 1813(br)m cm^{-1}.

Preparation of Aryldiazo derivatives

(a) $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (34) A solution of $Ru_3(CO)_{10}(dppm)$ (1) (100 mg, 0.103 mmol) in thf (10 ml) was treated with $K[HBBu^{\underline{s}}_3]$ (0.22 ml of a 0.5 mol l^{-1} solution in thf, 0.11 mmol). After stirring at 25°C for 5 h, solid

$[PhN_2][PF_6]$ (30 mg, 0.12 mmol) was added and the mixture stirred for 1 h. Evaporation and preparative tlc [light petroleum-acetone 95/5] gave six bands. Band 4, R

Band 4, R_f 0.38, yellow, recrystallised from Et_2O/MeOH to give yellow crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (14) (5 mg, 6%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 6, R_f 0.22, yellow, recrystallised from CH_2Cl_2/MeOH to give fine yellow needle-like crystals of $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (34) (77 mg, 77%), m.p. 141-144°C. [Found: C, 42.18; H, 1.94; N, 2.28; $C_{34}H_{22}N_2O_9P_2Ru_3$ requires C, 42.20; H, 2.29; N, 2.89%]. Infrared (cyclohexane): ν(CO) 2079w, 2059vs, 2023s, 2006w, 1994m, 1973w, 1958m; ν(NN) 1575 cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.60 [dd, *J*(PH) 10.5 and 11.5 Hz, 2H, CH_2], 6.65-8.0 (m, 20H, Ph). The remaining bands were present in trace amounts only and were not identified.

(b) $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (35) The cluster anion was prepared by the above method using $Ru_3(CO)_{10}$(dpam) (4) (300 mg, 0.284 mmol), thf (10 ml) and $K[HBBu^s_3]$ (0.60 ml of a 0.5 mol l^{-1} solution in thf, 0.30 mmol). Solid $[PhN_2][PF_6]$ (75 mg, 0.30 mmol) was added and the mixture stirred for 10 min. Evaporation and preparative tlc [light petroleum-acetone 80/20] gave 2 bands. Band 1, R_f 0.50, yellow recrystallised from Et_2O/MeOH to give a yellow powder of $Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (15) (10 mg, 1%), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample. Band 2, R_f 0.40, yellow-orange, recrystallised from CH_2Cl_2/MeOH to give orange needle-like crystals of $Ru_3(\mu\text{-}\eta^1\text{-}$

$N_2Ph)(\mu_3-AsPhCH_2AsPh_2)(CO)_9$ (35) (172 mg, 57%), m.p. 146-149 (dec). [Found: C, 38.79; H, 1.92; N, 2.64; $C_{34}H_{22}As_2N_2O_9Ru_3$ requires C, 38.69; H, 2.10; N, 2.65%]. Infrared (cyclohexane): ν(CO) 2078m, 2058vs, 2023vs, 2002m, 1994m, 1979w, 1959m; ν(NN) 1576w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.53 (s, 2H, CH_2), 6.65-7.8 (m, 20H, Ph).

(c) $Ru_3(\mu-\eta^1-C_6H_3Cl_2-2,4)(\mu_3-PPhCH_2PPh_2)(CO)_9$ (36) This complex was obtained after preparative tlc [light petroluem-acetone 90/10] from a reaction using $Ru_3(CO)_{10}(dppm)$ (1) (200 mg, 0.207 mmol), thf (10 ml) $K[HBBu^s_3]$ (0.22 ml of a 0.5 mol l^{-1} solution in thf, 0.21 mmol) and $[2,4-Cl_2C_6H_3N_2][BF_4]$, carried out as in (b) above. The yellow band with R_f 0.25 was recrystallised from CH_2Cl_2/MeOH to give orange crystals of $Ru_3(\mu-\eta^1-C_6H_3Cl_2-2,4)(\mu_3-PPhCH_2PPh_2)(CO)_9$ (36) (30 mg, 7%), m.p. >150°C (dec). [Found: C, 38.75; H, 1.85; N, 2.63; $C_{34}H_{20}Cl_2N_2O_9P_2Ru_3$ requires C, 39.40; H, 1.94; N, 2.70%]. Infrared (cyclohexane): ν(CO) 2081m, 2059vs, 2026vs, 2013w, 2000(sh), 1998s, 1971w, 1961m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 4.66 (m, 2H, CH_2), 6.60-8.20 (m, 18H, Ph and C_6H_3).

Cyclometallation reactions

(a) $Ru_3(\mu-H)(\mu-\eta^1,\eta^1-N_2C_6H_4)(\mu_3-PPhCH_2PPh_2)(CO)_8$ (37) A solution of $Ru_3(\mu-\eta^1-N_2Ph)(\mu_3-PPhCH_2PPh_2)(CO)_9$ (34) (30 mg, 0.031 mmol) was heated in refluxing cyclohexane (30 ml) for 1 h, after which time the reaction was adjudged complete (tlc). Evaporation and recrystallisation from CH_2Cl_2/MeOH gave large orange crystals of $Ru_3(\mu-H)(\mu-\eta^1,\eta^1-N_2C_6H_4)(\mu_3-PPhCH_2PPh_2)(CO)_8.0.5CH_2Cl_2$ (37) (23 mg, 73%), m.p. 158-160°C (dec). [Found: C, 41.11; H, 2.30; N, 2.83; $C_{35}H_{22}N_2O_8P_2Ru_3$.-$0.5CH_2Cl_2$ requires C, 40.97; H, 2.36; N, 2.85%]. Infrared (cyclohexane): ν(CO) 2085s, 2055vs, 2036vs, 2024m, 2008s, 2002(sh), 1994s, 1980vs, 1962w, 1941w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -11.45 [dd, J(PH) 2.5 and 15.5 Hz, 1H, RuH], 2.54 [AB(XY) pattern, 2H, CH_2], 7.15-8.25 (m, 19H, Ph and C_6H_4).

(b) $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_8$ (38)

A similar reaction of $Ru_3(\mu\text{-}\eta^1\text{-}N_2Ph)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9$ (35) (80 mg, 0.076 mmol) afforded orange crystals (from CH_2Cl_2/MeOH) of $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^1\text{-}N_2C_6H_4)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_8$ (38) (67 mg, 86%), m.p. 158-161 (dec). [Found: C, 38.73; H, 1.92; N, 2.66; $C_{33}H_{22}As_2N_2O_8Ru_3$ requires C, 38.57; H, 2.16; N, 2.73%]. Infrared (cyclohexane): ν(CO) 2084s, 2054vs, 2033vs, 2013w, 2007s, 1999m, 1996m, 1979s, 1958vs, 1940w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) -11.64 (s, 1H, RuH), 2.66 [AB quartet, J(AB) 12.9 Hz, 2H, CH_2], 7.10-8.20 (m, 19H, Ph and C_6H_4).

X-ray structure determinations of (6), (31) and (38)

The general procedure has been outlined in Chapter 1. Crystals of all three complexes were obtained from CH_2Cl_2/MeOH.

Crystal Data (6): $C_{35}H_{26}O_{10}P_2Ru_4$, M 1072.8, crystal size 0.69 x 0.38 x 0.38 mm, triclinic, space group $P\bar{1}$, a 10.206(2), b 11.412(3), c 18.860(3)Å, α 70.99(2), β 73.98(1), γ 72.27(2)°, U 1939.7$Å^3$, D_m 1.82(2), D_c 1.84 g cm^{-3} for Z = 2, F(000) 1044, μ(Mo-Kα) 16.01 cm^{-1}, λ(Mo-Kα) 0.7107Å, scan type ω(2/3)θ, ω scan angle (2.00 + 0.35 tanθ)°, horizontal aperture (2.4 +

0.50 tanθ)mm; Data: 5290 unique reflections collected in the range $2.4 < 2\theta < 46°$; the 4930 having $I > 2.5\sigma(I)$ were used in the refinement after correction for absorption. $R = 0.026$, $R_w = 0.035$, where $w = 1.0[\sigma^2(F) + 0.000671F^2]^{-1}$ A final difference synthesis showed no peak >0.6 eÅ^{-3}.

(31): $C_{30}H_{22}O_8P_2Ru_3$, *M* 875.7, crystal size 0.14 x 0.10 x 0.08 mm, triclinic, space group $P\bar{1}$, *a* 11.661(4), *b* 11.914(4), *c* 12.029(2)/, α 80.70(2), β 81.77(2), γ 69.79(4)°, *U* 1554.9Å^3, D_m 1.88(2), D_c 1.87 g cm^{-3} for $Z = 2$, *F*(000) 856, μ(Mo-*K*α) 15.26 cm^{-1}, λ(Mo-*K*α) 0.7107Å, scan type *ω*(1/3)θ, *ω* scan angle (1.60 + 0.35 tanθ)°, horizontal aperture (2.4 + 0.50 tanθ)mm; Data: 4184 unique reflections were collected in the range $2.4 < 2\theta < 46°$; the 3936 having $I > 2.5\sigma(I)$ were used in the refinement after correction for absorption. $R = 0.027$, $R_w = 0.034$ where $w = 3.5049[\sigma^2(F) + 0.000075F^2]^{-1}$. A final difference synthesis showed no peak > 0.8 eÅ^{-3}.

(38): $C_{33}H_{22}As_2N_2O_8Ru_3$, *M* 1027.7, crystal size 0.31 x 0.39 x 0.31 mm, triclinic, space group $P\bar{1}$, *a* 10.846(2), *b* 12.084(4), *c* 15.884(4)Å, α 72.63(2), β 68.25(2), γ 68.07(2)°, *U* 1762.4Å^3, D_m 1.94(2), D_c 1.94 g cm^{-3} for $Z = 2$, *F*(000) 992, μ(Mo-*K*α) 31.29 cm^{-1}, λ(Mo-*K*α) 0.7107Å, scan type *ω*(3/3)θ, *ω* scan angle (1.60 + 0.35 tanθ)°, horizontal aperture (2.4 + 0.50 tanθ)mm; Data: 4047 unique reflections were collected in the range $2.4 < 2\theta < 44°$; the 3676 having $I > 2.5\sigma(I)$ were used in the refinement. Absorption corrections were not applied. $R = 0.028$, $R_w = 0.034$ where $w = 4.2113[\sigma^2(F) + 0.000075F^2]^{-1}$. A final difference synthesis showed no peak >0.7 eÅ^{-3}.

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CHAPTER FOUR

PENTAKIS(METHOXYCARBONYL)CYCLOPENTADIENE: SOME ASPECTS OF ITS METAL CHEMISTRY.

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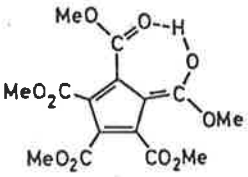
INTRODUCTION

Since the accidental discovery of ferrocene, $Fe(\eta-C_5H_5)_2$, in 1951[1,2] and the recognition of its remarkable properties,[3-6] the chemistry of cyclopentadienyl metal complexes has developed into one of the most active areas of organometallic chemistry.[7-10] With the exception of ferrocene, for which an extensive organic chemistry has been developed, substituted metallocenes are rare, and generally limited to those obtained from the readily-available methyl-[11] or pentamethyl-cyclopenta- diene.[12] The strong electron-donating properties of the latter ligand has resulted in the syntheses of many unusual complexes,[13] not least being those of the early transition elements[14,15] and those containing multiple metal-metal bonds.[16]

The chemistry of cyclopentadienyl ligands bearing five electron-withdrawing groups is less extensive. Indeed, we noted King's observation[16] that 'complete substitution of cyclopentadienyl hydrogens with electronegative groups such as cyano and alkoxycarbonyl should lead to removal of electron density from the filled ring $\underline{A}$ and $\underline{E}_1$ orbitals to the extent that stable pentahapto metal-ring bonds are no longer possible', which at the time appeared to be supported by the isolation of an iron (II) complex derived from pentakis-(methoxycarbonyl)cyclopentadiene which was soluble in water and appeared to have no ring-metal bonds.[17] Furthermore, the related compound derived from pentacyanocyclopentadiene is a light green, non-volatile, and extremely air-sensitive solid, suggesting it to be an iron (II) derivative rather than a ferrocene.[18] However, the syntheses of polychloro-ferrocenes and ruthenocenes have been described,[19] and the crystal structure of Ru(η^5-C_5Cl_5)$_2$ showed that this compound has the expected 'sandwich' structure.[20]

Pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ (1), was first synthesised by Diels in 1942,[21] and later was studied by LeGoff and LaCount[22] (1964) and by Cookson et al[23] (1961). The latter reported that (1) is a strong acid, aqueous solutions of which are capable of dissolving metallic iron with the evolution of hydrogen, and formation of $Fe[C_5(CO_2Me)_5]_2$.[17] Further investigations of its inorganic derivatives appear to be limited to the synthesis of the silver (I) derivative in situ, which has been used subsequently in alkylation studies, but not further characterised.[24]



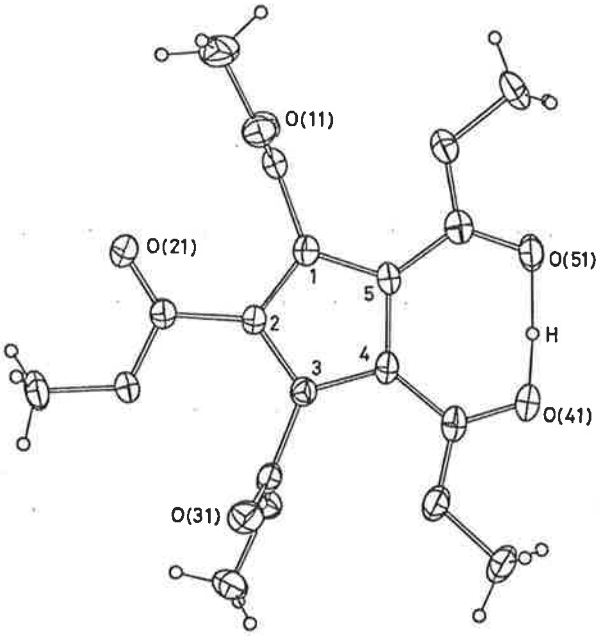
(1)

RESULTS AND DISCUSSION

This Chapter describes the syntheses and properties of some derivatives of the $[C_5(CO_2Me)_5]^-$ anion. The work involving this ligand has been explored jointly with J.K. Walton[25-32] and P.A. Humphrey.[33-35] Only the authors own work for the Degree of Doctor of Philosophy is described in the Experimental section unless stated otherwise. Much of this work has been reported elsewhere.[25-38]

Pentakis(methoxycarbonyl)cyclopentadiene

The diene (1) was prepared in *ca* 70% yield by a slight modification of the literature preparation: this reaction has been discussed in detail previously.[22] The compound forms white air-stable crystals which are soluble in solvents with a wide range of polarity. In polar solvents, such as water or acetone, the compound is fully ionised, as indicated by the equivalence of the CO_2Me groups in the ^1H n.m.r. spectrum; the Me groups resonate at δ 3.72 and δ 4.35 in water and acetone, respectively. The ^{13}C n.m.r. spectrum contained three resonances assigned to the Me (δ 53.56), ring (δ 118.18), and carbonyl carbons (δ 170.47) respectively. In contrast, in solutions in non-polar solvents such as benzene, the protons of the five Me groups now resonate as a broad singlet at δ 3.55; in $CDCl_3$ this resonance occurred at δ 3.95, while the acidic proton is greatly deshielded and was found at δ 31.10. The broadening found in non-polar solvents may be the result of incomplete ionisation or rapid tautomerism. The solid state structure of (1)[28] (Figure 1) corresponds to the hydroxyfulvene arrangement with the acidic hydrogen atom asymmetrically bridging two of the carbonyl oxygens of adjacent CO_2Me substituents [O-H...H 1.12(4) and 1.32(4)Å with O-H...O 117(3)°]. Within the C_5 ring, four C-C distances are essentially equal, [1.396(3)-1.410(5)Å] while the fifth, the bond between the carbons bearing the CO_2Me groups associated with the acidic hydrogen, is significantly longer at 1.453(5)Å. It is not possible for all five CO_2Me groups to be co-planar with the C_5 ring simultaneously; groups 2,4 and 5 are almost co-planar, while groups 1 and 3 are almost normal to the ring.



(Figure 1)

Salts of (1) with uni- and bi-valent cations

As reported earlier,[22] the potassium salt of (1), $K[C_5(CO_2Me)_5]$ (2), obtained by heating the octakis(methoxycarbonyl)cycloheptadiene isomers with potassium acetate, is initally obtained as a yellow crystalline material, which on recrystallisation from water or methanol afforded a pure white crystalline product. Ionic complexes of the type $M[C_5(CO_2Me)_5]_n$ (n = 1,2) have been prepared from reactions of (1) with metal carbonates or acetates [equations (i) and (ii), respectively], or from reactions of the thallium(I) derivative, $Tl[C_5(CO_2Me)_5]$ (3), with the metal chloride [equation (iii)]

$$\text{(i)}\ M_xCO_3 + xHC_5(CO_2Me)_5 \xrightarrow{H_2O} xM[C_5(CO_2Me)_5]_n + H_2O + CO_2\uparrow$$

[x = 2, n = 1: M = Li(4), Na(5), Tl(3);
x = 1, n = 2: M = Ca(6), Ba(7), Cd(8), Zn(9), Pb(10)]

$$\text{(ii)}\ Mg(O_2CMe)_2 + 2HC_5(CO_2Me)_5 \xrightarrow{MeOH} Mg[C_5(CO_2Me)_5]_2(11) + 2MeCO_2H$$

$$\text{(iii)}\ MCl_x + xTl[C_5(CO_2Me)_5] \xrightarrow{MeOH} M[C_5(CO_2Me)_5]_x + xTlCl\downarrow$$

[x = 1: M = Rb(12), Cs(13); x = 2: M = Sr(14)]

Salts of (1) with large cations of general formula $[R][C_5(CO_2Me)_5]$ [R = NMe_4 (15), NEt_4 (16), NPr^i_4 (17), NBu_4 (18), $AsPh_4$ (19), and $N(PPh_3)_2$ (20)] have also been prepared according to equation (iv).

$$\text{(iv)}\ [R]X + Tl[C_5(CO_2Me)_5] \xrightarrow{EtOH} [R][C_5(CO_2Me)_5] + TlX\downarrow$$

(X = Cl or Br)

All compounds formed white air- and moisture-stable crystals which were soluble in polar solvents such as water, acetone and alcohols. Analytical samples were dried in vacuo, and with the exception of the lithium, magnesium (monohydrates), lead (dihydrate), strontium and zinc (trihydrates) derivatives, gave values consistent with the non-solvated $[C_5(CO_2Me)_5]^-$ salts. In solution, all are completely ionised to give the $[C_5(CO_2Me)_5]^-$ ion and the appropriate solvated cation, as indicated by conductivity measurements and virtually identical electronic and n.m.r. spectra.

In the solid state, the i.r. spectra show several strong $\nu(C{=}O) + \nu(C{=}C)$ bands between 1650-1750 cm^{-1} and strong $\nu(C{-}O)$ bands between 1200-1250 cm^{-1}. The overall patterns of the spectra contain few common features; for example the lithium, sodium and potassium derivatives contain respectively two, three and four strong bands between 1650-1750 cm^{-1}. The molecular structures of the lithium (4), potassium (2), thallium (3)[28] and barium (7)[29] salts are shown in Figures 2, 3, 4 and 5 respectively and show that the metal ions are bonded to the carbonyl oxygens, with coordination numbers ranging from four to eight. The molecular structure of $[NMe_4][C_5(CO_2Me)_5]$[33] (Figure 6) contained isolated cations and anions with no close interactions between them.

The reaction between Me_3SnCl and $Tl[C_5(CO_2Me)_5]$ (3) in methanol afforded the bis-aquo complex $[Me_3Sn(OH_2)_2]$-$[C_5(CO_2Me)_5]$ (21) in high yield; presumably adventitious water was derived from the solvents on recrystallisation ($MeOH/Et_2O$). This complex, which was characterised by the usual methods (see Experimental), is similar to the analogous complex

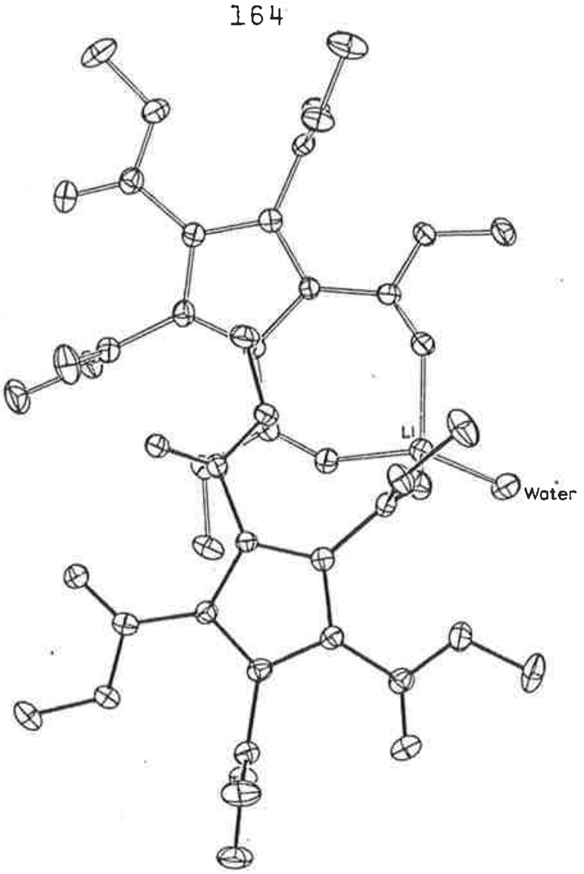


Figure 2: Fragment of the structure of Li$[C_5(CO_2Me)_5](H_2O)$ showing the association of the lithium atom with two anions and the water molecule (by B.W. Skelton and A.H. White).

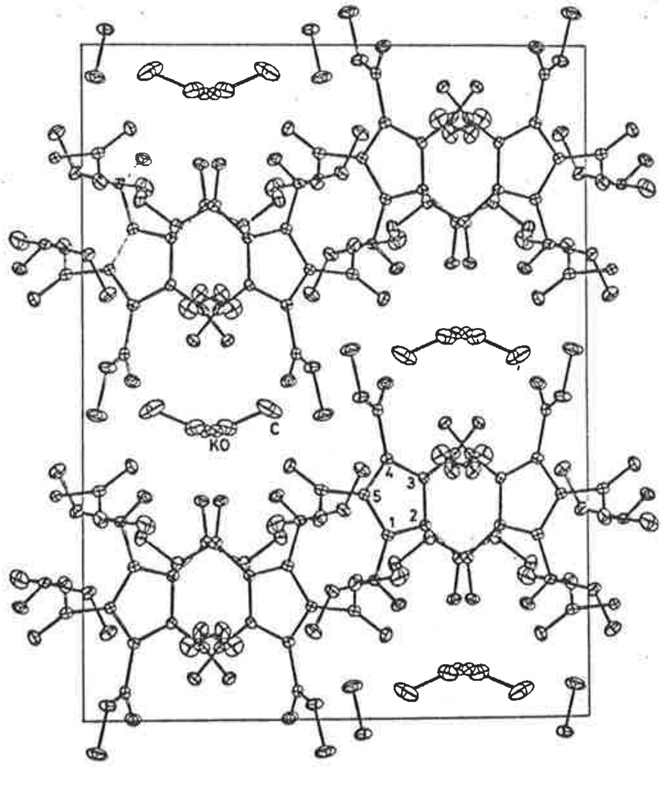


Figure 3: Unit-cell contents of K$[C_5(CO_2Me)_5]$ (2) (by B.W. Skelton and A.H. White).

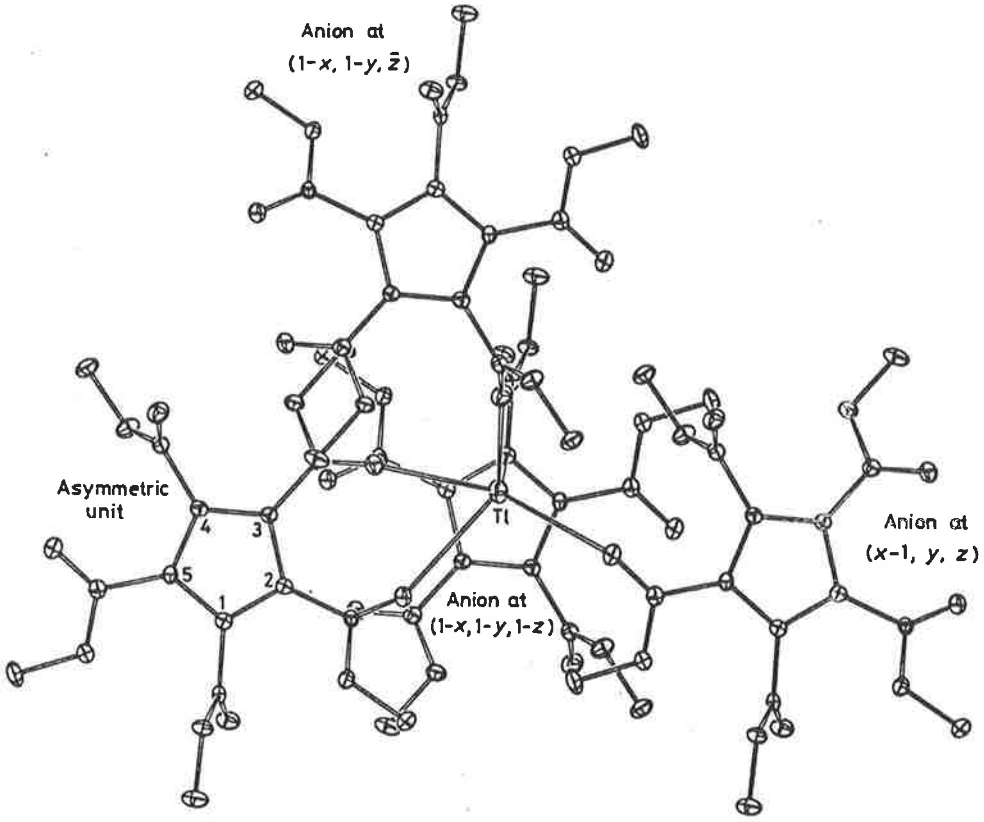


Figure 4: The thallium environment in $Tl[C_5(CO_2Me)_5]$ (3) (by B.W. Skelton and A.H. White).

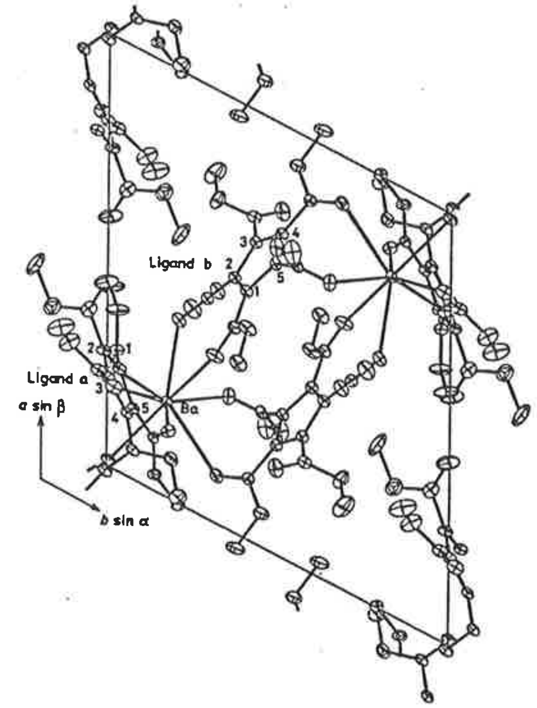


Figure 5: Unit-cell contents of $Ba[C_5(CO_2Me)_5]_2$ (7) (by B.W. Skelton and A.H. White)

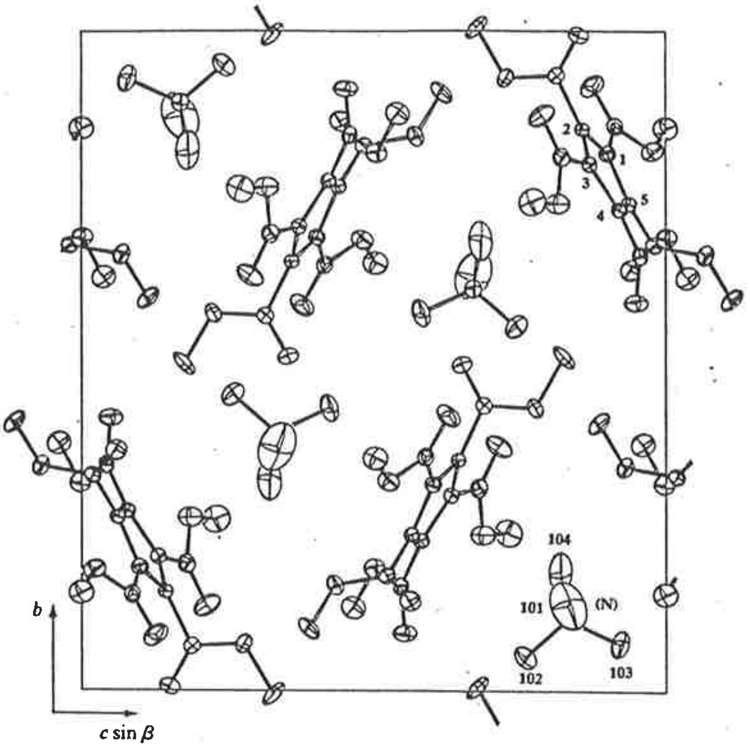


Figure 6: Unit-cell contents of $[NMe_4][C_5(CO_2Me)_5]$ (15) (by B.W. Skelton and A.H. White).

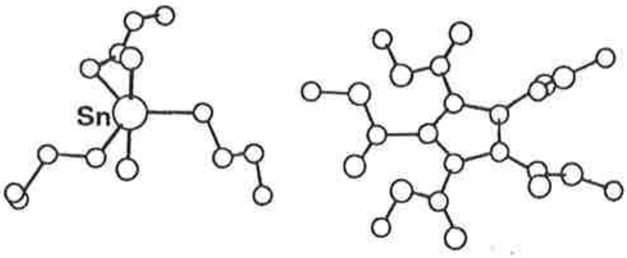


Figure 7: Molecular structure of $[Bu_3Sn(OH_2)_2][C_5(CO_2Me)_5]$.[39]

$[Bu_3Sn(OH_2)_2][C_5(CO_2Me)_5]$ which crystallised from a benzene solution of bis(tributyltin)oxide and (1).[39] The latter complex, which was characterised crystallographically, (Figure 7) contains a trigonal bipyramidal cation, with apical water molecules, and the non-coordinated $[C_5(CO_2Me)_5]^-$ anion.

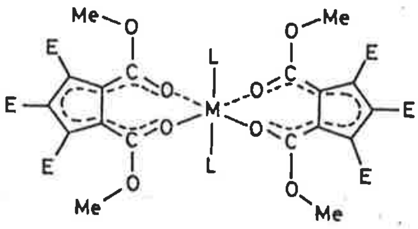
The group 2A metals, lithium, sodium, potassium, lead(II) and $Me_3Sn(IV)$ all form hydrocarbon analogues of the compounds reported above, which are unstable in air, and rapidly hydrolyse in contact with water.[40-46b] The zinc analogue $[Zn(C_5H_5)_2]$ has covalent ring-metal bonds, but is also air- and water-sensitive,[47] while $[Tl(C_5H_5)]_n$ contains $-M(C_5H_5)M(C_5H_5)-M(C_5H_5)-$ chains with each of the C_5 rings being η^5-bonded to two metal ions.[48] To the best of my knowledge, no hydrocarbon analogues have been reported for the remaining $[C_5(CO_2Me)_5]$ derivatives discussed above.

Some first-row transition-metal derivatives

The reaction of copper(II)acetate, or the carbonates of manganese(II), cobalt(II), nickel(II) or copper(II), with aqueous solutions of (1) (two equivalents) gave crystalline transition metal salts. The iron(II) derivative was prepared by the previously reported synthesis from the metal and (1).[17] The five compounds so obtained formed as water or methanol soluble salts which crystallised as $M[C_5(CO_2Me)_5]_2(L)_2$ [M = Mn (22), pale green; Fe (23), yellow; Co (24), pink; Ni (25), green; and Cu (26), orange; L = H_2O or MeOH]. In aqueous solution, conductivity measurements indicated they are 1:2 electrolytes; the solutions have colours of the corresponding aquo-cations, and the magnetic susceptibilities, determined by the Evans n.m.r. method,[49] show that these complexes have the same number of unpaired electrons as the well known $[M(OH_2)_6]^{2+}$ cations. In D_2O, the single resonance for the CO_2Me protons (δ 3.25-3.65) was more or less broadened by the paramagnetic cation. The U.V.-visible spectra were also consistent with the presence of these cations in solution, being the same as aqueous solutions of simple salts of the metal concerned; absorptions due to the $[C_5(CO_2Me)_5]^-$ anion were also present.

Complex (26) is notable as being the only cyclopentadienyl complex of copper(II) so far described. The orange colour is also unusual for this metal, and is a result of a Cu(II)-$C_5(CO_2Me)_5$ charge transfer interaction; in water, where the compound is fully ionised, blue solutions containing $[Cu(OH_2)_6]^{2+}$ are obtained.

In the solid state molecular structures of the Fe and Cu derivatives, two _trans_ octahedral coordination positions are occupied by MeOH ligands; for Co, two mutually _cis_ H_2O ligands are found; the remaining positions are occupied by two $C_5(CO_2Me)_5$ ligands, each chelating the metal ion via two adjacent ester carbonyl groups.[32]



	M	L
(23)	Fe	MeOH
(24)	Co*	H_2O
(26)	Cu	MeOH

E = CO_2Me
*_cis_ complex

The reaction between chromium(II) acetate and (1) in methanol afforded a water-soluble green solid, the analysis of which agrees with the formulation of a non-stoicheiometric hydrate of the chromium(III) complex $Cr[C_5(CO_2Me)_5]_3$ (27). The ^1H n.m.r. spectrum in D_2O contained a single resonance for the CO_2Me protons, broadened by the paramagnetic chromium(III) ion, and shifted[49] to an extent consistent with the presence of three unpaired electrons, as expected for $[Cr(OH_2)_6]^{3+}$. This cation was also shown by the electronic spectrum of (27) in aqueous solution. The molecular structure of (27),[30] which is shown in Figure 8, showed a tris-chelate complex, the chromium atom being chelated by two carbonyl oxygen atoms of adjacent carbonyl groups of three $[C_5(CO_2Me)_5]$ ligands.

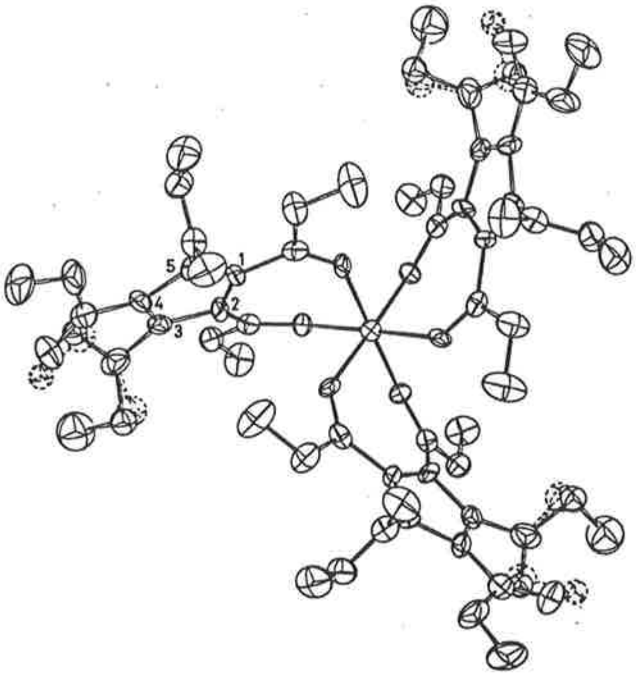
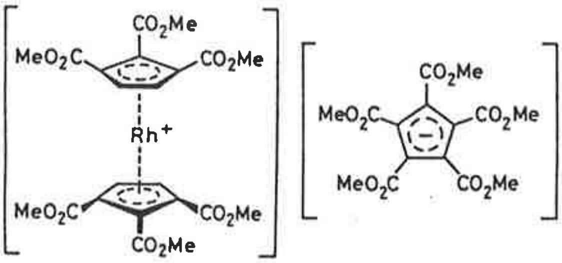


Figure 8: Molecular structure of $Cr[C_5(CO_2Me)_5]_3$ (by B.W. Skelton and A.H. White).

The π-type interaction of ring orbitals with the metals, as found with the $[C_5H_5]^-$ anion in $M(\eta\text{-}C_5H_5)_2$ [M = Cr, Fe, Co or Ni] is not found in the above complexes. The strongly electron withdrawing CO_2Me groups thus allows the anion of (1) to bond to the transition metal ions via the carbonyl oxygen atoms with the formation of classical coordination complexes. The orange copper(II) derivative has no C_5H_5 analogue.

Rhodium Complexes

The reaction between $Rh_2(O_2CMe)_4$ in refluxing methanol afforded red needles of $[Rh\{\eta\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ (28), which were soluble in polar solvents as a 1:1 electrolyte. An X-ray diffraction study of (28)^{27} has shown the complex is the $[C_5(CO_2Me)_5]^-$ salt of the $[Rh\{\eta\text{-}C_5H_2(CO_2Me)_3\}_2]^+$ cation. In the latter, both C_5 rings are η^5-bonded, and are fully staggered to allow the bulky CO_2Me groups to intermesh satisfactorily. The counterion is the pentagonal $[C_5(CO_2Me)_5]^-$ anion, which is similar to that found in $[NMe_4][C_5(CO_2Me)_5]$ (15).



(28)

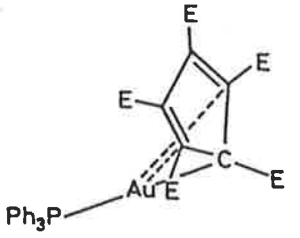
The precise mechanism for the formation of (28) cannot be proposed at this stage, however the driving force for the elimination of two CO_2Me groups from (1) to form the η^5-$C_5H_2(CO_2Me)_3$ ligand may arise from the removal of the steric interaction of the two $C_5(CO_2Me)_5$ rings; model studies have shown that η^5-attachment of two C_5 rings to a metal atom or ion is hindered if each ring contains five CO_2Me substituents.

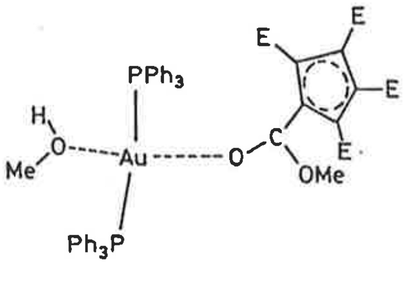
A similar reaction between $Rh_2(O_2CMe)_4$ and methyltetrakis-(methoxycarbonyl)cyclopentadiene $HC_5(CO_2Me)_4Me$, (obtained by the literature preparation^{50}), in refluxing methanol afforded red $Rh[C_5(CO_2Me)_4Me]_2$ (29) as the major product. The microanalytical and mass spectral data (parent ion at m/z 725) are consistent with the above formulation. Informative ^1H n.m.r. spectra were not obtained owing to the presence of the paramagnetic Rh(II) atom. Unlike all the previous complexes, (29) is insoluble in water and conductivity studies in acetone showed that (29) behaves as a non-electrolyte. These data suggest that the two rings may be π-bonded in a similar manner to that found in $Rh(C_5H_5)_2$, but so far the lack of suitable crystals has prevented X-ray confirmation of the molecular structure.

Group IB metal derivatives

The reaction of (1) with $Au(O_2CMe)(PPh_3)$ afforded $Au[C_5(CO_2Me)_5](PPh_3)$ (30); further reaction with one equivalent of PPh_3 afforded $[Au(PPh_3)_2][C_5(CO_2Me)_5].MeOH$ (31). Both complexes formed white air-stable crystals which are soluble in polar solvents such as alcohols, acetone and chloroform. In solution, conductivity measurements were consistent with complex (30) being a non-electrolyte and complex (31) being a 1:1 electrolyte, while the ^1H n.m.r. spectra of both complexes and all other Group IB complexes described show that all five CO_2Me groups are magnetically equivalent.

In the solid state, the C_5 ring in (30) is shown to interact with the gold in an unusual, asymmetric η^3 mode (Figure 9).[31] The central carbon of the three closest to the metal [Au-C(1) 2.199(4) Å] is almost collinear with the Au-P system [P-Au-C(1) 169.7(1)°]. The bonds from the gold to the adjacent ring carbons C(2) and C(5) are respectively 2.705(4), 2.813(4) Å; comparison with the complex $Au(C_5HPh_4)(PPh_3)$,[51] in which the $Au(PPh_3)$ group is considered to interact with three carbons of the ring at 2.15(1) [Au-C(1)], 2.67(1), and 2.76(1) Å [Au-C(2,5)], suggests that a similar coordination, intermediate between σ and η^3, occurs in complex (30).





E = CO_2Me

(30)

(31)

The structural determination of (31)[31] (Figure 10) shows the gold atom is essentially linearly two coordinate to two triphenylphosphine ligands [Au-P 2.300(3), 2.297(3) Å, P-Au-P 170.4(2)°]; the deviation from linearity probably arises as a

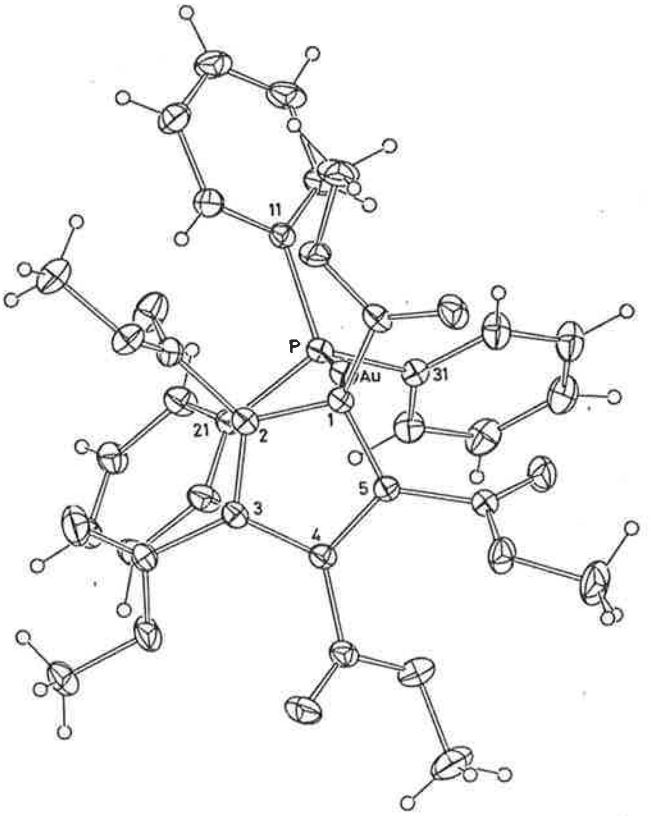


Figure 9: Projection of the 'molecule' of Au[$C_5(CO_2Me)_5$](PPh_3) (30) (by B.W. Skelton and A.H. White)

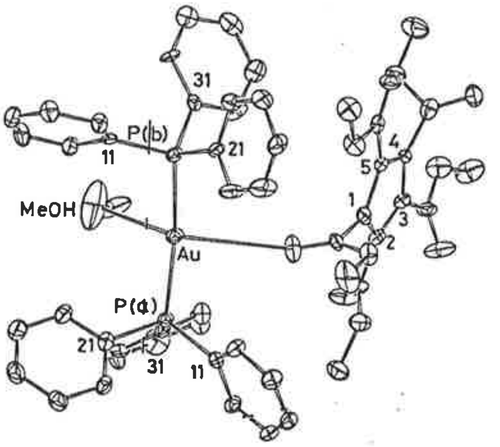


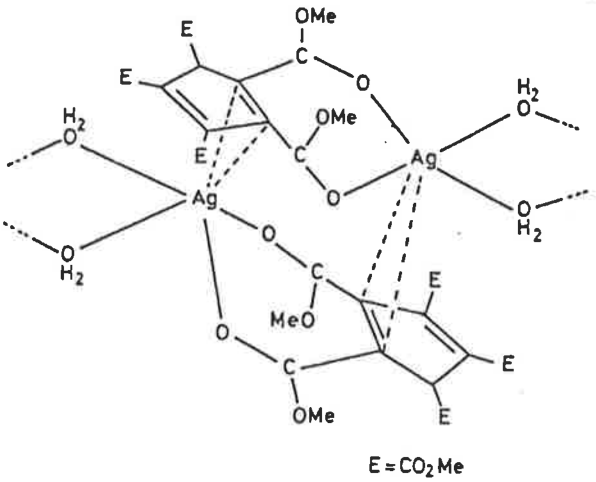
Figure 10: Projection of the 'molecule' of [Au(PPh_3)$_2$]-[$C_5(CO_2Me)_5$].MeOH (31) (by B.W. Skelton and A.H. White)

consequence of long interactions with the methanol solvate molecule [Au...O 3.343(17)Å] and the [$C_5(CO_2Me)_5$] ligand [Au...O 3.370(9)Å].

In (30), the gold ring interaction is strong enough to resist cleavage by polar solvents, however, addition of a strong donor ligand such as PPh_3, readily generates the $[Au(PPh_3)_2]^+$ cation, releasing the stable $[C_5(CO_2Me)_5]^-$ anion; dissolution in polar solvents is accompanied by complete ionisation.

The displacement of acetate from silver acetate by (1) affords the silver(I) derivative $Ag[C_5(CO_2Me)_5]$ (32). Compound (32) is a white solid with similar solubility properties to those of the group IA derivatives; both the solid and solution turn red quickly in light. The reaction of (32) with iodomethane gave the ring-methylated methylpentakis(methoxycarbonyl)cyclopentadiene (33); this compound has been obtained previously by methylating the solution obtained from (1) and silver oxide, although complex (32) was not isolated from the latter reaction.[22]

The crystal for the X-ray structure determination of (32) was chosen from a sample which had been recrystallised from water.[36] The basic unit of the structure is a dimeric species $[C_5(CO_2Me)_5]Ag(OH_2)_2Ag[C_5(CO_2Me)_5]$ (Figure 11) with the two silver atoms bridged by a pair of symmetrically disposed water oxygen atoms [Ag-O 2.450(5), 2.437(5)Å; Ag-O-Ag 94.7(2)°]. The silver atom is also coordinated by two of the carbonyl oxygens of adjacent CO_2Me substituents [Ag-O 2.391(5), 2.417(6)Å]. The four oxygen atoms coordinated to the silver are all disposed to one side of the atom; the void thus created is occupied by an



32

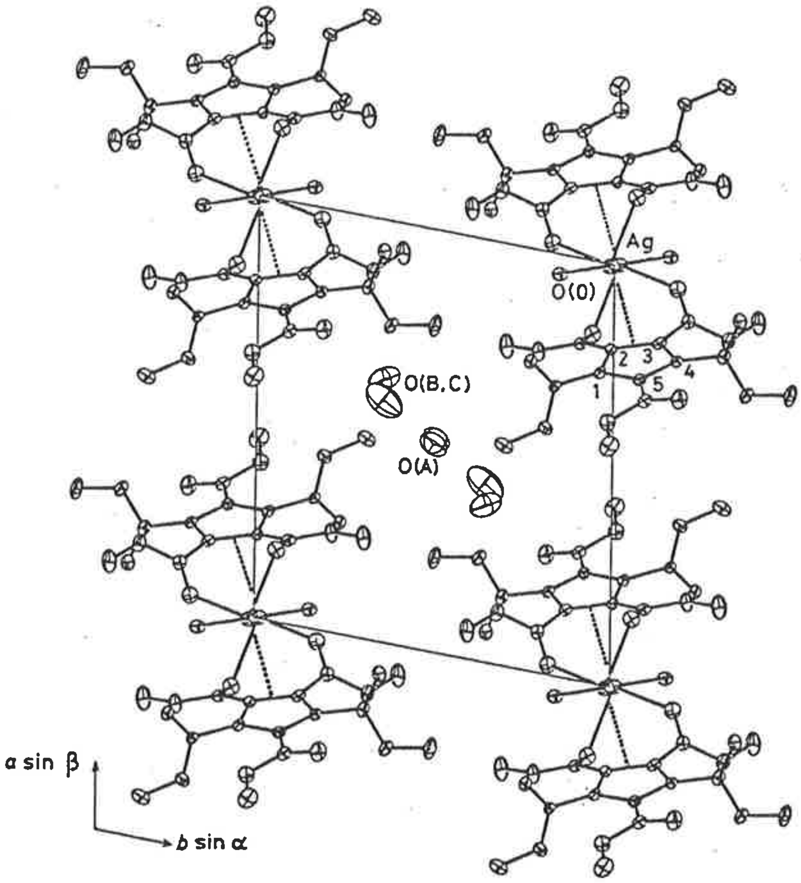
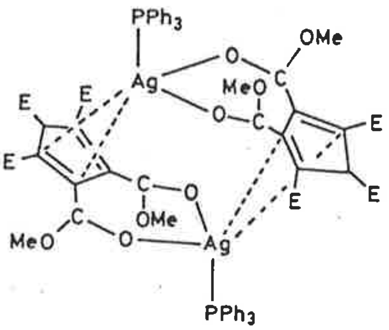


Figure 11: Unit cell contents of (32) projected down the b axis (by B.W. Skelton and A.H. White)

approach from a C=C double bond of an inversion-related $C_5(CO_2Me)_5$ ring [Ag-C 2.586(7), 2.807(7)Å]. The close interaction of one of these carbon atoms (approximating to σ-bonding) presumably activates the ring carbon towards alkylation.

Reactions between (32) and stoicheiometric amounts of tertiary phosphines in methanol at room temperature gave the complexes $\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2$ (34), $Ag[C_5(CO_2Me)_5](PPh_3)_2$ (35), $Ag[C_5(CO_2Me)_5](dppe)$ (36) and $Ag[C_5(CO_2Me)_5](tppme)$ (37). The complexes, which were also obtained from reactions between (1) and silver acetate in the presence of the tertiary phosphines, were obtained as white solids which were stable to air and water; some decomposition occurred if they were exposed to light or heat (>40°C) for prolonged periods. These compounds are soluble in solvents such as alcohols and acetone and have conductivities consistent with the solutes being 1:1 electrolytes; unlike (32), they are also soluble in benzene, dichloromethane and chloroform.



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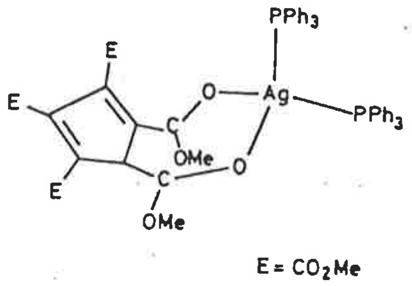


(35)

X-ray diffraction studies of (34) have shown that the silver atom is essentially four-coordinate (Figure 12);[36] being chelated by two adjacent carbonyl oxygens of a $C_5(CO_2Me)_5$ ring

[Ag-O 2.415(3), 2.613(3)Å], and bonded to the triphenylphosphine ligand [Ag-P 2.397(1)Å]. The fourth bond to silver is an asymmetric interaction with a C=C double bond of the ring carbons of an inversion-related $C_5(CO_2Me)_5$ ring [Ag-C 2.632(4), 2.472(4)Å].

The solid-state structure of (35) has also been determined by X-ray methods and is shown in Figure 13.[36] The complex is monomeric $Ag[C_5(CO_2Me)_5](PPh_3)_2$; the silver atom is again essentially four-coordinate. The two triphenylphosphine ligands are attached to the silver by slightly longer Ag-P bonds [2.428(2), 2.414(2)Å] than in (34). The P-Ag-P angle [136.64(5)°] is considerably larger than the ideal tetrahedral angle, probably as a result of steric interactions between the two phosphine ligands. The other two coordination sites about the silver are occupied by two carbonyl oxygen atoms of adjacent carboxyl groups [Ag-O (11,51) 2.465(4), 2.594(5)Å], the $C_5(CO_2Me)_5$ ligand again behaving as a chelate.

Two approaches to the synthesis of copper(I) complexes containing phosphines are available in principle: the reduction of an appropriate copper(II) derivative with the tertiary phosphine, and addition of the tertiary phosphine to a preformed copper(I) derivative. Only the second method can be used with tertiary arsines, which lack the pronounced reducing properties of their phosphorus(III) analogues.

The reaction of $Cu[C_5(CO_2Me)_5]_2$ (26) with excess PPh_3 afforded white $Cu[C_5(CO_2Me)_5](PPh_3)_2$ (38) which had solution properties like its silver analogue (35). This complex was also obtained by addition of PPh_3 to a solution of copper(I) oxide in methanolic $HC_5(CO_2Me)_5$; the $P(C_6H_4Me\text{-}\underline{p})_3$ derivative

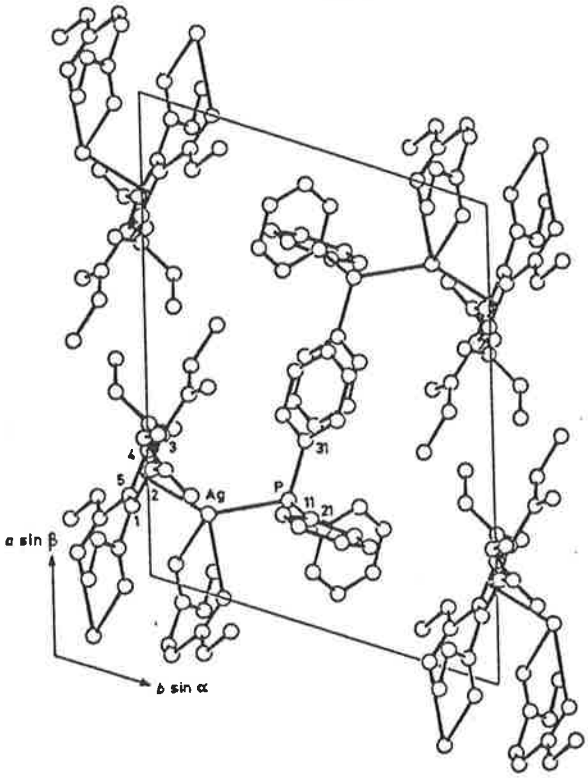


Figure 12: Unit cell contents of $\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2$ (34) (by B.W. Skelton and A.H. White)

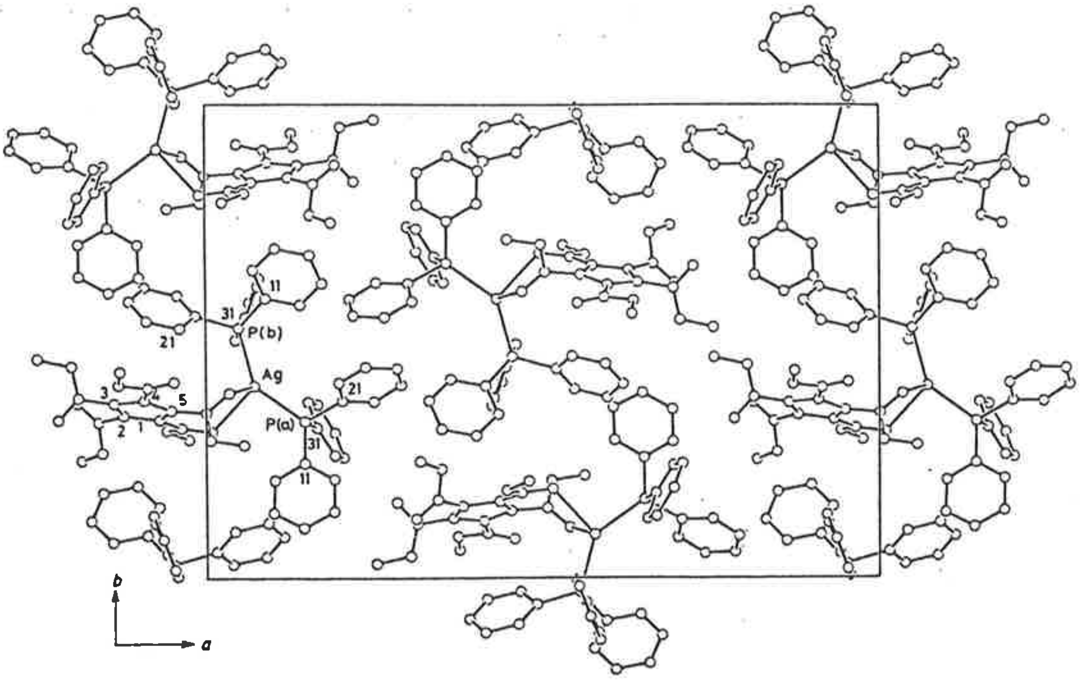


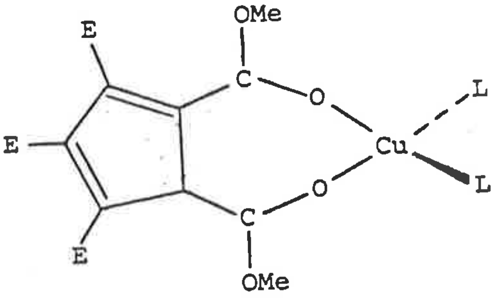
Figure 13: Unit cell contents of $Ag[C_5(CO_2Me)_5](PPh_3)_2$ (35) (by B.W. Skelton and A.H. White)

(39) was similarly prepared. A similar reaction carried out in the presence of dppe afforded the salt [Cu(dppe)$_2$][$C_5(CO_2Me)_5$] (40). The latter formulation is preferred over that of a possibly five- or six-coordinate copper(I) complex on the basis of the i.r. spectrum, which shows a much simpler ν(CO) region (two bands at 1715s, 1683vs cm^{-1}) compared with that of complexes (38) and (39) [at least three ν(CO) bands, with three shoulders].

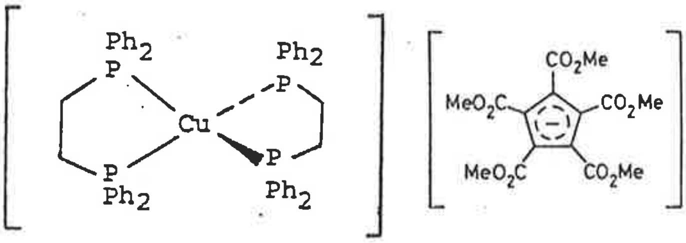
The $AsPh_3$ derivative (41) was obtained either by addition of the tertiary arsine to a solution of Cu_2O in methanolic $HC_5(CO_2Me)_5$, or by treating a solution of [CuI(NCMe)($AsPh_3$)]$_2$ in acetonitrile with Tl[$C_5(CO_2Me)_5$]. The white crystalline complex was characterised as Cu[$C_5(CO_2Me)_5$]($AsPh_3$)$_2$ **(41)** by the usual methods; it too was a 1:1 electrolyte in acetone solution.

As indicated above, however, the complexity of the ν(CO) region of the i.r. spectra of complexes (38), (39) and (41) (taken as nujol mulls) suggested that in the solid state, coordination of the diene to the copper(I) centre had occurred. The solid state structures of (38) and (41) have been determined by X-ray methods.^{34}

Both complexes are monomeric, and the unit cell contents confirm the stoicheiometry Cu[$C_5(CO_2Me)_5$](EPh_3)$_2$; the copper atom in each is approximately tetrahedral four-coordinate; a molecule of (41) is shown in Figure 14. In (38), the two tertiary phosphine ligands are attached with Cu-P distances [2.245(4), 2.255(4)Å], and subtend an angle of 125.7(1)° at the metal atom; for (41), the Cu-As distances are 2.329(1), 2.318(1)Å, and the As-Cu-As angle is 120.7(1)°. The larger



	L
(38)	PPh_3
(39)	$P(C_6H_4Me\text{-}\underline{p})_3$
(41)	$AsPh_3$



(40)

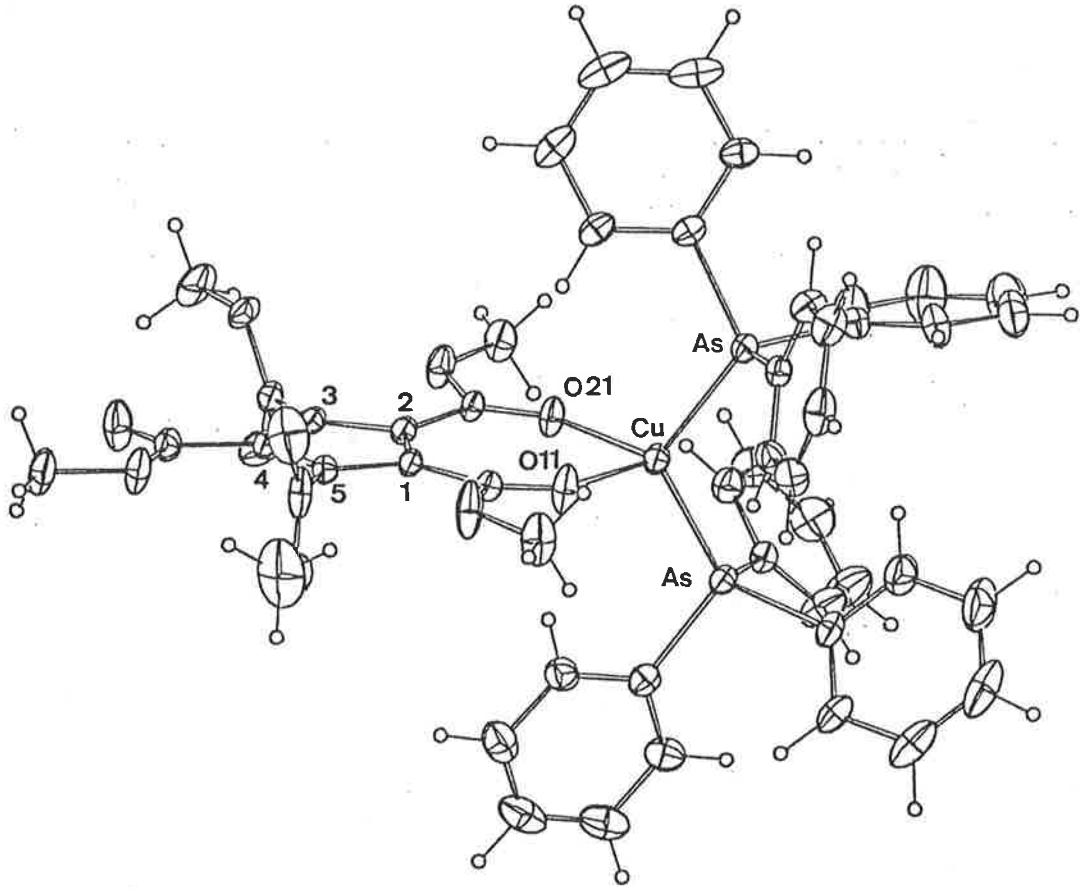


Figure 14: Molecular structure of $Cu[C_5(CO_2Me)_5](AsPh_3)_2$ (41) (by B.W. Skelton and A.H. White).

than tetrahedral angles probably result from steric intereactions between the two ligands.

The C_5 ligand is attached via the carbonyl oxygen atoms of two adjacent CO_2Me groups [Cu-O, 2.114(8), 2.115(8) Å for (38); 2.055(4), 2.068(4) Å for (41)]. The shortening of the Cu-O bond on going from P to As reflects the weaker σ-donor power of the tertiary arsine ligand, which results in stronger Cu-O bonding. It is also interesting to note that in the analogous silver complex (35), the Ag-P distances are *ca* 0.17 Å longer than the Cu-P distances in (38), but the Ag-O distances are *ca* 0.35-0.48 Å longer, reflecting the weaker attachment of the C_5 ligand to silver. Both C(1) and C(2) carboxylate substituents are nearly coplanar with the C_5 plane, the C(3) and C(5) substituents being pseudo-normal to this plane; this feature also contrasts with the situation in the silver analogue, where one of the coordinated oxygens belongs to one of the two carboxylate substituents which are normal to the C_5 ring plane.

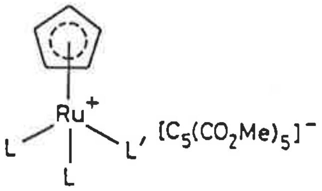
In none of the experiments was there any evidence for the formation of complexes of the type $[Cu\{C_5(CO_2Me)_5\}(L)]_n$ (L = PPh_3, $AsPh_3$, etc.) even when the amount of L was limited to one equivalent. Evidently copper(I) does not have the tendency to bond to the ring carbons exhibited by silver(I) or gold(I). We were also unsuccessful in obtaining a copper analogue of $[Ag\{C_5(CO_2Me)_5\}(OH_2)]_n$ (32); the only complex isolated from solutions of copper(I) oxide in aqueous or methanolic $HC_5(CO_2Me)_5$ was the orange copper(II) derivative (26).

Some ruthenium and osmium complexes

The initial approach to the synthesis of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_5]$ (42) was via the reaction between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and $Tl[C_5(CO_2Me)_5]$ (3). Previously it had been established that the reaction between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and $Tl(C_5H_5)$ gave a mixture of ruthenocene, PPh_3 and TlCl, no intermediate $\sigma-C_5H_5$ complex was detected.[52] The analogous reaction with (3), carried out in acetonitrile, afforded a bright yellow complex which contained PPh_3 and MeCN (n.m.r.). This compound (43) was readily characterised as the $[C_5(CO_2Me)_5]^-$ salt of the well-known cation $[Ru(NCMe)(PPh_3)_2(\eta-C_5H_5)]^+$. The osmium analogue $[Os(NCMe)(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (44) was obtained from the reaction of $OsBr(PPh_3)_2(\eta-C_5H_5)$ with (3) in the same solvent.[25,53]

The stability of these salts contrasts with the results obtained with $C_5H_5^-$. However, small and variable yields of a pale yellow-green compound were obtained after heating a mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ and (3) in other solvents such as thf, acetone or alcohols, and this compound was identified as the desired metallocene (42). The observation in one or more of the successful reactions, that triphenylphosphine oxide was also found, suggested that the reaction be attempted in air. This proved to be successful, and high, reproducible yeilds of (42) were obtained by running the reaction in MeOH in air. Complex (42) is also obtained from the reaction between $RuCl(CO)_2(\eta-C_5H_5)$ and (3).

The new metallocene forms pale yellowish-green crystals which melt without decomposition and are soluble in acetone, chlorinated solvents, ether and benzene but are insoluble in water. The i.r. spectrum is relatively simple, having bands assigned to ν(C=O) and the characteristic bands of a metallocene at 995 cm^{-1}; there is only a weak absorption at ca 1100 cm^{-1}. The n.m.r. spectra are also simple, all five CO_2Me groups being equivalent, and indicate that these groups are freely rotating (about the ring $C-CO_2Me$ bond) in solution (see Experimental). The mass spectrum contains a parent ion at m/z 522 (for ^{102}Ru) which fragments by loss of OMe, CO and C_2H_2O units. Conductivity measurements showed that (42) behaves as a non-electrolyte and magnetic suseptibility studies indicated that it is diamagnetic [conversely $Fe[C_5(CO_2Me)_5]_2$ (23) is a 1:2 electrolyte and is paramagnetic]. The above physical properties contrast with those of the first-row transition metal $C_5(CO_2Me)_5$ derivatives, but are similar to classical metallocenes such as ruthenocene.[54] This suggested that a π interaction occurs between both rings and the ruthenium atom. This was confirmed by an X-ray diffraction study.[37]



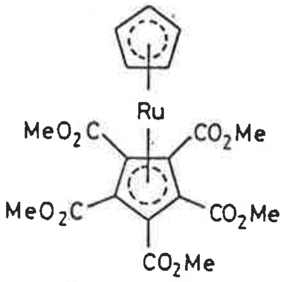
E = CO_2Me

(43) L = PPh_3, L' = NCMe

(46) L = PPh_3, L' = NCPh

(47) L_2 = dppe, L' = NCMe

A molecule of (42) is shown in Figure 15. As found for ruthenocene,[55,56] the carbon atoms of the two C_5 rings in complex (42) are eclipsed; the planes of the CO_2Me groups do not adopt any preferred positions. The dihedral angle between the two rings is 1.5°, which may be compared with the value of 0.0° found for ruthenocene. The Ru-C distances in C_5H_5 is 2.178(2)-2.186(3)Å [Ru-C(0) 1.817Å] while that in $C_5(CO_2Me)_5$ is 2.176(2)-2.178(2)Å [Ru-C(0) 1.796Å]. The range of values reported for Ru-C in $Ru(\eta-C_5H_5)_2$ is 2.181-2.188Å.[56]



42

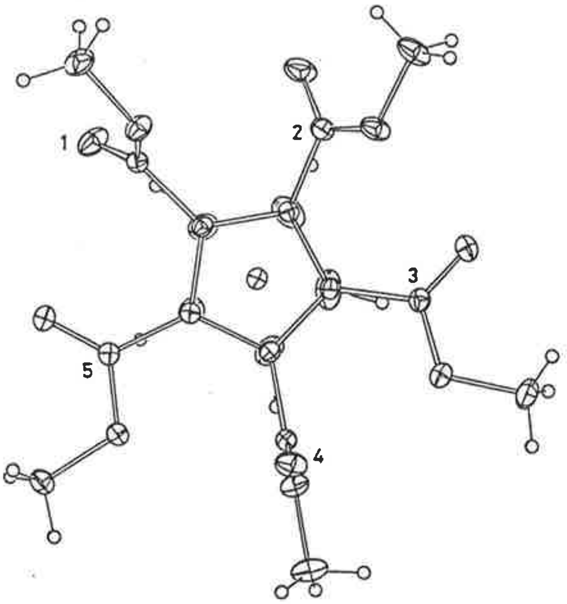


Figure 15: Molecular projection of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_5]$ normal to the C_5 ring plane (by B.W. Skelton and A.H. White).

Possible mechanisms for the reaction which affords complex (42) are of interest. Previously it has been noted that $RuCl(PPh_3)_2(\eta-C_5H_5)$ readily forms cationic complexes; with methanol, for example, equilibrium (v) lies to the right. However, oxygen-donor ligands such as alcohols and ethers are

(v) $RuCl(PPh_3)_2(\eta-C_5H_5) + MeOH \longrightarrow [Ru(MeOH)(PPh_3)_2(\eta-C_5H_5)]^+ + Cl^-$

weakly bonded, and are readily displaced by other ligands.[57] Nitrogen-donor ligands, such as acetonitrile, are more strongly attached to the metal atom, and it is relevant to observe that complex (42) cannot be obtained from the salt (43), even in oxygen.

It may be supposed, however, that the methanol ligand can be displaced by molecular oxygen to give an intermediate (undetected), which in turn undergoes an intermolecular oxygen transfer to phosphorus. The resulting $OPPh_3$ ligands are weakly coordinated through oxygen, and can be displaced by the entering $[C_5(CO_2Me)_5]^-$ ligand to give (42). If an excess of PPh_3 is present, coordination of this ligand would be preferred over that of the bulky $[C_5(CO_2Me)_5]^-$ anion, leading to a catalytic cycle [see below p. 187]. This process is similar to that proposed for the oxidation of PPh_3 by $[RuO(py)(bipy)_2]^{2+}$, in acetonitrile, which has been shown to involve an intermediate $OPPh_3$ complex.[58]

Similarly, the complex $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_4Me]$ (45) was obtained by reacting $RuCl(PPh_3)_2(\eta-C_5H_5)$ with $Tl[C_5(CO_2Me)_4Me]$ [prepared in situ from $Tl(O_2CMe)$ and $HC_5(CO_2Me)_4Me$] in methanol in air. Complex (45), which was identified by the usual methods (see Experimental), had similar physical properties to those of (42) (colour, solubilities and conductivity).

Reactions of $Ru(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CO_2Me)_5]$

As expected for a metallocene bearing electron-withdrawing substituents, (42) is stable towards aromatic electrophilic substitution (acetyl chloride in the presence of $AlCl_3$), and towards oxidation in air or oxygen, and also by molecular iodine; ruthenocene itself readily undergoes electrophilic substitution,[54,59] and readily affords the ruthenium(IV) derivative $[RuI(\eta\text{-}C_5H_5)_2]^+$ with the latter reagent.[60] The most interesting reaction is the ready displacement of the $[\eta\text{-}C_5(CO_2Me)_5]$ ligand by other donor ligands to give salts of the $[RuL_3(\eta\text{-}C_5H_5)]^+$ cations. Thus, complex (42) reacts with PPh_3 in acetonitrile to give (43); the similar compounds $[Ru(NCPh)(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (46) and $[Ru(NCMe)(dppe)(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (47) were obtained with PPh_3 in benzonitrile and with dppe in acetonitrile respectively. While fairly harsh reaction conditions were necessary, no added reagent (Lewis acid) is required, the displaced $[C_5(CO_2Me)_5]^-$ ligand being stable enough to act as the counter-ion. Although the displacement of one C_5H_5 ring from ferrocene by CO[61] or arenes[62-64] in the presence of $AlCl_3$, or from ruthenocene by arenes, also with $AlCl_3$ present,[65,66] has been reported, to our knowledge this is the first occasion on which simple displacement of a C_5 ring from a ruthenocene by simple two-electron donor ligands has been observed.

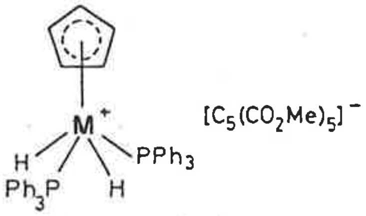
The displacement of the $[C_5(CO_2Me)_5]^-$ ligand is no surprise when we recall the greater stability of the resultant anion due to the electron-withdrawing CO_2Me groups. The greater stability of the Ru-C_5H_5 bond is also shown by the presence of the intense ion $[Ru(C_5H_5)]^+$ (m/z 167) in the mass spectrum of complex (42); the ion $[Ru\{C_5(CO_2Me)_5\}]^+$ is not found.

The ready displacement of the $[C_5(CO_2Me)_5]^-$ ring by PPh_3 in acetonitrile to form $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, and the observation that, in methanol in the presence of air, metallocene (42) is readily formed from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and (3), suggested that this system might act as a catalyst for the oxidation of PPh_3 to its oxide. Thus, the passage of oxygen into an ethanol solution of PPh_3 containing 0.01 mol equivalent of (42) for 6 h at 78°C afforded essentially a quantitative yield of $OPPh_3$. A control experiment showed that, in the absence of (42) no oxidation of PPh_3 occurred under the same conditions.

Use of $HC_5(CO_2Me)_5$ as a protonating agent

In an attempt to obtain complex (42) by displacement of the hydride ligand from $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ by the strongly acidic diene (1), we noticed that a suspension of yellow hydride in methanol was rapidly converted to a white precipitate. Isolation and characterisation of this substance showed that it was an adduct, best formulated as the salt $[RuH_2(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (48). Unfortunately, the compound was insoluble in most solvents, except chlorinated hydrocarbons, with which it reacted rapidly to afford

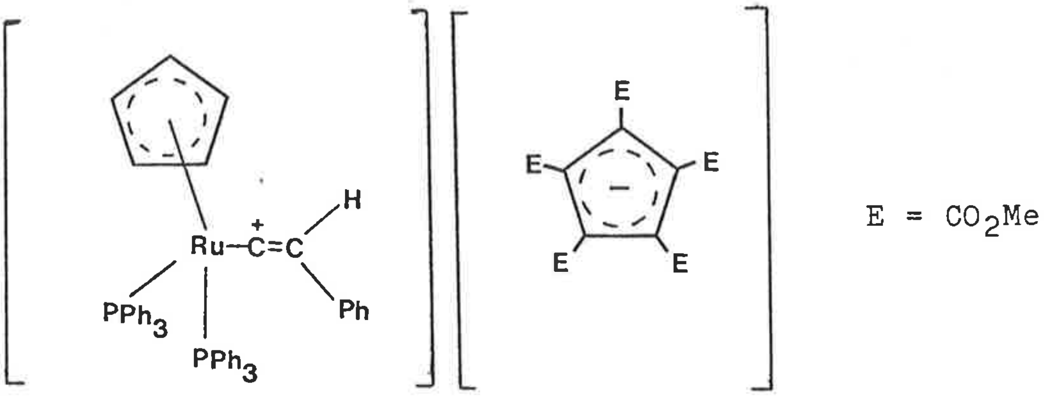
$RuCl(PPh_3)_2(\eta-C_5H_5)$. The osmium analogue $[OsH_2(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (49), which is stable in chlorinated solvents, was obtained from the reaction of $OsH(PPh_3)_2(\eta-C_5H_5)$ with (1). Both the dihydrido complexes were identified by elemental microanalyses and the presence of ν(RuH) and ν(C=O) bands in the i.r. spectra. The presence of the two hydride ligands in (49) were confirmed by the high-field two-proton triplet at δ -5.94 [J(PH) 30 Hz]. Previous work[67] has described the addition of HPF_6 to $MX(PR_3)_2(\eta-C_5H_5)$ (M = Ru, X = Cl; M = Os, X = Br; R = Me or Ph) to give the hydridometal (IV) salts $[MXH(PR_3)_2(\eta-C_5H_5)][PF_6]$.



M = Ru (48)
M = Os(49)

The diene (1) also proved to be an excellent reagent for protonating the acetylide complex $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ to give the $[C_5(CO_2Me)_5]^-$ salt of the cationic η^1-vinylidene complex $[Ru(C{=}CHPh)(PPh_3)_2(\eta-C_5H_5)]^+$ (50).[68] Similar reactions with HPF_6 has afforded $[Ru(C{=}CHPh)(PPh_3)_2(\eta-C_5H_5)][PF_6]$.[69] The reaction of $[Ru(C{=}CHPh)(PPh_3)_2(\eta-C_5H_5)]^+$ with dioxygen was reported to give $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)]^+$ and benzoic acid.[70] Thus the reaction of (50) [prepared in situ from $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ and (1)] with air affords $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (51). Complex (51) was identified by its characteristic[71] infrared [ν(CO) 1978 cm^{-1}], n.m.r. spectrum and microanalysis.

The above reactions provide more examples of the use of the strongly acidic nature of the diene (1), and the bulk of the $[C_5(CO_2Me)_5]^-$ anion, to isolate stable salts of protonated organometallics.



(50)

Conclusions

In most cases described above, the metal ion is coordinated by, or interacts electrostatically with, the carbonyl oxygens of the $[C_5(CO_2Me)_5]^-$ anion, rather than the ring carbons. This can be readily accounted for by the presence of the electronegative CO_2Me groups and the expected concentration of charge on the carbonyl oxygens. In the cases where a ring-metal bond is present, easy displacement of the stable $[C_5(CO_2Me)_5]^-$ anion by other donor ligands may occur. This large anion can also act as a non-coordinating counter-ion and has thus facilitated the isolation and crystallisation of cationic complexes of interest.

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1. ^1H n.m.r. spectra of compounds in D_2O solution were referenced to internal Bu^tOH (δ 1.28), and chemical shifts are given relative to $SiMe_4$. Magnetic measurements were obtained by the Gouy method,[72] and conductivity measurements at 25°C under nitrogen using a Phillips PR9500 AC conductance bridge. The ligands $HC_5(CO_2Me)_5$ [28] and $HC_5(CO_2Me)_4Me$,[50] and the complexes $Ag[C_5(CO_2Me)_5]$,[36] $Tl[C_5(CO_2Me)_5]$,[28] $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$,[73] $RuCl(CO)_2(\eta\text{-}C_5H_5)$,[74] $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$,[73] $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$,[75] $OsH(PPh_3)_2(\eta\text{-}C_5H_5)$[75] and $Rh_2(O_2CCH_3)_4$ [76] were prepared according to published procedures. Reactions involving silver complexes were protected from light. Only the authors own work for the Degree of Doctor of Philosophy is described in this section unless stated otherwise.

Preparation of $Pb[C_5(CO_2Me)_5]_2$ (10)

Lead(II) carbonate (200 mg, 0.75 mmol) was added to an aqueous solution of $HC_5(CO_2Me)_5$ (1) (500 mg, 1.4 mmol, in 10 ml). Rapid evolution of CO_2 occurred, after which the solution was filtered. The filtrate was then reduced in volume until colourless crystals of $Pb[C_5(CO_2Me)_5]_2.2H_2O$ (10) formed on cooling (610 mg, 95%) m.p. >150°C (dec). [Found: C, 37.92; H, 3.35; $C_{30}H_{30}O_{20}Pb.2H_2O$ requires C, 37.86; H, 3.60%]. Infrared (nujol): ν(CO) 3400m(br); ν(C=O) 1750m, 1575vs, 1645vs; other bands 1420w, 1310s, 1290w, 1260m, 1240vs, 1209vs, 1180s, 1084m, 1070w, 1009m, 940w, 881w, 860w, 840w, 810w, 791m, 752m cm^{-1}. ^1H n.m.r. : δ (D_2O) 4.32 (s, CH_3).

Preparation of $[Me_3Sn(OH_2)_2][C_5(CO_2Me)_5]$ (21)

Solutions of $Tl[C_5(CO_2Me)_5]$ (238 mg, 0.427 mmol) and Me_3SnCl (85 mg, 0.427 mmol) in methanol were mixed, resulting in an immediate precipitation of thallium chloride. After stirring for 1 h, the solution was filtered and the residue washed with methanol (2x5 ml). Evaporation of the combined filtrates and recrystallisation from $MeOH/Et_2O$ afforded a colourless powder of $[Me_3Sn(OH_2)_2][C_5(CO_2Me)_5]$ (21) (165 mg, 74%), m.p. 102-106°C. [Found: C, 39.12; H, 4.67; M (mass spectrum) 511. $C_{18}H_{24}O_{10}Sn.2H_2O$ requires C, 38.95; H, 5.08%, M ($-2H_2O$) 511 (for ^{111}Sn)]. Infrared (nujol): ν(OH) 3350m, 3180m; ν(C=O) 1612w, 1690s, 1649m; other bands 1418w, 1290w, 1235s, 1208s, 1180m, 1075w, 1009w, 996w, 835w, 790w, 764w, 721w cm^{-1}. ^1H n.m.r.: δ (D_2O) 0.63 (s, 9H, CH_3), 3.88 (s, 15H, OCH_3).

Preparation of $Rh[C_5(CO_2Me)_4Me]_2$ (29)

A mixture of $Rh_2(O_2CMe)_4$ (100 mg, 0.31 mmol) and $HC_5(CO_2Me)_4Me$ (112 mg, 0.36 mmol) was stirred in refluxing methanol (30 ml) for 72 h. Evaporation to ca 10 ml and filtration yielded blue crystals of $Rh_2(O_2CMe)_4$. The filtrate was cooled (-35°C) to give a red powder of $Rh[C_5(CO_2Me)_4Me]_2$ (29) (19 mg, 8%) m.p. 170°C (dec). [Found: C, 46.28; H, 4.33; O, 35.44; M (mass spectrum) 725. $C_{28}H_{30}O_{16}Rh$ requires C, 46.36; H, 4.17; O, 35.29%; M 725]. Infrared (nujol): ν(C=O) 1720vs; other bands 1435w, 1360w, 1325w, 1225s(br), 1170w, 1802w, 1060w, 1028w, 995w, 770m, 715m, 659m cm^{-1}. Conductivity (acetone) 1.0 $ohm^{-1}cm^{-1}mol^{-1}$.

Preparation of $Ag[C_5(CO_2Me)_5](PPh_3)$ (34) (from M.L. Williams Honours report[53])

A mixture of silver acetate (240 mg, 1.44 mmol), PPh_3 (390 mg, 1.5 mmol) and $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol) in methanol (50 ml) was stirred for 20 h at room temperature. Filtration and evaporation gave a white solid, which was recrystallised from MeOH to give white rod-like crystals of $Ag[C_5(CO_2Me)_5]$-(PPh_3) (650 mg, 65%), m.p. 198-200°C. [Found: C, 54.90; H, 4.00; $C_{33}H_{30}AgO_{10}P$ requires C, 54.65; H, 4.15%]. Infrared (nujol): ν(C=O) 1726s, 1720s, 1694s, 1670m; other bands 1435m, 1413m, 1362m, 1279s, 1220s, 1208s, 1175s, 1074m, 1006m, 994m, 778m, 753m, 750m, 745m, 700m, 694m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 3.75 (s, 15H, OMe), 7.35, 7.45 (both m, 15H, Ph). ^{13}C n.m.r.: δ ($CDCl_3$) 52.0 (s, OMe), 117.9 (s, ring C), 129.0-134.4 (m, Ph), 168.8 (s, $\underline{C}O_2Me$). Conductivity (acetone) 56 $ohm^{-1}cm^{-1}$ mol^{-1}.

Preparation of $Ag[C_5(CO_2Me)_5](PPh_3)_2$ (35) (from M.L. Williams Honours report[53])

A similar reaction to the above used silver acetate (120 mg, 0.7 mmol), PPh_3 (380 mg, 1.5 mmol) and $HC_5(CO_2Me)_5$ (250 mg, 0.7 mmol) in methanol (30 ml). After 18 h, evaporation, and washing with boiling light petroleum (2x50 ml) gave a white solid, which was recrystallised from methanol to give white rods of $Ag[C_5(CO_2Me)_5](PPh_3)_2$ (35) (560 mg, 81%), darkening and melting at 213-217°C. [Found: C, 62.22; H, 4.50; $C_{51}H_{45}AgO_{10}P_2$ requires C, 62.00; H, 4.60%]. Infrared (nujol): ν(C=O) 1693vs, 1621s; other bands 1455s, 1448m, 1434m, 1290s, 1220vs, 1203vs, 1172m, 1095m, 1070m, 1011m, 990m, 746m, 693m

cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 3.58 (s, 15H, OMe), 7.38 (m, 30H, Ph). ^{13}C n.m.r.: δ ($CDCl_3$) 51.1 (s, OMe), 117.8 (s, ring C), 128.9-134.0 (m, Ph), 168.5 (s, $\underline{C}O_2Me$). Conductivity (acetone) 86 $ohm^{-1}cm^{-1}mol^{-1}$.

Preparation of $Ag[C_5(CO_2Me)_5](dppe)$ (36)

A mixture of silver acetate (120 mg, 0.72 mmol), dppe (300 mg, 0.75 mmol) and $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) in methanol (30 ml) was stirred at room temperature for 18 h. After this time, the white solid was collected by filtration, washed with MeOH (2x5 ml) and Et_2O (2x5 ml) and dired. Evaporation of the filtrate to *ca* 15 ml and cooling afforded a second crop (total yeild 560 mg, 93%). Recrystallisation from MeOH afforded a white powder of $Ag[C_5(CO_2Me)_5](dppe)$ (36), m.p. 194-187°C (darkens at 180°C). [Found: C, 56.20; H, 4.50; $C_{41}H_{39}AgO_{10}P_2$ requires C, 57.15; H, 4.55%]. Infrared (nujol): ν(C=O) at 1723s, 1690s, 1674vs, 1637s; other bands 1588w, 1573w, 1455w, 1437w, 1415w, 1367w, 1288m, 1210s, 1195s, 1070m, 1009m, 1000w, 940w, 849w, 838w, 790m, 749m, 720m, 691m cm^{-1}. ^{1}H n.m.r.: δ ($CDCl_3$) 1.72 [s(br), 4H, CH_2], 3.68 (s, 15H, OMe), 7.30 [s(br), 20H, Ph]. ^{13}C n.m.r.: δ ($CDCl_3$) 51.56 (s, OMe), 118.0 (s, ring C), 129.6-132.9 (m, Ph), 168.9 (s, $\underline{C}O_2Me$). Conductivity (acetone) 84.7 $ohm^{-1}cm^{-1}mol^{-1}$.

Preparation of $Ag[C_5(CO_2Me)_5](tppme)$ (37)

A similar reaction using silver acetate (60 mg, 0.36 mmol), tppme (220 mg, 0.35 mmol) and $HC_5(CO_2Me)_5$ (130 mg, 0.37 mmol) afforded a white solid which was recrystallised from MeOH/Et_2O to give a white powder of $Ag[C_5(CO_2Me)_5](tppme)$ (37)

(270 mg, 70%), m.p. 147-153°C. [Found: C, 61.15; H, 5.10; $C_{56}H_{54}AgO_{10}P_3$ requires C, 51.85; H, 5.00%]. Infrared (nujol): ν(C=O) 1710s, 1690s, 1683w; other bands 1585vw, 1571vw, 1436w, 1367w, 1274m, 1200vs, 1174s, 1095w, 1068m, 1024vw, 1014w, 998w, 939w, 833w, 787w, 740m, 730w, 694m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 1.31 (s, 3H, Me), 2.57 [s(br), 6H, CH_2], 3.60 (s, 15H, OMe), 7.11 [s(br), 30H, Ph]. Conductivity (acetone) 70.7 $ohm^{-1}cm^{-1}$ mol^{-1}.

Preparation of $Ag[C_5(CO_2Me)_5](PPh_3)$ (34) from $Ag[C_5(CO_2Me)_5]$

A solution of $Ag[C_5(CO_2Me)_5]$ (32) (300 mg, 0.65 mmol) and PPh_3 (170 mg, 0.65 mmol) in methanol (30 ml) was stirred at room temperature for 20 h. Evaporation and crystallisation from MeOH afforded white crystals of $Ag[C_5(CO_2Me)_5](PPh_3)$ (34) (348 mg, 74%). Identified by comparison of its properties (i.r., n.m.r. and m.p.) with those of an authentic sample.

Similarly prepared were $Ag[C_5(CO_2Me)_5](PPh_3)_2$ (35) (86%); $Ag[C_5(CO_2Me)_5]$(dppe) (36) (95%) and $Ag[C_5(CO_2Me)_5]$(tppme) (37) (70%). All were identified by comparison of their properties (i.r., n.m.r. and m.p.) with those of authentic samples.

Reaction of $Ag[C_5(CO_2Me)_5]$ (32) with Iodomethane

Iodomethane (3 ml, excess) in methanol (15 ml) was added to a solution of $Ag[C_5(CO_2Me)_5]$ [prepared *in situ* from silver acetate (120 mg, 0.72 mmol) and $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) in methanol (20 ml)]; an olive green precipitate formed immediately. After stirring at room temperature for 6 h, the solution was filtered, and the solid washed with methanol (2x10 ml). The combined filtrates were evaporated to give

$MeC_5(CO_2Me)_4$ (240 mg, 93%) as a white solid; recrystallisation from methanol afforded clear colourless crystals, m.p. 99-100°C (lit.,[22] 101-102°C). ^1H n.m.r.: δ ($CDCl_3$) 1.70 (s, 3H, Me), 3.67 (s, 3H, OMe), 3.83, 3.88 (both s, 6H, OMe).

Preparation of $Cu[C_5(CO_2Me)_5](PPh_3)_2$ (38)

(a) From $Cu[C_5(CO_2Me)_5]_2$ and excess PPh_3 (from M.L. Williams Honours Report[53]) - A mixture of $Cu[C_5(CO_2Me)_5]_2$ (300 mg, 0.38 mmol) and PPh_3 (210 mg, 0.80 mmol) was heated in refluxing methanol (40 ml) for 20 h. The resulting pale orange solution was evaporated to dryness and the residue was extracted with boiling light petroleum (40-60°C) (4x50 ml). Addition of cold methanol (10 ml) to the residue resulted in the precipitation of white microcrystals which were collected and washed with cold methanol (2x20 ml). Recrystallisation from acetone/light petroleum gave white crystals of $Cu[C_5(CO_2Me)_5](PPh_3)_2$ (38) (160 mg, 46%), m.p. 198-199°C. [Found: C, 64.68; H, 4.73; $C_{51}H_{45}CuO_{10}P_2$ requires C, 64.93; H, 4.81%]. Infrared (Nujol): ν(C=O) 1725s, 1704s, 1655vs, 1620w; other bands 1357m, 1291s, 1261w, 1211vs, 1195s, 1187s, 1174s, 1095s, 1078s, 998m, 749s, 695s cm^{-1}. ^1H n.m.r.: δ($CDCl_3$) 3.58 (s, 15H, OMe) 7.25, (s, 30H, Ph). ^{13}C n.m.r.: δ($CDCl_3$) 51.4 (s, OMe), 118.4 (s, $\underline{C}_5(CO_2Me)_5$), 128.6-133.5 (m, Ph), 168.4 (s, $\underline{C}O_2Me$). Conductivity (acetone) 54.4 $ohm^{-1}cm^{-1}mol^{-1}$.

(b) From Cu_2O. - A solution of $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) in MeOH (25 ml) was added dropwise over a period of 30 mins to a suspension of Cu_2O (50 mg, 0.35 mmol) and PPh_3 (380 mg, 1.45 mmol) in methanol (50 ml). The mixture was stirred at room temperature (20°C) for 18 h to give a colourless solution which was filtered and evaporated to dryness. Recrystallisation of the white solid from methanol yielded clear white crystals of $Cu[C_5(CO_2Me)_5](PPh_3)_2$ (38) (490 mg, 75%), identical with the material prepared in (a) above.

Similarly prepared was $Cu[C_5(CO_2Me)_5][P(\underline{p}\text{-tol})_3]_2$ (39) (88%) as a white solid (from CH_2Cl_2/hexane), m.p. 75-79°C. [Found: C, 66.83, H, 6.02; $C_{57}H_{57}CuO_{10}P_2$ requires C, 66.62, H, 5.59%]. Infrared (nujol): ν(C=O) 1730m, 1700m, 1665s, 1600w; other bands 1500w, 1400w, 1295m, 1210s, 1188s, 1175s, 1119w, 1099m, 1080w, 1068w, 1027m, 805m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 2.31 (s, 18H, Me), 3.61 (s, 15H, OMe), 7.20 (m, 24H, C_6H_4).

Preparation of $Cu[C_5(CO_2Me)_5](AsPh_3)_2$ (41)

As for the PPh_3 analogue, Cu_2O (57 mg, 0.40 mmol), $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) and $AsPh_3$ (440 mg, 1.45 mmol) gave clear white crystals of $Cu[C_5(CO_2Me)_5](AsPh_3)_2$ (41) (450 mg, 62%), m.p. 171-173°C. [Found: C, 59.33, H, 4.47; $C_{51}H_{45}As_2CuO_{10}$ requires C, 59.40; H, 4.40%]. ^1H n.m.r.: δ ($CDCl_3$) 3.61 (s, 15H, OMe), 7.26 (m, 30H, Ph). Infrared (Nujol): ν(C=O) 1738(sh), 1727s, 1705s, 1660vs, 1625(sh); other bands 1582m, 1575(sh), 1437m, 1295m, 1273m, 1211vs, 1197vs, 1175s, 1160(sh), 1075s, 1070(sh), 1023m, 1000m, 941m, 791m, 739s, 725(sh), 694s cm^{-1}. Conductivity (acetone) 84.7 ohm^{-1} $cm^{-1}mol^{-1}$.

Preparation of $[Cu(dppe)_2][C_5(CO_2Me)_5]$ (40)

A solution of $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) in methanol (25 ml) was added dropwise over a period of 1 h to a suspension of Cu_2O (57 mg, 0.40 mmol) and dppe (380 mg, 1.45 mmol) in methanol (50 ml). The mixture was stirred at room temperature (20°C) for 18 h to give a colourless solution which was filtered and evaporated to dryness. Recrystallisation of the white solid from methanol yielded clear white crystals of $[Cu(dppe)_2][C_5(CO_2Me)_5]$ (40) (710 mg, 83%), m.p. 215-218°C [Found: C, 65.74; H, 5.00; $C_{67}H_{63}CuO_{10}P_4$ requires C, 66.20; H, 5.22%]. ^1H n.m.r.: δ ($CDCl_3$) 2.38 [t, J(PH) 6 Hz, 8H, CH_2], 3.63 (s, 15H, OMe), 7.17 (s, 40H, Ph). Infrared (nujol): ν(C=O) 1715s, 1683vs; other bands 1270m, 1196vs, 1170vs, 1160(sh), 1100m, 1065m, 999m, 787m, 778(sh), 741s, 694s cm^{-1}. Conductivity (acetone) 86.0 $ohm^{-1}cm^{-1}mol^{-1}$.

Reaction of Cu_2O with $HC_5(CO_2Me)_5$

A mixture of Cu_2O (50 mg, 0.35 mmol) and $HC_5(CO_2Me)_5$ (250 mg, 0.70 mmol) in methanol (30 ml) was stirred at room temperature in the dark for 18 h. Filtration removed copper metal, and concentration of the orange filtrate to *ca* 2 ml and cooling afforded orange microcrystals of $Cu[C_5(CO_2Me)_5]_2$ (26) (230 mg, 88%), identified from its i.r. spectrum and m.p.

A similar reaction using Cu_2O, $HC_5(CO_2Me)_5$ and PPh_3 (1 mole equivalent) afforded a mixture of copper metal, $Cu[C_5(CO_2Me)_5]_2$ (26) and $Cu[C_5(CO_2Me)_5](PPh_3)_2$ (38).

Preparation of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_5]$ (42)

(a) From $RuCl(PPh_3)_2(\eta-C_5H_5)$ A mixture of $Tl[C_5(CO_2Me)_5]$ (780 mg, 1.40 mmol) and $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1000 mg, 1.38 mmol) in methanol (40 ml) was stirred at 60°C for 2 h in air. The white precipitate (TlCl) was filtered off and washed with MeOH (5 ml); the combined pale yellow filtrates were cooled overnight (-30°C) to give well formed pale yellow-green crystals of pure $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_5]$ (42) (610 mg, 85%), m.p. 145-146°C. [Found: C, 45.75; 3.80%; M (mass spectrum) 522. $C_{20}H_{20}O_{10}Ru$ requires C, 46.05; H, 3.85%; M 522]. Infrared (nujol): ν(C=O) 1758s, 1745w, 1734vs, 1723vs; other bands 1409s, 1399s, 1378w, 1357w, 1263s, 1225s, 1181s, 1105w, 1063m, 995s, 985m, 952w, 871m, 851w, 844w, 825m, 807m, 785m, 773m, 757w, 678m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 3.80 (s, 15H, OMe), 4.93 (s, 5H, C_5H_5). ^{13}C n.m.r.: δ ($CDCl_3$) 52.96 (s, OMe), 78.83 (s, C_5H_5), 82.23 [s, $\underline{C}_5(CO_2Me)_5$], 165.98 (s, $\underline{C}O_2Me$). Conductivity (acetone): 1.0 $ohm^{-1}cm^{-1}mol^{-1}$. Magnetic susceptibility (21°C): $\chi_{\underline{M}} = 124.67 \times 10^{-6}$ c.g.s. units. The filtrate was evaporated, and the resulting solid extracted with boiling light petroleum (3x20 ml). Filtration and cooling (0°C) gave white crystals of $OPPh_3$ (422 mg, 55%), m.p. 151-154°C. Infrared nujol): ν(PO) 1187s cm^{-1}.

(b) A similar reaction using $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1000 mg, 1.38 mmol), $HC_5(CO_2Me)_5$ (500 mg, 1.40 mmol), and $Tl(O_2CMe)$ (370 mg, 1.40 mmol) afforded (42) in 83% yield.

(c) From $[RuCl(CO)_2(\eta-C_5H_5)]$. The salt $Tl[C_5(CO_2Me)_5]$ (109 mg, 0.195 mmol) was added to $[RuCl(CO)_2(\eta-C_5H_5)]$ (50 mg, 0.194

mmol) dissolved in MeOH (40 ml). After stirring at reflux for 16 h, a yellow-green solution containing a white precipitate (TlCl) was obtained. The filtered solution was reduced in volume to *ca* 10 ml, from which well formed yellow-green crystals of (42) (60 mg, 60%) were deposited on cooling.

Preparation of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_4Me]$ (45)

A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (700 mg, 0.96 mmol), $HC_5(CO_2Me)_4Me$ (300 mg, 0.97 mmol), and $Tl(O_2CMe)$ (255 mg, 0.97 mmol) in methanol (50 ml) was stirred at 35°C for 4 h in air. The white precipitate (TlCl) was filtered off and washed with methanol (5 ml); evaporation and preparative tlc (Et_2O) afforded one pale yellow band, R_f 0.80, which was recrystallised from Et_2O to give fine yellow-green crystals of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_4Me]$ (45) (274 mg, 60%) m.p. 120-122°C. [Found: C, 47.50; H, 4.22; $C_{19}H_{20}O_8Ru$ requires C, 47.80; H, 4.22%]. Infrared (nujol): $\nu(C{=}O)$ 1730vs, 1720vs; other bands 1420w, 1412m, 1400w, 1255s, 1219s, 1193m, 1182m, 1125w, 1110w, 1093m, 1070w, 1039w, 994m, 988w, 855w, 820m, 804w, 786w, 778w, 723m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 2.34 (s, 3H, Me), 3.79 and 3.80 (both s, 12H, OMe), 4.78 (s, 5H, C_5H_5). Conductivity (acetone): 1.0 $ohm^{-1}cm^{-1}mol^{-1}$.

Reactions of $Ru(\eta-C_5H_5)[\eta-C_5(CO_2Me)_5]$ (42)

(a) With PPh_3 in acetonitrile A mixture of $Ru(\eta-C_5H_5)$-$[\eta-[C_5(CO_2Me)_5]$ (42) (100 mg, 0.19 mmol) and PPh_3 (200 mg, 0.76 mmol) was heated in refluxing MeCN (50 ml) for 5 days. During this time the colour of the initially yellow-green solution intensified to bright yellow. Evaporation and preparative tlc (ether) afforded three bands. Band 1, $\underline{R_f}$ 0.9, colourless, PPh_3. Band 2, $\underline{R_f}$ 0.40, recovered $Ru(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CO_2Me)_5]$ (42) (17 mg, 17%). Band 3, $\underline{R_f}$ 0.0, yellow, recrystallised from MeOH to give yellow crystals of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)]$-$[C_5(CO_2Me)_5]$ (43) (120 mg, 55%), identified by comparison of its properties (i.r., n.m.r. and m.p.) with those of an authentic sample.[37]

(b) <u>With PPh_3 in benzonitrile</u> Similarly, a mixture of $Ru(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CO_2Me)_5]$ (42) (100 mg, 0.19 mmol) and PPh_3 (100 mg, 0.38 mmol) was heated at 120°C in benzonitrile (15 ml) for 72 h. Evaporation of the resulting yellow solution, extraction of the residue with boiling light petroleum (3x25 ml) and Et_2O (3x25 ml), and recrystallisation from $MeOH/Et_2O$ of the remaining solid gave yellow crystals of $[Ru(NCPh)(PPh_3)_2$-$(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (46) (70 mg, 32%), m.p. 145-148°C. [Found: C, 65.75; H, 5.00; N, 1.20; $C_{63}H_{55}NO_{10}P_2Ru$ requires C, 65.85; H, 4.80; N, 1.20%]. Infrared (nujol): $\nu(C{\equiv}N)$ 2228w; $\nu(C{=}O)$ 1739w, 1734w, 1710s, 1700w, 1687vs; other bands 1587w, 1574w, 1480w, 1436m, 1312w, 1275m, 1200vs, 1175s, 1090m, 1087m, 1070m, 1012m, 1000m, 975w, 940m, 849m, 835m, 799w, 788w, 751s, 721w, 698s, 685m cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 3.70 (s, 15H, OMe), 4.50 (s, 5H, C_5H_5), 7.23 (m, 35H, Ph).

(c) <u>With dppe in acetonitrile</u> A mixture of $Ru(\eta\text{-}C_5H_5)$-$[C_5(CO_2Me)_5]$ (42) (250 mg, 0.48 mmol) and dppe (200 mg, 0.5 mmol) in acetonitrile (50 ml) was heated in an autoclave under nitrogen (140°C, 45 atm, 15 h). Evaporation of the resulting yellow solution, extraction of the residue with boiling light petroleum (3x50 ml), and Et_2O (3x50 ml), and recrystallisation from MeOH/Et_2O afforded large bright yellow crystals of $[Ru(NCMe)(dppe)(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5].0.25MeCN$ (47) (256 mg, 56%), m.p. 148-152°C. [Found: C, 59.05; H, 5.05; N, 1.40; $C_{48}H_{47}NO_{10}P_2Ru.0.25MeCN$ requires C, 60.00; H, 4.95; N, 1.80%]. Infrared (nujol): ν(C≡N) 2278w; ν(C=O) 1725w, 1721w, 1714vs, 1695vs, 1677s; other bands 1587w, 1572w, 1436m, 1310w, 1277m, 1207vs, 1169s, 1100m, 1069m, 1015m, 999m, 939w, 870w, 841m, 835w, 812m, 790w, 754m, 741w, 701s, 679w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 1.35 [s, 3H, MeCN (coordinated)], 1.97 [s, 0.75H, MeCN (free)], 2.37, 2.57 [s(br), 2H each, CH_2], 3.66 (s, 15H, OMe), 4.60 (s, 5H, C_5H_5), 7.50 (m, 20H, Ph).

Catalytic oxidation of triphenylphosphine

Oxygen was bubbled through a mixture of $Ru(\eta\text{-}C_5H_5)\text{-}[\eta\text{-}C_5(CO_2Me)_5]$ (42) (20 mg, 0.038 mmol) and PPh_3 (1000 mg, 3.81 mmol) in refluxing EtOH (50 ml) for 6 h. The solution was taken to dryness and the off-white solid was extracted with hot light petroleum (5x20 ml), filtered and the combined extracts cooled to give white crystals of $OPPh_3$ (850 mg, 80%), m.p. 148-153°C, ν(PO) 1187s cm^{-1}, identified by comparison with an authentic sample.

Preparation of $[RuH_2(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (48)

Twice-recrystallised $HC_5(CO_2Me)_5$ (330 mg, 0.9 mmol) was added to a suspension of $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ (600 mg, 0.84 mmol) in methanol (45 ml), whereupon the colour rapidly faded. After 30 min the white precipitate was filtered off, washed with methanol (4x20 ml) and diethyl ether (2x10 ml), and dried to give $[RuH_2(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (48) (830 mg, 94%), m.p. 136-137°C (turns orange at 134°C). [Found: C, 63.95; H, 5.20; $C_{56}H_{52}O_{10}P_2Ru$ requires C, 64.2; H, 5.00%]. Infrared (nujol): ν(RuH) 2013w; ν(C=O) 1730w, 1708vs, 1691vs; other bands 1435m, 1277m, 1200vs, 1163vs, 1093s, 1075m, 1065m, 1009m, 1001m, 839s, 834s, 751s, 720m, 698s, 660m cm^{-1}. The complex is insoluble in most solvents (alkanes, benzene, Et_2O, CS_2, 1,2-dimethoxyethane, MeCN, Me_2CO, alcohols, and water); it dissolves with rapid reaction in chlorinated solvents to give $RuCl(PPh_3)_2(\eta-C_5H_5)$.

Preparation of $[OsH_2(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (49)

A similar reaction using $HC_5(CO_2Me)_5$ (85 mg, 0.27 mmol) and $OsH(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.26 mmol) in methanol afforded white $[OsH_2(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (49) (220 mg, 74%), m.p. 210-215°C (dec). [Found: C, 58.06; H, 4.82%; $C_{56}H_{52}O_{10}OsP_2$ requires C, 59.15; H, 4.61%]. Infrared (nujol): ν(OsH) 2129w, 2100vw; ν(C=O) 1730w, 1718vs, 1691vs; other bands 1436m, 1276m, 1200vs, 1173s, 1094s, 1010m, 842m, 833m, 790w, 743m, 698s, 686w cm^{-1}. ^1H n.m.r.: δ $(CDCl_3)$ -5.94 [t, *J*(PH) 30 Hz, 2H, OsH], 3.67 (s, 15H, OCH_3), 4.86 (s, 5H, C_5H_5), 7.30 (s, 30H, Ph). Prolonged exposure to chlorinated solvents (days) affords $OsCl(PPh_3)_2(\eta-C_5H_5)$.

Preparation of $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (51)

A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (150 mg, 0.195 mmol) and $HC_5(CO_2Me)_5$ (72 mg, 0.202 mmol) in CH_2Cl_2 (30 ml) was stirred at room temperature in air for 2 h. Evaporation to *ca* 5 ml and dropwise filtration into stirred Et_2O (50 ml) gave a fine tan powder of $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)][C_5(CO_2Me)_5]$ (51)

(140 mg, 65%), m.p. 80-83°C. [Found: C, 63.15; H, 4.63; $C_{57}H_{50}O_{11}P_2Ru$ requires C, 63.74; H, 4.69%]. Infrared (nujol): ν(C≡O) 1978s; ν(C=O) 1715vs, 1690vs; other bands 1585w, 1575w, 1435w, 1310w, 1275m, 1205vs, 1175vs, 1091m, 1069m, 1015s, 1000w, 940w, 837w, 790w, 750m, 699s cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) 3.68 (s, 15H, OMe), 4.81 (s, 5H, C_5H_5), 7.20 (m, 30H, Ph).

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