



A STUDY OF TRANSITION METAL COMPLEXES

by

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Concise abstract *Approved*

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SUMMARY

The chemistry of cyclopentadienyl ligands bearing five electron withdrawing groups is less extensive than that of the well-known C_5H_5 ligand. The first Chapter of this Thesis describes some complexes containing the $C_5(CO_2Me)_5$ ligand. The ligand is bonded to the metal either by the ester carbonyl oxygens or the ring carbons. The first examples of complexes containing covalent bonds between the carbonyl oxygens and the metal which are preserved in solution were found (e.g. $Ru(O_2CMe)\{C_5(CO_2Me)_5\} - (PPh_3)_2$ and $Rh(azb)_2\{C_5(CO_2Me)_5\}$ ($azb = C_6H_4N=NPh$)). Ring-C interactions were found in complexes such as $Rh(\eta^4-C_8H_{12})-\{\eta^5-C_5(CO_2Me)_5\}$; displacement of the $C_5(CO_2Me)_5$ ligand as $[C_5(CO_2Me)_5]^-$ was easily achieved by addition of dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) yielding $[Rh(\eta^4-C_8H_{12})(dppe)][C_5(CO_2Me)_5]$. The reaction between $Tl[C_5(CO_2Me)_5]$ and $\{RhCl(CO)_2\}_2$ afforded $Rh\{\eta^5-C_5H_2(CO_2Me)_3 - 1,2,3\}\{\eta^4-C_5H_3(CO_2Me)_3 - 1,3\text{-diene}\}$ as the major product. In addition, a number of ionic complexes were synthesised in which $[C_5(CO_2Me)_5]^-$ acts as a non-coordinating counter-ion.

Several complexes of the ligand $C_5Me(CO_2Me)_4$ have also been obtained. There appear to be no essential differences between these complexes and the analogous $C_5(CO_2Me)_5$ complexes, except for obvious spectroscopic changes. The molecular structure of $Au\{C_5Me(CO_2Me)_4\}(PPh_3)$ closely resembles that of $Au\{C_5(CO_2Me)_5\}(PPh_3)$; the methyl group is found on the ring carbon adjacent to that which most closely interacts with the $Au(PPh_3)$ group.

The second Chapter describes the synthesis of mixed metal clusters containing gold using a novel source of ' $\text{Au}_2(\text{PPh}_3)_2$ ' groups, namely $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ and $[\text{ppn}][\text{X}]$ ($\text{X} = \text{Co}(\text{CO})_4$, OAc or Cl). This reagent combination has given products in which a CO ligand is replaced by $\text{Au}_2(\text{PPh}_3)_2$. The isolobal relationship between H and $\text{Au}(\text{PR}_3)$ groups suggests that formation of complexes containing two $\text{Au}(\text{PR}_3)$ groups may model the addition of H_2 to clusters. Clusters synthesised using this route include $\text{Ru}_3(\mu_3-\text{NPh})-(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ and $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$, both containing an Ru_3Au_2 trigonal bipyramidal. In $\text{Ru}_3-(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$, the metal core consists of a capped distorted square pyramid. The triangle of Au atoms is centred over one of the Ru atoms. The structure of $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PPh}_3)\}_2$ consists of an Ru_6 octahedron, two opposite edges of which are bridged by $\text{Au}(\text{PPh}_3)$ groups. Reactions of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ with ruthenium and osmium hydrido clusters also gave mainly clusters containing Au_2 units. This work has been extended to include reactions of $[\text{O}\{\text{Au}[\text{P}(\text{OMe})_3]\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$, to give, for example, $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_8[\text{Au}_2\{\text{P}(\text{OMe})_3\}_2]$ which contains a trigonal bipyramidal Ru_3Au_2 core.

The chemistry of $\text{Ru}_3(\mu-\text{dppm})(\text{CO})_{10}$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) has been investigated in some detail, and is described in Chapter 3. Addition of terminal acetylenes gave $\text{Ru}_3(\mu-\text{H})-(\mu_3-\text{C}\equiv\text{CR})(\mu-\text{dppm})(\text{CO})_7$ ($\text{R} = \text{Ph}, \text{C}_6\text{F}_5, \text{But}^t$ and SiMe_3) while the addition of $\text{Au}(\text{C}\equiv\text{CPh})(\text{PR}'_3)$ yielded the analogous gold compounds $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\mu-\text{dppm})(\text{CO})_7\{\text{Au}(\text{PR}'_3)\}$ ($\text{R}' = \text{Ph}, \text{C}_6\text{H}_4\text{Me}-p$). Addition of one equivalent of $\text{C}_2(\text{CO}_2\text{Me})_2$

afforded $\text{Ru}_3\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7$ and $\text{Ru}_3\{\mu_3-\text{C}_4(\text{CO}_2\text{Me})_4\}(\mu-\text{dppm})(\text{CO})_6$ although longer reaction times also yielded a mixture of products including $\text{Ru}_3(\mu-\text{H})_2\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{dppm})(\text{CO})_7$ and $\text{Ru}_4(\mu_3-\text{H})-\{\mu_4-\text{C}_2(\text{CO}_2\text{Me})_2\}\{\mu-\text{PPh}(\text{C}_6\text{H}_4)\text{CH}_2\text{PPh}_2\}(\text{CO})_9$. The addition of two equivalents of $\text{C}_2(\text{CO}_2\text{Me})_2$ gave a high yield of $\text{Ru}_3\{\mu_3-\text{C}_4(\text{CO}_2\text{Me})_4\}(\mu-\text{dppm})(\text{CO})_6$.

Reactions of $\text{Ru}_3(\mu-\text{dppm})(\text{CO})_{10}$ with I_2 and allyl bromide afforded $\text{Ru}_2(\mu-\text{I})_2(\mu-\text{dppm})(\text{CO})_4$ and $\text{Ru}_2(\mu-\text{Br})-(\mu-\text{C}_3\text{H}_5)(\mu-\text{dppm})(\text{CO})_4$, respectively.

Addition of I_2 to $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{C}\equiv\text{CPh})(\mu-\text{dppm})(\text{CO})_7$ yielded $\text{Ru}_2(\mu-\text{I})(\mu-\text{C}_2\text{Ph})(\mu-\text{dppm})(\text{CO})_4$, while pyrolysis of $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{C}\equiv\text{CBu}^t)(\mu-\text{dppm})(\text{CO})_7$ yielded $\text{Ru}_3(\mu-\text{H})_2-(\mu_3-\text{Bu}^t\text{C}_2\text{Ph})(\mu_3-\text{PPhCH}_2\text{PPh}_2)(\text{CO})_6$, in which a phenyl group has migrated from the dppm ligand to the acetylene.

Some related chemistry of $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$ and $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (a pyrolysis product of $\text{Ru}_3(\mu-\text{dppm})(\text{CO})_{10}$) is also discussed in this Chapter.

STATEMENT

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

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

PAUL A. HUMPHREY

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ABBREVIATIONS

In general

° Å	angstroms
AR	Analytical Reagent
atm	atmospheres
av.	average
azb	C ₆ H ₄ N=NC ₆ H ₅
b.p.	boiling point
bqH	benzo[<i>h</i>]quinoline
Bu	normal butyl
Bu ^s	secondary butyl
Bu ^t	tertiary butyl
ca	circa
cp	cyclopentadienyl
d	days
dec.	decomposed
dpam	bis(diphenylarsino)methane
dppae	1-diphenylphosphino-2-diphenylarsino ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
e	electron
e.g.	for example
Et	ethyl
Fig.	Figure
g	grams
h	hours
hy	hybrid
Hz	hertz
i.e.	that is
K	degrees Kelvin

kV	kilovolts
L	ligand or litre
lit.	literature value
LR	Laboratory Reagent
<i>m</i>	meta
M	metal or Molarity
Me	methyl
mg	milligrams
MHz	megahertz
min	minutes
ml	millilitres
mmol	millimoles
MO	molecular orbital
m.p.	melting point
OAc	acetate
<i>p</i>	para
Ph	phenyl
phen	1,10-phenanthroline
ppn	bis(triphenylphosphine)iminium
Pr	normal propyl
Pr ⁱ	isopropyl
R	alkyl or aryl
rt	room temperature
<i>R_f</i>	retardation factor (TLC)
s	solid
thf	tetrahydrofuran
TLC	thin layer chromatography
vac.	vacuum
X	anion

For Electronic Absorption Spectroscopy (UV/Visible)

λ wavelength (nm)
 ϵ extinction coefficient ($M^{-1}cm^{-1}$)

For Infrared Spectroscopy (IR)

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

For Mass Spectrometry (MS)

EI MS Electron Impact Mass Spectra
FAB MS Fast Atom Bombardment Mass Spectra
m molecular ion
 m/z mass per unit charge

For Nuclear Magnetic Resonance Spectroscopy (NMR)

δ chemical shift (ppm)
d doublet
dd doublet of doublets
dt doublet of triplets
 J coupling constant
m multiplet
ppm parts per million
s singlet
t triplet

NUMBERING OF COMPLEXES

The numbering of complexes applies only to the chapter being discussed in the text as each chapter is self-contained.



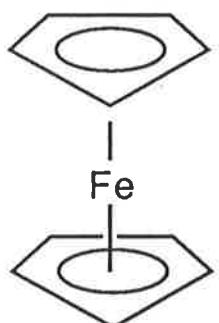
CHAPTER ONE

SOME CHEMISTRY OF
PENTAKIS (METHOXYSARBONYL) CYCLOPENTADIENE,
 $\text{HC}_5(\text{CO}_2\text{Me})_5$, AND 1-METHYL-2,3,4,5-
TETRAKIS (METHOXYSARBONYL) CYCLOPENTADIENE,
 $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$

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INTRODUCTION

The discovery of ferrocene $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ (1) in 1951, by two independent research groups^{1, 2}, resulted in extensive research into cyclopentadienyl chemistry, so that for every metal, main group, transition or f-block there is at least one cyclopentadienyl derivative.^{3, 4}



(1)

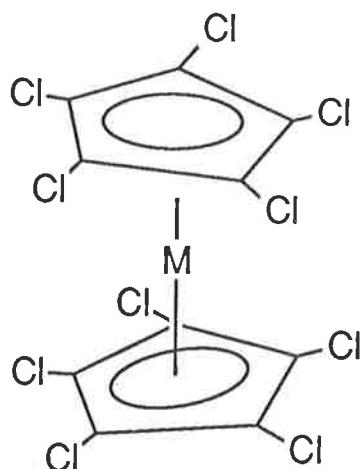
Ferrocene and other cyclopentadienyl metal complexes undergo electrophilic substitution reactions which are typical for aromatic compounds.⁵ In general, however, attempts to make penta- or deca-substituted derivatives, in which half or all the ring hydrogen atoms are replaced by other functional groups, usually by successive substitution reactions, have not been successful, although exceptions to this include decachloro-ferrocene and -ruthenocene (2, 3)⁶ and the recently reported superferrocene.^{7, 8}

The use of pentasubstituted cyclopentadienes is another approach which has been particularly successful in the case of the electron releasing pentamethylcyclopentadienyl group, C_5Me_5 , which has enabled the synthesis of

compounds for which C_5H_5 analogues do not exist and the subsequent development of their chemistry. Specific examples include the early transition metals,^{9,10,11} complexes containing metal-metal multiple bonds,¹² and their application to C-H bond activation systems.^{13,14,15}

The chemistry of cyclopentadienyl ligands bearing five electron-withdrawing groups is less extensive. King¹² postulated that "complete substitution of cyclopentadienyl hydrogens with electronegative groups such as cyano and alkoxy carbonyl should lead to removal of electron density from the filled ring A and E_1 orbitals to the extent that stable pentahapto metal-ring bonds are no longer possible." This statement was apparently supported by (i) the existence of iron compounds derived from dicyanobis (ethoxycarbonyl) and tetracyano-cyclopentadiene which were described as "ferrous salts, which were not ferrocenes"¹⁶, (ii) the so-called decacyano-ferrocene which is a light green, non-volatile and extremely air-sensitive solid, suggesting it is an iron (II) derivative rather than a ferrocene¹⁷ and (iii) the iron (II) complex derived from pentakis(methoxycarbonyl) cyclopentadiene which is soluble in water and does not have any covalent properties.¹⁸ The previously mentioned decachloro-ruthenocene, however, had been confirmed as a sandwich structure by X-ray studies.⁶

The $C_5(CO_2Me)_5$ ligand contains five strongly electron-withdrawing CO_2Me groups, whose presence in metal complexes would be expected to confer properties different from those exhibited by similar compounds of C_5H_5 or C_5Me_5 .



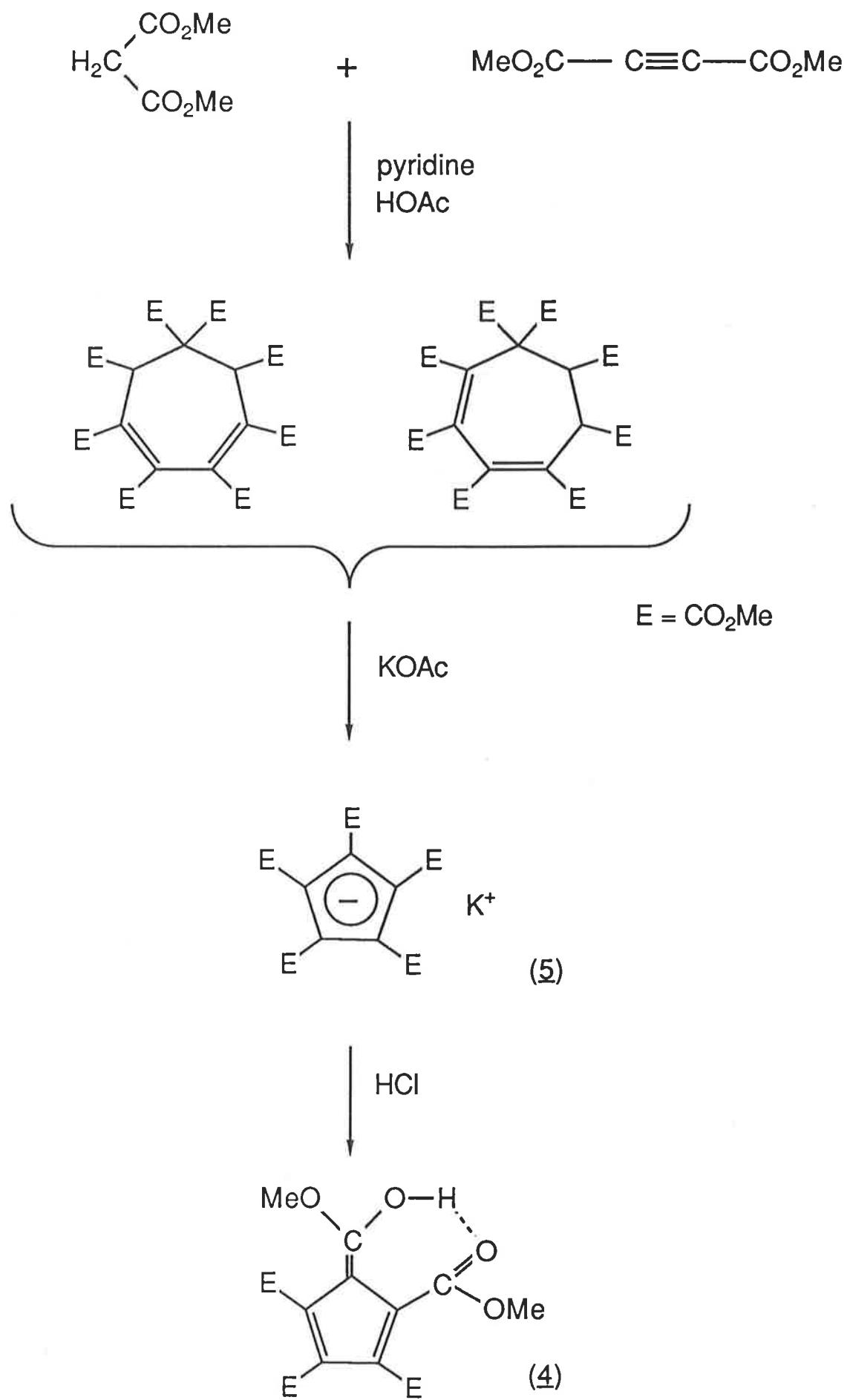
(2) $M = Fe$

(3) $M = Ru$

Pentakis(methoxycarbonyl)cyclopentadiene $HC_5(CO_2Me)_5$

$HC_5(CO_2Me)_5$ (4) was reported initially by Diels¹⁹ in 1942 as among the products of the reactions of the dimethyl acetylenedicarboxylate-dimethyl malonate adduct. Subsequent studies have shown the adduct to be two (3,5 and 4,6) isomers of 1,1,2,3,4,5,6,7 octakis-(carbomethoxy)cycloheptadiene. Both of the isomers react with potassium acetate to give the potassium salt (5) of the diene (Scheme 1). Addition of strong acid to a concentrated aqueous solution of the potassium salt results in the precipitation of the free acid $HC_5(CO_2Me)_5$.^{18,20,21}

Cookson *et al*¹⁸ reported that $HC_5(CO_2Me)_5$ is a strong acid, aqueous solutions of which are capable of dissolving metallic iron with the evolution of hydrogen, and the formation of $Fe\{C_5(CO_2Me)_5\}_2$, which was considered to be a ferrous iron salt, not a ferrocene, i.e. not containing iron covalently bonded to the C_5 rings.



Scheme 1

The spectroscopic data for the diene are consistent with the acidic proton being bound to an ester oxygen atom. An x-ray study (Figure 1) shows that the acidic proton is located asymmetrically between two of the carbonyl oxygen atoms of adjacent CO_2Me groups.²¹ The size of the CO_2Me groups prohibits all five carbomethoxy groups from being coplanar with the ring; groups 2, 4 and 5 are almost co-planar, while the substituents of the carbons labelled 1 and 3 are almost normal to the ring plane. The carbon-carbon bond lengths for the ring are all of approximately equal length (av. 1.404\AA) except for the C4-C5 bond, which is longer at $1.453(5)\text{\AA}$, because it does not participate in the delocalisation of the negative charge.

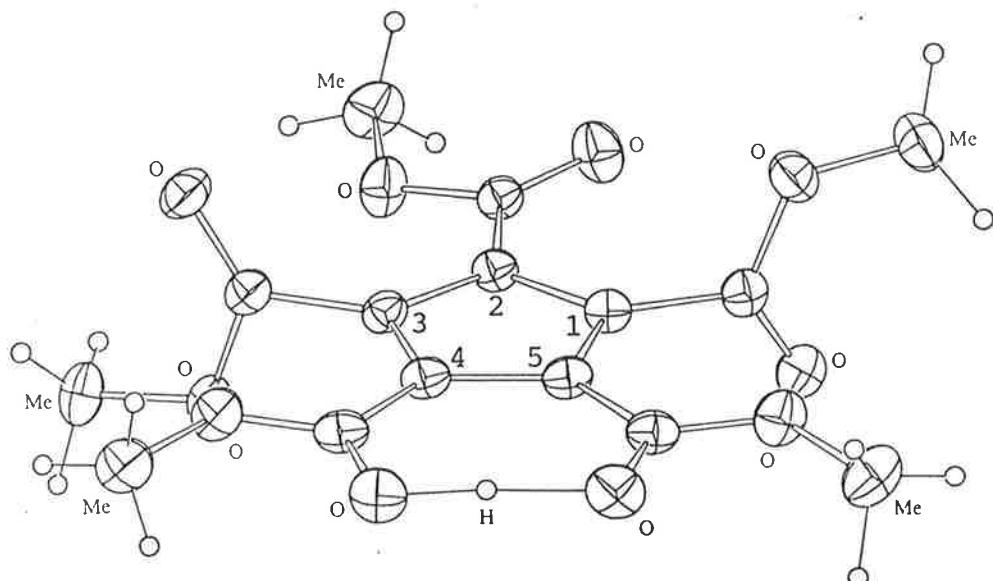
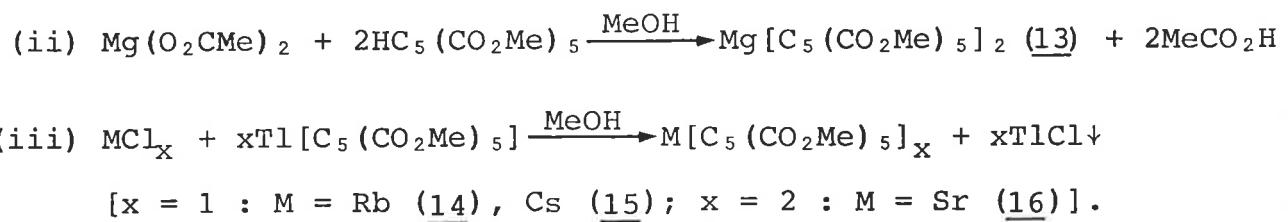
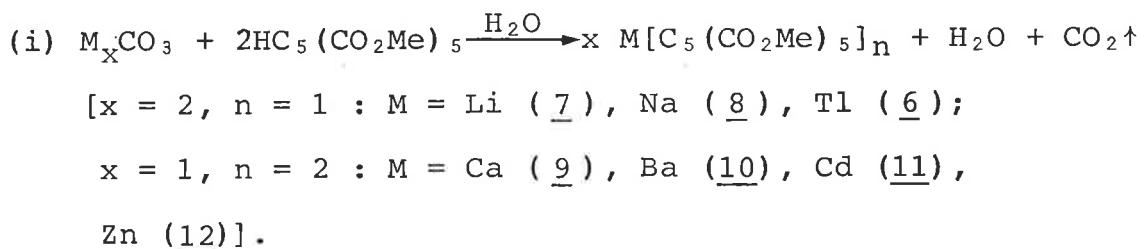


Figure 1: Molecular structure of $\text{HC}_5(\text{CO}_2\text{Me})_5$ (4)²¹

Salts of the $[C_5(CO_2Me)_5]^-$ anion with uni-
and bi-valent cations

Being a strong acid, $HC_5(CO_2Me)_5$ will displace weaker acids from their salts; ionic complexes of the type $M[C_5(CO_2Me)_5]_n$ ($n = 1, 2$) were prepared from reactions of (4) with metal carbonates or acetates [Equations (i) and (ii), respectively], or from reactions of the thallium (I) derivative, $Tl[C_5(CO_2Me)_5]$ (6), with the metal chloride [Equation (iii)].^{21, 22}



All compounds formed white, air- and moisture-stable crystals which were soluble in polar solvents such as water, acetone and alcohols. 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 NMR spectra. The molecular structures of the lithium (7), potassium (5), thallium (6)²¹ and barium (10)²² salts (Figures 2, 3, 4 and 5) show that the metal ions are bonded to the carbonyl oxygens, with coordination numbers ranging from four to eight.

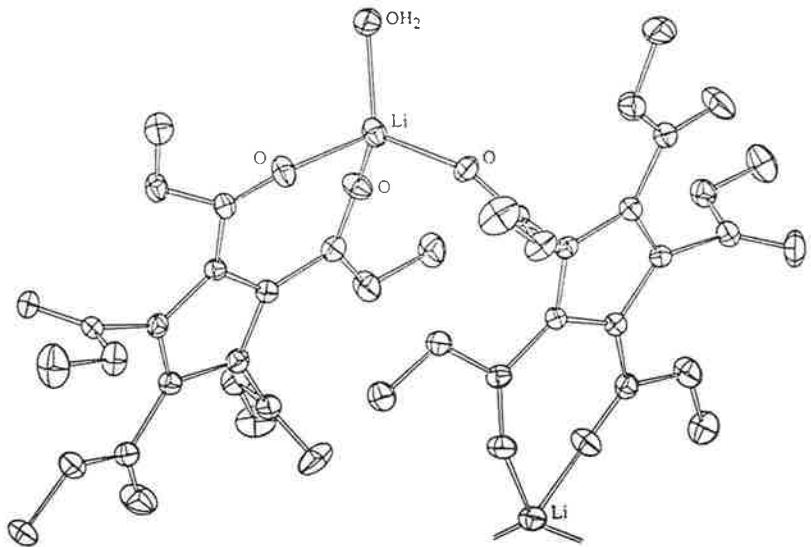


Fig. 2

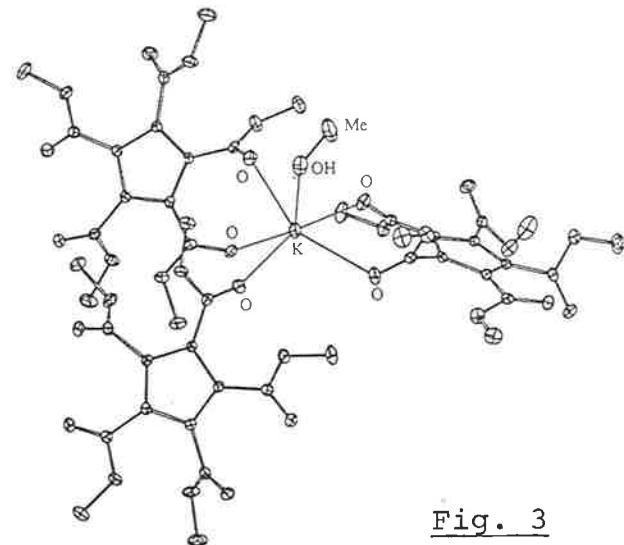


Fig. 3

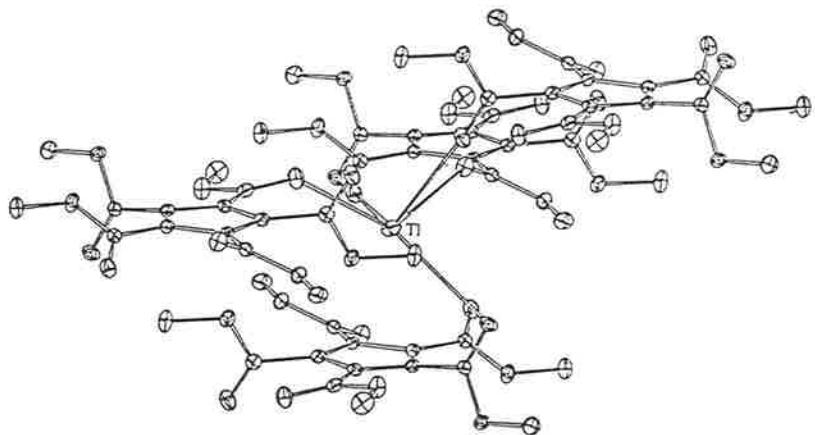


Fig. 4

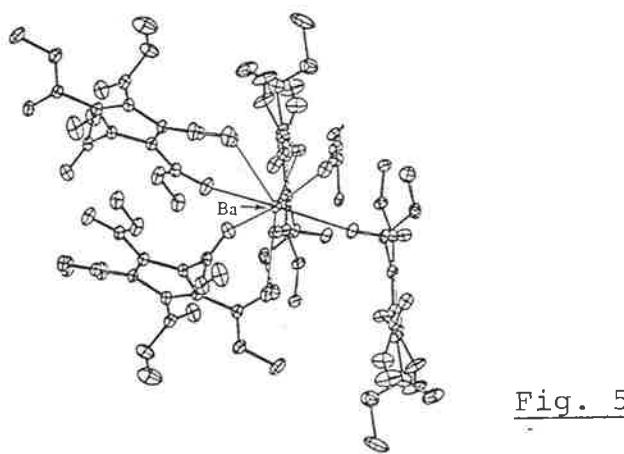


Fig. 5

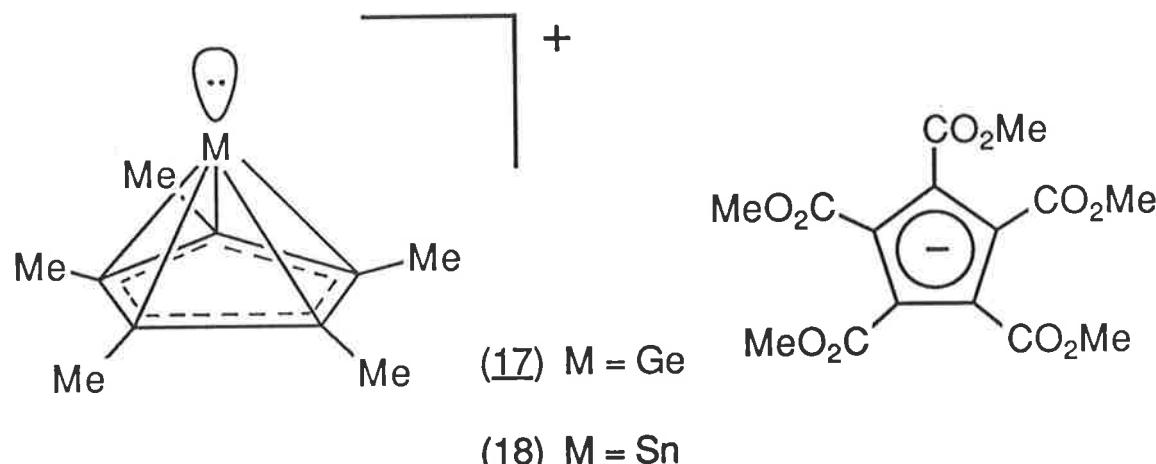
Figures 2-5: X-ray structures of $\text{Li}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (7), $\text{K}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (5), $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (6) and $\text{Ba}[\text{C}_5(\text{CO}_2\text{Me})_5]_2$ (10), respectively

Rare earths

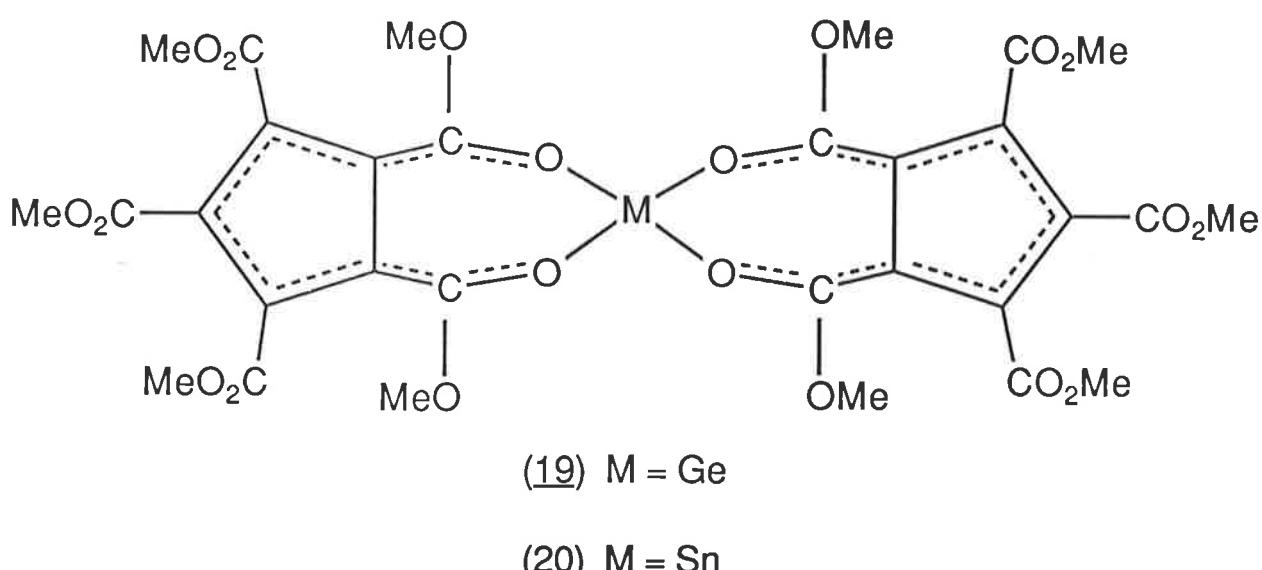
Air-stable, water-soluble salts of the lanthanides, $\text{Ln}[\text{C}_5(\text{CO}_2\text{Me})_5]_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) have been prepared from $\text{HC}_5(\text{CO}_2\text{Me})_5$ and the carbonates. These compounds are ionic, although in some cases, $\text{Ln}-\text{O}$ bonds are formed.²³

Group IVA derivatives

The reaction of $\text{M}(\text{C}_5\text{Me}_5)_2$ [$\text{M} = \text{Ge}, \text{Sn}$] with one equivalent of (4) gave $[\text{M}(\eta^5-\text{C}_5\text{Me}_5)][\text{C}_5(\text{CO}_2\text{Me})_5]$ [$\text{M} = \text{Ge}$ (17), Sn (18)] - these compounds are very air-sensitive.^{24, 25}



Addition of another equivalent of (4) gave $\text{M}[\text{C}_5(\text{CO}_2\text{Me})_5]_2$ [$\text{M} = \text{Ge}$ (19), Sn (20)].^{24, 25}

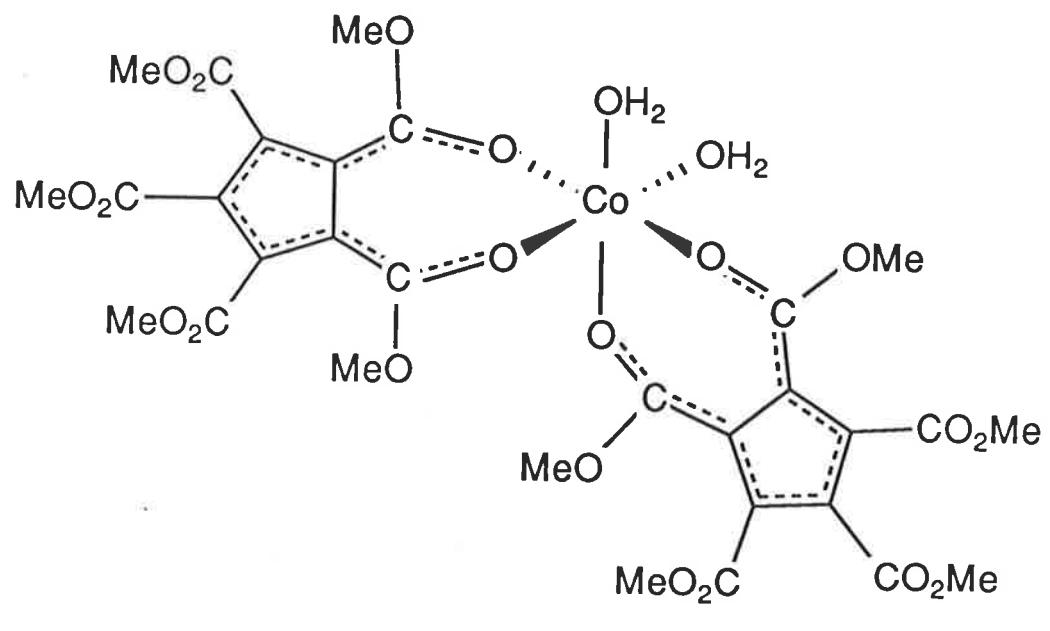
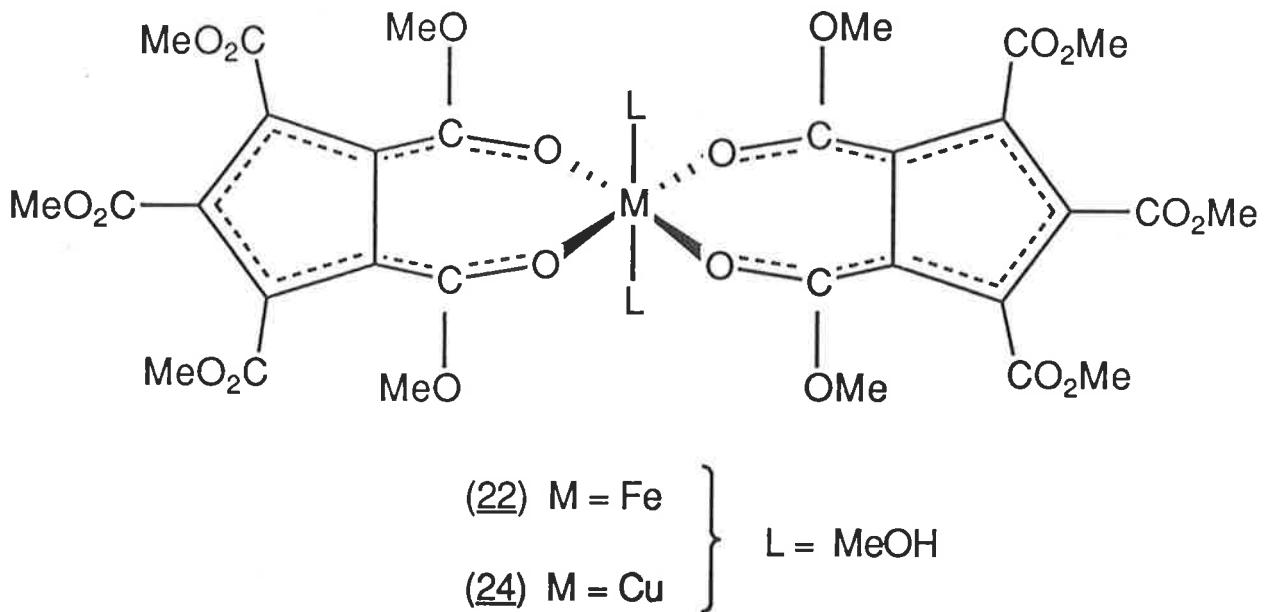


The reaction of $(\text{SnBu}_3)_2\text{O}$ with (4) in benzene gave the salt $[\text{SnBu}_3(\text{OH}_2)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$.²⁶ The related compound, $[\text{SnMe}_3(\text{OH}_2)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ was obtained from the reaction between SnClMe_3 and $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ in methanol.²⁷ Lead (II) carbonate reacted with $\text{HC}_5(\text{CO}_2\text{Me})_5$ to give white crystalline $\text{Pb}[\text{C}_5(\text{CO}_2\text{Me})_5]_2 \cdot 2\text{H}_2\text{O}$, the structure of which is unknown.²⁷

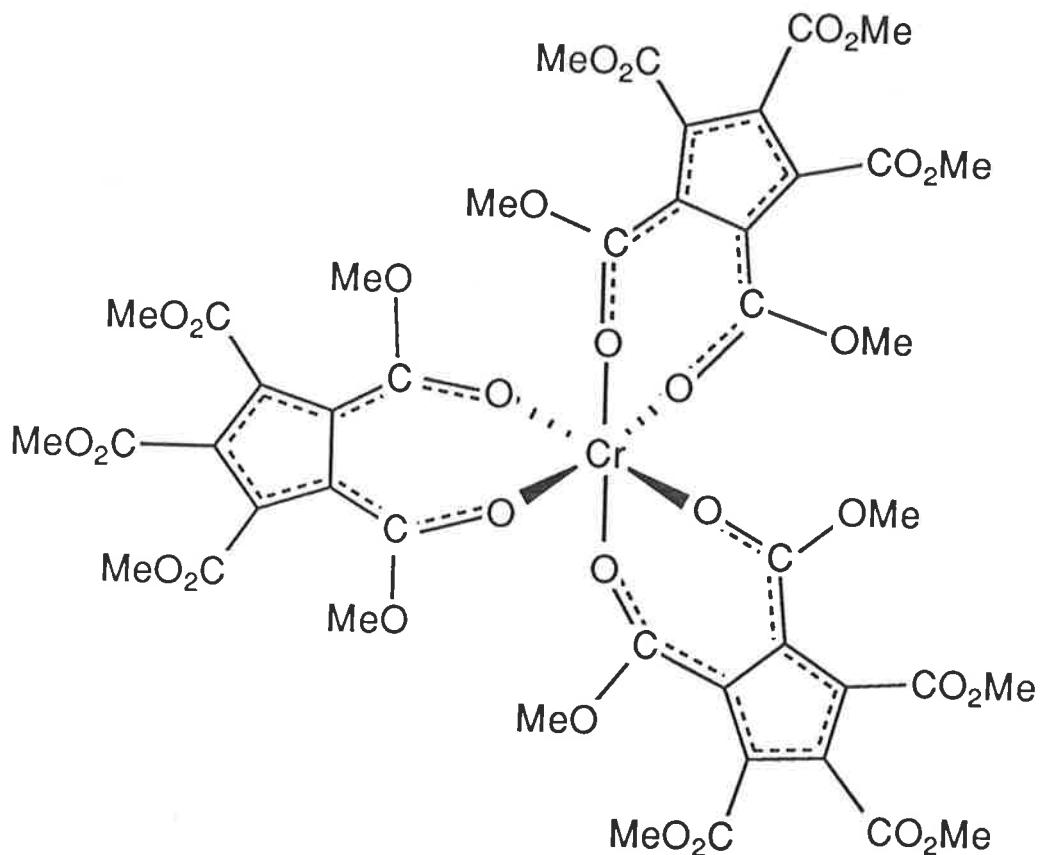
Transition metal derivatives

(a) First series - Crystalline derivatives of manganese (II), cobalt (II), nickel (II) and copper (II) were obtained²⁸ from reactions of acetates or carbonates with two equivalents of $\text{HC}_5(\text{CO}_2\text{Me})_5$ in aqueous solution, while the iron (II) derivative was prepared by Cookson as mentioned above.¹⁸ Their compositions correspond to $\text{M}[\text{C}_5(\text{CO}_2\text{Me})_5]_2$ [$\text{M} = \text{Mn}$ (21) (pale green); Fe (22) (yellow); Co (23) (pink); Cu (24) (orange) or the dihydrate $\text{M} = \text{Ni}$ (25) (green)]. In aqueous solutions, conductivity measurements indicated that they are 1:2 electrolytes, which have the colour of the corresponding aquo cations $[\text{M}(\text{OH}_2)_6]^{2+}$.

The copper (II) complex is the only cyclopentadienyl derivative of copper in this oxidation state. In water, blue solutions are formed, while in methanol, solutions are orange.²⁸ In the solid state structures of these compounds, the metal atoms are chelated by oxygens from two pairs of chelating ester groups. In the isomorphous iron and copper derivatives these occupy four equatorial sites of an octahedron, the two remaining *trans* sites being occupied by MeOH molecules. The C-C bonds not involved in the delocalised system show the usual lengthening, to 1.44\AA . The cobalt (II) complex (23), a dihydrate, contains the water molecules in two *cis* sites.²⁸

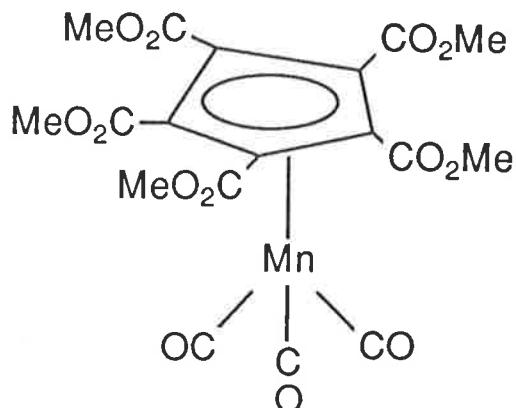


The reaction of $\text{Cr}_2(\text{OAc})_4$ with $\text{HC}_5(\text{CO}_2\text{Me})_5$ gave a small yield of the green hydrated chromium (III) derivative, $\text{Cr}\{\text{C}_5(\text{CO}_2\text{Me})_5\}_3$ (26),²⁹ instead of the expected chromium (II) complex.



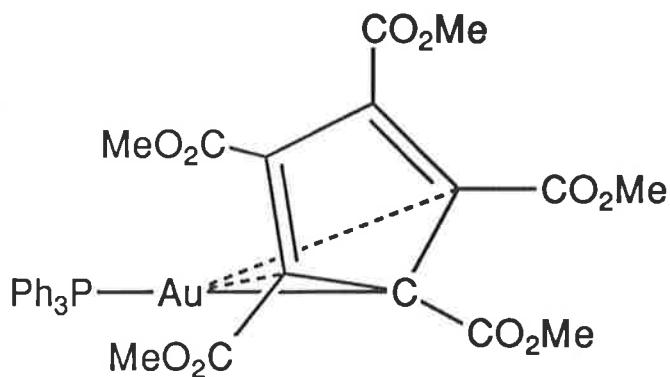
(26)

In contrast with the other first-row transition metal complexes in which the $\text{C}_5(\text{CO}_2\text{Me})_5$ bonds via the ester carbonyl oxygen atoms, the reaction between $\text{K}[\text{C}_5(\text{CO}_2\text{Me})_5]$ and $\text{MnBr}(\text{CO})_5$ or $\{\text{Mn}(\mu-\text{Br})(\text{CO})_4\}_2$ yielded $\text{Mn}(\text{CO})_3\{\eta^5-\text{C}_5(\text{CO}_2\text{Me})_5\}$ (27) in 80% yield.³⁰



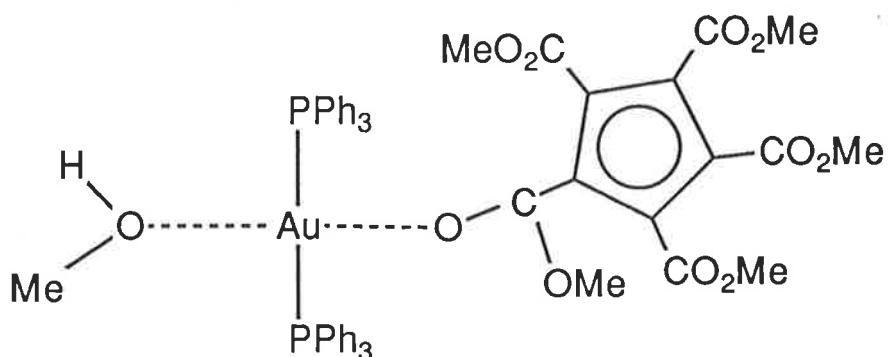
(27)

(b) Group IB metal derivatives - The reaction of $\text{HC}_5(\text{CO}_2\text{Me})_5$ with $\text{Au}(\text{O}_2\text{CMe})(\text{PPh}_3)$ afforded $\text{Au}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)$ (28).³¹ In the solid state, the C_5 ring is shown to interact with the gold in an unusual, asymmetric η^3 mode. There is essentially linear two-coordinate gold attached to triphenylphosphine and one of the C_5 ring carbons [Au-C 2.199(4) \AA]. The adjacent ring carbons are also within (weak) bonding distance.³¹



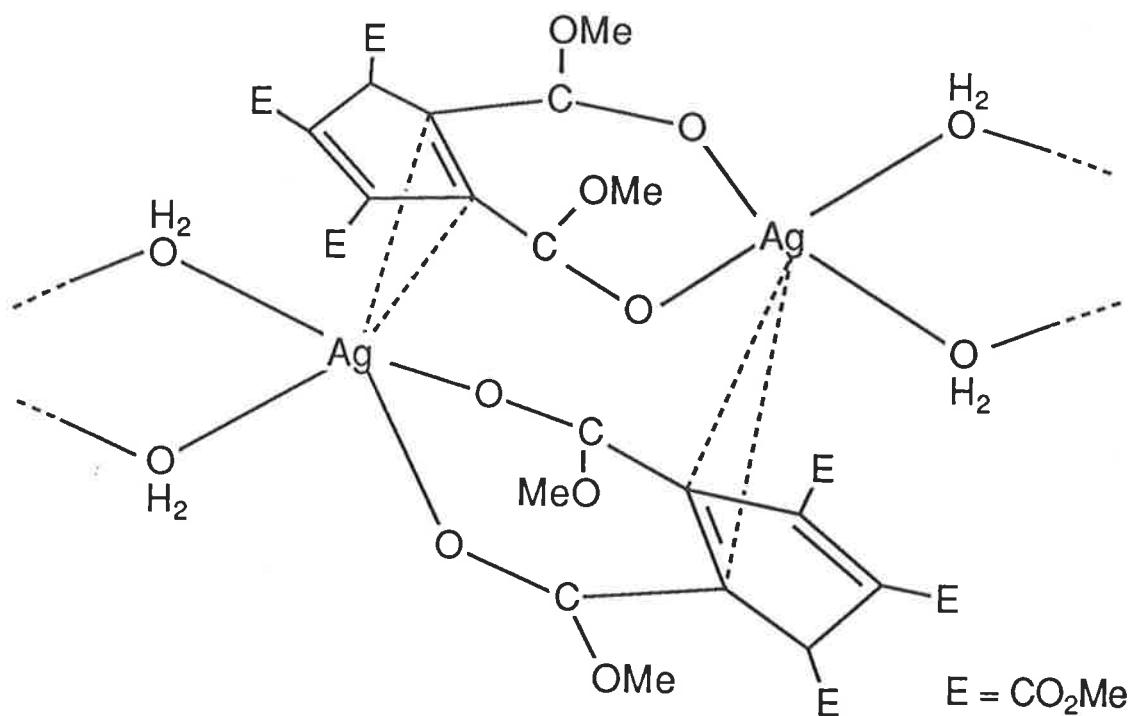
(28)

Addition of another equivalent of PPh_3 to (28) yielded $[\text{Au}(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]\cdot\text{MeOH}$ (29). ³¹ An X-ray study shows that the gold atom is essentially linearly two coordinate to two triphenylphosphine ligands with long distance interactions of the gold with MeOH and the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand. ³¹



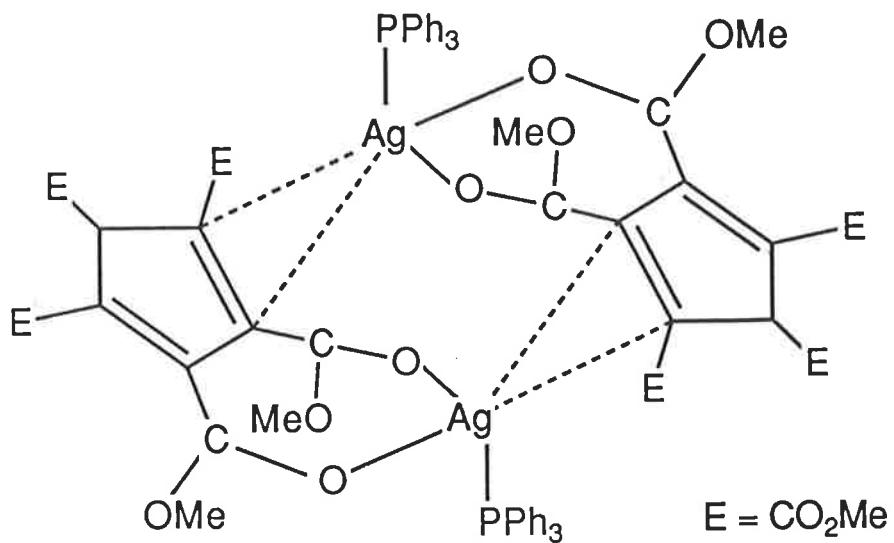
(29)

Silver acetate and $\text{HC}_5(\text{CO}_2\text{Me})_5$ reacted to yield the silver (I) derivative $\text{Ag}\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (30). ³² The X-ray structural determination of a sample recrystallised from water shows that the basic unit of the structure is a dimeric species, $\{\text{C}_5(\text{CO}_2\text{Me})_5\}\text{Ag}(\text{OH}_2)_2\text{Ag}\{\text{C}_5(\text{CO}_2\text{Me})_5\}$. The C_5 ligand is coordinated via two ester oxygens, while a void in the coordination sphere is occupied by a C=C bond from a second C_5 ring, albeit with rather long Ag-C distances [2.586(7), 2.807(7) \AA]. The silver atom has approximate square pyramidal geometry, with the four oxygens forming the basal plane. The C=C interaction generates an infinite polymer, and the interstitial water molecules form strong hydrogen bonds to ester carbonyl groups. ³²



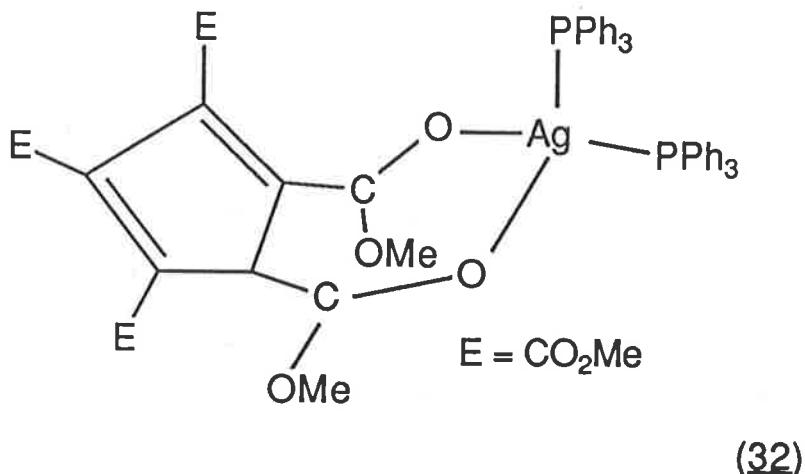
(30)

The addition of triphenylphosphine generated two types of complex. The addition of one molecule displaced the water and formed a dimer (31) in which each silver is coordinated by the tertiary phosphine and the C=C bond, and chelated by ester carbonyl groups of the second C₅ ligand.³² Further addition of



(31)

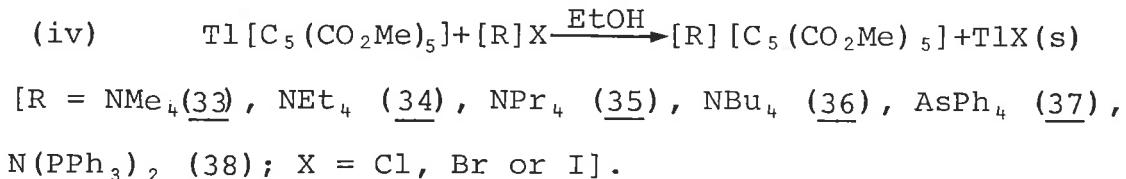
triphenyl phosphine displaced the C=C bond, and the monomeric $\text{Ag}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)_2$ (32) was obtained, in which the silver is again essentially four coordinate.³²



This chapter further explores the types of structures assumed by complexes containing the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand and, in Section B, the closely related ligand $\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4$.

RESULTS AND DISCUSSIONSECTION A1. Salts containing the $[C_5(CO_2Me)_5]^-$ anion

(a) Onium salts - Salts of (4) with large cations of general formula $[R][C_5(CO_2Me)_5]$ have been prepared according to Equation (iv).



On mixing equimolar quantities of the reactants in ethanol, the thallium(I) halide is immediately precipitated; after filtration and evaporation to dryness, the salts were isolated as white solids which are air- and moisture-stable. With the exception of the $[NMe_4]^+$ salt, all are soluble in polar solvents such as water, acetone, alcohols, chloroform and dichloromethane, while being insoluble in diethyl ether or light petroleum. The tetramethylammonium salt is insoluble in dichloromethane and chloroform, and only sparingly soluble in water or acetone.

The infrared spectra of these salts contain several strong absorptions between 1650 and 1750 cm^{-1} , which are assigned to $\nu(\text{C=O}) + \nu(\text{C=C})$ vibrations; strong $\nu(\text{C-O})$ absorptions are found between 1200 and 1250 cm^{-1} . The ^1H NMR spectra each contain a singlet for the CO_2Me protons between $\delta 3.60$ and 3.75, in addition to other resonances characteristic of the cation.

The molecular structure of $[NMe_4][C_5(CO_2Me)_5]$ (Figure 6) shows isolated cations and anions with no close interactions between them.

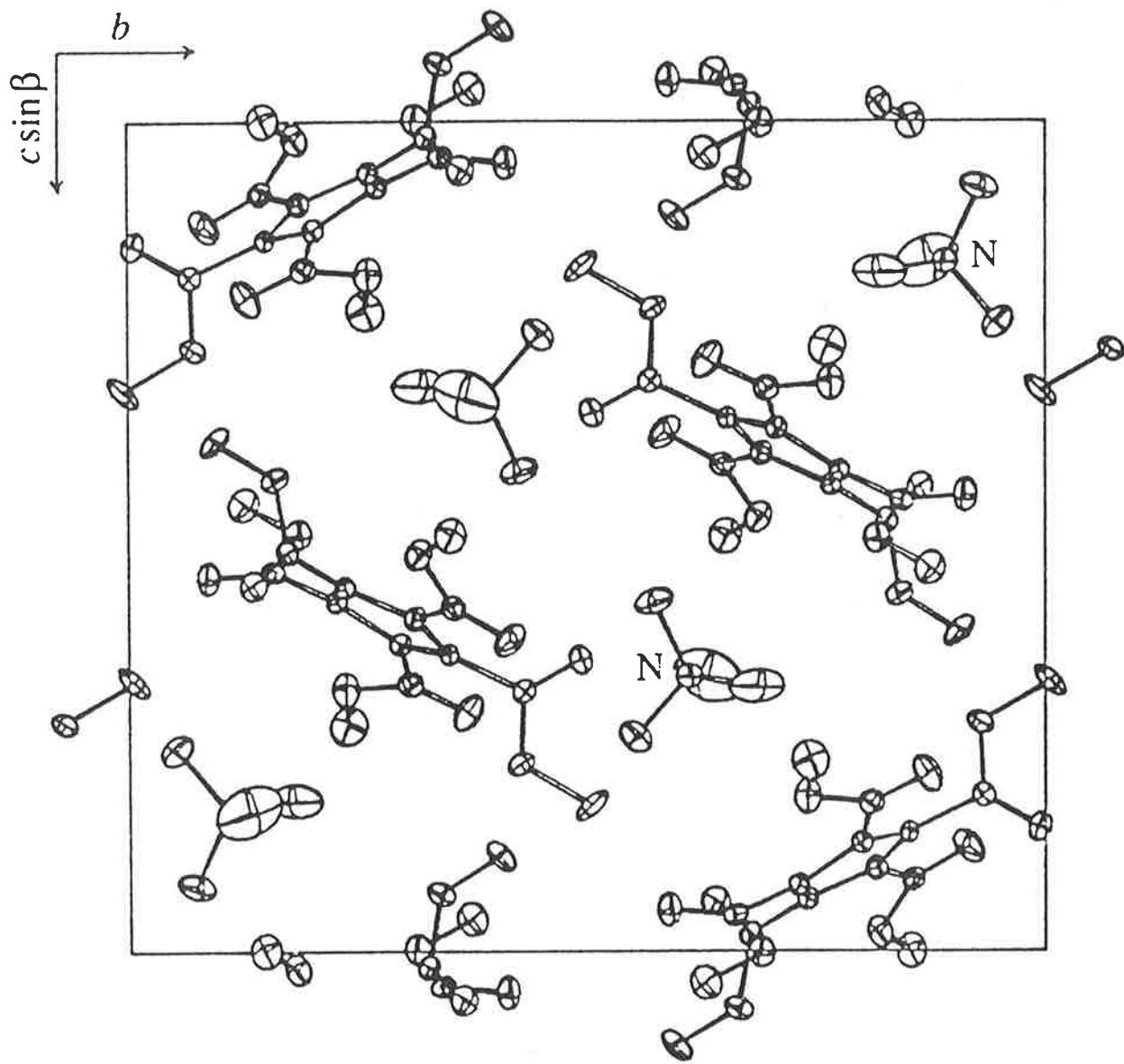


Figure 6 : Unit-cell contents of $[NMe_4][C_5(CO_2Me)_5]$ (33)

(by B.W. Skelton and A.H. White)

(b) Tropylium salt - The orange tropylium salt, $[C_7H_7][C_5(CO_2Me)_5]$ (39), was synthesised and the structure determined, as it was considered to be of some interest to show the presence of structural features consistent with the 'charge-transfer' proposal. (Previous references to salts containing organic cations³³ and their spectroscopic properties^{34, 35, 36} reported that such complexes are colourless in solution, but coloured as solids, as a consequence of charge transfer interactions.) It was synthesised by a modification of the previous method,³³ from $K[C_5(CO_2Me)_5]$ and $[C_7H_7][PF_6]$. The 1H NMR spectrum of (39) shows the OMe protons as a singlet at δ 3.72, while the C_7H_7 ligand is found as a singlet at δ 8.30. The ^{13}C NMR spectrum shows three signals at δ 51.9, 117.7 and 150.6 assigned to OMe, C_7 and C_5 carbons, respectively.

Contrary to previous reports, (39) dissolved in polar solvents such as methanol, acetone or acetonitrile to give orange-red to deep red solutions. The band responsible for the orange colour has a maximum at *ca* 450 nm, although the precise position is solvent dependent, ranging from 440 nm (in MeOH) to 470 nm (in CH_2Cl_2). In acetonitrile, the values for ϵ are concentration-dependent, ranging from 220 (for 1-3 mM) to 400 $dm^3 mol^{-1} cm^{-1}$ (for 4.5 mM); λ_{max} is not affected by changes in concentration, so that increasing ion-association and resultant charge transfer give rise to this effect. Solutions in acetone do decolourise on standing; the species present in the colourless solution has not been identified.

Tropylium pentakis(methoxycarbonyl)cyclopentadienide crystallises in the form of long (several centimetres) but very thin needles from polar solvents such as methanol or acetone, assumed to be due to the stacking of alternate $[C_7H_7]^+$ and $[C_5(CO_2Me)_5]^-$ ions.

A single crystal (from dichloromethane/hexane) was subjected to an X-ray study (Figure 7) which shows the presence of an infinite sandwich of alternate planar anions and cations, with an interplanar spacing of 3.5\AA . This study confirms the expectation of ion stacking; several C_5-C_7 ring carbon contacts are found between $3.3-3.5\text{\AA}^\circ$, which must be close enough for a degree of charge transfer to occur, as evidenced by the colour of this unusual compound.

2. Copper complexes

The reaction of $Cu[C_5(CO_2Me)_5]_2$ (24) with excess triphenylphosphine afforded the white copper (I) complex $Cu\{C_5(CO_2Me)_5\}(PPh_3)_2$ (40). This compound was also formed by the addition of triphenylphosphine to a solution of Cu_2O in methanolic $HC_5(CO_2Me)_5$. This complex behaves as a 1:1 electrolyte in polar solvents such as acetone, and the 1H and ^{13}C NMR spectra show all five CO_2Me groups to be equivalent.

The triphenylarsine derivative (41) was obtained either by the addition of the tertiary arsine to a solution of Cu_2O in methanolic $HC_5(CO_2Me)_5$, or by reacting $Tl[C_5(CO_2Me)_5]$ with a solution of $[CuI(NCMe)(AsPh_3)]_2$ in acetonitrile. 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.

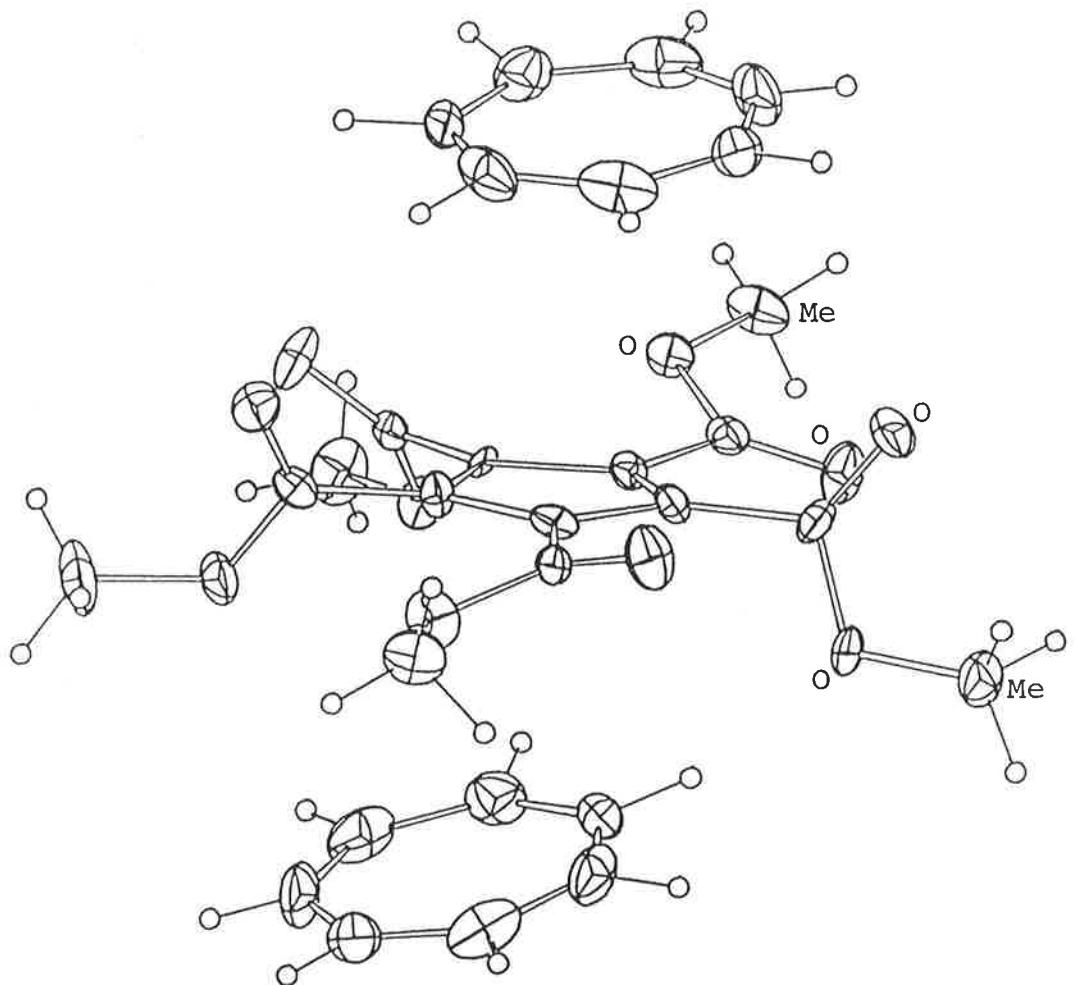


Figure 7: X-ray structure of $[C_7H_7][C_5(CO_2Me)_5]$ (39)
showing cation-anion-cation stacking
(by B.W. Skelton and A.H. White)

The complexity of the $\nu(\text{CO})$ region of (40) and (41) (taken as Nujol mulls) however, suggested that in the solid state, coordination of the diene ester groups to the copper (I) centre had occurred.

X-ray structural studies of (40) and (41) show that both complexes are monomeric, and the unit-cell contents confirm the stoichiometry, $\text{Cu}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{EPh}_3)_2$; the monomer comprises the asymmetric unit. The copper atom in each is approximately tetrahedral four-coordinate; a molecule of (41) is shown in Figure 8. In (40), the two tertiary phosphine ligands are attached through phosphorus, with the Cu-P bonds [2.245(4) and 2.255(4) \AA] forming an angle of 125.7(1) $^\circ$ at the metal atom; for (41), the Cu-As distances are 2.329(1) and 2.328(1) \AA , and the As-Cu-As angle is 120.7(1) $^\circ$. The larger than tetrahedral angles probably result from steric interactions between the two ligands.

The C_5 ligand is attached through the carbonyl oxygen atoms of two adjacent CO_2Me groups [Cu-O, 2.114(8), 2.115(8) \AA for (40), 2.055(4), 2.068(4) \AA for (41)]. The shortening of the Cu-O bond on going from phosphorus to arsenic reflects the weaker σ -donor power of the tertiary arsine ligand, which results in stronger Cu-O bonding. It is interesting to note that, in the analogous silver complex (32), the Ag-P distances [2.428(2) and 2.414(2) \AA] are ca 0.17 \AA longer than the Cu-P distances in (40), but the Ag-O distances [2.465(4) and 2.594(5) \AA] are ca 0.35-0.48 \AA longer, reflecting the weaker attachment of the C_5 ligand to silver.³² 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

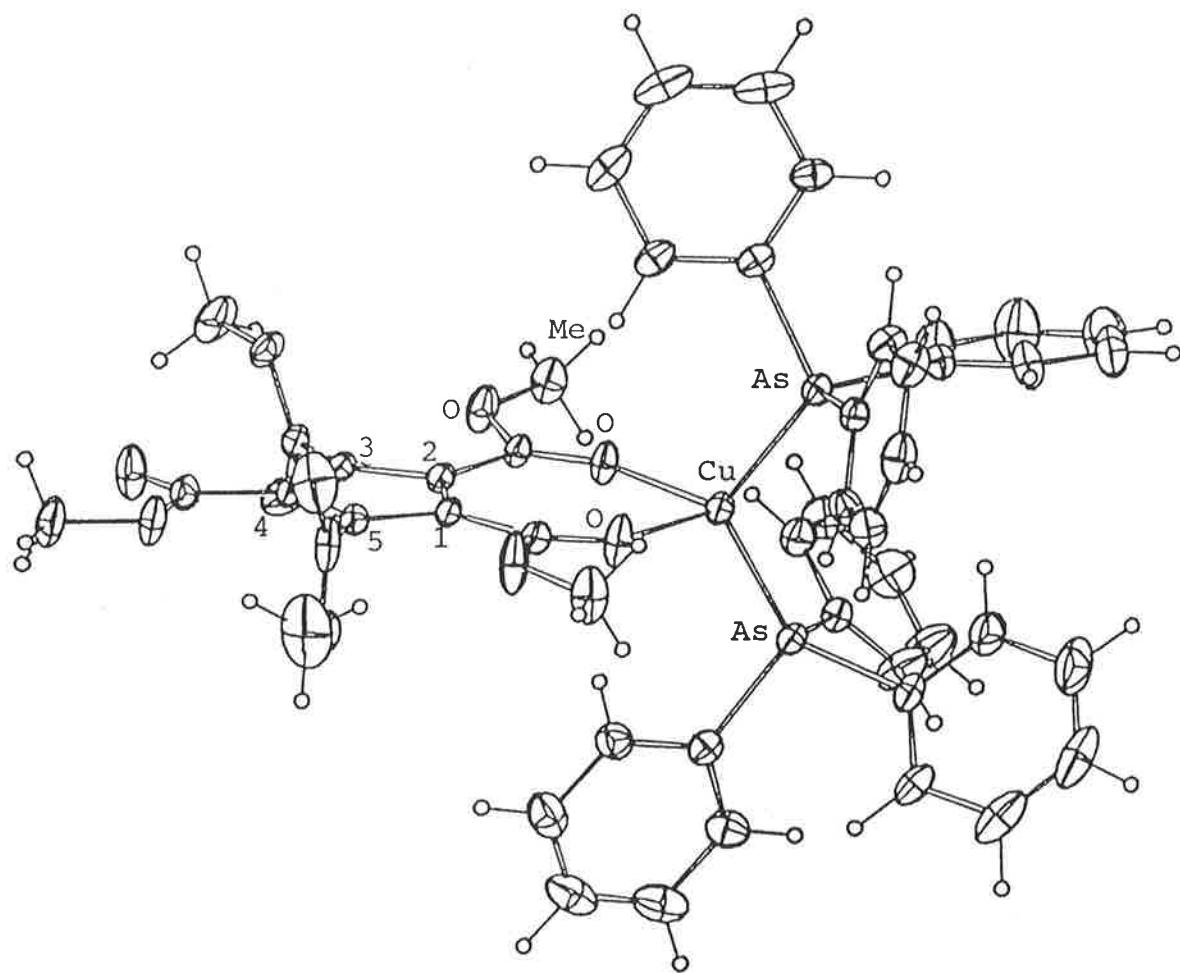
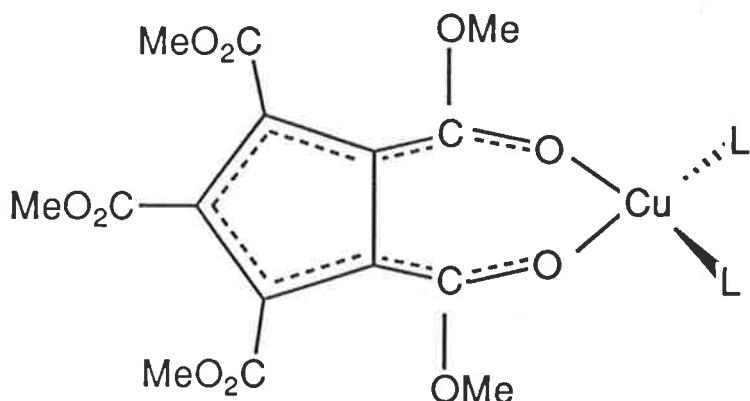


Figure 8 : Molecular structure of $\text{Cu}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{AsPh}_3)_2$
(41) (by B.W. Skelton and A.H. White)

in the silver analogue, where one of the coordinated oxygens belongs to one of the two carboxylate substituents which are normal to the C₅ ring plane. Finally, there is no significant lengthening of any of the ring C-C bonds; all five are between 1.41(1) and 1.43(1) \AA [average 1.42(1) \AA].

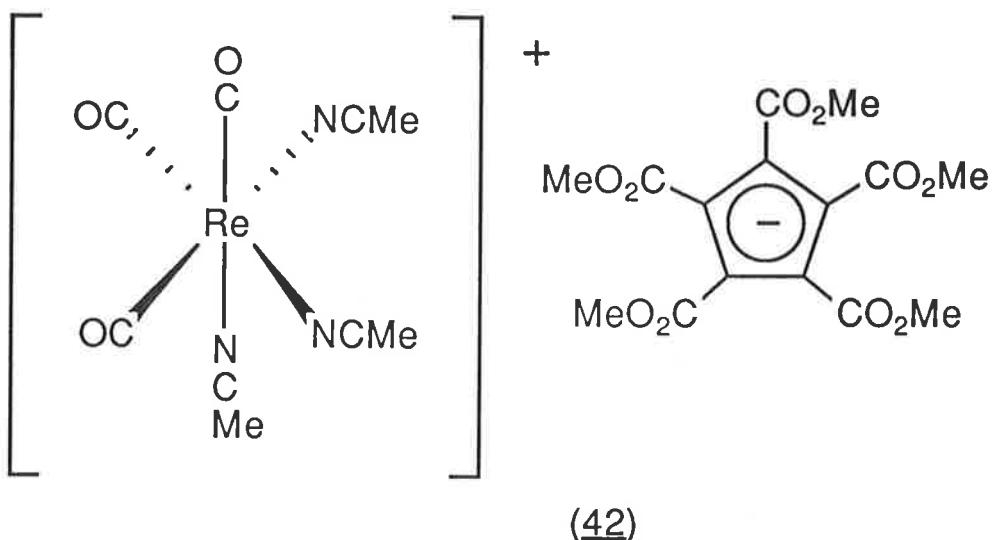


No evidence was found for the formation of complexes of the type [Cu{C₅(CO₂Me)₅}(L)]_n (L = PPh₃, AsPh₃) even when the amount of L was limited to one equivalent. Evidently copper (I) does not have the tendency to bond to the ring carbons exhibited by silver (I)³² or gold (I)³¹. Attempts to obtain a copper analogue of [Ag{C₅(CO₂Me)₅}(OH₂)]_n were also unsuccessful; the only complex isolated from solutions of copper (I) oxide in aqueous or methanolic HC₅(CO₂Me)₅ was the orange copper (II) derivative.

3. Second and third transition series derivatives

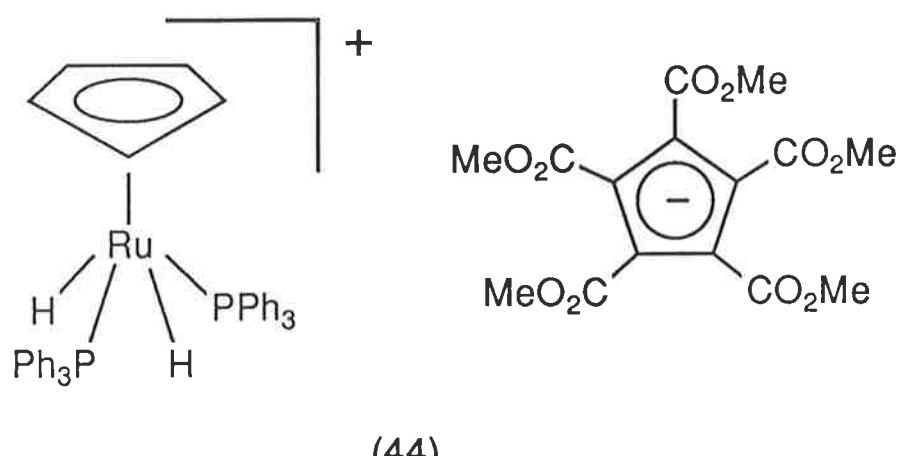
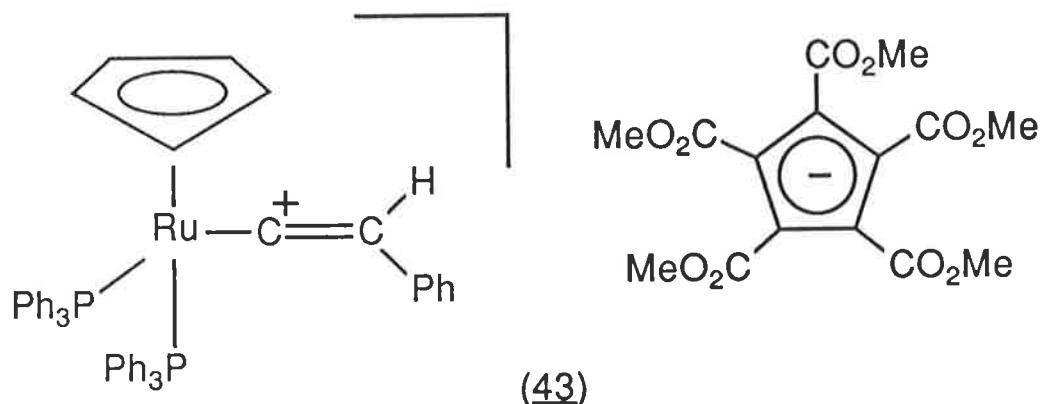
The elements of the second and third row transition metals have given a wider range of bonding situations with the $C_5(CO_2Me)_5$ ligand than the first series, with complexes containing the ligand bonded to the metal via oxygen or carbon, while more examples of salts containing the $[C_5(CO_2Me)_5]^-$ anion have been identified.

(a) Rhenium - The reaction of $Tl[C_5(CO_2Me)_5]$ with $\{Re(CO)_4Cl\}_2$ in acetonitrile afforded the $[C_5(CO_2Me)_5]^-$ salt of the known $[Re(CO)_3(NCMe)_3]^+$ cation (42).³⁷ Identification was made on the basis of spectroscopic and microanalytical data. The infrared spectrum shows, in addition to the usual strong $\nu(C=O)$ bands from 1690-1750 cm^{-1} and strong $\nu(C-O)$ bands between 1200-1250 cm^{-1} , $\nu(C\equiv O)$ bands between 1900-2080 cm^{-1} and weak $\nu(C\equiv N)$ bands around 2300 cm^{-1} . The 1H NMR spectrum shows singlets at

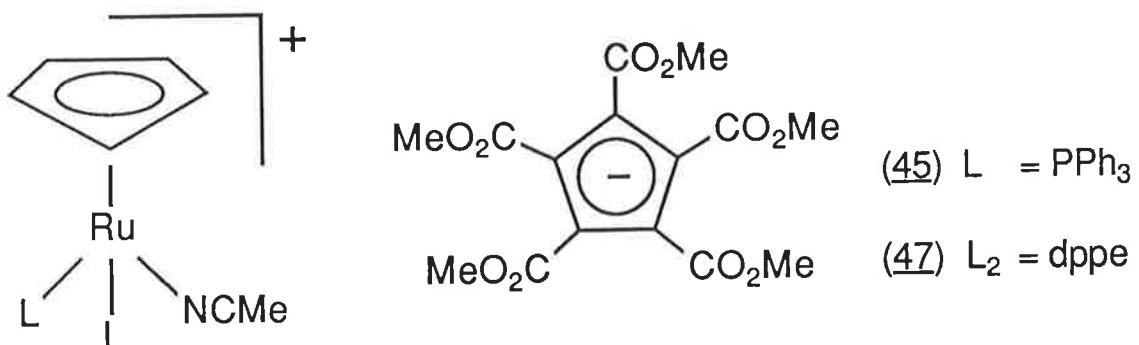
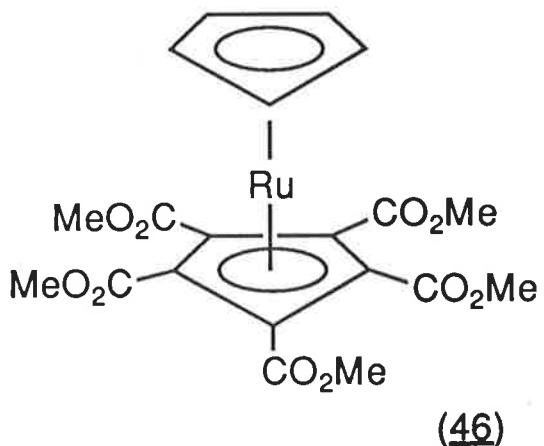


δ 2.38 and 3.73 assigned to MeCN and OMe hydrogens, respectively. The FAB mass spectrum shows the base peak at $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^+$, then peaks due to loss of one and two MeCN ligands. The negative ion spectrum shows the major peaks at m/z 355, which is due to $[\text{L}]^-$, with breakdown peaks at m/z 341 ($[\text{HL} - \text{Me}]^-$) and m/z 309 and m/z 251 assigned to $[\text{L} - \text{OMe}]^-$ and $[\text{HL} - \text{Me} - \text{OMe} - \text{CO}_2\text{Me}]^-$, respectively.

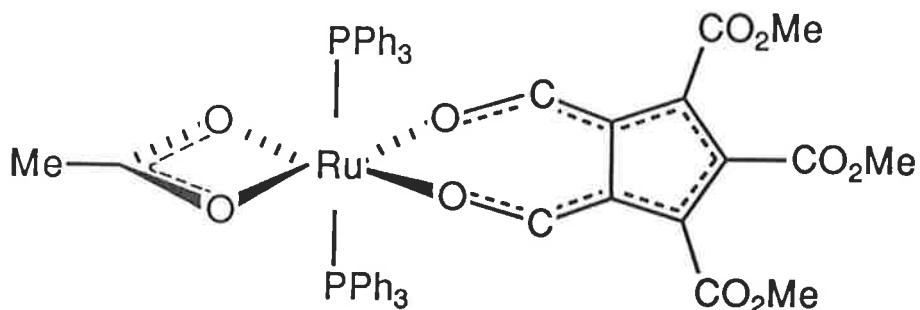
(b) Ruthenium complexes - The strongly acidic nature of $\text{HC}_5(\text{CO}_2\text{Me})_5$ is demonstrated in the reactions with $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta-\text{C}_5\text{H}_5)$ or $\text{RuH}(\text{PPh}_3)_2(\eta-\text{C}_5\text{H}_5)$, in which the phenylvinylidene complex $[\text{Ru}(\text{C}=\text{CHPh})(\text{PPh}_3)_2(\eta-\text{C}_5\text{H}_5)][\text{C}_5(\text{CO}_2\text{Me})_5]$ (43)³⁸ and $[\text{RuH}_2(\text{PPh}_3)_2(\eta-\text{C}_5\text{H}_5)][\text{C}_5(\text{CO}_2\text{Me})_5]$ (44)³⁹, respectively, are formed.



The addition of $\text{Ti}[\text{C}_5(\text{CO}_2\text{Me})_5]$ to $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ in acetonitrile gave the salt $[\text{Ru}(\text{NCMe})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^-$ $[\text{C}_5(\text{CO}_2\text{Me})_5]$ (45), while the same reaction in methanol in air yielded the first example of a metallocene containing the $\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5$ group, $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (46).³⁹ The same compound was obtained from $\text{RuCl}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Ti}[\text{C}_5(\text{CO}_2\text{Me})_5]$ in methanol.³⁹ The X-ray study of (46) showed a typical metallocene structure, with the C_5H_5 ring being ca 0.02\AA further away from the metal than the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand.³⁹ Although the similar Ru-ring C distances might suggest similar Ru-ring bond strengths, the solution behaviour proves that the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand has the weaker attachment. Thus, in acetonitrile, it is readily displaced by tertiary phosphines to give $[\text{Ru}(\text{NCMe})(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)]^-$ $[\text{C}_5(\text{CO}_2\text{Me})_5]$ [$\text{PR}_3 = \text{PPh}_3$ (45), $\frac{1}{2}$ dppe (47)].³⁹

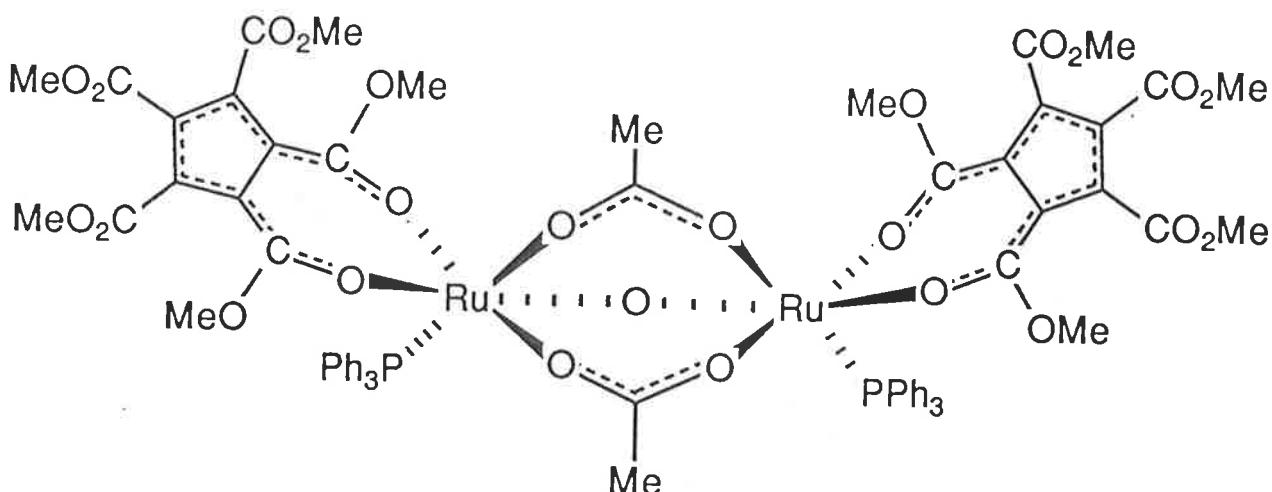


$\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3)_2$ reacted with $\text{HC}_5(\text{CO}_2\text{Me})_5$ in benzene at room temperature to give orange crystals of $\text{Ru}\{\text{C}_5(\text{CO}_2\text{Me})_5\}-(\text{O}_2\text{CMe})(\text{PPh}_3)_2$ (48), after crystallisation from methanol. In this complex, the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand is probably attached via the ester CO groups as found in the solid state structures of the first series transition metal derivatives; in this case, however, ^1H NMR studies clearly show that the chelate structure is retained in solution (four OMe resonances with relative intensities 1:2:1:1). The FAB spectrum of $\text{Ru}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{O}_2\text{CMe})-(\text{PPh}_3)_2$ shows a weak molecular ion, then peaks corresponding to loss of O_2CMe , $\text{C}_5(\text{CO}_2\text{Me})_5$ (the base peak) and PPh_3 .



(48)

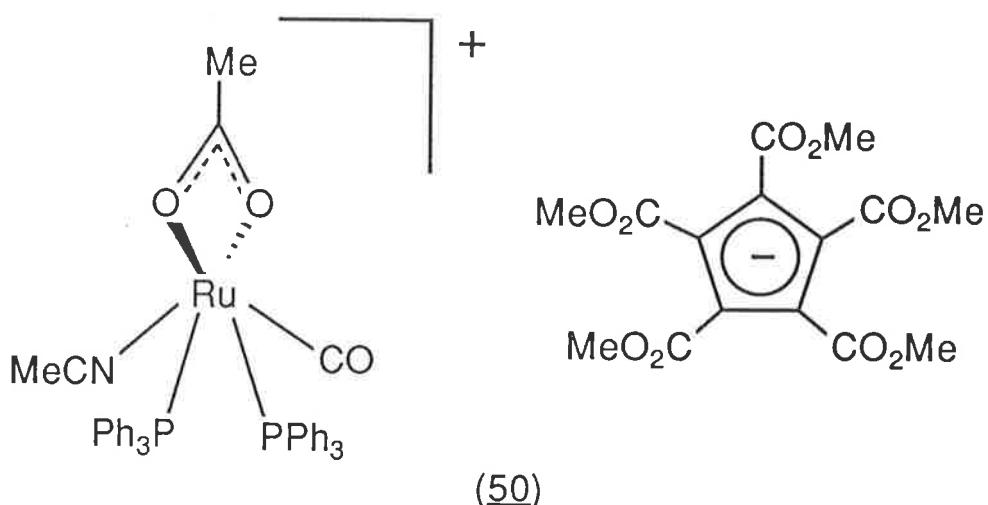
$\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3)_2$ is also orange, but readily changes colour to purple in solution; the product is the oxygen-bridged dimer $\{\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3)\}_2\text{O}$.⁴⁰ Similar behaviour is found for the $\text{C}_5(\text{CO}_2\text{Me})_5$ derivative, which forms $\{\text{Ru}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{O}_2\text{CMe})-(\text{PPh}_3)\}_2\text{O}$ (49). The ^1H NMR spectrum again confirms the chelate structure with three OMe resonances with relative intensities 2:2:1. The FAB spectrum shows the molecular ion which loses the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand to give a peak at m/z 1217. Further breakdown gives peaks assigned to $[\text{Ru}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)]^+$ and $[\text{Ru}_2\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{O}_2\text{CMe})_2]^+$. The most abundant peaks, however, are found at m/z 735, assigned to $[\text{Ru}\{\text{C}_5(\text{CO}_2\text{Me})_5\}-$



(49)

$(\text{Ph}_3\text{PO})]^+$ and at m/z 278 $([\text{Ph}_3\text{PO}]^+)$.

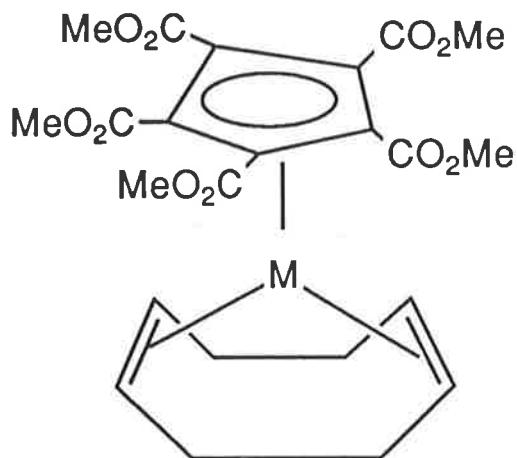
The reaction of $\text{RuCl}(\text{CO})(\text{O}_2\text{CMe})(\text{PPh}_3)_2$ with $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ in refluxing acetonitrile afforded a high yield of a cream coloured compound, formulated as $[\text{Ru}(\text{CO})(\text{O}_2\text{CMe})(\text{PPh}_3)_2(\text{NCMe})]^-[\text{C}_5(\text{CO}_2\text{Me})_5]$ (50), after filtration and crystallisation from dichloromethane/diethyl ether. The ^1H NMR spectrum shows singlet resonances at δ 0.46 and 1.37 assigned to MeCN and CMe hydrogens, respectively. The OMe protons are found as a singlet at δ 3.72, while the phenyl protons resonate as a multiplet around δ 7.47. The FAB mass spectrum shows the base peak at m/z 754 assigned to $[\text{Ru}(\text{CO})(\text{O}_2\text{CMe})(\text{PPh}_3)_2-(\text{NCMe})]^+$, which fragments by the loss of MeCN, then one PPh_3 , then CO. The negative ion spectrum shows the base peak at $[\text{L}]^-$ as expected, with the same anion breakdown pattern as found in the negative ion spectrum of $[\text{Re}(\text{CO})_3(\text{NCMe})_3]^-[\text{C}_5(\text{CO}_2\text{Me})_5]$ (42). Conductivity measurements confirm a 1:1 electrolyte.



(c) Rhodium and Iridium Complexes - The addition of $\{\text{RhCl}(\eta^4\text{-C}_8\text{H}_{12})\}_2$ to $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ in acetonitrile gave an immediate precipitate of TlCl and orange crystals of $\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (51) were isolated from the solution in good yield. Characterisation of the complex was from elemental microanalysis, the IR spectrum which contained the multitude of $\nu(\text{CO})$ bands around 1700 and 1200 cm^{-1} characteristic of the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand, and the ^1H NMR spectrum, which contained only a single OMe resonance at $\delta 3.83$ in addition to the usual CH and CH_2 resonances of the C_8H_{12} ligand. This suggested that the C_5 ligand was symmetrically bonded to the rhodium, since (51) was shown not to dissociate in solution (conductivity). The analogous iridium complex (52) formed yellow crystals, with similar properties. The FAB mass spectrum of (51) contained the molecular ion as the base peak, which showed loss of OMe and CO_2Me groups as the major fragmentation routes. The negative ion spectrum contained a weak ion

$[\text{Rh}(\text{C}_8\text{H}_{12})\{\text{C}_5(\text{CO}_2\text{Me})_4\}]^-$, but the major ion was found at m/z 355, corresponding to $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$.

The presence of the $\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5$ ligand was confirmed by a single-crystal X-ray diffraction study of (51). Two independent pseudo-symmetrically related molecules comprise the asymmetric unit of the structure (Fig. 9); it can be seen that the structure is similar to that of $\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\text{-}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})$.⁴¹ The Rh-C(cp) distances in the latter average 2.262°\AA , while in (51) they have lengthened to 2.28°\AA ; the C_8 ligand is coordinated in the usual chelating "tub" form, with a Rh-C(olefin) separation of 2.13°\AA compared with 2.11°\AA in $\text{Rh}(\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_4\text{CO}_2\text{Me})$. Comparison with the only other $\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5$ ligand which has been structurally characterised,³⁹ in $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (46), shows that metal-ring carbon distances to the C_5H_5 and $\text{C}_5(\text{CO}_2\text{Me})_5$ ligands, respectively, are 2.181 and 2.173°\AA [in (46)] and 2.262 and 2.28°\AA (in the two Rh complexes discussed above). While for the two ligands



(51) $M = \text{Rh}$

(52) $M = \text{Ir}$

attached to the same metal, the differences are small, the differences in the lengths of the bonds to Ru and Rh exceed the difference between the covalent radii of the metals.

About the C₅ ring in (51), the dihedral angles of the carboxylate substituents are 79.9, 36.7, 42.7, 65.4, 11.0° (molecule A); 56.3, 47.7, 16.8, 90.0, 16.7° (molecule B), consistent with only approximate pseudo-symmetry.

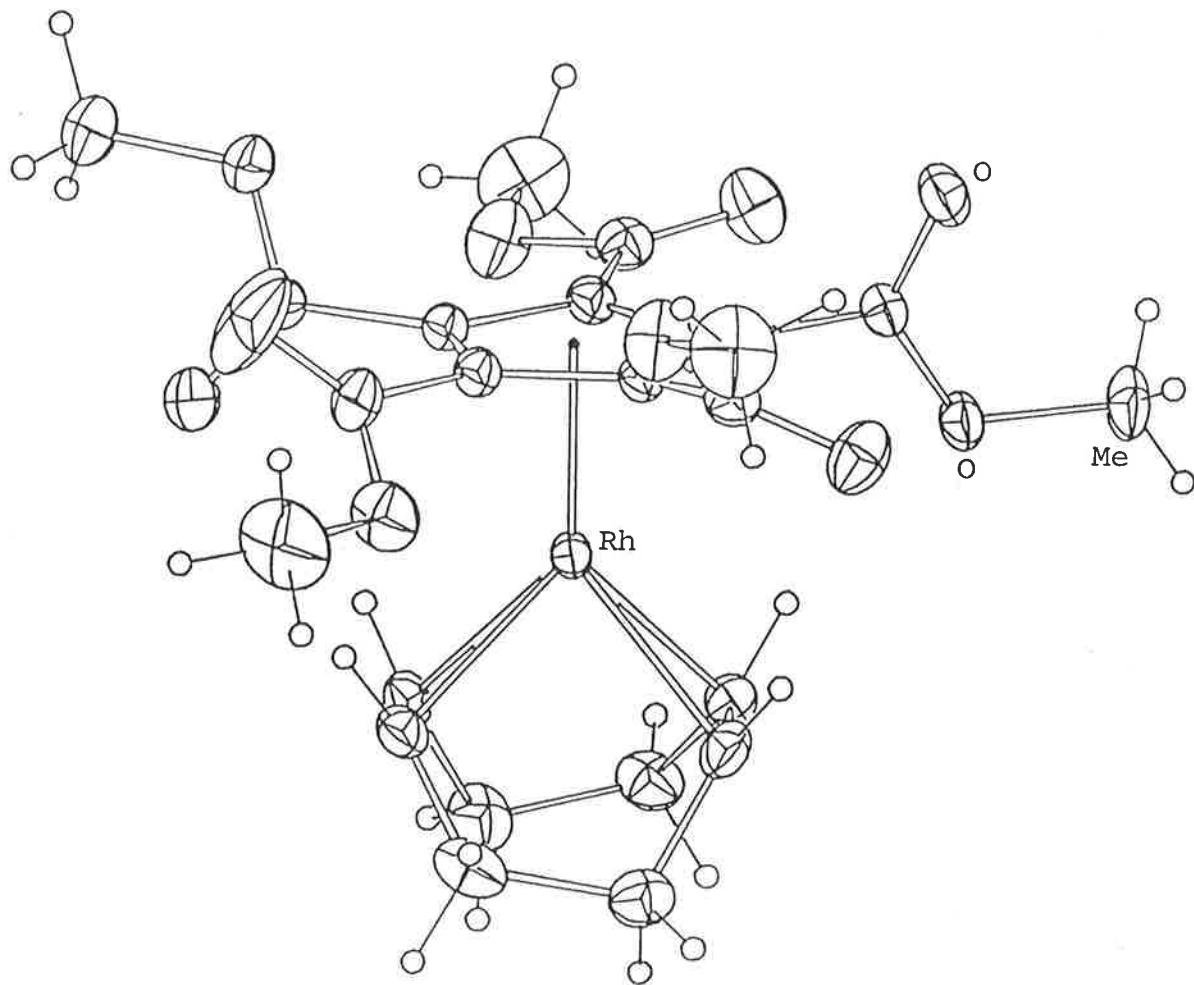
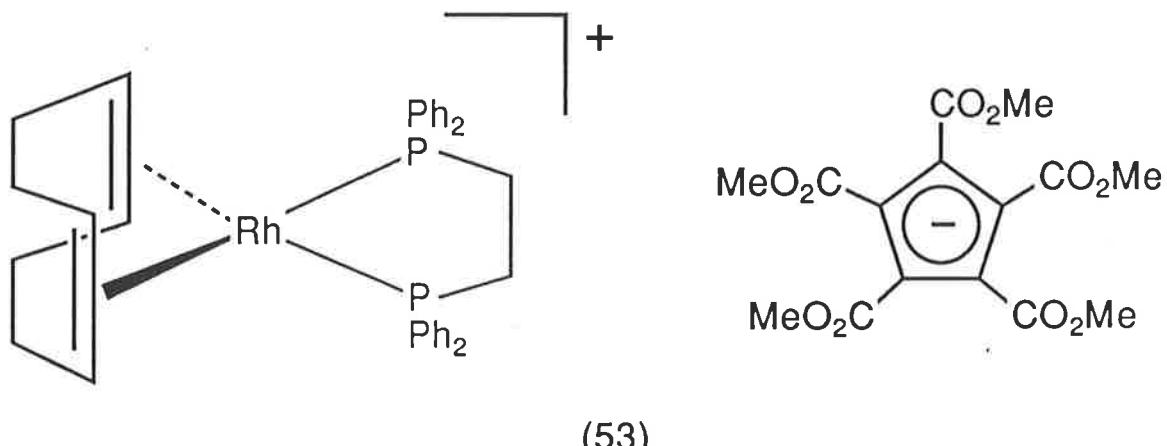


Figure 9: Molecule A of $\text{Rh}(\eta^4\text{-C}_6\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (51)
(by B.W. Skelton and A.H. White)

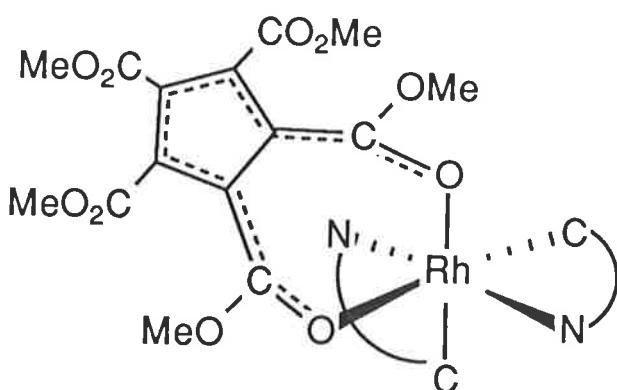
The reaction between (51) and the chelating bis-tertiary phosphine $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppe) afforded an ionic product which proved to be the $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ salt of the known^{42, 43} $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{dppe})]^+$ cation (53).

In this complex, the OMe resonance of the anion was found at $\delta 3.63$; conductivity measurements confirmed the 1:1 electrolyte formulation. In the FAB mass spectrum, the base peak corresponds to the cation $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{dppe})]^+$, which fragments to $[\text{Rh}(\text{dppe})]^+$ and $[\text{Rh}(\text{C}_8\text{H}_{12})]^+$. A weak ion at m/z 856 can be assigned to $[\text{Rh}(\text{dppe})\{\text{C}_5(\text{CO}_2\text{Me})_5\}]^+$, while in the negative ion spectrum, the only peak of significant intensity is the expected m/z 355, $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$.

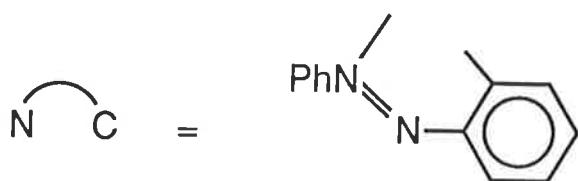


This reaction demonstrates the relatively weak Rh-C₅ bond in (51), and parallels similar observations on the ruthenium complex (46) mentioned above.³⁹

The reaction between $\{\text{RhCl}(\text{azb})_2\}_2$ ($\text{azb} = \text{C}_6\text{H}_4\text{N}=\text{NPh}$) and $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ in acetonitrile gave a red complex, characterised as the mononuclear complex $\text{Rh}(\text{azb})_2\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (54). The presence of the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand was evident from the IR spectrum, but the ^1H NMR spectrum contained three OMe resonances, at $\delta 3.32$, 3.69 , and 3.75 , with relative intensities 2:1:2. The complex resonances for the azb ligands had a similar profile to those for other complexes containing this chelating ligand, so that a reasonable structure was one in which the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand was bonded through two carbonyl oxygen atoms in the manner



(54)



found in the solid state structures of first-row transition metal derivatives^{28, 29} but not preserved in solution.

The proposed formulation was confirmed by an X-ray study (Figure 10). The C_5 ligand, chelating through the carbonyl oxygens of CO_2Me groups 1 and 2, is seen to have three

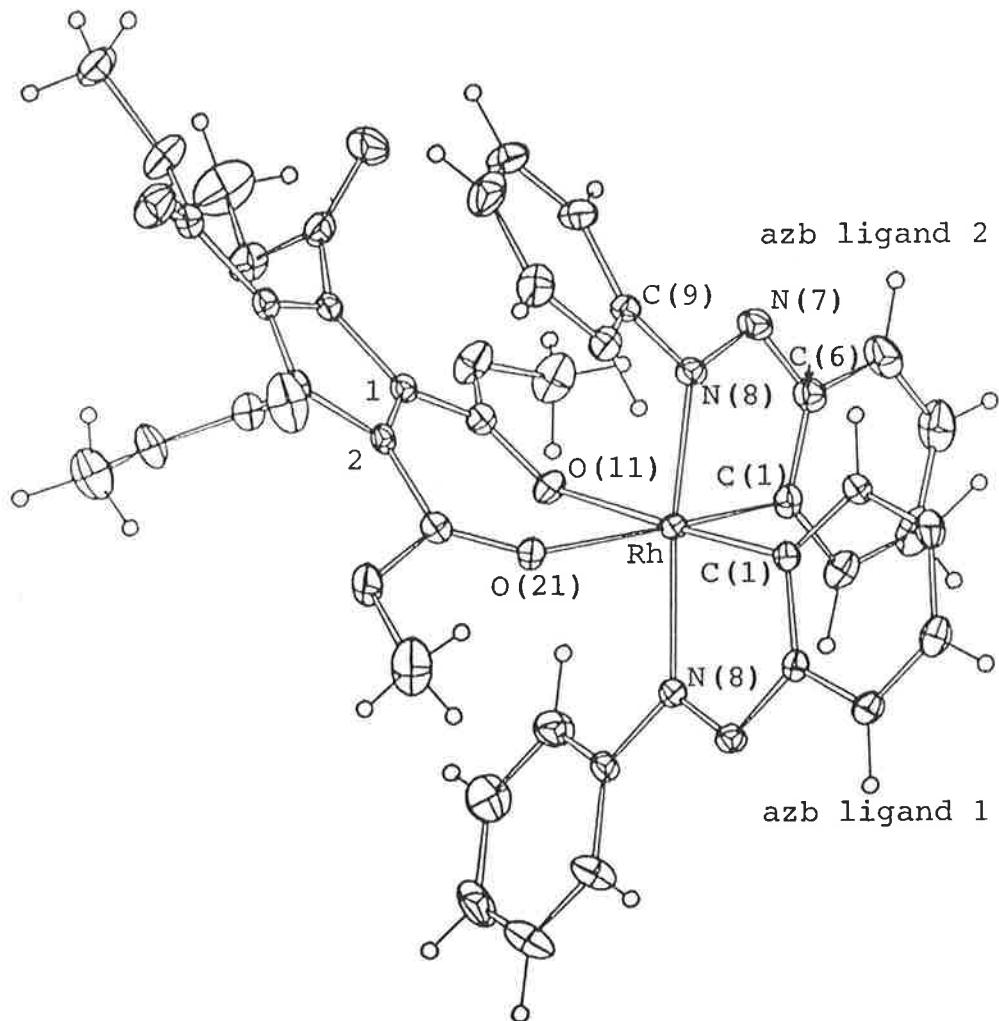


Figure 10: A molecule of $\text{Rh}(\text{azb})_2\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (54)
 (by B.W. Skelton and A.H. White). Selected
 bond lengths: Rh-O(11) 2.222(3); Rh-O(21) 2.197(3);
 Rh-C(101) 1.959(4); Rh-N(108) 2.073(3); Rh-C(201)
 1.957(4); Rh-N(208) 2.006(3).

environmentally different CO_2Me groups, in agreement with the ^1H NMR results.

The data for the seven-membered chelate ring are similar to those found in earlier structural studies,^{28, 29} the C(1)-C(2) distance being the longest of the five C-C separations in the C_5 ring [1.450(6) vs. 1.40(av.) \AA], and C(n1)-O(n1) are also correspondingly elongated. The two metallated aryl carbons are each *trans* to an oxygen of the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand, with the coordinated nitrogen atoms mutually *trans*. While the $\text{RhC}_2\text{N}_2\text{O}_2$ molecular core has potential D_2 symmetry, very substantial departures from this ideal are observed for the metal-ligand distances, presumably as a consequence of steric interaction between the ligand planes. The aromatic system of the azb chelate rings is strongly coupled with that of the metallated phenyl ring, and not at all with that of the pendant phenyl ring, in spite of its coplanarity; C(6)-N(7) are 1.39 \AA (av.), while N(8)-C(9) are 1.44 \AA (av.).

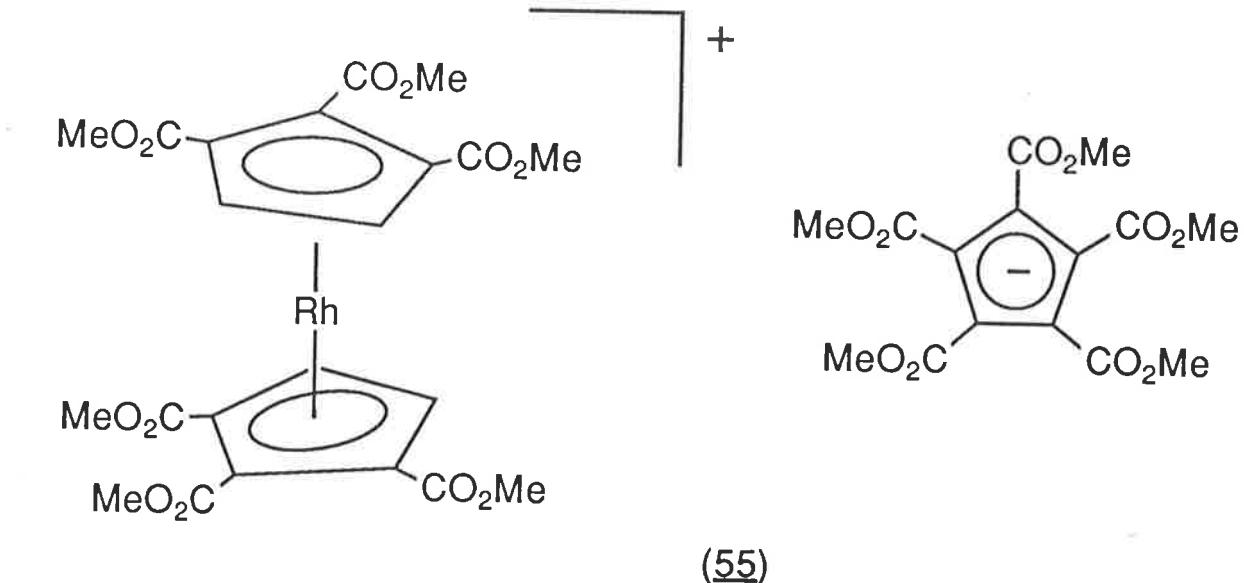
Two other complexes containing the $\text{Rh}(\text{azb})_2$ moiety have been structurally studied, namely $\text{Rh}(\text{OAc})(\text{azb})_2$ and $(\text{azb})_2\text{Rh}(\mu-\text{Cl})_2\text{Rh}(\text{CO})_2$.^{44, 45} In all three cases the two azb ligands are similar, with the metal-bonded nitrogen occupying mutually *trans* sites about the octahedrally coordinated rhodium.

Complexes (51) and (54) thus show an interesting difference in respect of the coordination of the $\text{C}_5(\text{CO}_2\text{Me})_5$ ligand. In the former, a rhodium(I) complex, interaction of the metal with the ring carbons gives a complex containing a symmetrical η^5 -bonded ligand, while in the rhodium(III) derivative there is a chelating O-bonded ligand. While

these two complexes do not have any other ligands in common, it is useful to relate the bonding mode of the $C_5(CO_2Me)_5$ ligand to the nature of the metal centre, with the relatively electron-rich soft rhodium(I) bonding to the soft ring carbons in (51) and the more highly oxidised centre attaching to the hard oxygen donors in (54).

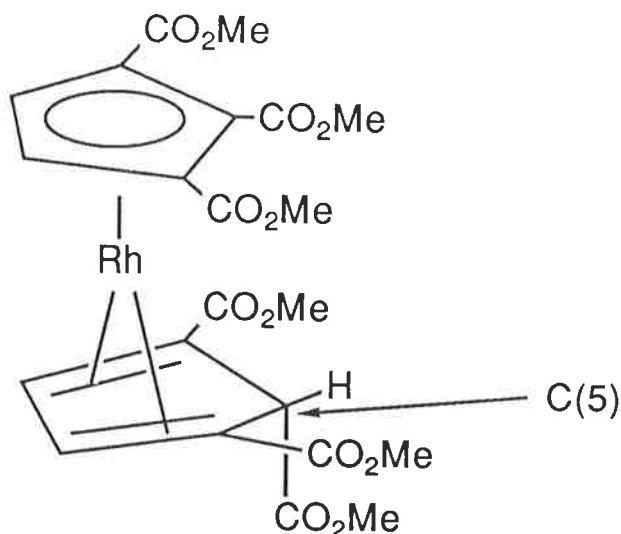
Previous work had shown that the reaction between $Rh_2(OAc)_4$ and $HC_5(CO_2Me)_5$ gave red needles of a complex (55), shown by conductivity measurements to behave as a 1:1 electrolyte in polar solvents such as water or acetone. Microanalytical figures and an osmometric molecular weight of $1100 \pm 10\%$ in chloroform, suggested the presence of both ionic and covalently-bound C_5 fragments.⁴⁶

A single-crystal X-ray diffraction study⁴⁶ showed that (55) has the illustrated structure, $[Rh\{\eta^5-C_5H_2(CO_2Me)_3-1,2,3\}_2][C_5(CO_2Me)_5]$, in which the cations and anions stack along the long axis of the needle crystals. The 1H NMR spectrum contains three resonances at $\delta 3.75$, 3.89 and 6.30 , of relative intensities 18:15:4, which are assigned to accidentally equivalent CO_2Me groups of the $C_5H_2(CO_2Me)_3$ ligand, the $C_5(CO_2Me)_5$ anion, and the ring protons, respectively. The ^{13}C NMR spectrum is more informative, containing three inequivalent OMe resonances between $\delta 51.4$ and 54.6 and three carbonyl resonances between $\delta 159.7$ and 176.6 ; the ring carbons of the $C_5(CO_2Me)_5$ group resonate at $\delta 117.45$, while those of the other η^5 ligands are found between $\delta 91.3$ and 105.0 .



In this study, the reaction between $Tl[C_5(CO_2Me)_5]$ and $\{RhCl(CO)_2\}_2$ was carried out in methanol. After several days at reflux point, preparative TLC showed the presence of a large number of products, of which only one has been isolated in a pure state. This compound (56) formed orange crystals, the EI mass spectrum of which contained the highest mass ion at m/z 582. Similarly, the FAB mass spectrum shows a weak ion at m/z 582, with the major ion at m/z 522 assigned to $[M - CO_2Me - H]^+$. In the 1H NMR spectrum, seven singlet resonances of relative intensities 2:2:1:3:6:6:3 were present. These observations, together with the finding that complex (55) contained two $C_5H_2(CO_2Me)_3$ ligands, suggested that (56) also contained similar groups. Both the analytical results and the ion at m/z 582 were consistent with the formula $RhH\{C_5H_2(CO_2Me)_3\}_2$; no high-field 1H resonance was found, and a single-crystal X-ray diffraction study was carried out to confirm the suggested diene-dienyl structure and to determine the precise CO_2Me substitution.

pattern of (56).



(56)

As can be seen from Fig. 11, which shows a plot of one of the two independent molecules found in the unit cell, complex (56) is indeed another example of an 18e $\text{Rh}(\eta^4\text{-diene})(\eta^5\text{-dienyl})$ complex. The rhodium is attached to an $\eta^5\text{-C}_5\text{H}_2(\text{CO}_2\text{Me})_3\text{-1,2,3}$ group and to the 1,3-diene system of the related 1,4,5-tris(methoxycarbonyl)-cyclopenta-1,3-diene ligand. The ^1H NMR spectrum can be interpreted on the basis of this structure and comparing it with that of (55); the singlet at $\delta 4.19$ is assigned to the *endo* proton on C(5), while the equivalent pairs of protons on the η^4 and η^5 ligands resonate at $\delta 5.64$ and 5.98, respectively. Assignment of the two sets of CO_2Me resonances is not straightforward, apart from the obvious distinction between the single central and two outer CO_2Me groups on each ligand.

The Rh-C(cp) distances (2.24\AA) are comparable with those found in $\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (2.28\AA ⁴⁷), but considerably longer than those in (55), as would be

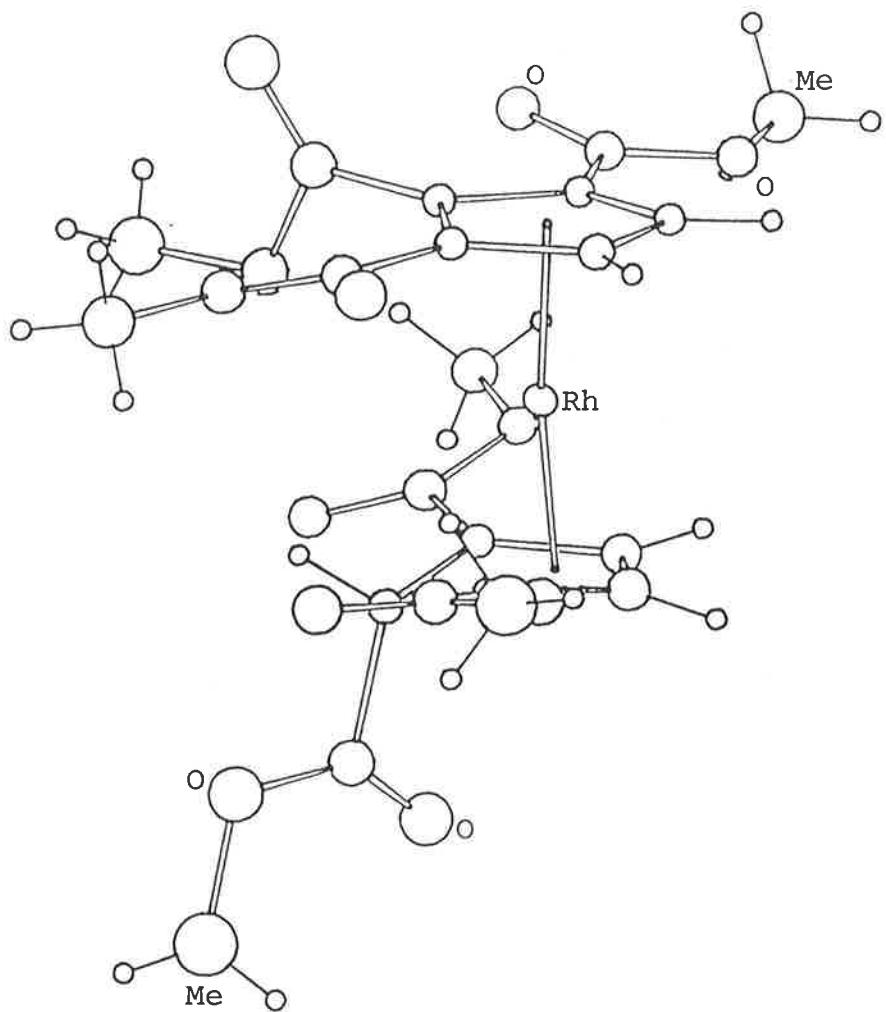


Figure 11: Molecular structure of
 $\text{Rh}\{\eta^4-\text{C}_5\text{H}_3(\text{CO}_2\text{Me})_3\}\{\eta^5-\text{C}_5\text{H}_2(\text{CO}_2\text{Me})_3\}$ (56)
(by B.W. Skelton and A.H. White)

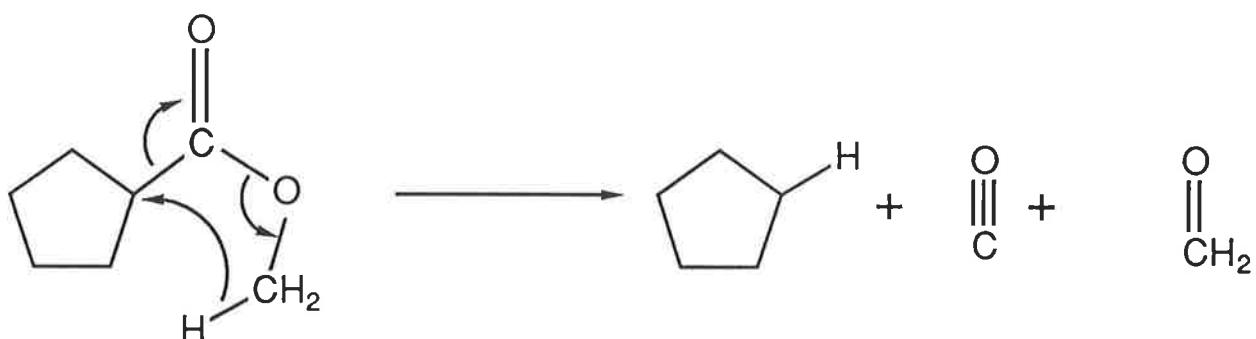
expected when comparing neutral and cationic systems.

The Rh-C(diene) separations (2.14\AA) are 0.1\AA shorter, and are similar to those found in $\text{Rh}(\eta^4\text{-C}_6\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (2.13\AA) (51).⁴⁷ The bulky CO_2Me group attached to C(5) of the diene is *exo*, while in the cp ligand, the middle substituent is twisted about its attachment similarly to ease steric strain.

In both cases, the isolation of (55) and (56) only after prolonged reaction times has precluded any studies designed to elucidate the manner in which the two CO_2Me groups are replaced by H. Model studies suggest that steric interactions between the CO_2Me groups of complexes $\text{M}\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}_2$ having metallocene 'sandwich' structures, would be severe as a result of the impossibility of all CO_2Me groups being able to adopt a configuration close to coplanarity with the C_5 ring. Inspection of the structure of (55) shows that the least sterically demanding conformation of the two rings is adopted, such that the CO_2Me groups of one ring lie above the H atoms of the second. No such constraint applies to (56) since the central CO_2Me group on the η^5 -ring whose plane has a dihedral of *ca* 80° with the C_5 ring plane, lies above and to one side of the proton attached to C(5) of the η^4 -ring, i.e. the carbon furthest away (2.65\AA) from the metal, and thus is in the most open position. In consequence, the two CH-CH portions of the rings are approximately staggered but overlapping, with respect to one another.

The steric interactions of CO_2Me groups on separate η^5 -rings may provide the driving force for the reaction which results in the replacement of two of these groups on each ring with H. The reaction corresponds to a net

elimination of "C₂H₂O₂" from each group. Similar processes have been observed in the mass spectra of Ru(η^5 -C₅H₅)-{ η^5 -C₅(CO₂Me)₅},⁴⁸ where a stepwise conversion of the molecular ion of this complex to the molecular ion of ruthenocene, [Ru(C₅H₅)₂]⁺, occurs. In that case, one can propose a cyclic elimination of CO and CH₂O (Scheme 2).

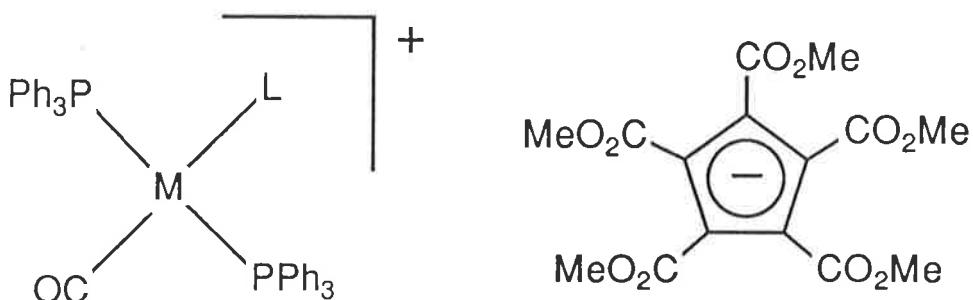


Scheme 2

Complexes (55) and (56) are related by hydride transfer reactions, as found previously for [Rh(η -C₅H₅)₂]⁺ and nucleophiles such as Ph⁻.⁴⁹

Reactions between Tl[C₅(CO₂Me)₅] and MCl(CO)(PPh₃)₂ (M = Rh or Ir) also proceed readily in polar solvents, such as acetonitrile, but the only products which have been isolated are the [C₅(CO₂Me)₅]⁻ salts of the acetonitrile cations [M(CO)(NCMe)(PPh₃)₂]⁺. These were characterised by the usual methods, and have properties consistent with the illustrated structures (57) and (58). The IR spectra contain bands at ca 2300 and 2010 cm⁻¹, assigned to ν (CN) and ν (CO), respectively, and complex absorptions between 1650-1750 cm⁻¹ from the ester CO groups. The ¹H NMR spectra contain the expected resonances at

δ 1.2 (MeCN), 3.6 (CO_2Me) and 7.4 (PPh_3). The FAB mass spectra contains weak ions corresponding to $[\text{M}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]^+$, while the base peak is $[\text{Rh}(\text{PPh}_3)_2]^+$ for (57) and $[\text{Ir}(\text{CO})(\text{PPh}_3)_2]^+$ for (58). Other significant peaks are $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]^+$ and $[\text{Ir}(\text{PPh}_3)_2]^+$. Finally, elemental analyses were consistent with values calculated for the formulations given, and conductivity measurements showed that the complexes were 1:1 electrolytes.

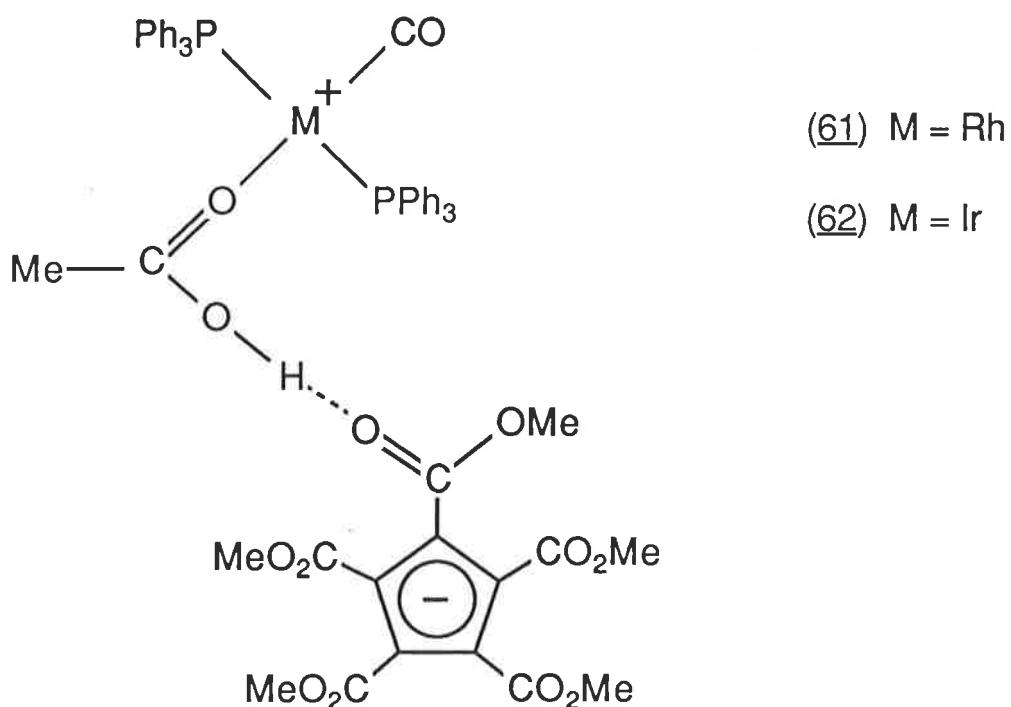


- (57) M = Rh, L = NCMe
- (58) M = Ir, L = NCMe
- (59) M = Rh, L = bqH
- (60) M = Rh, L = phen

These cations were described earlier,^{43, 50} and undergo ready exchange of the acetonitrile for other nitrogen donors. The benzoquinoline (59) and 1,10-phenanthroline (60) cations⁵¹ were both isolated with $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ counterions in this way. Both were identified by spectroscopic and microanalytical data, while conductivity measurements show 1:1 electrolytes. These results further illustrate

the utility of the stable $[C_5(CO_2Me)_5]^-$ anion in the isolation of cationic species, but we have not yet been able to induce either complex to undergo loss of MeCN or CO to give species containing a covalently bonded $C_5(CO_2Me)_5$ ligand.

Crystals of the supposed salts of the acetonitrile cations were subjected to crystallographic studies, but in both cases, the structures revealed a unit cell composed of $[M(X)(CO)(PPh_3)_2]^+$ cations and $[C_5(CO_2Me)_5]^-$ anions (61 and 62). As shown in Figure 12. the ligand X refined as



a four-atom, branched chain fragment, and was not consistent with the presence of acetonitrile (a linear three-atom ligand). The most satisfactory refinement was in terms of monodentate acetato or acetamide group [Rh-O 2.123(9), Ir-O 2.074(10) \AA]. The remainder of the cationic geometry is square planar, with mutually *trans* PPh_3 ligands [Rh-P 2.327(3), 2.323(3); Ir-P 2.317(3), 2.318(3) \AA] and CO

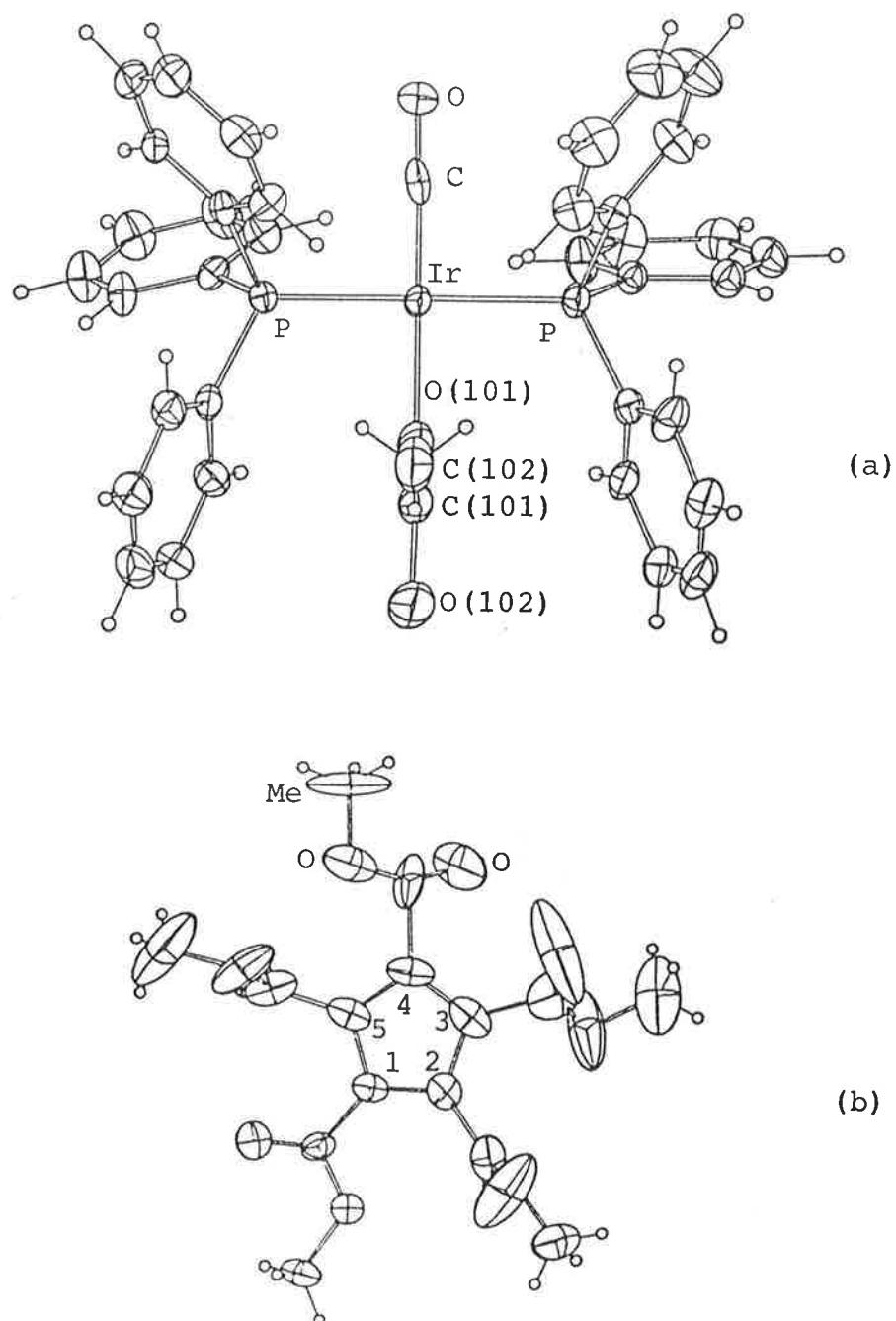


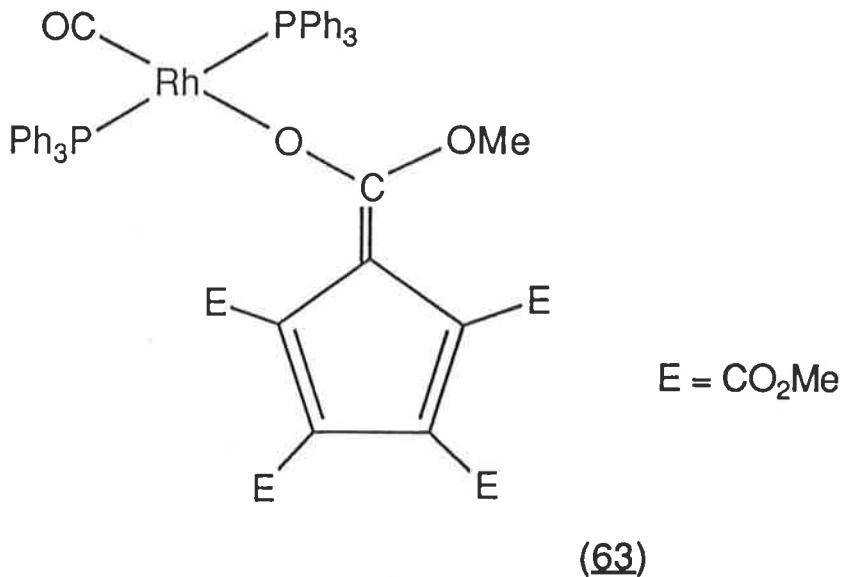
Figure 12: X-ray structure of (a) cation and (b) anion
in $[\text{Ir}\{\text{OC(OH)Me}\}(\text{CO})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (62)
(by B.W. Skelton and A.H. White)

trans to X [Rh-CO 1.814(10), Ir-CO 1.740(14) Å], and does not require further comment.

The anionic fragment was satisfactorily modelled on the basis of a regular pentagonal $C_5(CO_2Me)_5$ group, as found previously in $[NMe_4][C_5(CO_2Me)_5]$ (33)⁵² and $[Rh\{\eta^5-C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$, (55),⁴⁶ with the planes of the CO_2Me groups taking up a random orientation relative to the C_5 ring plane; only $CO_2Me(1)$ is almost coplanar with the ring.

However, interpretation of the structure in terms of $[M\{O_2CMe\}(CO)(PPh_3)_2]^+$ cations and $[C_5(CO_2Me)_5]^-$ anions obviously violates the usual electron-counting rules applied to these systems; the diamagnetic (NMR) nature of these salts precludes them from being derivatives of rhodium(II) or iridium(II). Inspection of the unit-cell contents shows that the closest contact is O(21)...O(101) ($x, y-1, z$) (2.86 Å), and that O(51) and O(102) are only 3.09 Å apart; the associated geometry is consistent with the possibility of a hydrogen bond between the two groups. The structure can thus be viewed as an aggregate of neutral $M\{OC(O)Me\}(CO)(PPh_3)_2$ and $HC_5(CO_2Me)_5$ molecules, joined by the hydrogen bond, or as a salt of the acetic acid cation $[M\{OC(OH)Me\}(CO)(PPh_3)_2]^+$ and $[C_5(CO_2Me)_5]^-$ anion [$M = Rh$ (61); $M = Ir$ (62)]. We incline to the latter view, based on the well-known stability of the anionic species, and the expected relative basicities of coordinated acetate and free $[C_5(CO_2Me)_5]^-$ anions; the determined geometry is not helpful in this respect as the CO_2Me substituent libration is generally very high.

The acetic acid may be formed by hydration of acetonitrile, catalysed by the metal complex or strong acid; we have also considered the possibility that the ligand is acetamide. Attempted syntheses of these salts from $[M(NCMe)(CO)(PPh_3)_2]^-$ $[C_5(CO_2Me)_5]$ and the ligand were unsuccessful. The converse approach, the reaction between $HC_5(CO_2Me)_5$ and $Rh(OAc)(CO)(PPh_3)_2$ in a non-coordinating solvent (benzene) gave a yellow powder which analysed for $Rh\{C_5(CO_2Me)_5\}(CO)(PPh_3)_2$ (63). Attempts to obtain a suitable crystalline sample of this compound were unsuccessful, as it is insoluble in all but coordinating solvents; from the latter, only the salts $[Rh(S)(CO)(PPh_3)_2][C_5(CO_2Me)_5]$ ($S = \text{solvent}$) could be obtained. The FAB mass spectrum shows only $[Rh(CO)(PPh_3)_2]^+$ or $[C_5(CO_2Me)_5]^-$ and associated fragment



ions, possibly because the matrix (3-nitrobenzyl alcohol) is sufficiently polar to coordinate to the rhodium. It is possible that this complex has the illustrated square planar structure, with an O-bonded $C_5(CO_2Me)_5$ group. An alternative structure containing a covalent chelating, O-bonded $C_5(CO_2Me)_5$ group, with five-coordinate rhodium(I), cannot be ruled out.

SECTION B

This section of work describes the synthesis and characterisation of some metal containing derivatives of $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$.

Derivatives of 1-methyl-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadiene

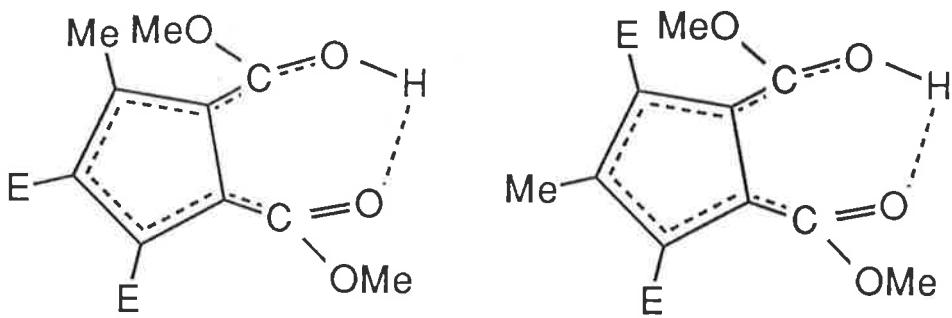
Following the method described earlier by Hoffmann and co-workers,⁵³ addition of iodomethane to silver(I) oxide in a dichloromethane solution of (4) gave an olive-green precipitate (AgI). Workup of the solution afforded $\text{C}_5\text{Me}(\text{CO}_2\text{Me})_5$ (64) in 87% yield. The white crystalline solid had the expected resonances in its ^1H NMR spectrum at δ 1.70, 3.67, 3.83 and 3.88 (1:1:2:2) assigned to the Me and three types of CO_2Me groups, respectively. The FAB mass spectrum shows a pseudomolecular ion at $[M + \text{H}]^+$ while major fragmentation routes are via loss of OMe or CO_2Me . The negative ion spectrum shows a molecular ion, then loss of Me or OMe with the base peak at m/z 311 due to $[M - \text{CO}_2\text{Me}]^-$. The ion of lowest mass with significant intensity is at m/z 265, assigned to $[M - \text{CO}_2\text{Me} - \text{OMe} - \text{Me}]^-$.

The compound reacts with sodium methoxide in refluxing methanol to give $\text{Na}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]$ (65), isolated as a white solid. The FAB mass spectrum shows that aggregation phenomena resulted in the formation of ions due to $[\text{Na}_4\text{L}_3]^+$ [$\text{L} = \text{C}_5\text{Me}(\text{CO}_2\text{Me})_4$], $[\text{Na}_3\text{L}_2]^+$, while the base peak is due to $[\text{Na}_2\text{L}]^+$. The negative ion spectrum similarly shows a weak peak at m/z 645 assigned to $[\text{NaL}_2]^-$.

Acidification (concentrated HCl) of an aqueous solution of (65) gave a white precipitate of $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ (66), which

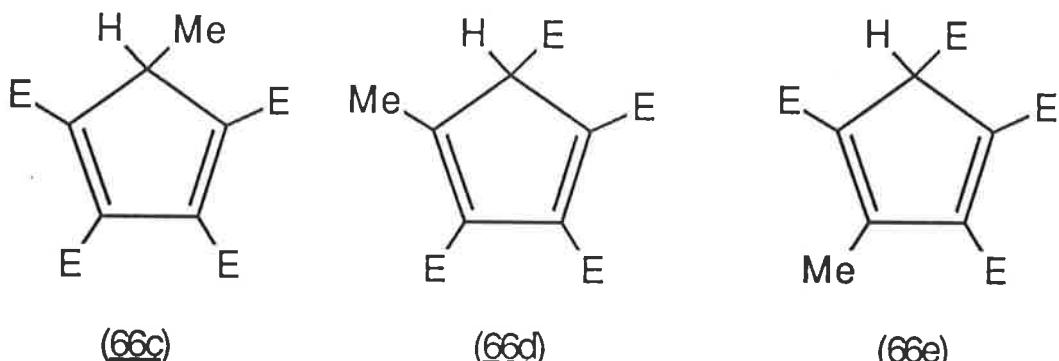
was isolated in 95% yield. Diene (66) forms white needles from diethyl ether; as expected, the infrared spectrum is dominated by very strong $\nu(\text{CO})$ absorptions between 1600-1740 and 1050-1280 cm^{-1} . The NMR spectra are highly solvent dependent. In D_2O , in which (66) is fully ionised, three ^1H resonances at δ 2.43, 3.86 and 3.88 are found corresponding to the ring-Me and two types of CO_2Me groups; the ^{13}C NMR spectrum similarly contains eight resonances for the ring-Me group, the three types of ring carbons, and the Me and carbonyl carbons of the two types of CO_2Me groups. In less polar solvents, complex spectra are obtained as a result of the presence of isomeric forms of the non-ionised diene [e.g. (66a-e)]. Thus, in C_6D_6 , a signal at δ 20.3 is assigned to the acidic proton; there are three Me resonances, one at δ 2.36, and two closely spaced at δ 2.49 and 2.50, while between δ 3.1-4.1, there are at least 13 OMe resonances of differing relative intensities. Similarly, in CDCl_3 , the acidic proton occurs at δ 20.0; four Me resonances are found between δ 2.35-2.65, and at least nine separate OMe signals between δ 3.7-4.4. In both cases, addition of a drop of D_2O resulted in the disappearance of the low-field proton signal, and some changes in relative intensities of the other resonances. In $(\text{CD}_3)_2\text{CO}$, only four Me (δ 2.45-2.75) and seven OMe signals (δ 3.8-4.0) were resolved. Further studies of the complex isomeric equilibria are necessary to assign the predominant structures present in these solutions.

The FAB mass spectrum of $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ showed a molecular ion, then loss of OMe. The base peak at m/z



(66a)

(66b)



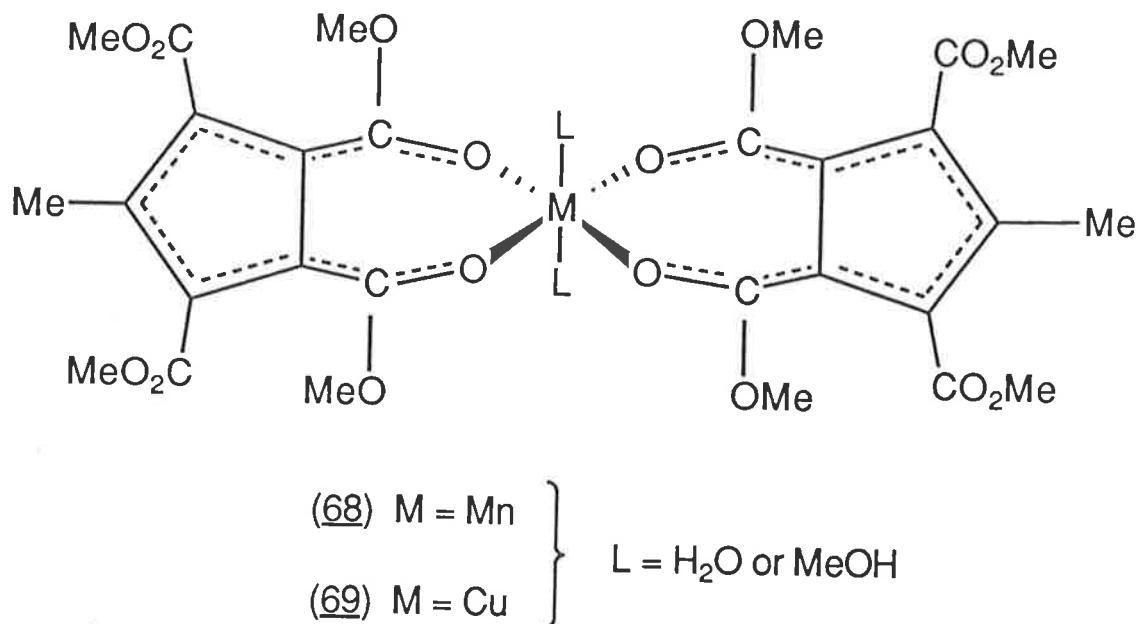
93, is unassigned. The negative ion spectrum shows the base peak due to $[L]^-$, while fragmentation of the ligand gives peaks of m/z 297 due to $[HL - Me]^-$, m/z 265 due to $[L - OMe - Me]^-$, m/z 253 due to $[HL - CO_2Me]^-$ and m/z 207 due to $[HC_5(CO)(CO_2Me)_2]^-$.

Metal derivatives of (66) were obtained by using similar methodology to that employed for (4). Thus, the thallium(I) derivative is a useful reagent for replacement of halide by the $C_5Me(CO_2Me)_4$ group; this compound was readily obtained by dissolving Tl_2CO_3 in a dilute aqueous solution of (66). Crystallisation from methanol gave pure $Tl[C_5Me(CO_2Me)_4]$ (67); the 1H NMR spectrum suggests that it

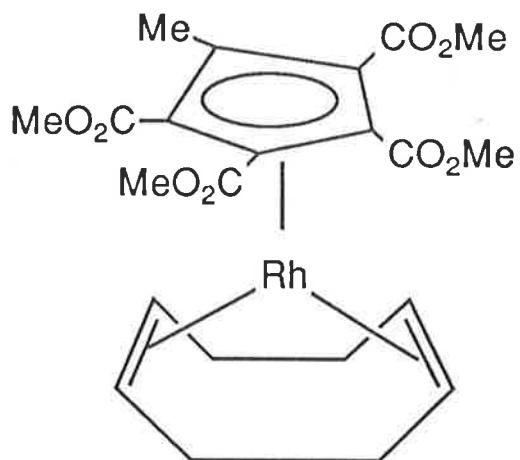
is fully ionised in D₂O solution, while the chemical shifts of the three Me groups show little change in CDCl₃. The FAB mass spectrum again shows aggregation with a peak due to [Tl₂L]⁺, while the negative ion spectrum shows a weak peak assigned to [TlL₂]⁻. The base peaks are [Tl]⁺ and [L]⁻, the latter of which shows the usual ligand fragmentation pattern.

As mentioned previously, displacement of a weak acid from its salts is a preferred method of preparation of several derivatives of the more strongly acidic diene (4); this is also true for (66). The white manganese (II) (68) and red-brown copper(II) salts (69) were obtained from the metal acetates and methanolic solutions of (66). Both compounds are soluble in water with complete ionisation; in methanol, solutions of (69) are red-orange, in which property it resembles Cu[C₅(CO₂Me)₅]₂²⁸ (24). Analytical results suggest that both (68) and (69) are solvated, but we have been unable to determine whether water or methanol (or a mixture of the two) occupies the two remaining coordination sites around the octahedrally coordinated metal atoms, as found for the C₅(CO₂Me)₅ complexes of iron(II), cobalt(II) and copper(II).²⁸ The FAB mass spectrum of the manganese complex shows aggregation peaks at *m/z* 1720 and 1043 due to [Mn₃L₅]⁺ and [Mn₂L₃]⁺, respectively, while the base peak is assigned to [Mn(HL) - 2CO₂Me]⁺. The negative ion spectrum shows a peak at 988 due to [MnL₃]⁻, while the base peak is again due to [L]⁻.

Orange crystalline Rh(η^4 -C₈H₁₂) $\{\eta^5$ -C₅Me(CO₂Me)₄ $\}$ (70) was obtained in 67% yield from the reaction between



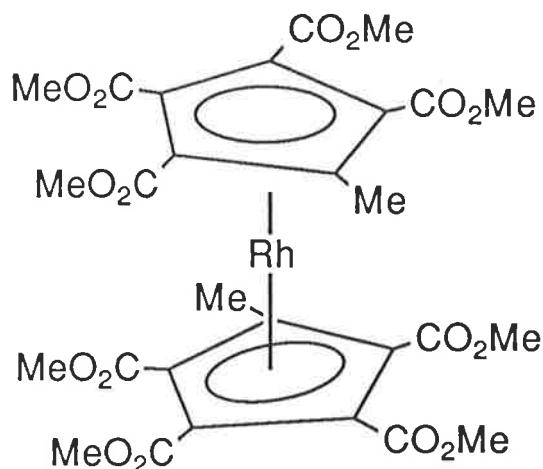
$\{\text{RhCl}(\eta^4-\text{C}_8\text{H}_{12})\}_2$ and $\text{Tl}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]$ in acetonitrile. The molecular structure is assumed to be similar to that of the crystallographically characterised $\eta^5-\text{C}_5(\text{CO}_2\text{Me})_5$ analogue (51), mentioned earlier.^{4,7} This is supported by the ^1H NMR spectrum, which contains singlet resonances at δ 3.80 and 3.84 (CO_2Me groups) and multiplets at δ 2.15 and 4.18 for the CH_2 and CH protons, respectively, of the chelating cycloocta-1,5-diene ligand; the ring-Me resonance is overlapped by the former. The FAB mass spectrum of (70) shows the molecular ion as the base peak, while the negative spectrum is again dominated by the anion $[\text{L}]^-$, although there is a very weak peak at $[\text{M}]^-$.



(70)

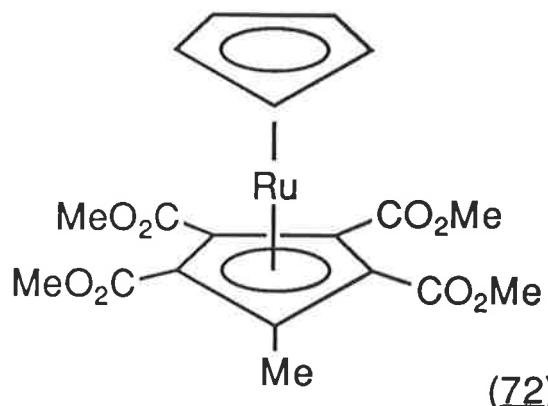
With $\text{Rh}_2(\text{OAc})_4$, a complex formulated as $\text{Rh}\{\text{C}_5\text{Me}-(\text{CO}_2\text{Me})_4\}_2$ (71) was isolated in low yield. It has not been possible to obtain X-ray quality crystals of this material, so its precise structure is uncertain. Of the obvious possibilities, the η^4 -diene/ η^5 -dienyl structure $\text{Rh}\{\eta^4-\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4\}\{\eta^5-\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}$ appears to be ruled out by its paramagnetism, which broadened the ${}^1\text{H}$ NMR resonances. The latter is also inconsistent with a binuclear structure involving $\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4$ ligands bridging an $\text{Rh} \equiv \text{Rh}$ quadruple bond via the ester carbonyl groups. The remaining possibility is the rhodium(II) metallocene structure, $\text{Rh}\{\eta^5-\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}_2$, which is expected to be paramagnetic (d^7). Model studies suggest some difficulty in accommodating the eight CO_2Me groups in a sandwich structure; mass spectral studies have also

been unable to resolve the problem, and for the time being, the identity of this compound remains in doubt.

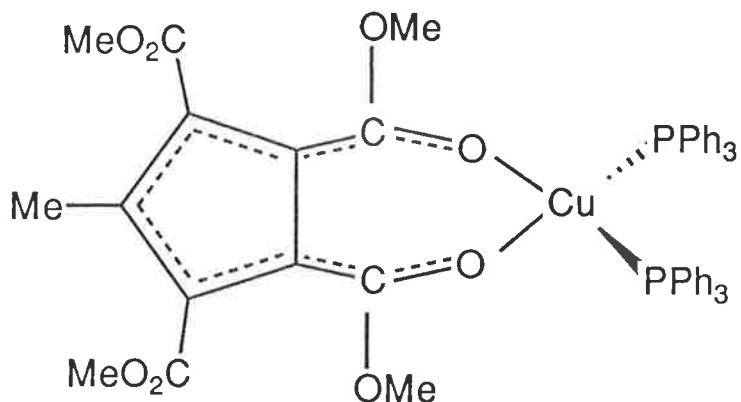


(71)

As found for the $C_5(CO_2Me)_5$ derivative,³⁹ the reaction between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and $Tl[C_5Me(CO_2Me)_4]$ in methanol, carried out in the presence of air, afforded the pale yellow ruthenocene derivative, $Ru(\eta-C_5H_5)\{\eta^5-C_5Me(CO_2Me)_4\}$ (72). The proposed structure is supported by the 1H NMR spectrum, which contains singlet resonances at δ 2.34 (Me), 3.79 and 3.80 (CO_2Me), and 4.78 (C_5H_5), and its properties, which are generally similar to those of $Ru(\eta-C_5H_5)\{\eta^5-C_5(CO_2Me)_5\}$ (46), described earlier.



(72)

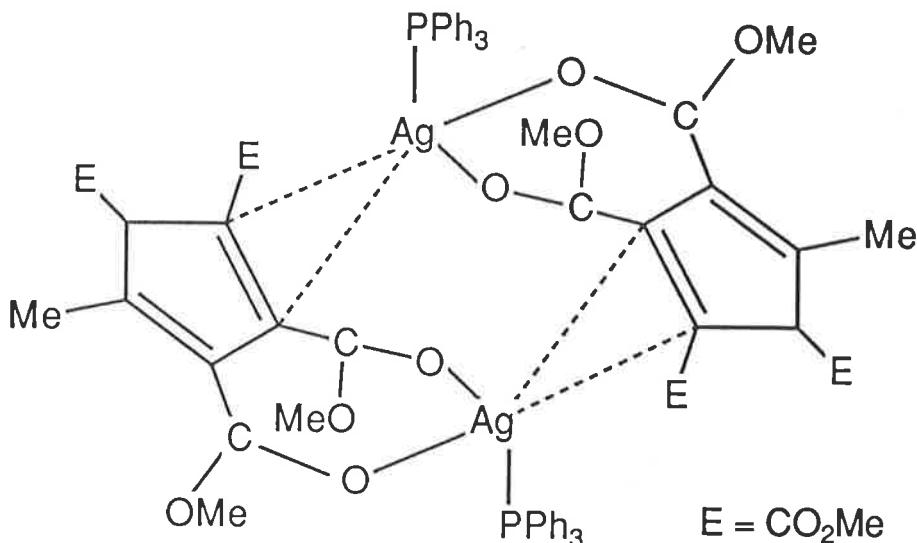


(73)

As discussed earlier, some of the more interesting results in the chemistry of (4) were found with the ^{31, 32, 54} univalent Group IB metals.⁵⁴ In a similar manner, Cu{C₅Me(CO₂Me)₄} (PPh₃)₂ (73) was obtained from a mixture of Cu₂O, triphenylphosphine and (66) in methanol. The ¹H NMR spectrum contains resonances at δ 2.34 (Me), 3.52 and 3.55 (CO₂Me) and 7.23 (Ph) (relative intensities 1:2:2:10), which is consistent with the symmetrical O-bonded chelate structure found for the C₅(CO₂Me)₅ analogue, with pseudo-tetrahedral copper(I).⁵⁴ The FAB mass spectrum shows a weak peak assigned to [M + Cu]⁺, while the base peak is at m/z 588 due to loss of the diene. The other peak of significant intensity is [Cu(PPh₃)]⁺. The only significant peak in the negative spectrum is [L]⁻.

The silver derivative (74) was obtained from a reaction of silver acetate, triphenylphosphine and (66). In this case, analytical and spectroscopic results are consistent with the formulation Ag{C₅Me(CO₂Me)₄} (PPh₃), the ¹H NMR spectrum containing four resonances, at δ 2.48 (Me), 3.71

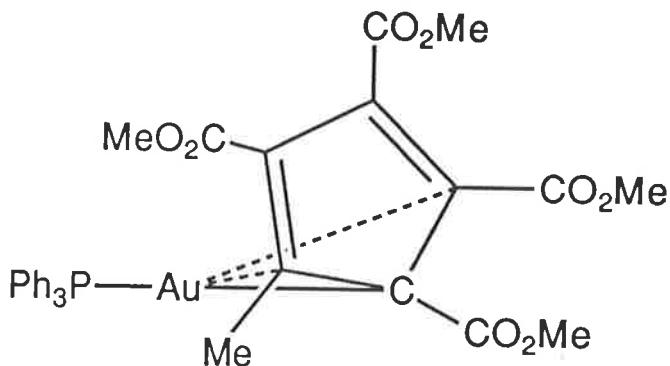
and 3.77 (CO_2Me), and 7.42 (Ph), with relative intensities 1:2:2:5. The structure of (74) is probably analogous to that of $\text{Ag}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)$ (31), in which a distorted tetrahedral silver atom is coordinated by two ester carbonyl



groups of one $\text{C}_5(\text{CO}_2\text{Me})_5$ group, the PPh_3 ligand, and a C=C double bond from the second $\text{C}_5(\text{CO}_2\text{Me})_5$ in a dimeric assembly.³² The simple ^1H NMR spectrum suggests that some fluxional process equilibrates the CO_2Me group environments.

A gold(I) complex (75) of similar stoichiometry was readily prepared from $\text{Au}(\text{OAc})(\text{PPh}_3)$ and diene (66) as white crystals. The molecular formula was established by analysis and spectroscopically, and the structure was confirmed as being entirely analogous to that of $\text{Au}\{\text{C}_5-(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)$ (28)³¹ by a single-crystal X-ray study (see below). Of interest, however, is the ^1H NMR spectrum, with the usual four resonances at δ 2.64 (Me), 3.76 and 3.80 (CO_2Me), and 7.5 (Ph), showing that some fluxional

process is occurring in solution to give only two types of CO_2Me group; the most likely situation is a rapid shift of the $\text{Au}(\text{PPh}_3)$ group around the C_5 ring. The FAB mass spectra of (74) and (75) are very similar. Both show weak ions corresponding to $[\text{M}_2(\text{PPh}_3)_2(\text{L})]^+$ ($\text{M} = \text{Ag}, \text{Au}$), $[\text{M}]^+$ and $[\text{M} - \text{OMe}]^+$. Ions of significant intensity are found at $[\text{M}(\text{PPh}_3)_2]^+$ and $[\text{M}(\text{PPh}_3)]^+$ which is the base peak.



(75)

Structure of $\text{Au}\{\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)$ (75) (Figure 13)

The crystals of $\text{Au}\{\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)$ are not isomorphous with those of the parent $\text{Au}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)$ (28). Nevertheless, in both complexes, one molecule comprises the asymmetric unit of the structure, and the disposition of ligands about the gold atom in both cases is very similar. In (75), Au-P , C(1) are 2.252(2), 2.186(6), with Au-C(2,5) 2.721(7), 2.743(7) \AA , and P-Au-C(1) , 169.9(2) $^\circ$; in the parent, corresponding values are 2.253(1), 2.199(4), 2.705(4), 2.813(4) \AA and 169.7(1) $^\circ$, differing significantly only in respect of the slightly more asymmetrical disposition of the gold atom *vis-a-vis* the C_5 ring. As in the parent,³¹ bond localisation is indicated: C(2)-C(3) , C(4)-C(5) , by the distances [around the ring from C(1)] 1.46(1), 1.37(1), 1.44(1), 1.36(1) and 1.47(1) \AA .

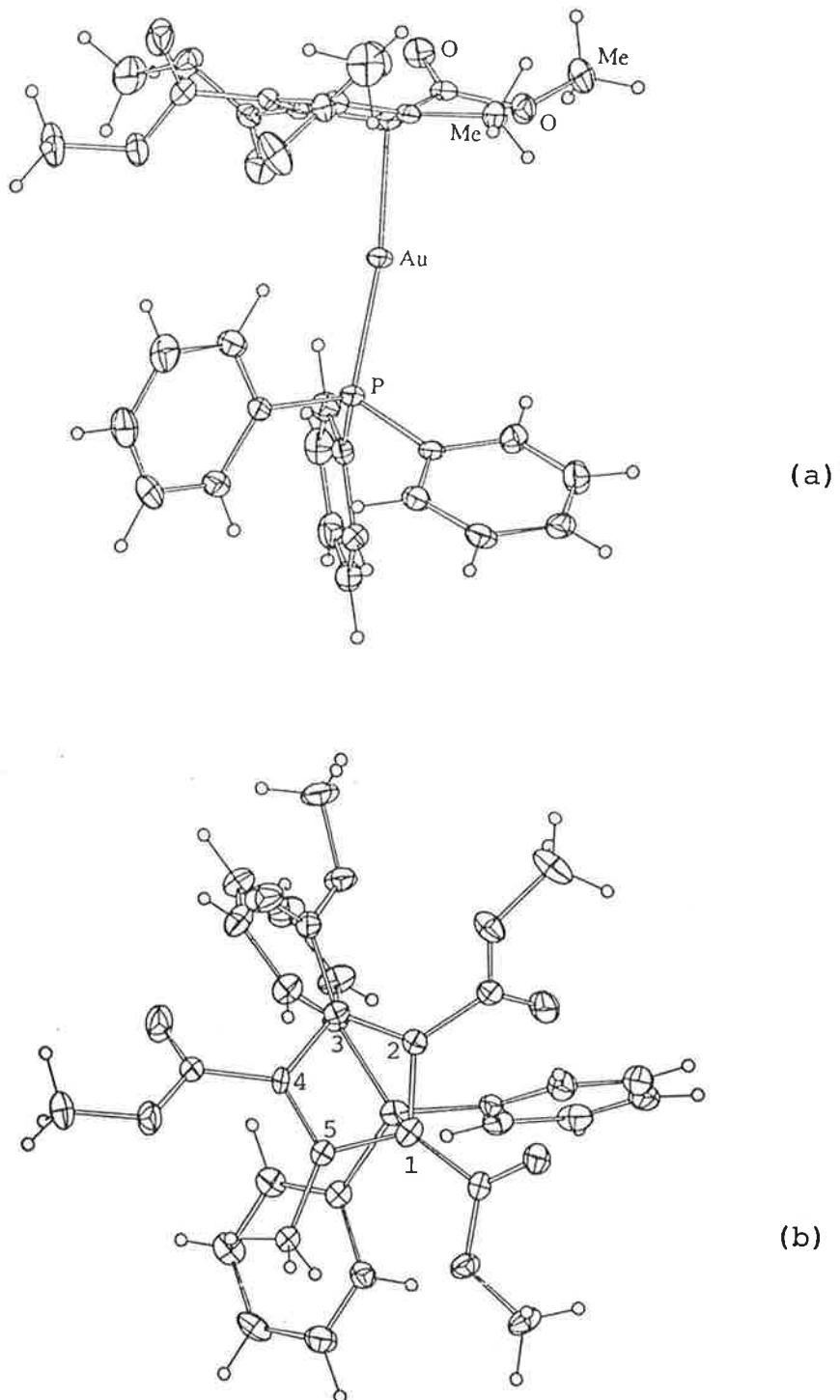


Figure 13: Molecular structure of $\text{Au}\{\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)$ (75)
 (a) side view. (b) projection down Au-P axis
 by B.W. Skelton and A.H. White

CONCLUSION

The $C_5(CO_2Me)_5$ ligand has been shown to interact with the metal ion, either through the carbonyl oxygens or through its C_5 ring. The propensity for bonding through the carbonyl oxygens is easily explained by the electronegative CO_2Me groups and the expected concentration of charge on the carbonyl oxygens. The first examples of complexes containing covalent bonds between the carbonyl oxygens and the metal, which are strong enough to be preserved in solution, were found. Ring C - metal interactions, however, have been found to be quite weak, so that for $Rh(\eta^4-C_8H_{12})\{C_5(CO_2Me)_5\}$, displacement of the $C_5(CO_2Me)_5$ ligand as $[C_5(CO_2Me)_5]^-$ by dppe was easily achieved. A number of compounds have also been synthesised in which $[C_5(CO_2Me)_5]^-$ acts as a non-coordinating counter ion, allowing the isolation of various ionic compounds.

Similarly, the $C_5Me(CO_2Me)_4$ ligand has been shown to form metal complexes bonding either through the carbonyl oxygens or in η^5 mode in the case of $Rh(\eta^4-C_8H_{12})\{\eta^5-C_5Me(CO_2Me)_4\}$. There appears to be no significant differences between these compounds and analogous species derived from $HC_5(CO_2Me)_5$, except for the expected spectroscopic changes. Similarly, the molecular structure of $Au\{C_5Me(CO_2Me)_4\}(PPh_3)$ closely resembles that of $Au\{C_5(CO_2Me)_5\}(PPh_3)$, the methyl group being on the ring carbon adjacent to that which most closely interacts with the $Au(PPh_3)$ group.

EXPERIMENTALGeneral Experimental Conditions

All reactions were performed under a nitrogen atmosphere, using dried degassed solvents. No special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids and for short times in solution. Chemical reagents were commercial products and were used as received, unless indicated otherwise. The nitrogen used was high purity grade (Commonwealth Industrial Gases). Solvents used for chromatography were LR grade; spectroscopic grade solvents were used for spectroscopy; all other solvents used were AR grade and/or were dried and distilled under a nitrogen atmosphere, as described in Vogel.⁵⁵ Light petroleum refers to a fraction of b.p. 62 - 65°C.

Melting points were measured in sealed capillaries using a Gallenkamp melting point apparatus and are uncorrected.

Conductivity measurements were obtained at 25°C under nitrogen using a Phillips PR 9500 AC conductance bridge.

Thin layer chromatography (TLC) was carried out on 20 x 20 cm glass plates coated with Kieselgel 60 GF₂₅₄ (Merck, Darmstadt).

Elemental microanalyses were determined by the Canadian Microanalytical Service, Delta, British Columbia, Canada.

Instrumentation

Infrared: Perkin-Elmer 683 double-beam and 1720X FT spectrometers, NaCl optics, calibrated using polystyrene absorption at 1601.5 cm⁻¹.

NMR: Bruker WP 80 (¹H NMR at 80 MHz, ¹³C NMR at 20.1 MHz) and Bruker CXP 300 (¹H NMR at 300.13 MHz, ³¹P NMR at 121.49 MHz,

^{13}C NMR at 75.47 MHz) spectrometers. Chemical shifts (300 K) to low field are denoted positive; the internal reference was SiMe₄ (^1H and ^{13}C NMR); the external reference for ^{31}P NMR was 0.01M H₃PO₄/0.1M HCl in D₂O (δ + 0.8 ppm). The shifts quoted for the ^{31}P NMR spectra are relative to 85% H₃PO₄. ^1H NMR spectra and ^{13}C NMR spectra of compounds in D₂O solutions were referenced to internal Bu^tOH (δ 1.28 for ^1H NMR and δ 30.79 for ^{13}C NMR), and chemical shifts for both are given relative to SiMe₄.

Mass spectra. FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon or xenon were used as FAB gases, with source pressures typically 10^{-6} bar; the FAB gun voltage was 7.5 kV, current 1mA. The ion-accelerating potential was 7kV. The samples were made up as ca 0.5 M solutions in CH₂Cl₂. A drop of solution was added to a drop of matrix (3 - nitrobenzyl alcohol), and the mixture was applied to the FAB probe tip. Spectra are reported in the form: m/z , assignment, relative intensity; multi-isotopic species are normalised on the most abundant metal isotope. FAB mass spectra are for positive ions unless otherwise noted. For negative ion spectra, L refers to C₅(CO₂Me)₅ in Section A and C₅Me(CO₂Me)₄ in Section B. EI mass spectra were obtained on a GEC - Kratos MS 3074 mass spectrometer (70 eV ionising energy, 4 kV accelerating potential).

Starting materials

The ligand $\text{HC}_5(\text{CO}_2\text{Me})_5$ ²¹ and the complexes $\text{K}[\text{C}_5(\text{CO}_2\text{Me})_5]$,²¹ $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$,²¹ $\{\text{Re}(\text{CO})_4\text{Cl}\}_2$,⁵⁶ $\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3)_2$,⁴⁰ $\text{RuCl}(\text{CO})-(\text{O}_2\text{CMe})(\text{PPh}_3)_2$,⁵⁷ $\{\text{RhCl}(\eta^4-\text{C}_8\text{H}_{12})\}_2$,⁵⁸ $\{\text{IrCl}(\eta^4-\text{C}_8\text{H}_{12})\}_2$,⁵⁹ $\{\text{RhCl}(\text{azb})_2\}_2$,⁶⁰ $\{\text{RhCl}(\text{CO})_2\}_2$,⁶¹ $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$,⁶² $\text{IrCl}(\text{CO})-(\text{PPh}_3)_2$,⁶³ $\text{Rh}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2$,⁶⁴ and $\text{Au}(\text{O}_2\text{CMe})(\text{PPh}_3)$ ⁶⁵ were prepared according to published procedures. $[\text{C}_7\text{H}_7][\text{PF}_6]$ was obtained from Cationics Inc., Cleveland, Ohio, and vacuum dried prior to use. Compounds (71) and (72) were prepared by Dr. M.L. Williams.⁶⁶

SECTION APreparation of $[\text{NMe}_4][\text{C}_5(\text{CO}_2\text{Me})_5]$ (33)

To a stirred solution of tetramethyl ammonium bromide (110 mg, 0.714 mmol) in EtOH (30 ml) was added a solution of $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (407 mg, 0.727 mmol) in EtOH (70 ml) giving a precipitate of thallium bromide. After stirring for a further two hours, the solution was filtered and the filtrate evaporated to dryness under vacuum. Crystallisation from MeOH yielded white crystals of $[\text{NMe}_4][\text{C}_5(\text{CO}_2\text{Me})_5]$ (33) (280 mg, 91%), m.p. 181-183°C. (Found: C, 53.44; H, 6.39; N, 3.29; $\text{C}_{19}\text{H}_{27}\text{NO}_{10}$ requires C, 53.14; H, 6.34, N, 3.26%). Infrared (Nujol): $\nu(\text{C=O})$ 1745(sh), 1732(sh), 1722(sh), 1718(sh), 1717s, 1713(sh), 1700(sh), 1697s, 1690(sh), 1676s, 1667(sh), 1657m; other bands 1511(sh), 1499s, 1488s, 1430s, 1392m, 1384m, 1284(sh), 1277s, 1218(sh), 1215s(br), 1207s(br), 1180s, 1080w, 1064s, 1018s, 992s, 968w, 950m, 940m, 868w, 859m, 832m, 800vw, 786m, 778(sh), 761w, 750m, 720vw, 692vw, 640w cm^{-1} . ^1H NMR: $\delta[(\text{CD}_3)_2\text{CO}]$ 3.28 (s, 12H, Me), 3.60 (s, 15H, OMe).

Similarly prepared were: $[\text{NET}_4][\text{C}_5(\text{CO}_2\text{Me})_5]$ (34) (81%), white crystals, m.p. 133-135°C. (Found: C, 57.17;

H, 7.49; N, 2.87; $C_{23}H_{35}NO_{10}$ requires C, 56.90; H, 7.27; N, 2.88%). $[NPr_4][C_5(CO_2Me)_5]$ (35) (88%), white crystals, m.p. 178-181°C. (Found: 59.77; H, 8.39; N, 2.60; $C_{27}H_{43}NO_{10}$ requires C, 59.87; H, 8.00; N, 2.59%). $[NBu_4][C_5(CO_2Me)_5]$ (36) (78%), white crystals, m.p. 226-228°C [lit.¹⁸: m.p. 224°C]. (Found: C, 61.50; H, 8.69; N, 2.37; $C_{31}H_{51}NO_{10}$ requires C, 62.29; H, 8.60; N, 2.34%). $[AsPh_4][C_5(CO_2Me)_5]$ (37) (86%), white crystals, m.p. 155-157°C. (Found: C, 63.66; H, 4.86; $C_{39}H_{35}AsO_{10}$ requires C, 63.42; H, 4.78%). $[N(PPh_3)_2][C_5(CO_2Me)_5]$ (38) (87%), white crystals, m.p. 177-179°C. (Found: C, 68.24; H, 5.16; N, 1.57; $C_{51}H_{45}NO_{10}P_2$ requires C, 68.53; H, 5.07; N, 1.57%).

Preparation of $[C_7H_7][C_5(CO_2Me)_5]$ (39)

To a stirred solution of $[C_7H_7][PF_6]$ (169 mg, 0.716 mmol) in acetone (50 ml) was added $K[C_5(CO_2Me)_5]$ (275 mg, 0.697 mmol), resulting in the immediate formation of a red solution. After stirring for 0.5 h, partial evaporation afforded an orange precipitate, which was collected by filtration and recrystallised from CH_2Cl_2 /hexane to give $[C_7H_7][C_5(CO_2Me)_5]$ (39) (278 mg, 89%), m.p. 143-145°C after turning black at 129-131°C [lit.³³: m.p. 157-159°C (vac.)]. (Found: C, 59.11; H, 5.01; $C_{22}H_{22}O_{10}$ requires C, 59.19; 4.97%). Infrared (Nujol): $\nu(C=O)$ 1725s, 1718s, 1715s, 1702s, 1695s, 1690s, 1685s; other bands 1480s, 1278m, 1215s(br), 1175s, 1080m, 1070m, 1012m, 1000m, 863m, 830m, 791m, 643m cm^{-1} . 1H NMR: $\delta(CDCl_3)$ 3.72 (s, 15H, OMe), 8.30 (s, 7H, C_7H_7). ^{13}C NMR: $\delta(CDCl_3)$ 51.9 (s, OMe), 117.7 (s, C_7), 150.6 (s, C_5).

Solutions of $[C_7H_7][C_5(CO_2Me)_5]$ in polar solvents are orange-red to deep red in colour. The uv-vis spectra of such solutions show the following absorptions [solvent (concentration), λ_{max} , ϵ]: MeOH (2.50mM), 320.4 (1035), 439.2 (235); acetone (0.94mM), 331.9 (1511), 464.9 (683); CH_2Cl_2 (0.31mM), 331.9 (7140), 469.4 (866); MeCN (1.34mM), 307.0 (1887), 448.1 (220); MeCN (2.51mM), 307.7 (1014), 449.0 (354); MeCN (3.14mM), 311.5 (815), 449.0 (368); MeCN (4.48mM), 447.2 (400).

Preparation of $Cu\{C_5(CO_2Me)_5\}(AsPh_3)_2$ (41)

(a) From Cu_2O and $HC_5(CO_2Me)_5$ - 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 min to a suspension of Cu_2O (57 mg, 0.40 mmol) and $AsPh_3$ (440 mg, 1.45 mmol) in MeOH (50 ml). The mixture was stirred at room temperature for 18 h to give a colourless solution which was filtered and evaporated to dryness. Recrystallisation of the white solid from MeOH yielded colourless 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%). Infrared (Nujol): $\nu(C=O)$ 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} . 1H NMR: $\delta(CDCl_3)$ 3.61 (s, 15H, OMe), 7.26 (m, 30H, Ph). Conductivity (acetone) $84.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(b) From CuI and $Tl[C_5(CO_2Me)_5]$ - A mixture of CuI (167 mg, 0.88 mmol) and $AsPh_3$ (269 mg, 0.88 mmol) was heated in refluxing MeCN (30 ml) for 15 h. A solution of $AsPh_3$ (269 mg, 0.88 mmol) in MeCN (15 ml) was then added dropwise

over 5 min, followed immediately by $Tl[C_5(CO_2Me)_5]$ (490 mg, 0.88 mmol), giving a yellow precipitate (TII). The filtered solution was evaporated to dryness. Recrystallisation from MeOH gave white crystals of (41) (651 mg, 74%), m.p. 169-170°C. (Found: C, 59.14; H, 4.35%).

Reaction of $\{Re(CO)_4Cl\}_2$ with $Tl[C_5(CO_2Me)_5]$

To a stirred solution of $Tl[C_5(CO_2Me)_5]$ (260 mg, 0.465 mmol) in MeCN (25 ml) was added a solution of $\{Re(CO)_4Cl\}_2$ (155 mg, 0.232 mmol) in the same solvent (20 ml). After refluxing for 18 h, the reaction mixture was filtered by gravity and the filtrate evaporated to an oil (rotary evaporator). Crystallisation from MeOH/Et₂O gave feathery white crystals of $[Re(CO)_3(NCMe)_3]^- [C_5(CO_2Me)_5]$ (42) (185 mg, 53%), m.p. 92-94°C. (Found: C, 37.43; H, 3.36; N, 5.39; C₂₄H₂₄N₃O₁₃Re requires C, 38.50; H, 3.23; N, 5.61%). Infrared (CH₂Cl₂): $\nu(C\equiv O)$ 2055s, 2043m, 1954s(br) cm⁻¹; Infrared (Nujol): $\nu(C\equiv N)$ 2333w, 2300w; $\nu(C\equiv O)$ 2059s, 1940(sh), 1921s, 1915s, 1900s; $\nu(C=O)$ 1742(sh), 1738m, 1734(sh), 1720s, 1705s, 1696s; other bands 1280m, 1230s, 1225s, 1208s, 1185m, 1176m, 1078(sh), 1070w, 1010w, 1000w, 944w, 842w, 760w, 722w cm⁻¹. ¹H NMR: δ (CDCl₃) 2.38 (s, 9H, MeCN), 3.73 (s, 15H, OMe). FAB MS: 426, -, 18; 394, $[Re(CO)_3(NCMe)_3]^+ \equiv M^+$, 100; 353, $[M - MeCN]^+$, 98; 312, $[M - 2MeCN]^+$, 24; negative ion: 355, $[L]^-$, 100; 341, $[HL - Me]^-$, 4; 309, $[L - OMe - Me]^-$, 9; 251, $[HL - Me - OMe - CO_2Me]^-$, 5.

Preparation of Ru{C₅(CO₂Me)₅}(O₂CMe)(PPh₃)₂ (48)

To a stirred solution of Ru(O₂CMe)₂(PPh₃)₂ (250 mg, 0.336 mmol) in benzene (25 ml) was added HC₅(CO₂Me)₅ (120 mg, 0.337 mmol). After stirring at room temperature overnight, evaporation to dryness gave an orange solid. Addition of MeOH (*ca* 2 ml) initially gave a red-orange solution and after approximately 1 min an orange compound precipitated, which was collected on a sintered glass funnel and washed with cold MeOH (2 x 2 ml). Recrystallisation from CH₂Cl₂/MeOH gave orange crystals of Ru{C₅(CO₂Me)₅}(O₂CMe)(PPh₃)₂ (48) (208 mg, 60%) m.p. (darkens *ca* 170°C) 179–180°C. (Found: C, 61.21; H, 4.66; C₅₃H₄₈O₁₂P₂Ru requires C, 61.21; H, 4.65%). Infrared (Nujol): ν (C=O) 1752(sh), 1743m, 1735(sh), 1731s, 1728(sh), 1720(sh), 1715(sh), 1710s, 1660(sh), 1655(sh), 1640(sh), 1637vs, 1629(sh); other bands 1442s, 1438s, 1417m, 1314m, 1269m, 1222s, 1208s, 1186m, 1183m, 1176m, 1162m, 1099(sh), 1090m, 1070w, 1013w, 1000w, 949w, 890w, 863w, 792w, 749m, 722w, 700m, 685m cm⁻¹. ¹H NMR: δ (CDCl₃) 1.20 (s, 3H, CMe), 2.19 (s, 3H, OMe), 3.19 (s, 3H, OMe), 3.72 (s, 6H, OMe), 3.81 (s, 3H, OMe), 7.24 (m, 30H, Ph). FAB MS: 1040, [M]⁺, 7; 981, [M - O₂CMe]⁺, 10; 778, [M - PPh₃]⁺, 14; 719, [Ru{C₅(CO₂Me)₅}(PPh₃)]⁺, 56; 685, [M - {C₅(CO₂Me)₅}]⁺, 100; 625, [Ru(PPh₃)₂ - H]⁺, 80; 547, [Ru(PPh₃)(PPh₂) - 2H]⁺, 82; 423, [Ru(PPh₃)(O₂CMe)]⁺, 29; 363, [Ru(PPh₃) - H]⁺, 90.

Preparation of {Ru[C₅(CO₂Me)₅](O₂CMe)(PPh₃)₂O (49)}

Solutions of Ru{C₅(CO₂Me)₅}(O₂CMe)(PPh₃)₂ (48) in MeOH change colour from orange to purple over a period of several hours. On one occasion cooling the purple solution (-30°C) afforded purple crystals of {Ru[C₅(CO₂Me)₅](O₂CMe)(PPh₃)₂O (49)} m.p. >150 °C (Found: C, 54.52; H, 4.40; C₇₀H₆₆O₂₅P₂Ru requires C, 53.51; H, 4.23%). Infrared (Nujol) ν (C=O)

1752(sh), 1745m, 1742m, 1734m, 1724m, 1712m, 1708s, 1703(sh), 1636(sh), 1631s, 1624s, 1617s, 1611(sh); other bands 1578m, 1570m, 1556m, 1550m, 1440m, 1418m, 1322s, 1230s, 1208s, 1170s, 1098m, 1090m, 1070w, 1011w, 792w, 753w, 696w cm^{-1} .
 ^1H NMR: δ (CDCl₃) 1.29 (s, 6H, CMe), 2.31 (s, 6H, OMe), 3.68 (s, 12H, OMe), 3.86 (s, 12H, OMe), 7.33-7.44 (m, 30H, Ph).
FAB MS: 1572, [M]⁺, 7; 1217, [M - L]⁺, 11; 735, [RuO-{C₅(CO₂Me)₅}(Ph₃P)]⁺, 100; 719, [Ru{C₅(CO₂Me)₅}(PPh₃)]⁺, 71; 677, [Ru₂{C₅(CO₂Me)₅}(O₂CMe)₂]⁺, 50; 278, [Ph₃PO]⁺, 100; negative ion: 1570, [M - 2H]⁻, 2; 355, [L]⁻, 100.

Reaction of Tl[C₅(CO₂Me)₅] with RuCl(CO)(O₂CMe)(PPh₃)₂

To a stirred solution of Tl[C₅(CO₂Me)₅] (65 mg, 0.116 mmol) in MeCN (10 ml) was added RuCl(CO)(O₂CMe)(PPh₃)₂ (86 mg, 0.115 mmol). After refluxing for ca 1 h, the TlCl which had formed was filtered off, and washed with MeCN (2 x 3 ml). The combined filtrates were evaporated to dryness (rotary evaporator) and then crystallised from CH₂Cl₂/Et₂O to give cream coloured clumps of [Ru(CO)-(O₂CMe)(PPh₃)₂(NCMe)][C₅(CO₂Me)₅] (50) (110 mg, 86%), m.p. 197-200 °C (dec.). (Found: C, 59.17; H, 4.60; N, 1.42; C₅₆H₅₁NO₁₃P₂Ru requires C, 60.65; H, 4.64; N, 1.26%). Infrared (CH₂Cl₂): ν (C≡O) 1986 cm^{-1} ; Infrared (Nujol): ν (C≡O) 1986s; ν (C=O) 1750m, 1725s, 1716s, 1695s, 1687s, 1684s, 1675s; other bands 1587w, 1575w, 1570w, 1492(sh), 1485s, 1437s, 1435s, 1275m(br), 1203s(br), 1174s, 1096m, 1070m, 1015w, 997w, 937w, 835w, 787w, 752m, 708m, 695s cm^{-1} . ^1H NMR: δ (CDCl₃) 0.46 (s, 3H, MeCN), 1.37 (s, 3H, CMe), 3.72 (s, 15H, OMe), 7.47 (m, 30H, Ph). FAB MS: 768, - , 3; 754, [Ru(CO)(O₂CMe)(PPh₃)₂(NCMe)]⁺ ≡ M⁺, 100; 713, [M - MeCN],

51; 685, $[M - \text{MeCN} - \text{CO}]^+$, 5; 653, $[\text{Ru}(\text{CO})(\text{PPh}_3)_2 - \text{H}]^+$, 14; 625, $[\text{Ru}(\text{PPh}_3)_2 - \text{H}]^+$, 36; 547, $[\text{Ru}(\text{PPh}_3)(\text{PPh}_2) - 2\text{H}]^+$, 26; 492, $[M - \text{PPh}_3]^+$, 26; 469, $[\text{Ru}(\text{PPh}_2)_2 - 3\text{H}]^+$, 8; 451, $[M - \text{PPh}_3 - \text{MeCN}]^+$, 49; 439, -, 10; 423, $[\text{Ru}(\text{O}_2\text{CMe})(\text{PPh}_3)]^+$, 65; 392, $[\text{Ru}(\text{PPh}_2)(\text{PPh}) - 3\text{H}]^+$, 10; 379, -, 28; 363, $[\text{Ru}(\text{PPh}_3) - \text{H}]^+$, 94; negative ion: 355, $[\text{L}]^-$, 100; 341, $[\text{HL} - \text{Me}]^-$, 5; 309, $[\text{L} - \text{Me} - \text{OMe}]^-$, 6; 251, $[\text{HL} - \text{Me} - \text{OMe} - \text{CO}_2\text{Me}]^-$, 3.

Preparation of $M(\eta^4-\text{C}_8\text{H}_{12})\{\eta^5-\text{C}_5(\text{CO}_2\text{Me})_5\}$ ($M = \text{Rh}, \text{Ir}$)

(i) $M = \text{Rh}$ - Addition of $\{\text{RhCl}(\eta^4-\text{C}_8\text{H}_{12})\}_2$ (119 mg, 0.24 mmol) to a stirred solution of $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (271 mg, 0.48 mmol) in MeCN (20 ml) resulted in immediate separation of TlCl from a yellow solution. After 3 h stirring the TlCl was filtered off, and washed with MeCN (2 ml). The combined filtrates were evaporated to dryness. Crystallisation of the residue (MeOH, -30°C) afforded orange crystals of $\text{Rh}(\eta^4-\text{C}_8\text{H}_{12})\{\eta^5-\text{C}_5(\text{CO}_2\text{Me})_5\}$ (51) (213 mg, 78%), m.p. 124-126°C. (Found: C, 48.71; H, 4.98; $\text{C}_{23}\text{H}_{27}\text{O}_{10}\text{Rh}$ requires C, 48.78; H, 4.81%). Infrared (Nujol): $\nu(\text{C=O})$ 1770(sh), 1764(sh), 1750(sh), 1742s, 1736s, 1727s, 1718s, 1715(sh), 1705(sh), 1678(sh); other bands 1448s, 1420m, 1412m, 1408(sh), 1390s, 1331m, 1308m, 1304(sh), 1255s, 1228s(br), 1180s, 1075m, 1065m, 1000s, 990s, 980m, 807m, 674(sh), 636m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 1.94-2.33 (m, 8H, CH_2), 3.83 (s, 15H, OMe), 4.43 (s, 4H, CH). FAB MS: 566, M^+ , 100; 535, $[M - \text{OMe}]^+$, 60; 505, $[M - \text{CO}_2\text{Me} - 2\text{H}]^+$, 9; 447, $[M - 2\text{CO}_2\text{Me} - \text{H}]^+$, 28; negative ion: 507, $[M - \text{CO}_2\text{Me}]^-$, 8; 355, $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$, 100. Conductivity (acetone): 10.7 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

(ii) M = Ir - A similar procedure starting from $\{\text{IrCl}(\eta^4\text{-C}_8\text{H}_{12})\}_2$ (92 mg, 0.14 mmol) and $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (152 mg, 0.27 mmol) in MeCN (15 ml) afforded yellow crystals of $\text{Ir}(\eta^4\text{-C}_8\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (52) (128 mg, 72%) m.p. 110-112°C. (Found: C, 42.08; H, 4.16; $\text{C}_{23}\text{H}_{27}\text{IrO}_{10}$ requires C, 42.13; H, 4.15%). Infrared (Nujol): $\nu(\text{C=O})$ 1750(sh), 1745s, 1741(sh), 1730s, 1718s, 1709(sh), 1700(sh); other bands 1410m, 1298(sh), 1263(sh), 1256(sh), 1225vs(br), 1180s, 1170(sh), 1155(sh), 1075m, 998s, 987s, 846(sh), 809m, 632m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 1.92-2.22 (m, 8H, CH_2), 3.82 (s, 15H, OMe), 4.33 (s, 4H, CH).

Reaction of $\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (51) with dppe

The addition of dppe (133 mg, 0.33 mmol) to a stirred solution of $\text{Rh}(\text{C}_8\text{H}_{12})\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (187 mg, 0.33 mmol) in MeOH (15 ml) resulted in an immediate colour change from yellow to orange. The mixture was refluxed for approximately 18 h and then evaporated to dryness (rotary evaporator). Crystallisation (MeOH) gave orange-red crystals of $[\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\text{-}(\text{dppe})]\text{[C}_5(\text{CO}_2\text{Me})_5]$ (53) (233 mg, 73%) m.p. 156-158°C. (Found: C, 60.33; H, 5.43; $\text{C}_{49}\text{H}_{51}\text{O}_{10}\text{P}_2\text{Rh}$ requires C, 61.00; H, 5.33%). Infrared (Nujol): $\nu(\text{C=O})$ 1742m, 1732(sh), 1718s, 1706s, 1700s, 1697s, 1690(sh), 1677(sh), 1655m, 1642m; other bands 1495m, 1490(sh), 1480m, 1437s, 1424m, 1418m, 1265s, 1197s, 1190s, 1175s, 1170s, 1105s, 1065s, 1020m, 709m, 699s, 680m, 677(sh), 645m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.01-2.31 (m, 12H, CH_2), 3.63 (s, 15H, OMe), 4.88 (s, 4H, CH), 7.50 (s, 20H, Ph). FAB MS: 856, $[\text{Rh}(\text{dppe})\{\text{C}_5(\text{CO}_2\text{Me})_5\}]^+$, ~1; 609, $[\text{Rh}(\text{C}_8\text{H}_{12})\text{(dppe)}]^+$, 100; 501, $[\text{Rh}(\text{dppe})]^+$, 77; 211,

$[\text{Rh}(\text{C}_8\text{H}_{12})]^+$, 17; negative ion: 355, $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$, 100.

Conductivity (acetone): 75.5 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Preparation of $\text{Rh}(\text{azb})_2\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (54)

A mixture of $\{\text{RhCl}(\text{azb})_2\}_2$ (150 mg, 0.15 mmol) and $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (167 mg, 0.30 mmol) in MeCN (15 ml) was refluxed for approximately 18 h to give a red-brown solution over an off-white precipitate. The precipitate (TlCl) was filtered off and washed with MeCN (2 ml). The combined filtrates were evaporated to dryness (rotary evaporator). Purification by preparative TLC (acetone/light petroleum 1:1) showed a major product ($R_f = 0.37$) which was crystallised (MeOH/Et₂O) to give red crystals of $\text{Rh}(\text{azb})_2\{\text{C}_5(\text{CO}_2\text{Me})_5\}$ (54) (78 mg, 32%), m.p. 209–210°C (dec.). (Found C, 56.29; H, 4.19; N, 6.60; $\text{C}_{39}\text{H}_{33}\text{N}_4\text{O}_{10}\text{Rh}$ requires C, 57.08; H, 4.05; N, 6.83%). Infrared (Nujol): $\nu(\text{C=O})$ 1750(sh), 1746(sh), 1742s, 1711m, 1707s, 1700s, 1670m, 1660s, 1655(sh), 1649vs, 1645vs, 1640(sh), 1629s, 1625(sh), 1618m; other bands 1595s, 1590(sh), 1582s, 1578s, 1560m, 1558m, 1495m, 1490m, 1420m, 1410m, 1362m, 1322m, 1310s, 1260s, 1242m, 1235m, 1220(sh), 1212s, 1208s, 1200s, 1178s, 1168s, 1160s, 1082m, 1065m, 1045m, 1011m, 772s, 760m, 728m, 718m, 685m, 655m cm^{-1} . ¹H NMR: $\delta(\text{CDCl}_3)$ 3.32 (s, 6H, OMe), 3.69 (s, 3H, OMe), 3.75 (s, 6H, OMe), 7.0–8.3 (m, 18H, Ph).

Reaction between $\{\text{RhCl}(\text{CO})_2\}_2$ and $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$

To a stirred solution of $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (400 mg, 0.72 mmol) in MeOH (40 ml) was added $\{\text{RhCl}(\text{CO})_2\}_2$ (150 mg, 0.38 mmol), to give a yellow solution. The mixture was refluxed for approximately 130 h to give a grey-black precipitate

and a red-brown solution. The precipitate was filtered off and washed with MeOH (5 ml). The combined filtrates were evaporated to dryness (rotary evaporator). Preparative TLC of a CH_2Cl_2 extract of the residue (acetone/light petroleum 3:2) separated the major product ($R_f = 0.88$) from a large number of minor unidentified components. Crystallisation from MeOH gave orange crystals of $\text{Rh}\{\eta^4-\text{C}_5\text{H}_3-(\text{CO}_2\text{Me})_3\}\{\eta^5-\text{C}_5\text{H}_2(\text{CO}_2\text{Me})_3\}$ (56) (74 mg, 18%), m.p. 134–136°C. (Found: C, 44.94; H, 4.03; M (mass spectrometry), 582; $\text{C}_{22}\text{H}_{23}\text{O}_{12}\text{Rh}$ requires C, 45.38; H, 3.98%; M, 582). Infrared (Nujol): $\nu(\text{C=O})$ 1750s, 1742s, 1735s, 1725s, 1717s, 1713s, 1708s, 1702(sh), 1690(sh), 1678(sh); other bands 1440s, 1426m, 1411m, 1407(sh), 1350m, 1340m, 1332m, 1312s, 1297m, 1280m, 1257s, 1246(sh), 1205s, 1185s, 1170m, 1162(sh), 1140s, 1128m, 1074s, 1037(sh), 1033m, 1028m, 1000m, 960m, 778m, 770m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.55 (s, 3H, OMe), 3.70 (s, 6H, OMe), 3.81 (s, 6H, OMe), 3.91 (s, 3H, OMe), 4.19 (s, 1H, CH), 5.64 (s, 2H, CH), 5.98 (s, 2H, CH). FAB MS: 582, $[\text{M}]^+$, 4; 580, $[\text{M} - 2\text{H}]^+$, 4; 551, $[\text{M} - \text{OMe}]^+$, 14; 522, $[\text{M} - \text{CO}_2\text{Me} - \text{H}]^+$, 100; 508, $[\text{M} - \text{CO}_2\text{Me} - \text{Me}]^+$, 6; 464, $[\text{M} - 2\text{CO}_2\text{Me}]^+$, 9; 289, -, 5; 231, -, 8.

Reactions between $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ and $\text{MCl}(\text{CO})(\text{PPh}_3)_2$ (M = Rh, Ir)

(i) M = Rh – Addition of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (365 mg, 0.53 mmol) to a stirred solution of $\text{Tl}[\text{C}_5(\text{CO}_2\text{Me})_5]$ (296 mg, 0.53 mmol) in MeCN (35 ml) caused immediate separation of a white precipitate. After 1 h this was filtered off and washed with MeCN (5 ml). Evaporation of the combined filtrates, dissolution of the residue in hot MeOH (3 ml), and cooling the filtered solution gave yellow crystals of $[\text{Rh}(\text{CO})(\text{NCMe})-$

$(PPh_3)_2] [C_5(CO_2Me)_5]$ (57) (418 mg, 75%), m.p. 170–172°C.
 (Found: C, 61.78; H, 4.59; N, 1.33; $C_{54}H_{48}NO_{11}P_2Rh$
 requires C, 61.66; H, 4.60; N, 1.33%). Infrared (CH_2Cl_2):
 $\nu(C\equiv O)$ 2020 cm^{-1} ; Infrared (Nujol): $\nu(C\equiv N)$ 2302w; $\nu(C\equiv O)$
 2016s, 1970w; $\nu(C=O)$ 1741m, 1738s, 1725s, 1718s, 1714(sh),
 1708(sh), 1702(sh), 1696s, 1691s, 1687(sh), 1680(sh),
 1668(sh), 1655(sh); other bands 1495(sh), 1490m, 1482m,
 1478m, 1441s, 1439s, 1275(sh), 1272m, 1209s, 1202s, 1185s,
 1180s, 1173s, 1165s, 1155s, 1135(sh), 1100s, 1080(sh),
 1075m, 1065m, 710m, 705(sh), 696s, 690m cm^{-1} . 1H NMR:
 $\delta(CDCl_3)$ 1.20 (s, 3H, MeCN), 3.58 (s, 15H, OMe), 7.38 (m,
 30H, Ph). FAB MS: 696, $[Rh(CO)(NCMe)(PPh_3)_2]^+ \equiv M^+$, 2; 655,
 $[M - MeCN]^+$, 54; 627, $[Rh(PPh_3)_2]^+$, 100; 550, $[Rh(PPh_2) -$
 $(PPh_3)]^+$, 11; 393, $[Rh(CO)(PPh_3)]^+$, 4; 288, $[Rh(PPh_2)]^+$,

33. Conductivity (acetone): $86.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(ii) M = Ir – A similar reaction between $Tl[C_5(CO_2Me)_5]$ (212 mg, 0.38 mmol) and $IrCl(CO)(PPh_3)_2$ (296 mg, 0.38 mmol) in MeCN (25 ml) afforded yellow crystals of $[Ir(CO)(NCMe) -$
 $(PPh_3)_2] [C_5(CO_2Me)_5]$ (58) (365 mg, 84%), m.p. 175–176°C
 (dec.). (Found: C, 56.65; H, 4.24; N, 1.25; $C_{54}H_{48}IrNO_{11}P_2$
 requires C, 56.84; H, 4.24; N, 1.23%). Infrared (CH_2Cl_2):
 $\nu(C\equiv O)$ 2006 cm^{-1} ; Infrared (Nujol): $\nu(C\equiv N)$ 2300w; $\nu(C\equiv O)$
 2000vs, 1955w; $\nu(C=O)$ 1747m, 1742(sh), 1740s, 1727(sh),
 1723vs, 1719vs, 1715vs, 1705s, 1695s, 1690vs, 1687s, 1680(sh),
 1675s, 1670(sh), 1665(sh), 1652m, 1645m, 1640(sh); other bands
 1495m, 1485s, 1480s, 1435vs, 1417m, 1398m, 1394m, 1269s,
 1207(sh), 1202vs, 1197s, 1185s, 1180s, 1170s, 1160s, 1152(sh),
 1098s, 1071m, 1061m, 1013m, 999m, 750m, 710m, 701m, 692s,
 685m cm^{-1} . 1H NMR: $\delta(CDCl_3)$ 1.25 (s, 3H, MeCN), 3.62 (s,
 15H, OMe), 7.43 (m, 30H, Ph). FAB MS: 786, $[Ir(CO)(NCMe) -$

$(\text{PPh}_3)_2]^+ \equiv M^+$, 12; 745, $[M - \text{MeCN}]^+$, 100; 715, $[\text{Ir}(\text{PPh}_3)_2 - 2\text{H}]^+$, 69; 483, $[\text{Ir}(\text{CO})(\text{PPh}_3)]^+$, 25; 453, $[\text{Ir}(\text{PPh}_3) - 2\text{H}]^+$, 25; 375, $[\text{Ir}(\text{PPh}_2) - 3\text{H}]^+$, 50.

Conductivity (acetone): 79.7, (MeCN) $94.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Reactions of $[\text{Rh}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$

(i) With benzo[*h*]quinoline - Benzo[*h*]quinoline

(19 mg, 0.11 mmol) was added to a solution of $[\text{Rh}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (87 mg, 0.083 mmol) in CHCl_3 (5 ml). The mixture was stirred at room temperature for 1 h, then the solvent was removed and the residue crystallised ($\text{CHCl}_3/\text{Et}_2\text{O}$) to give pale yellow crystals of $[\text{Rh}(\text{CO})(\text{bqH})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (59) (79 mg, 80%), m.p. 170°C (dec.). (Found: C, 64.94; H, 4.51; N, 1.20; $\text{C}_{6.5}\text{H}_{5.4}\text{NO}_{1.1}\text{P}_2\text{Rh}$ requires C, 65.61; H, 4.57; N, 1.18%).

Infrared (CH_2Cl_2): $\nu(\text{C}\equiv\text{O})$ 2006 cm^{-1} ; Infrared (Nujol): $\nu(\text{C}\equiv\text{O})$ 2008vs, 1965w; $\nu(\text{C}=\text{O})$ 1740(sh), 1725s, 1722(sh), 1711s, 1707s, 1702(sh), 1695s, 1690s, 1688(sh), 1675s; other bands 1495(sh), 1482s, 1438s, 1425(sh), 1403(sh), 1397m, 1282m, 1275(sh), 1205vs(br), 1179(sh), 1175s, 1145(sh), 1097m, 1072(sh), 1065m, 1052(sh), 1011m, 760(sh), 754s, 747(sh), 741m, 709m, 695s, 622m cm^{-1} .

^1H NMR: $\delta(\text{CDCl}_3)$ 3.60 (s, 15H, OMe), 6.65-7.90 (m, 39H, Ph + bq). FAB MS: 834, $[\text{Rh}(\text{CO})(\text{bqH})(\text{PPh}_3)_2]^+ \equiv M^+$, 13; 655, $[M - \text{bqH}]^+$, 42; 627, $[\text{Rh}(\text{PPh}_3)_2]^+$, 100; 550, $[\text{Rh}(\text{PPh}_2)(\text{PPh}_3)]^+$, 16; 544, $[\text{Rh}(\text{bqH})(\text{PPh}_3)]^+$, 17; 393, $[\text{Rh}(\text{CO})(\text{PPh}_3)]^+$, 7; 288, $[\text{Rh}(\text{PPh}_2)]^+$, 72. Conductivity (acetone): $87.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(ii) With 1,10-phenanthroline - A similar procedure was carried out with 1,10-phenanthroline (24 mg, 0.13 mmol) and $[\text{Rh}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (129 mg, 0.12 mmol) in CHCl_3 (12 ml). There was an immediate colour change from yellow to orange-yellow. After 18 h, evaporation and crystallisation of the residue ($\text{CHCl}_3/\text{Et}_2\text{O}$) gave pale orange crystals of $[\text{Rh}(\text{CO})(\text{phen})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5] \cdot \text{CHCl}_3$ (60) (96 mg, 61%), m.p. 173°C (dec.). (Found: C, 59.08; H, 4.13; N, 2.14; $\text{C}_{64}\text{H}_{53}\text{N}_2\text{O}_{11}\text{P}_2\text{Rh} \cdot \text{CHCl}_3$ requires C, 59.58; H, 4.15; N, 2.13%). Infrared (CH_2Cl_2): $\nu(\text{C}\equiv\text{O})$ 1947s cm^{-1} ; Infrared (Nujol): $\nu(\text{C}\equiv\text{O})$ 1931vs, 1885w; $\nu(\text{C}=\text{O})$ 1745(sh), 1739(sh), 1728s, 1721(sh), 1705m, 1701(sh), 1698m, 1693m, 1691(sh), 1685(sh), 1681m, 1678m; other bands 1482m, 1441m, 1438m, 1429(sh), 1421m, 1212s, 1178m, 1167(sh), 1095m, 755m, 748m, 708m, 698m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.72 (s, 15H, OMe), 7.27 (s, 1H, CHCl_3), 7.17-8.98 (m, 38H, Ph + phen). FAB MS: 573, $[\text{Rh}(\text{CO})(\text{phen})(\text{PPh}_3)]^+$, 100; 545, $[\text{Rh}(\text{phen})-(\text{PPh}_3)]^+$, 33; 283, $[\text{Rh}(\text{phen})]^+$, 69; 154, -, 53. Conductivity (acetone): 103 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Reactions between $\text{HC}_5(\text{CO}_2\text{Me})_5$ and $\text{Rh}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2$

(i) In benzene - $\text{HC}_5(\text{CO}_2\text{Me})_5$ (56 mg, 0.157 mmol) was added to a stirred solution of $\text{Rh}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2$ (112 mg, 0.157 mmol) in benzene (20 ml) immediately forming a yellow precipitate. After stirring for 30 min the solid was collected, washed with light petroleum, and dried, to give $\text{Rh}[\text{C}_5(\text{CO}_2\text{Me})_5](\text{CO})(\text{PPh}_3)_2$ (63) (123 mg, 78%), m.p. 180-182°C after darkening at 116-118°C. (Found: C, 61.54; H, 4.60; N, <0.05; $\text{C}_{52}\text{H}_{45}\text{O}_{11}\text{P}_2\text{Rh}$ requires C, 61.79; H, 4.49; N, 0.0%).

Infrared (Nujol): ν (C≡O) 1970s, 1925w; ν (C=O) 1745(sh), 1740(sh), 1735s, 1727m, 1715s, 1708s, 1701m, 1698s, 1693s, 1682, 1675s, 1671(sh), 1667(sh), 1653w; other bands 1442s, 1438s, 1295m, 1282m, 1278m, 1198s, 1175s, 1170s, 1167(sh), 1096s, 1000m, 979m, 940(sh), 760m, 746m, 721m, 706m, 692s cm^{-1} . FAB MS: 655, $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]^+$, 17; 627, $[\text{Rh}(\text{PPh}_3)_2]^+$, 32; 550, $[\text{Rh}(\text{PPh}_2)(\text{PPh}_3)]^+$, 7; 393, $[\text{Rh}(\text{CO})(\text{PPh}_3)]^+$, 4; 278, $[\text{OPPh}_3]^+$, 20; negative ion: 355, $[\text{L}]^-$, 100; 341, $[\text{HL} - \text{Me}]^-$, 3; 309, $[\text{L} - \text{Me} - \text{OMe}]^-$, 5; 251, $[\text{HL} - \text{Me} - \text{OMe} - \text{CO}_2\text{Me}]^-$, 3.

(ii) In acetonitrile - A solution of $\text{HC}_5(\text{CO}_2\text{Me})_5$ (47 mg, 0.132 mmol) and $\text{Rh}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2$ (94 mg, 0.132 mmol) in MeCN (15 ml) was stirred at room temperature for 6 h. Evaporation of the solvent gave a yellow solid, which was recrystallised (MeOH, -30°C) to give yellow crystals of $[\text{Rh}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2][\text{C}_5(\text{CO}_2\text{Me})_5]$ (73 mg, 53%) identical (m.p., IR, NMR) with the salt (57) prepared as described above.

SECTION BPreparation of HC₅Me(CO₂Me)₄

(a) C₅Me(CO₂Me)₅ (64) - Silver(I) oxide (3.0 g, 12.95 mmol) was added to a solution of HC₅(CO₂Me)₅ (3.0 g, 8.42 mmol) in CH₂Cl₂ (10 ml), followed by iodomethane (10 ml) in the same solvent (20 ml), giving an olive-green precipitate. After stirring overnight at room temperature, the reaction mixture was filtered, and the solid residue was washed with CH₂Cl₂ (2 x 5 ml). Evaporation of the combined filtrates and crystallisation (MeOH) gave white crystals of C₅Me(CO₂Me)₅ (64) (2.7 g, 87%), m.p. 99-100°C (lit.¹⁸: m.p. 102-103°C). Infrared (Nujol): ν (C=O) 1768(sh), 1755s, 1750s, 1745s, 1738s, 1730s, 1726(sh), 1722(sh), 1630m; other bands 1586m, 1443s, 1436s, 1353s, 1332s, 1300m, 1258s, 1235s(br), 1215s, 1178m, 1167m, 1087m, 1082(sh), 1071m, 1020m, 1000m, 980m, 967m, 937w, 927w, 899w, 858m, 847m, 799m, 788w, 780w, 768w, 745w, 719w, 678w cm⁻¹. ¹H NMR: δ (CDCl₃) 1.70 (s, 3H, Me), 3.67 (s, 3H, OMe), 3.83 (s, 6H, OMe), 3.88 (s, 6H, OMe). FAB MS: 371, [M + H]⁺, 45; 339, [M - OMe]⁺, 62; 295, [M - CO₂Me - CH₄]⁺, 100; 249, [M - CO₂Me - 2OMe]⁺, 54; negative ion: 370, [M]⁻, 24; 355, [M - Me]⁻, 19; 339, [M - OMe]⁻, 4; 311, [M - CO₂Me]⁻, 100; 265, [M - CO₂Me - OMe - Me]⁻, 11.

(b) Na[C₅Me(CO₂Me)₄] (65) - The diene C₅Me(CO₂Me)₅ (2.0 g, 5.4 mmol) was added to a sodium methoxide solution [sodium (500 mg) dissolved in MeOH (25 ml)] and the mixture was heated at reflux point for 3 h. Evaporation to dryness then gave Na[C₅Me(CO₂Me)₄] (65) as a white solid, which was used directly in the next step. Infrared (Nujol) [of a

recrystallised (MeOH) sample]: ν (C=O) 1708m, 1704s, 1699s, 1695s, 1687s, 1679m, 1662s, 1656s, 1652s, 1646s, 1635s, 1630s; other bands 1403m, 1340m, 1336m, 1293s, 1290s, 1281s, 1278s, 1205m, 1190m, 1180m, 1172m, 1168m, 1100m, 1009w, 938w, 810m, 788m, 781m, 721m cm^{-1} . FAB MS: 1025, $[\text{Na}_4\text{L}_3]^+$, <1; 691, $[\text{Na}_3\text{L}_2]^+$, 11; 469, -, 59; 407, -, 59; 357, $[\text{Na}_2\text{L}]^+$, 100; 335, $[\text{M} + \text{H}]^+$, 37; 334, $[\text{M}]^+$, 37; 303, $[\text{M} - \text{OMe}]^+$, 78; 249, $[\text{L} - 2\text{OMe}]^+$, 33; 207, $[\text{HC}_5(\text{CO})(\text{CO}_2\text{Me})_2]^+$, 41; negative ion: 645, $[\text{NaL}_2]^-$, 6; 311, $[\text{L}]^-$, 100; 297, $[\text{HL} - \text{Me}]^-$, 4; 281, $[\text{L} - 2\text{Me}]^-$, 4; 265, $[\text{L} - \text{OMe} - \text{Me}]^-$, 20; 253, $[\text{HL} - \text{CO}_2\text{Me}]^-$, 6; 207, $[\text{HC}_5(\text{CO})(\text{CO}_2\text{Me})_2]^-$, 8.

(c) $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ (66) - $\text{Na}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]$ prepared as above was dissolved in cold water (40 ml). Concentrated hydrochloric acid was added dropwise until precipitation of the white solid was complete. This was collected and dried to give $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ (66) (1.60 g, 95%). Recrystallisation (twice) from hot Et_2O gave white needles, m.p. 86°C (lit. 18 m.p. 86°C). (Found: C, 53.74; H, 5.06; $\text{C}_{14}\text{H}_{16}\text{O}_8$ requires C, 53.85; H, 5.16%). Infrared (Nujol): ν (C=O) 1740s, 1728m, 1709vs, 1600vs(br); other bands 1402m, 1278m, 1268m, 1240s, 1212s, 1188s, 1178s, 1125m, 1099s, 1078s, 1046s cm^{-1} . ^1H NMR: δ (D_2O) 2.43 (s, 3H, Me), 3.86 (s, 6H, OMe), 3.88 (s, 6H, OMe); δ (CDCl_3) 2.35-2.65 (4 x s, 3H, Me), 3.7-4.1 (9 x s, 12H, OMe), 20.01 (s, 1H, acidic H). ^{13}C NMR: δ (D_2O , internal reference Bu^tOH) 14.13 (s, Me), 53.15 (s, OMe), 53.99 (s, OMe), 71.38, 119.6, 132.6 (s, 3x ring C), 171.2 (s, CO_2Me), 172.3 (s, CO_2Me). FAB MS: 312, $[\text{M}]^+$, 22; 281, $[\text{M} - \text{OMe}]^+$, 64; 248, -, 79; 185, -, 28; 115, -, 45; 93, -, 100; negative ion: 311, $[\text{L}]^-$, 100; 297, $[\text{HL} - \text{Me}]^-$, 20; 265, $[\text{L} - \text{OMe} - \text{Me}]^-$, 26; 253, $[\text{HL} - \text{CO}_2\text{Me}]^-$, 32; 207, $[\text{HC}_5(\text{CO})(\text{CO}_2\text{Me})_2]^-$, 12.

Preparation of metal complexes

(a) Tl[C₅Me(CO₂Me)₄]₂ (67) - Solid Tl₂CO₃ (98 mg, 0.21 mmol) was added to a solution of HC₅Me(CO₂Me)₄ (129 mg, 0.413 mmol) in water (25 ml); the reaction mixture, protected from light, was stirred for 3 h. Evaporation of the filtered solution and crystallisation (MeOH) gave white crystals of Tl[C₅Me(CO₂Me)₄]₂ (67) (103 mg, 48%), m.p. 143–145°C. (Found: C, 32.61; H, 3.25; C₁₄H₁₅O₈Tl requires C, 32.61; H, 2.93%). Infrared (Nujol): ν (C=O) 1744s, 1687s, 1680s, 1660s, 1654s, 1648s, 1642s, 1638s; other bands 1420m, 1404m, 1285s, 1252m, 1211s(br), 1195s, 1180s, 1170s, 1096s, 1080s, 1021m, 1009m, 940m, 789m, 783m cm⁻¹. ¹H NMR: δ (D₂O) 2.43 (s, 3H, Me), 3.86 (s, 6H, OMe), 3.88 (s, 6H, OMe). FAB MS: 909, -, 4; 721, [Tl₂L]⁺, 22; 485, [M - OMe]⁺, 8; 441, -, 10; 297, [HL - Me]⁺, 3; 205, [Tl]⁺, 100; negative ion: 827, [TlL₂]⁻, 1; 311, [L]⁻, 100; 297, [HL - Me]⁻, 11; 281, [L - 2Me]⁻, 11; 265, [L - OMe - Me]⁻, 35; 253, [HL - CO₂Me]⁻, 9; 207, [HC₅(CO)(CO₂Me)₂]⁻, 13.

(b) Mn[C₅Me(CO₂Me)₄]₂ (68) - Solid Mn(O₂CMe)₂(OH₂)₄ (30 mg, 0.122 mmol) was added to a solution of HC₅Me(CO₂Me)₄ (98 mg, 0.314 mmol) in MeOH (15 ml). After stirring overnight, evaporation of the filtered solution gave a white solid, which was crystallised (MeOH/Et₂O, -30°C) to give Mn[C₅Me(CO₂Me)₄]₂·2H₂O (68) (64 mg, 77%) as a white powder, m.p. 210°C (dec.). (Found: C, 46.43; H, 4.81; C₂₈H₃₀MnO₁₆·2H₂O requires C, 47.13; H, 4.80%). Infrared (Nujol): ν (OH) 3460m(br); ν (C=O) 1725s, 1718s, 1690s, 1682s, 1676s, 1672s, 1660s, 1652s, 1649s, 1637s, 1629s; other bands 1309s, 1281m, 1212s, 1185m(br), 1099s, 1082m cm⁻¹. FAB MS: 1720,

$[\text{Mn}_3\text{L}_5]^+$, 2; 1043, $[\text{Mn}_2\text{L}_3]^+$, 20; 763, -, 24; 677, $[\text{M}]^+$, 18; 646, $[\text{M} - \text{OMe}]^+$, 85; 587, $[\text{M} - \text{CO}_2\text{Me} - \text{OMe}]^+$, 16; 556, $[\text{M} - \text{CO}_2\text{Me} - 2\text{OMe}]^+$, 10; 366, $[\text{MnL}]^+$, 92; 352, $[\text{Mn}(\text{HL}) - \text{Me}]^+$, 10; 336, $[\text{MnL} - 2\text{Me}]^+$, 83; 307, $[\text{MnL} - \text{CO}_2\text{Me}]^+$, 7; 249, $[\text{Mn}(\text{HL}) - 2\text{CO}_2\text{Me}]^+$, 100; negative ion: 1664, -, 3; 1505, -, 4; 988, $[\text{MnL}_3]^-$, 34; 830, -, 35; 723, -, 10; 311, $[\text{L}]^-$, 100; 265, $[\text{L} - \text{OMe} - \text{Me}]^-$, 25; 207, $[\text{HC}_5(\text{CO})(\text{CO}_2\text{Me})_2]^-$, 6.

(c) $\text{Cu}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]_2$ (69)-Similarly, $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ (75 mg, 0.24 mmol) was added to $\text{Cu}(\text{O}_2\text{CMe})_2(\text{OH}_2)_2$ (24 mg, 0.06 mmol) in MeOH (6 ml), giving an immediate colour change from blue-green to red-orange. The mixture was stirred at room temperature for 45 min and evaporated to dryness. The residue was then crystallised (MeOH) to give red-brown crystals of $\text{Cu}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]_2 \cdot 2\text{MeOH}$ (69) (52 mg, 63%), m.p. ca 185°C. (Found: C, 47.59; H, 4.54; $\text{C}_{28}\text{H}_{30}\text{CuO}_{16} \cdot 2\text{MeOH}$ requires C, 48.03; H, 5.11%). Infrared (Nujol): $\nu(\text{OH})$ 3250m(br); $\nu(\text{C=O})$ 1732m, 1705(sh), 1695s, 1660(sh), 1647s, 1608s, 1590s, 1585(sh); other bands 1420m, 1405m, 1328s, 1320s, 1265s, 1250s, 1208s, 1200(sh), 1180s, 1103m, 1083m, 1008m, 1004m cm^{-1} . FAB MS: 685, $[\text{M}]^+$, 2; 654, $[\text{M} - \text{OMe}]^+$, 4; 592, $[\text{M} - 3\text{OMe}]^+$, 100; 374, $[\text{CuL}]^+$, 5; 343, $[\text{CuL} - \text{OMe}]^+$, 19; 249, $[\text{L} - 2\text{OMe}]^+$, 34; negative ion: 685, $[\text{M}]^-$, 9; 644, -, 1; 525, -, 2; 437, -, 3; 311, $[\text{L}]^-$, 100; 265, $[\text{L} - \text{OMe} - \text{Me}]^-$, 16; 253, $[\text{HL} - \text{CO}_2\text{Me}]^-$, 5.

(d) $\text{Rh}(\eta^4-\text{C}_8\text{H}_{12})\{\eta^5-\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}$ (70)-Addition of $\{\text{RhCl}(\eta^4-\text{C}_8\text{H}_{12})\}_2$ (75 mg, 0.152 mmol) to a solution of $\text{Tl}[\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4]$ (157 mg, 0.304 mmol) in MeCN (20 ml) gave an immediate precipitate (TlCl). After stirring overnight,

evaporation of the filtered solution and crystallisation of the residue (MeOH, -30°C) afforded orange crystals of Rh(η^4 -C₈H₁₂) $\{\eta^5$ -C₅Me(CO₂Me)₄ $\}$ (70) (106 mg, 67%), m.p. 100-102°C. (Found: C, 50.55; H, 5.14; C₂₂H₂₇O₈Rh requires C, 50.59; H, 5.21%). Infrared (Nujol): ν (C=O) 1763(sh), 1752s, 1733s, 1718s, 1713s, 1709(sh), 1705(sh), 1693(sh), 1688(sh), 1680(sh), 1674(sh), 1660(sh), 1655m, 1650m, 1643m, 1638m, 1635(sh), 1630(sh), 1622(sh); other bands 1410s, 1405(sh), 1395s, 1337m, 1332m, 1307m, 1289(sh), 1280s, 1249(sh), 1232s, 1227s, 1217s, 1208s, 1191(sh), 1188s, 1180(sh), 1172s, 1096s, 1085m, 1072s, 1044s, 1007m, 989m, 980m, 880m, 872(sh), 823m, 786(sh), 781(sh), 779m, 720m cm⁻¹. ¹H NMR: δ (CDCl₃) 1.94-2.35 (m, 11H, 4CH₂ + Me). 3.80 (s, 6H, OMe), 3.84 (s, 6H, OMe), 4.18 (s, 4H, CH). FAB MS: 522, [M]⁺, 100; 491, [M - OMe]⁺, 26; 461, [M - CO₂Me - 2H]⁺, 19; 404, [M - 2CO₂Me]⁺, 37; negative ion: 522, [M]⁻, 1; 520, [M - 2H]⁻, 3; 507, [M - Me]⁻, 8; 463, [M - CO₂Me]⁻, 16; 432, [M - CO₂Me - OMe]⁻, 4; 311, [L]⁻, 100; 253, [HL - CO₂Me]⁻, 60.

(e) Cu{C₅Me(CO₂Me)₄} (PPh₃)₂ (73) - A solution of HC₅Me(CO₂Me)₄ (49 mg, 0.157 mmol) in MeOH (10 ml) was added dropwise over a period of 15 min to a suspension of Cu₂O (13 mg, 0.091 mmol) and PPh₃ (82 mg, 0.313 mmol) in MeOH (15 ml). The reaction mixture was stirred at room temperature for 18 h, and then filtered. After washing the residue (MeOH, 2 ml), the combined filtrates were evaporated to dryness (rotary evaporator). Recrystallisation of the white solid (MeOH) afforded colourless crystals of Cu{C₅Me(CO₂Me)₄} (PPh₃)₂ (73) (85 mg, 60%) m.p. 210-212°C.

(Found: C, 66.64; H, 5.01; $C_{50}H_{45}CuO_8P_2$ requires C, 66.67; H, 5.04%). Infrared (Nujol): $\nu(C=O)$ 1740(sh), 1735(sh), 1731m, 1725m, 1722(sh), 1706m, 1701(sh), 1690s, 1687m, 1670(sh), 1660s, 1654s, 1649s, 1640(sh), 1627(sh), 1619m, 1604m; other bands 1589m, 1575m, 1573(sh), 1485s, 1479s, 1439s, 1425m, 1421m, 1403m, 1314(sh), 1292s, 1257s, 1205(sh), 1191s, 1173s, 1163(sh), 1095s, 1075m, 755m, 747m, 722m, 702(sh), 697s, 690(sh) cm^{-1} . 1H NMR: $\delta(CDCl_3)$ 2.34 (s, 3H, Me), 3.52 (s, 6H, OMe), 3.55 (s, 6H, OMe), 7.23 (m, 3OH, Ph). FAB MS: 961, $[M + Cu]^+$, <1; 676, -, 12; 603, $[M - C_5(CO_2Me)_4]^+$, 9; 588, $[M - L]^+$, 100; 510, $[M - L - C_6H_6]^+$, 3; 326, $[Cu(PPh_3)]^+$, 52; 262, $[PPh_3]^+$, 10; negative ion: 311, $[L]^-$, 100; 265, $[L - OMe - Me]^-$, 6.

(f) $\underline{Ag\{C_5Me(CO_2Me)_4\}(PPh_3)}$ (74) - A mixture of $HC_5Me - (CO_2Me)_4$ (153 mg, 0.490 mmol), silver acetate (82 mg, 0.490 mmol) and PPh_3 (128 mg, 0.488 mmol) in MeOH (25 ml) was stirred at room temperature in the dark for 18 h. After filtration and evaporation to dryness (rotary evaporator), crystallisation (MeOH) afforded $\underline{Ag\{C_5Me(CO_2Me)_4\}(PPh_3)}$ (74) as a white powder (153 mg, 46%) m.p. 170°C (dec.). (Found: C, 56.47; H, 4.42; $C_{32}H_{30}AgO_8P$ requires C, 56.40; H, 4.44%). Infrared (Nujol): $\nu(C=O)$ 1710s, 1707s, 1701(sh), 1697(sh), 1691s, 1686s, 1680(sh), 1678(sh), 1661s, 1651(sh), 1649s, 1639(sh), 1625(sh), 1620(sh); other bands 1504(sh), 1495(sh), 1491m, 1485s, 1480s, 1420m, 1411m, 1405m, 1351m, 1311(sh), 1289(sh), 1275s, 1255s, 1210s, 1195s, 1190s, 1182s, 1170s, 1158s, 1096s, 1071s, 1004m, 845m, 799m, 785(sh), 780m, 762(sh), 756m, 749m, 722m, 711m, 699s, 690(sh) cm^{-1} . 1H NMR: $\delta(CDCl_3)$ 2.48 (s, 3H, Me), 3.71 (s, 6H, OMe), 3.77

(s, 6H, OMe), 7.42 (m, 15H, Ph). FAB MS: 1049, $[\text{Ag}_2(\text{PPh}_3)_2 - (\text{L})]^+$, 2; 680, $[\text{M}]^+$, 7; 649, $[\text{M} - \text{OMe}]^+$, 7; 631, $[\text{Ag}(\text{PPh}_3)_2]^+$, 54; 369, $[\text{Ag}(\text{PPh}_3)]^+$, 100; negative ion: 311, $[\text{L}]^-$, 100; 265, $[\text{L} - \text{OMe} - \text{Me}]^-$, 4.

(g) $\text{Au}\{\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)$ (75)-To a stirred solution of $\text{HC}_5\text{Me}(\text{CO}_2\text{Me})_4$ (87 mg, 0.279 mmol) in MeOH (10 ml) was added $\text{Au}(\text{O}_2\text{CMe})(\text{PPh}_3)$ (144 mg, 0.278 mmol). After stirring at room temperature for 18 h in the dark, the mixture was filtered. After washing the residue (MeOH), the combined filtrates were evaporated to dryness (rotary evaporator) to give a pink solid; crystallisation (MeOH) gave colourless crystals of $\text{Au}\{\text{C}_5\text{Me}(\text{CO}_2\text{Me})_4\}(\text{PPh}_3)$ (75) (53 mg, 37%), m.p. 157-159°C. (Found: C, 49.25; H, 3.89; $\text{C}_{32}\text{H}_{30}\text{AuO}_8\text{P}$ requires C, 49.88; H, 3.92%). Infrared (Nujol): $\nu(\text{C=O})$ 1735(sh), 1731m, 1724m, 1717s, 1712s, 1707vs, 1704(sh), 1699(sh), 1696(sh), 1652m, 1646m, 1641m, 1635m, 1627(sh); other bands 1496(sh), 1480m, 1437s, 1401m, 1290m, 1280s, 1274s, 1269(sh), 1255(sh), 1205m, 1188m, 1179m, 1162m, 1158m, 1101s, 1080m, 1070(sh), 750m, 712m, 691m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.64 (s, 3H, Me), 3.76 (s, 6H, OMe), 3.80 (s, 6H, OMe), 7.43-7.50 (m, 15H, Ph). FAB MS: 1229, $[\text{Au}_2(\text{PPh}_3)_2(\text{L})]^+$, 1; 770 $[\text{M}]^+$, 3; 739, $[\text{M} - \text{OMe}]^+$, 4; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 41; 644, $[\text{Au}(\text{PPh}_2)(\text{PPh}_3)]^+$, 2; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100.

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Note: The chemistry of $\text{HC}_5(\text{CO}_2\text{Me})_5$ and related molecules has been the subject of a recent review.^{6,7}

CHAPTER TWO

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GOLD IN MIXED-METAL CLUSTERS	
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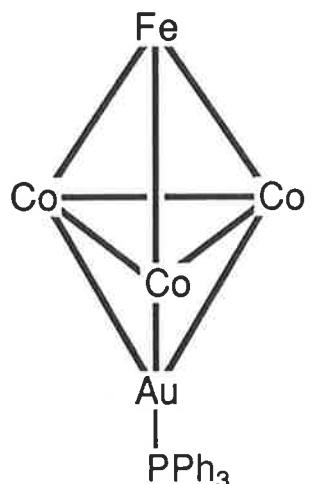
INTRODUCTION

Heteronuclear transition metal cluster compounds have attracted great interest for many years,¹ but it is only since the start of the 1980's that mixed-metal cluster compounds containing one or more Group IB metal atoms have attracted much attention. A large number of such compounds have now been described, especially those containing gold-transition metal bonds. Bimetallic clusters of gold were reviewed by Braunstein and Rosé in 1985,² while Hall and Mingos reviewed both homo- and heteronuclear gold clusters in 1984.³ In addition, Salter has recently reviewed the copper-, silver- and gold-containing heteronuclear cluster compounds,⁴ and has also surveyed the stereochemical non-rigidity exhibited in solution by the metal skeletons of some mixed-metal clusters containing copper, silver and gold.⁵

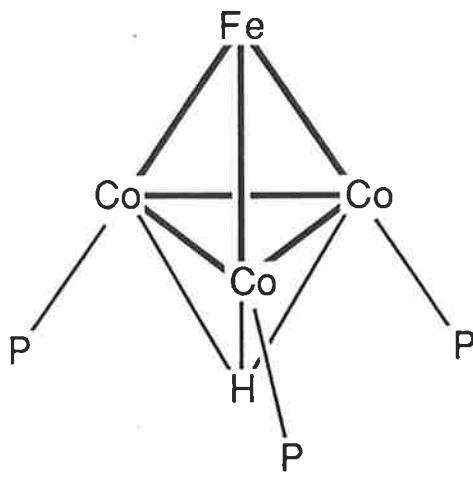
Much of the interest in gold-containing heterometallic clusters arose from the proposal⁶ that the Au(PR₃) moiety is isolobal with a H atom, which means that they have similar frontier orbitals containing a single electron.

Lauher and Wald⁶ pointed out the close structural relationship between certain hydrido-metal complexes and AuPPh₃ derivatives, exemplified by such pairs of compounds as the complexes AuCo(CO)₄(PPh₃)⁷ and HCo(CO)₄⁸ with capped tetrahedral geometries, and Fe(CO)₄{Au(PPh₃)₂}⁹ and the hydride Fe(CO)₄H₂⁸ with bicapped tetrahedral geometries. They prepared and determined the structure of FeCo₃(CO)₁₂-{Au(PPh₃)₂} (1)⁶ (a trigonal-bipyramidal array of metal atoms with the gold atom at one apical position), which

proved to be similar to that of $\text{HFeCO}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$ (2), which was determined by Kaesz¹⁰ and confirmed in a neutron study by Koetzle and Bau,¹¹ and which contained a hydride capping the three Co atoms.

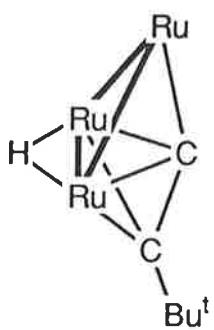


(1)

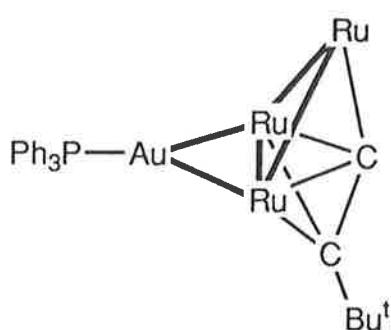


(2)

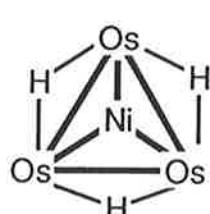
This relationship between a $\text{Au}(\text{PR}_3)$ group and a H atom has been further verified in $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CBu}^t)(\text{CO})_9$ (3)¹² and $\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_9(\eta\text{-C}_5\text{H}_5)$ (4),¹³ in which the hydride/s have been located. The corresponding Ru_3Au (5)¹⁴ and NiOs_3Au (6)¹⁵ clusters have been shown to have the $\text{Au}(\text{PPh}_3)$ fragment occupying the position of the H atom which it replaces.



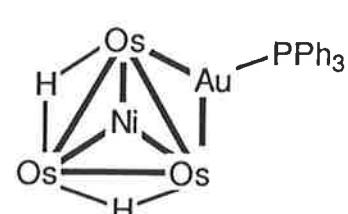
(3)



(5)



(4)



(6)

It would appear that a gold phosphine group and a hydride would have little in common from either an electronic or steric viewpoint, but closer analysis shows that they are not so different. The larger gold atoms result in longer bonds to the transition metal. Hydrogen bonds to a metal by using its 1s orbital while gold uses primarily its 6s orbital. This was later refined to use a 6sp(hy) or (s-z)hy orbital in the latter case (hy = hybrid).¹⁶

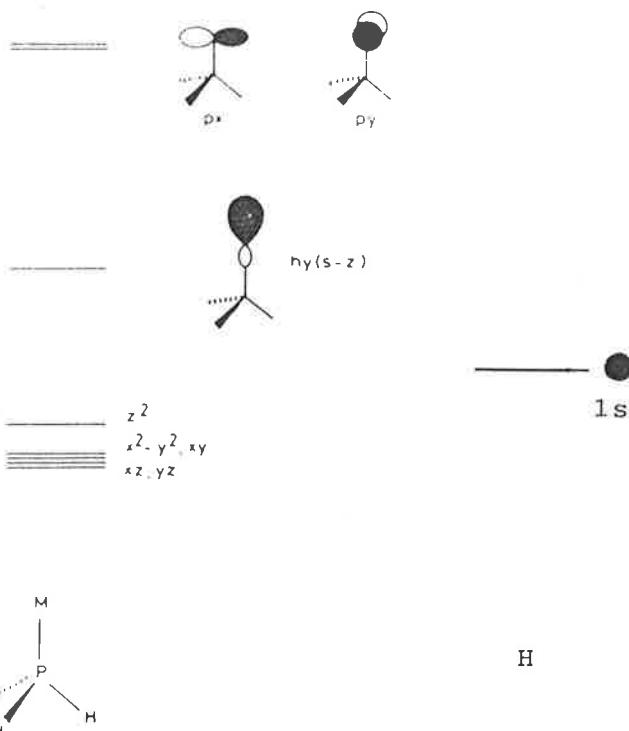


Figure 1: A comparison of the frontier orbitals of $\text{Au}(\text{PH}_3)$ and H . Adapted from ref. 16.

The isolobal relationship has been particularly useful in predicting the synthesis and structures of many clusters containing one $\text{Au}(\text{PR}_3)$ fragment because it usually occupies the edge-bridging or face-capping position of the H in the corresponding hydrido cluster. Alternatively, structures of complexes with the $\text{Au}(\text{PR}_3)$ group may provide information on the structures

of analogous hydrido complexes in cases where the H atom cannot be found directly by diffraction methods.

If the isolobal relationship $H \longleftrightarrow \text{Au}(\text{PR}_3)$ holds, then the question arises whether H_2 is isolobal with $\text{Au}_2(\text{PPh}_3)_2$. However, when two or more $\text{Au}(\text{PR}_3)$ groups are present in clusters, the isolobal analogy does not appear to be valid because of the propensity for formation of Au-Au bonds between adjacent groups. The σ_g Au-Au bonding orbital is the in-phase combination of sp_z orbitals on each gold leading to strong σ -bonding between the two gold atoms. At higher energies are found in-phase (π_u) and out-of-phase (π_g^*) combinations of the gold $6p_x$ and $6p_y$ orbitals. These orbitals are also available for bonding to the metal atoms in the cluster (Figure 2).¹⁷

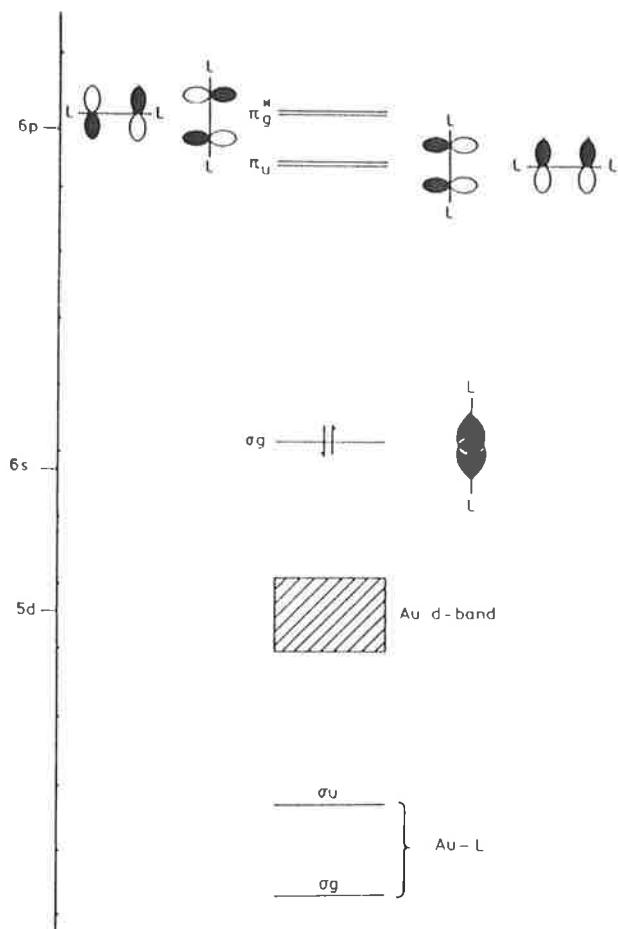
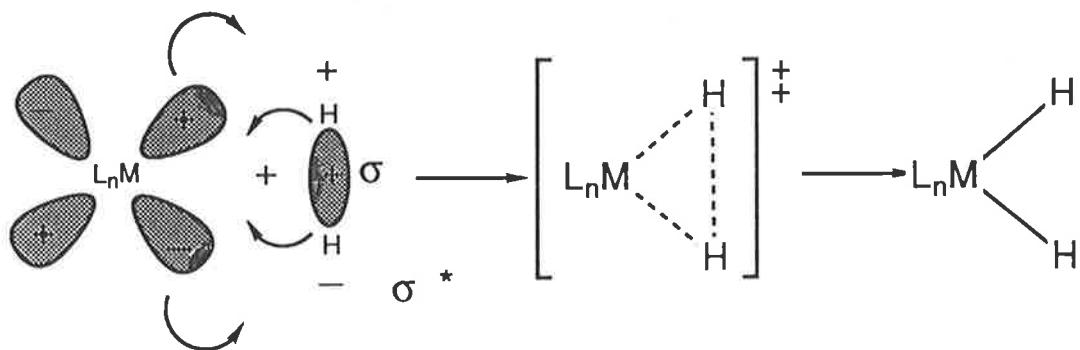


Figure 2: Frontier orbitals of an Au_2L_2 fragment¹⁷

No cluster complexes containing molecular H₂ are known at present [although mononuclear complexes such as W(H₂) (CO)₃(PPr₂)₂¹⁸ have been known for some years]. The reason for the lack of hydrogen-hydrogen bonding is explained by the fact that kinetic data for the oxidative addition of H₂ suggest a "three-centre" concerted process with a non-polar transition state. Electron density in a filled valence d orbital on M (a metal) flows into the empty σ* MO of H₂, thus forming two M-H bonding interactions while weakening the H-H bond in the transition state. In addition, electron density in the occupied σ MO, that defines the H-H single bond, flows into an empty valence orbital on the metal atom. The H-H bond is eventually cleaved, and two M-H single bonds form (Scheme 1).¹⁹



Scheme 1

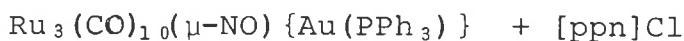
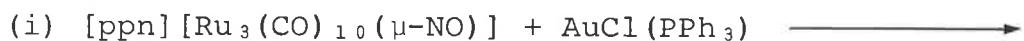
The structures of di-gold complexes would, therefore, be expected to be significantly different to those of dihydride complexes, but it is possible that they may serve as useful models for the initial attack of H₂ on a cluster.

At present the methods of introducing Au(PR₃) units into clusters are:

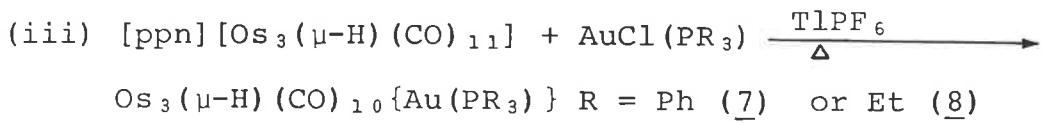
(I) Reactions of anionic complexes with Au(PR₃) precursors

(a) AuX(PR₃) (X = Cl, NO₃ etc.)

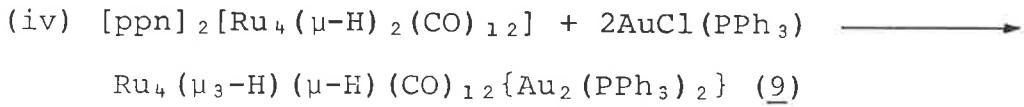
Many clusters have been prepared by the reaction of an anionic mono-, di- or polynuclear complex with AuCl(PPh₃) or Au(NO₃)(PPh₃). Examples are shown in Equations (i)²⁰ and (ii)⁶.



It has been found that the yield could be increased by using TlPF₆ (or some other halide abstractor) to remove Cl⁻ from the reaction mixture as insoluble TlCl [e.g. Equation (iii)].²¹



Two Au(PR₃) groups can be introduced into a preformed cluster dianion [e.g. Equation (iv)].²²

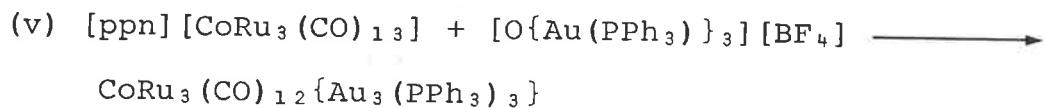


(b) [O{Au(PR₃)₃}][BF₄]

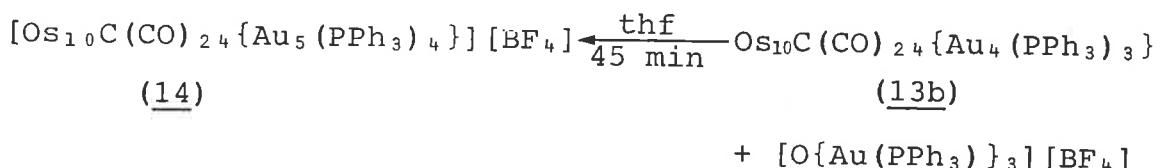
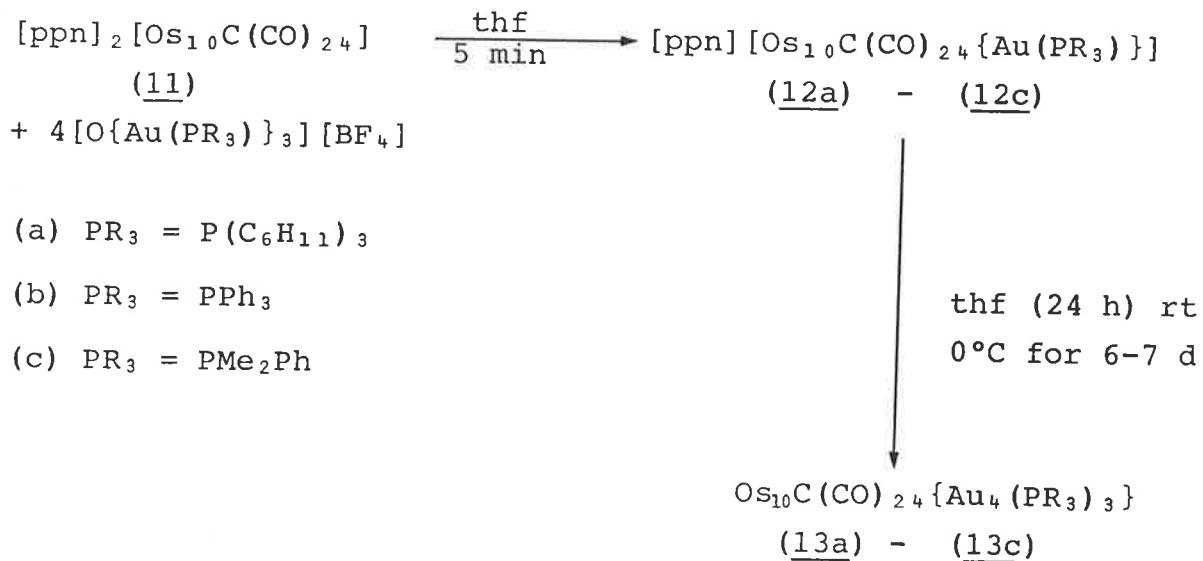
The gold oxonium reagent [O{Au(PPh₃)₃}][BF₄]²³ was first synthesised by Russian workers and has been used to replace reactive hydrogen atoms in organic molecules such as CH₂(CN)₂,²⁴ C₅H₆,²⁴ C₅H₂Ph₄^{25,26} and ferrocene,²⁴ by Au(PPh₃) groups to give Au₂{C(CN)₂}(PPh₃)₂, C₅H₅Au(PPh₃), Au(C₅HPh₄)(PPh₃) and

$\text{Au}_2(\text{C}_5\text{Ph}_4)(\text{PPh}_3)_2$, and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\{\eta\text{-C}_5\text{H}_4\text{Au}_2(\text{PPh}_3)_2\}][\text{BF}_4]$, respectively.

Bruce and co-workers have demonstrated that $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (10) can replace a CO group or two hydride ligands in cluster anions by $\text{Au}_2(\text{PPh}_3)_2$ fragments as well as acting as a source of $[\text{Au}(\text{PPh}_3)]^+$. Therefore, the complex can be used to incorporate up to three $\text{Au}(\text{PPh}_3)$ units into a cluster monoanion. An example of the use of this reagent is given in Equation (v).²⁷



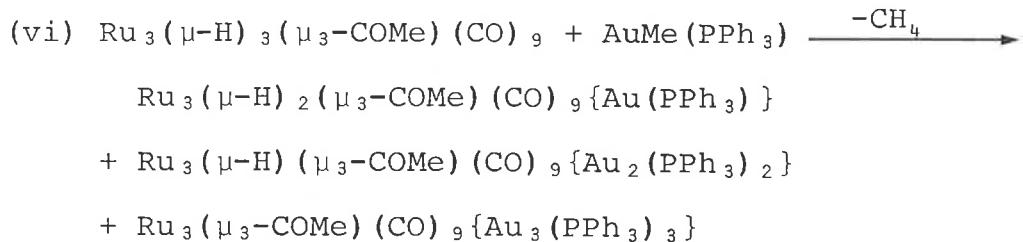
Lewis *et al* have recently used the gold oxonium reagent to incorporate four or five gold atoms into a cluster (Scheme 2).²⁸



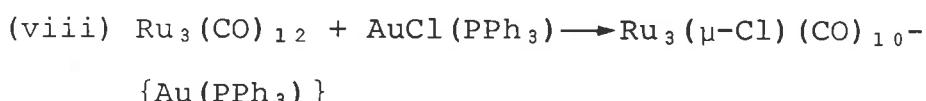
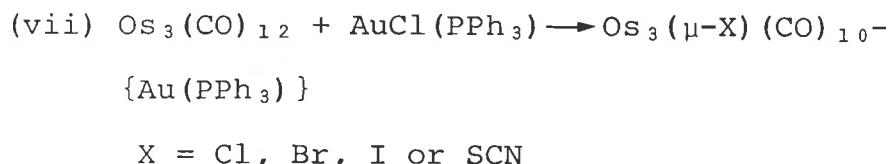
Scheme 2

(II) Synthetic routes using neutral precursors

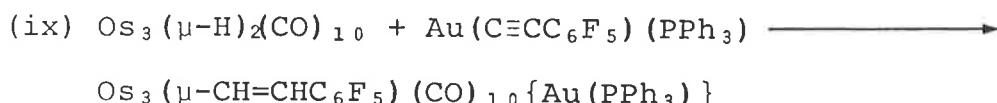
One method for introducing $\text{Au}(\text{PR}_3)$ fragments into neutral clusters involves a condensation reaction, with the elimination of methane, between a hydrido cluster and $\text{AuMe}(\text{PPh}_3)$ [e.g. Equation (vi)].²⁹



Oxidative addition reactions have also been used to synthesise heteronuclear gold clusters [e.g. Equations (vii)³⁰ and (viii)].³¹



Oxidative addition reactions, however, do not always produce the expected single product. A reaction between the cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ and $\text{Au}(\text{C}\equiv\text{CC}_6\text{F}_5)(\text{PPh}_3)$ proceeded via oxidative addition and hydrogen migration steps to afford $\text{Os}_3(\mu\text{-CH=CHC}_6\text{F}_5)(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}$ cleanly and in high yield [Equation (ix)].³²



Similar reactions using $\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$ and $\text{Au}(\text{C}\equiv\text{CPh})(\text{PMe}_3)$, however, gave a complex mixture of products.

It is apparent that there is no satisfactory method for adding two $\text{Au}(\text{PR}_3)$ moieties to clusters which do not possess hydrides to be eliminated as methane.

(III) Addition of 'Au₂(PPh₃)₂' to clusters

It has been shown recently that the addition of [O{Au(PPh₃)₃}][BF₄] (10) and [ppn][Co(CO)₄] (15) to a tetrahydrofuran solution of a cluster leads to the addition of two Au(PPh₃) units to the cluster. For example, the addition of (10) and (15) to Ru₅(μ₅-η²,P-C₂PPh₂)(μ-PPh₂)(CO)₁₃ gave Ru₅(μ₅-η²,P-C₂PPh₂)(μ-PPh₂)(CO)₁₂{Au₂(PPh₃)₂} in high yield; AuCo(CO)₄(PPh₃) was also isolated in high yield.³³ Similarly, the addition of (10) and (15) to Fe₂M(μ₃-η²-C≡CPh)-(CO)₈(PPh₃) resulted in the formation of the pentanuclear clusters Fe₂M(μ₃-η²-C≡CPh)(CO)₇(PPh₃) {Au₂(PPh₃)₂} (M = Ir, Rh).³⁴ It, therefore, appears that the [O{Au(PPh₃)₃}][BF₄]/[ppn]-[Co(CO)₄] system may be useful in introducing 'Au₂(PR₃)₂' units into neutral clusters under mild conditions.

In this Chapter a survey of the reactions of neutral clusters (both with and without hydrides) with [O{Au(PR₃)₃}][BF₄] (R = Ph, OMe)/[ppn][X] [X = Co(CO)₄, Cl, OAc] is given. These were carried out concurrently with those just mentioned to investigate the effectiveness of this reaction to add two Au(PR₃) units under mild conditions to clusters with various functional groups. The structures of the products may be considered as models for the initial addition of H₂ to the clusters. The ³¹P NMR spectra of some of these complexes will also be discussed. A brief mention is made of some oxidative addition reactions of Ru₃(CO)₁₂ with other gold acetylides.

Fast Atom Bombardment Mass Spectrometry of Mixed-MetalClusters containing gold

Fast atom bombardment mass spectrometry (FAB MS) is a technique which uses a stream of neutral atoms (argon or xenon) to sputter ions from solids or liquids. The utility of the method lies in its ability to generate ions from solutions in relatively non-volatile liquid matrices (glycerol, thiodiglycol), allowing the recording of spectra (both of negative and positive ions) of polar molecules, ionic complexes, and of high molecular weight organometallic molecules, all of which are labile under 'normal' electron impact source conditions.³⁵

This technique proved very useful in the identification of the mixed-metal clusters prepared in this Chapter. The spectra obtained in this Chapter show a number of similarities. The ion of greatest mass is usually the molecular ion - further peaks are formed by the stepwise loss of the carbonyl ligands. The dominant peaks in all of the spectra, however, are assigned to $[Au(PR_3)_2]^+$ and $[Au(PR_3)]^+$ ($R = Ph, OMe$).

Given these similarities, the discussion of the FAB mass spectra will, in general, be simplified and restricted to noteworthy peaks.

Note: Di-gold complexes discussed in this Chapter are listed as $M_n(CO)_x\{Au_2(PR_3)_2\}$ in cases where (a) it is known that Au-Au bonding occurs or (b) where it is thought to occur. Complexes in which it is known that there is no bonding are listed as $M_n(CO)_x\{Au(PR_3)\}_2$.

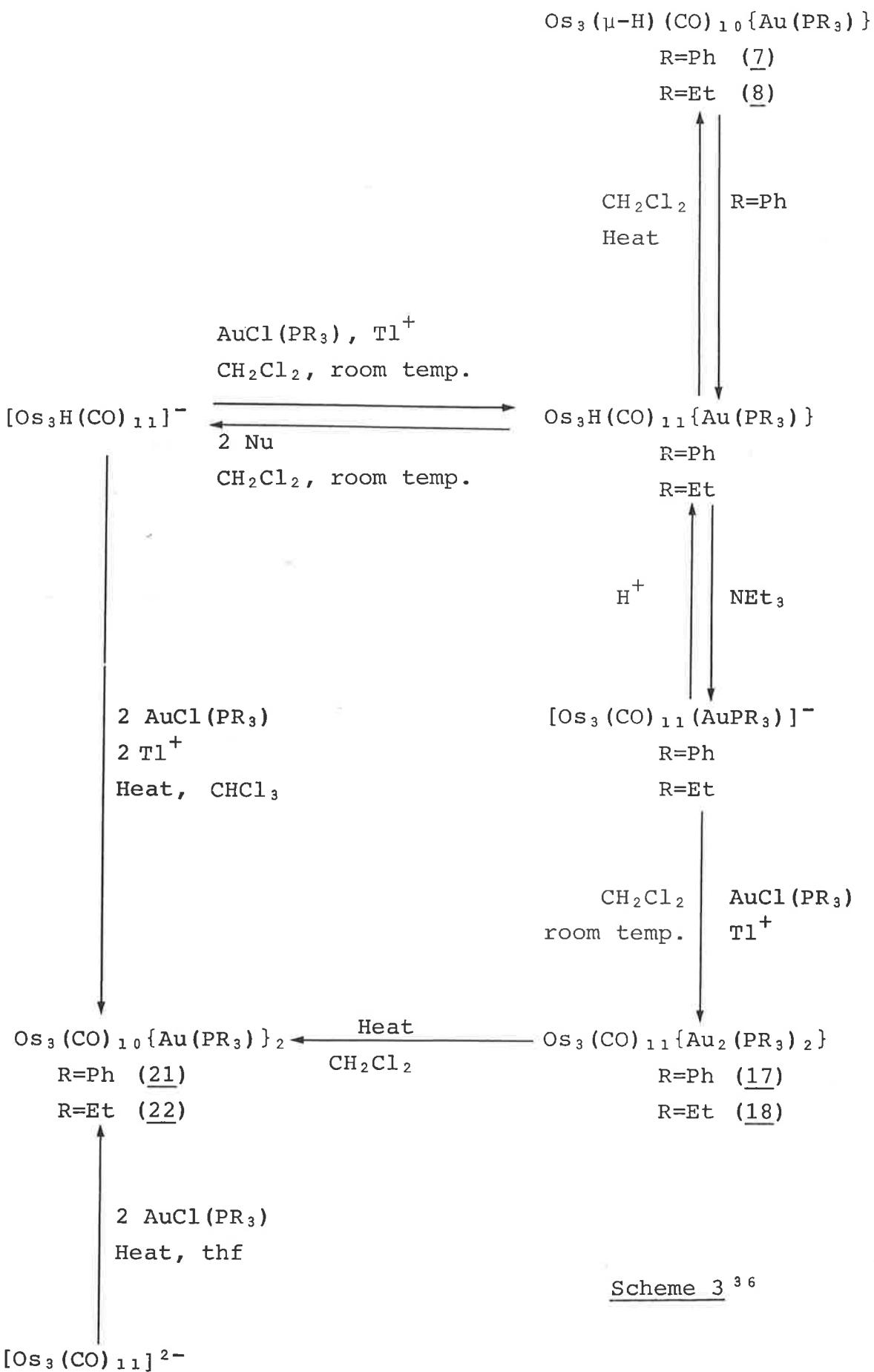
In some diagrams only core atoms and significant functional groups have been depicted for reasons of clarity.

RESULTS AND DISCUSSIONReactions of Osmium and Ruthenium Clusters with $[O\{Au(PR_3)\}_3]^-$ -
[BF₄] (R=Ph, OMe) in the presence of [ppn]⁺ saltsPreparation of Osmium-Gold Complexes

Addition of $[O\{Au(PPh_3)\}_3]^-$ -[BF₄] (10) / [ppn][Co(CO)₄] (15) to a solution of Os₃(CO)₁₂ (16) in tetrahydrofuran resulted in immediate darkening of the solution. After removal of [ppn]-[BF₄], preparative TLC gave AuCo(CO)₄(PPh₃) (identified by IR and FAB mass spectra) and an orange compound which was obtained in high yield. This was identified as Os₃(CO)₁₁{Au₂-(PPh₃)₂} (17) on the basis of its FAB mass spectrum and microanalytical data. The FAB mass spectrum shows a weak molecular ion at *m/z* 1798, and ions formed by stepwise loss of seven carbonyl ligands. Strong peaks are also found at *m/z* 721 and 459, assigned to [Au(PPh₃)₂]⁺ and [Au(PPh₃)]⁺, respectively. The solution IR spectrum shows eight bands in the $\nu(CO)$ region, while the ¹H NMR spectrum shows the phenyl protons as a multiplet around δ7.30.

This compound was previously obtained by Lewis *et al*³⁶ via the reaction pathway in Scheme 3, although their IR $\nu(CO)$ spectrum was significantly different (see Experimental section). The X-ray structure of (17) was reported earlier, and showed that a Au-Au interaction exists [2.845(1) $\overset{\circ}{\text{A}}$].³⁷

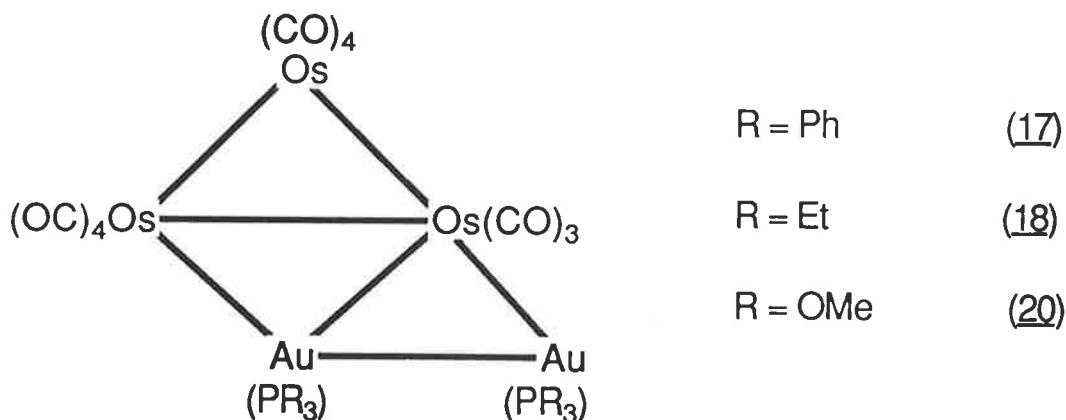
A similar reaction of Os₃(CO)₁₂ with $[O\{Au(PPh_3)\}_3]^-$ -[BF₄]/[ppn][OAc] gave a comparable yield of (17) after preparative TLC together with AuOAc(PPh₃), while the reaction of (16), (10) and [ppn][Cl] also afforded (17) as the major product after a similar work-up [together with AuCl(PPh₃)], although the yield of (17) was lower than found in the other two reactions.





It should be noted that, as a general rule, a side product of the reactions of $[O\{Au(PR_3)\}_3][BF_4]$ ($R = Ph, OMe$) / [ppn] [X] [$X = Co(CO)_4, OAc, Cl$] with neutral clusters was identified (if not isolated) as $AuX(PR_3)$ by solution IR spectroscopy and/or spot TLC (see Experimental section) and will not be discussed further.

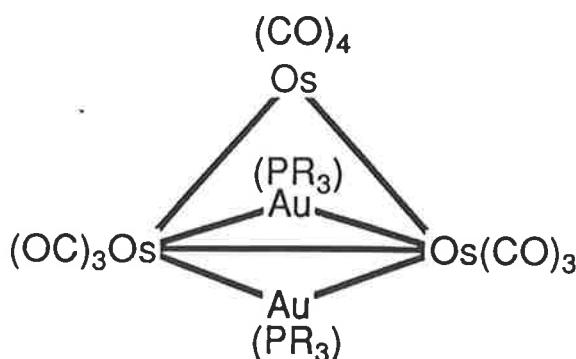
The reaction of $Os_3(CO)_{12}$ with the new oxonium complex $[O\{Au[P(OMe)_3]\}_3][BF_4]$ (19) and [ppn] $[Co(CO)_4]$ in tetrahydrofuran similarly yielded orange crystals of $Os_3(CO)_{11}\{Au_2[P(OMe)_3]_2\}$ (20), identified on the basis of microanalytical and spectroscopic data. The solution IR spectrum is very similar to that of



(17), suggesting that the $\{Au_2[P(OMe)_3]_2\}$ complex has the same stereochemistry as the $\{Au_2(PPh_3)_2\}$ complex, while the 1H NMR spectrum shows the methyl protons as a doublet at $\delta 3.79$ [$J(PH) = 13.5\text{Hz}$]. The FAB mass spectrum contains a molecular ion and peaks corresponding to the sequential loss of seven carbonyls; the base peak at m/z 445 is assigned to $[Au\{P(OMe)_3\}_2]^+$.

A reaction of (10) and (15) with $Ru_3(CO)_{12}$ in tetrahydrofuran gave a number of products, none of which have been isolated thus far.

The reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ / [ppn] $[\text{Co}(\text{CO})_4]$ gave green crystals of $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ (21) in moderate yield after chromatographic separation. Identification was made on the basis of solution IR and FAB mass spectra. The $\nu(\text{CO})$ spectrum shows five bands, while the FAB mass spectrum shows a molecular ion and stepwise loss of six carbonyl ligands with the base peak corresponding to $[\text{Au}(\text{PPh}_3)_2]^+$; a peak at m/z 1255 is assigned to $[\text{M} - 2\text{CO} - \text{Au}(\text{PPh}_3)]^+$. Complex (21) had been previously synthesised by the decarbonylation of (17) or by the direct reaction of $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$ or $[\text{Os}_3(\text{CO})_{11}]^{2-}$ [obtained by the reduction of $\text{Os}_3(\text{CO})_{12}$ in tetrahydrofuran] with two equivalents of $\text{AuCl}(\text{PPh}_3)$ (Scheme 3).³⁶ A single-crystal X-ray diffraction study of the analogous compound $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PEt}_3)\}_2$ (22), shows the three Os atoms form an isosceles triangle, the shorter edge of which is bridged on both sides of the Os plane by the two $\text{Au}(\text{PEt}_3)$ units. There is no interaction between the Au atoms [the interatomic separation is $4.304(2)^\circ\text{\AA}$].³⁶ The structure of (22) is, therefore, closely related to that of the formally unsaturated dihydride $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$, in which the hydride bridged Os-Os bond is significantly shorter [$2.681(1)^\circ\text{\AA}$] than the other two Os-Os bonds.³⁸ In (22), the Au-bridged Os-Os bond has a similar length [$2.684(1)^\circ\text{\AA}$], to that observed for the dihydride.



$R = \text{Ph}$ (21)

$R = \text{Et}$ (22)

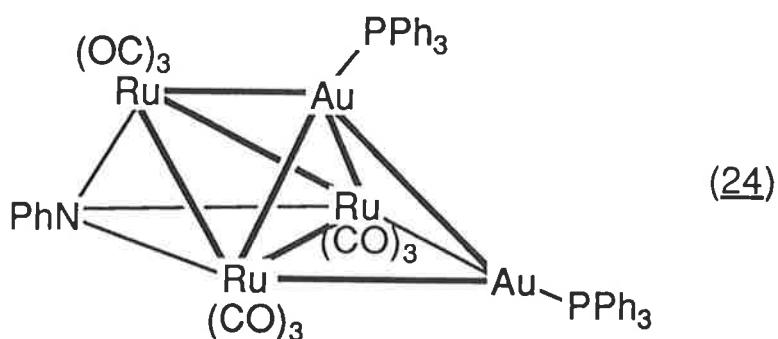
Preparation of Ruthenium-Gold Complexes

Preparation of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24)

Addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to a solution of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_{10}$ (23) in tetrahydrofuran afforded, after preparative TLC and crystallisation from dichloromethane/methanol, red crystals of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24) in good yield. The solution IR spectrum contains five bands, while the ^1H NMR spectrum shows the phenyl protons as a multiplet around $\delta 7.31$. The FAB mass spectrum shows the usual peaks as well as peaks at m/z 1328 assigned to $[\text{M} - 8\text{CO} - \text{N}]^+$ and a peak at m/z 1237 assigned to $[\text{M} - 9\text{CO} - \text{Ph}]^+$; peaks assigned to $[\text{Au}-(\text{PPh}_3)_2]^+$ and $[\text{M} - 5\text{CO}]^+$ are the base peaks.

Structure of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24)

An X-ray diffraction study of (24) was undertaken and is shown in Figure 3 (see also Table 1). It consists of a trigonal-bipyramidal Ru_3Au_2 core (three CO ligands on each ruthenium atom) with the Au atoms in an apical and an equatorial site. This metal core is symmetrically capped on the Ru_3 face by a $\mu_3\text{-NPh}$ unit as found for the parent complex.



The triply bridging CO found in (23) has been replaced by two $\text{Au}(\text{PPh}_3)$ groups. The $\text{Au}-\text{Au}$ bond length of $2.955(1)\text{\AA}$ is unexceptional (the reported range of $\text{Au}-\text{Au}$ distances is $2.60\text{--}3.10\text{\AA}$), as are all the $\text{Au}-\text{Ru}$ bonds, which range from $2.784(1)\text{--}$

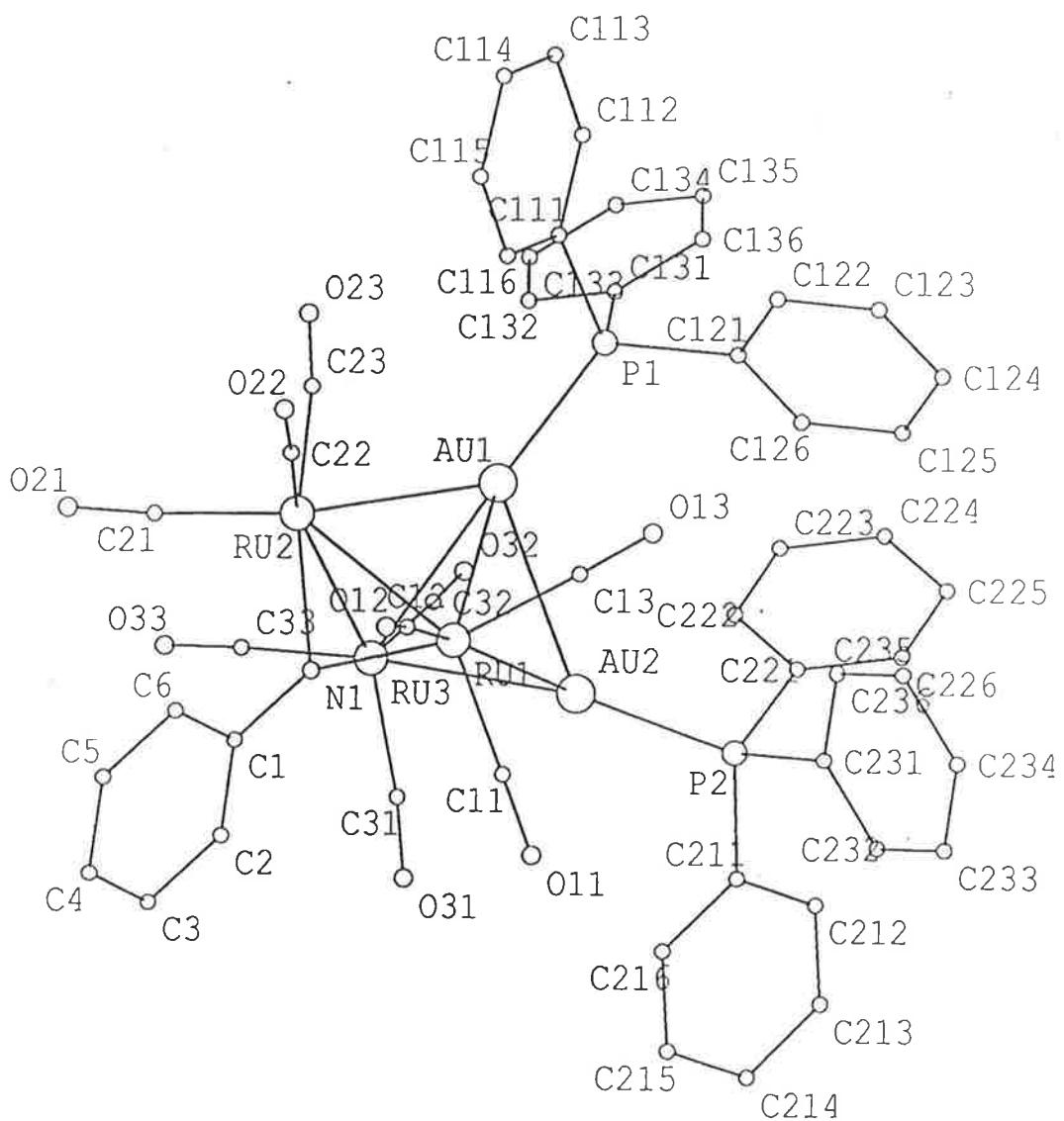


Figure 3 : PLUTO plot of the molecular structure of
 $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24)
 (by E. Horn and E.R.T. Tiekink)

$2.828(1)\text{\AA}^\circ$. These bond lengths are similar to those found in the closely related complex $\text{Ru}_3(\mu_3\text{-S})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (25) [$\text{Au-Au } 2.967(2)\text{\AA}^\circ$, $\text{Au-Ru } 2.783(2)-2.867(2)\text{\AA}^\circ$].³⁹ The Ru-Ru bond lengths in (24) range from $2.730(1)-2.909(1)\text{\AA}^\circ$, while those of the parent complex range from $2.735(1)-2.750(1)\text{\AA}^\circ$ (molecule A) and $2.734(1)-2.760(1)\text{\AA}^\circ$ (molecule B).⁴⁰ [The average Ru-Ru bond in $\text{Ru}_3(\text{CO})_{12}$ is $2.854(4)\text{\AA}^\circ$.]⁴¹ The Ru-N bond lengths in (24) range from $2.057(9)-2.083(9)\text{\AA}^\circ$, while those of (23) range from $2.053(4)-2.055(4)\text{\AA}^\circ$ (molecule A) and $2.054(4)-2.060(4)\text{\AA}^\circ$ (molecule B).

Table 1: Selected interatomic parameters for (24)

Bond distances (\AA°)

$\text{Au}(2) - \text{Au}(1)$	$2.955(1)$	$\text{Ru}(1) - \text{Au}(1)$	$2.828(1)$
$\text{Ru}(2) - \text{Au}(1)$	$2.804(1)$	$\text{Ru}(3) - \text{Au}(1)$	$2.937(1)$
$\text{P}(1) - \text{Au}(1)$	$2.309(3)$	$\text{Ru}(1) - \text{Au}(2)$	$2.811(1)$
$\text{Ru}(3) - \text{Au}(2)$	$2.784(1)$	$\text{P}(2) - \text{Au}(2)$	$2.300(3)$
$\text{Ru}(3) - \text{Ru}(1)$	$2.909(1)$	$\text{Ru}(2) - \text{Ru}(1)$	$2.821(1)$
$\text{N}(1) - \text{Ru}(1)$	$2.057(9)$	$\text{Ru}(3) - \text{Ru}(2)$	$2.730(1)$
$\text{N}(1) - \text{Ru}(3)$	$2.083(9)$	$\text{N}(1) - \text{Ru}(2)$	$2.063(8)$

Bond angles ($^\circ$)

$\text{Ru}(1) - \text{Au}(1) - \text{Au}(2)$	$58.1(1)$	$\text{Ru}(2) - \text{Au}(1) - \text{Au}(2)$	$103.8(1)$
$\text{Ru}(2) - \text{Au}(1) - \text{Ru}(1)$	$60.1(1)$	$\text{Ru}(3) - \text{Au}(1) - \text{Au}(2)$	$56.4(1)$
$\text{Ru}(3) - \text{Au}(1) - \text{Ru}(1)$	$60.6(1)$	$\text{Ru}(3) - \text{Au}(1) - \text{Ru}(2)$	$56.7(1)$
$\text{Ru}(3) - \text{Au}(2) - \text{Au}(1)$	$61.5(1)$	$\text{Ru}(1) - \text{Au}(2) - \text{Au}(1)$	$58.7(1)$
$\text{Ru}(2) - \text{Ru}(1) - \text{Au}(1)$	$59.5(1)$	$\text{Ru}(3) - \text{Au}(2) - \text{Ru}(1)$	$62.7(1)$
$\text{Ru}(3) - \text{Ru}(1) - \text{Au}(1)$	$61.6(1)$	$\text{Au}(2) - \text{Ru}(1) - \text{Au}(1)$	$63.2(1)$
$\text{Ru}(3) - \text{Ru}(1) - \text{Ru}(2)$	$56.9(1)$	$\text{Ru}(2) - \text{Ru}(1) - \text{Au}(2)$	$107.1(1)$
$\text{Ru}(3) - \text{Ru}(2) - \text{Au}(1)$	$64.1(1)$	$\text{Ru}(3) - \text{Ru}(1) - \text{Au}(2)$	$58.2(1)$
$\text{Au}(2) - \text{Ru}(3) - \text{Au}(1)$	$62.1(1)$	$\text{Ru}(1) - \text{Ru}(2) - \text{Au}(1)$	$60.4(1)$
$\text{Ru}(1) - \text{Ru}(3) - \text{Au}(2)$	$59.1(1)$	$\text{Ru}(3) - \text{Ru}(2) - \text{Ru}(1)$	$63.2(1)$
$\text{Ru}(2) - \text{Ru}(3) - \text{Au}(2)$	$110.5(1)$	$\text{Ru}(1) - \text{Ru}(3) - \text{Au}(1)$	$57.9(1)$
$\text{Ru}(3) - \text{N}(1) - \text{Ru}(1)$	$89.3(3)$	$\text{Ru}(2) - \text{Ru}(3) - \text{Au}(1)$	$59.2(1)$
$\text{Ru}(3) - \text{N}(1) - \text{Ru}(2)$	$82.4(3)$	$\text{Ru}(2) - \text{Ru}(3) - \text{Ru}(1)$	$59.9(1)$
		$\text{Ru}(2) - \text{N}(1) - \text{Ru}(1)$	$86.4(3)$

Preparation of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (27)

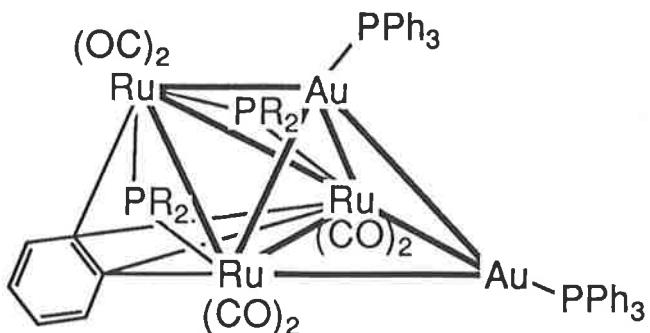
and $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_3\text{Me})\{\mu\text{-P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (28)

The reaction of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_7$, (26) with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ in tetrahydrofuran afforded, after preparative TLC and crystallisation from dichloromethane/n-hexane, dark purple crystals of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (27) in good yield. Identification was made from spectroscopic and microanalytical data. The solution IR spectrum of (27) shows three broad $\nu(\text{CO})$ bands, while the FAB mass spectrum contains the usual peaks. In addition, peaks corresponding to $[M - n\text{CO} - \text{PPh}_3]^+$ ($n = 1-6$) are observed; further fragmentation occurs via the loss of one or two phenyl groups. Peaks at m/z 1133 and 1056 are assigned to $[M - 6\text{CO} - \text{Au}(\text{PPh}_3) - n\text{Ph}]^+$ ($n = 1, 2$).

A similar reaction of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_3\text{Me})\{\mu\text{-P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_7$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ yielded $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_3\text{Me}) - \{\mu\text{-P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (28). The solution IR spectrum is very similar to that of (27), with three $\nu(\text{CO})$ bands. The ^1H NMR spectrum shows the methyl protons as singlets at δ 1.87, 2.13 and 2.18 (relative intensities 3:6:6), and the phenyl, C_6H_4 and C_6H_3 protons as a multiplet at δ 6.06-7.62. The FAB mass spectrum of (28) shows a weak molecular ion and a peak at m/z 1879 corresponding to $[M - \text{CO}]^+$, although no further peaks are observed corresponding to the loss of the other carbonyl ligands. Peaks at $[M - n\text{CO} - \text{PPh}_3]^+$ ($n = 1, 4$ and 6) are observed, however, as well as peaks at m/z 1386 and 1189 assigned to $[M - 6\text{CO} - \text{PPh}_3 - \text{C}_6\text{H}_4\text{Me}]^+$ and $[M - 6\text{CO} - \text{Au}(\text{PPh}_3) - \text{C}_6\text{H}_4\text{Me}]^+$, respectively. In the FAB mass spectra of both (27) and (28) the dominant peak is assigned to $[\text{Au}(\text{PPh}_3)_2]^+$.

Molecular Structure of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6^-$ { $\text{Au}_2(\text{PPh}_3)_2$ } (27)

The molecular structure of (27) is shown in Figure 4 (see also Table 2). It consists of a trigonal-bipyramidal Ru_3Au_2 core (two carbonyl ligands on each Ru atom) with the Au atoms in an apical and equatorial site. The three Ru atoms are attached to a benzyne ligand. Two Ru atoms are attached by M-C σ -bonds to *ortho* carbons [Ru(1)-C(1) 2.09(2) and Ru(3)-C(6) 2.16(2) \AA] while the third [Ru(2)] is attached to these carbons in an η^2 -mode [Ru(2)-C(1), C(6) 2.29(2), 2.35(2) \AA]. Bonds Ru(3)-Ru(1) and Ru(3)-Ru(2) are both bridged by PPh₂ groups. The structure is, therefore, very similar to that of the parent complex (26).^{4,2} The semi-bridging CO between Ru(1) and Ru(2) in (26) has been lost with concomitant formation of the Ru-Au bonds. The Ru(3)-Ru(1) bond in (27) is significantly longer [3.012(4) \AA] than the bonds Ru(2)-Ru(1) [2.831(4) \AA] and Ru(3)-Ru(2) [2.847(4) \AA]. In the parent complex, the Ru(3)-Ru(1) bond length is 2.956(1) \AA , while the other two Ru-Ru bond lengths are again significantly shorter [Ru(3)-Ru(2) 2.776(1) \AA , Ru(2)-Ru(1) 2.759(1) \AA].^{4,2} The Ru-Au bond lengths in (27) range from 2.690(4) \AA -3.094(3) \AA while the Au-Au separation is 3.032(2) \AA .



$R = \text{C}_6\text{H}_5$ (27)

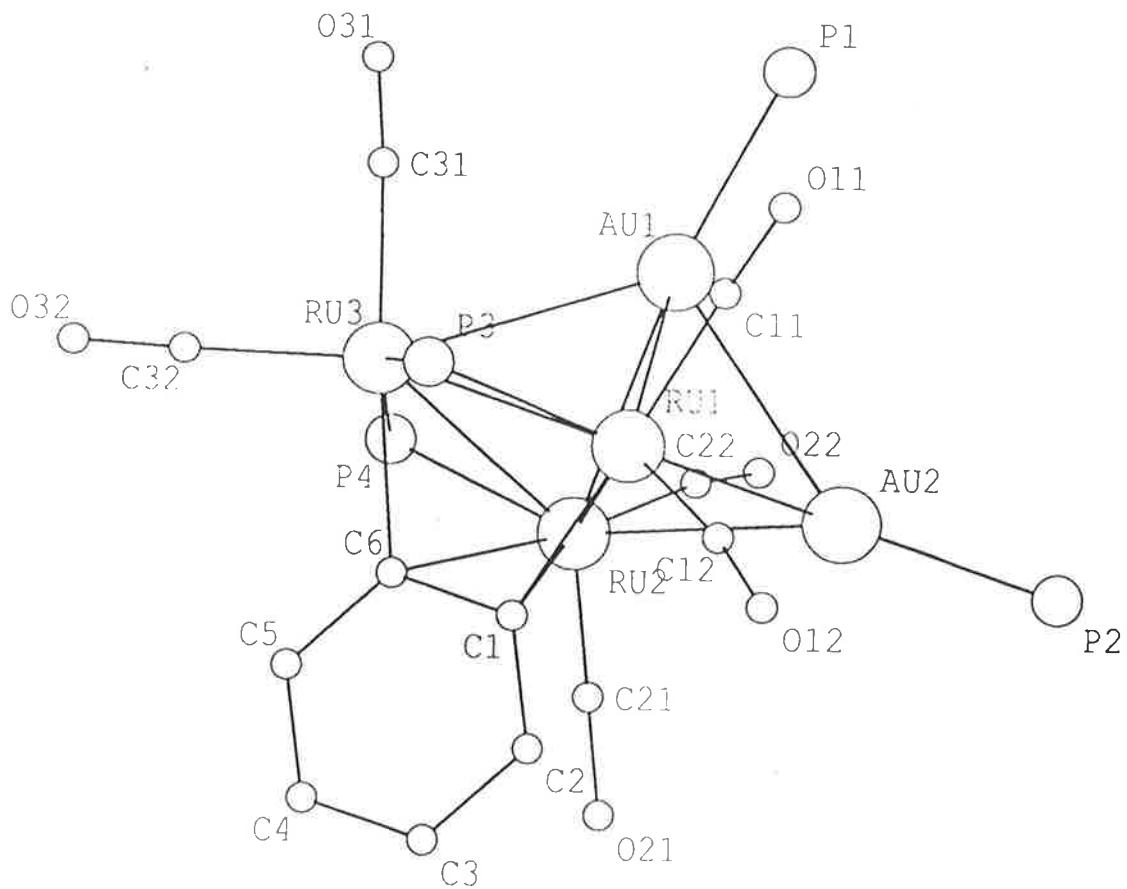


Figure 4 : PLUTO plot of the molecular structure of
 $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (27)
 (by E. Horn and E.R.T. Tiekink)

Note: phenyl groups have been omitted for
 reasons of clarity

Table 2: Selected interatomic parameters for (27)

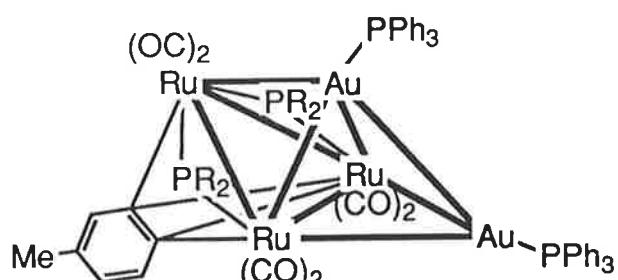
Bond distances (Å)

Au(2) - Au(1)	3.032(2)	Ru(1) - Au(1)	2.728(3)
Ru(2) - Au(1)	2.845(3)	Ru(3) - Au(1)	3.094(3)
P(1) - Au(1)	2.327(8)	Ru(2) - Au(2)	2.835(3)
Ru(1) - Au(2)	2.690(4)	Ru(2) - Ru(1)	2.831(4)
P(2) - Au(2)	2.282(9)	Ru(3) - Ru(2)	2.847(4)
Ru(3) - Ru(1)	3.012(4)	C(1) - Ru(2)	2.29 (2)
C(1) - Ru(1)	2.09 (2)	C(6) - Ru(3)	2.16 (2)
C(6) - Ru(2)	2.35 (2)		

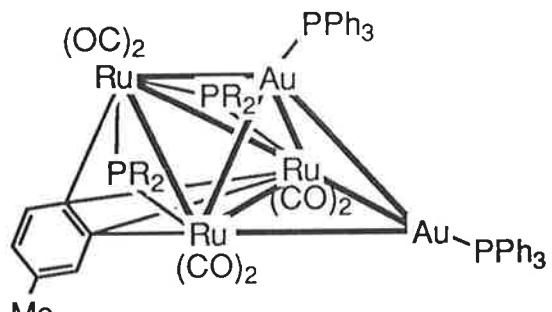
Bond angles (°)

Ru(1) - Au(1) - Au(2)	55.4(1)	Ru(2) - Au(1) - Au(2)	57.6(1)
Ru(2) - Au(1) - Ru(1)	61.0(1)	Ru(3) - Au(1) - Au(2)	104.1(1)
Ru(3) - Au(1) - Ru(1)	61.9(1)	Ru(3) - Au(1) - Ru(2)	57.1(1)
Ru(2) - Au(2) - Au(1)	57.9(1)	Ru(1) - Au(2) - Au(1)	56.6(1)
Ru(2) - Ru(1) - Au(1)	61.5(1)	Ru(2) - Au(2) - Ru(1)	61.6(1)
Ru(3) - Ru(1) - Au(1)	65.0(1)	Au(2) - Ru(1) - Au(1)	68.0(1)
Ru(3) - Ru(1) - Ru(2)	58.2(1)	Ru(2) - Ru(1) - Au(2)	61.7(1)
Ru(1) - Ru(2) - Au(1)	57.5(1)	Ru(3) - Ru(1) - Au(2)	115.7(1)
Ru(3) - Ru(2) - Au(1)	65.9(1)	Au(2) - Ru(2) - Au(1)	64.5(1)
Ru(3) - Ru(2) - Ru(1)	64.1(1)	Ru(1) - Ru(3) - Au(1)	53.1(1)
Ru(2) - Ru(3) - Au(1)	57.0(1)	Ru(2) - Ru(3) - Ru(1)	57.7(1)
Ru(3) - C(6) - Ru(2)	78.1(6)	Ru(3) - P(3) - Ru(1)	80.7(3)
Ru(3) - P(4) - Ru(2)	75.6(3)	Ru(2) - C(1) - Ru(1)	80.4(6)
Ru(1) - Ru(2) - Au(2)	56.7(1)	Ru(3) - Ru(2) - Au(2)	116.4(1)

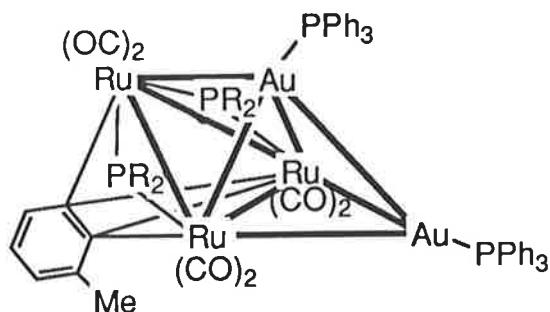
Compound (28) is assumed to have a similar structure to (27) although unambiguous assignment of the position of the Me group of the C_6H_3Me benzyne ligand in (28) is not possible with the available 1H NMR data. Of the four possible isomers (28a-d), (28a) and (28b) are favoured as being the most likely sterically and on the basis that these were found to be the isomers present in $Os_3(\mu\text{-H})(\mu_3\text{-}C_6H_3Me)(\mu\text{-AsMe}_2)\text{-}(CO)_9$.⁴³ Conversely, isomers of the type (28c) and (28d) were found for $Os_3(\mu\text{-H})(\mu_3\text{-}C_6H_3OMe)(\mu\text{-AsMe}_2)(CO)_9$.⁴³ Given these results, Arce and Deeming then postulated that the position of substitution depends on electronic effects rather than steric effects.⁴³



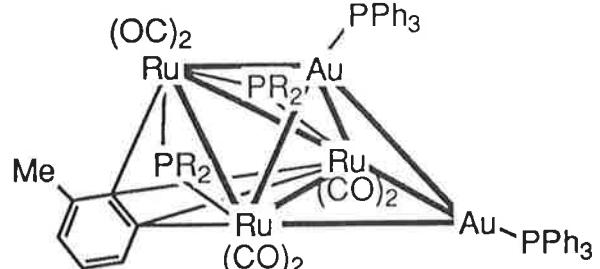
(28a)



(28b)



(28c)



(28d)

$R = C_6H_4Me - m$

The complexity of these systems was confirmed by Lewis *et al*, who later found a mixture of isomers for $\text{Os}_3(\mu\text{-H})_2 - (\mu_3\text{-C}_6\text{H}_3\text{Me})(\text{CO})_9$ [1:4 ratio favouring the assignment found for $\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_6\text{H}_3\text{Me})(\mu\text{-AsMe}_2)(\text{CO})_9$] and $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-C}_6\text{H}_3\text{Cl}) - (\text{CO})_9$ [3:1 favouring the assignment found for $\text{Os}_3(\mu\text{-H}) - (\mu_3\text{-C}_6\text{H}_3\text{OMe})(\mu\text{-AsMe}_2)(\text{CO})_9$].⁴⁴

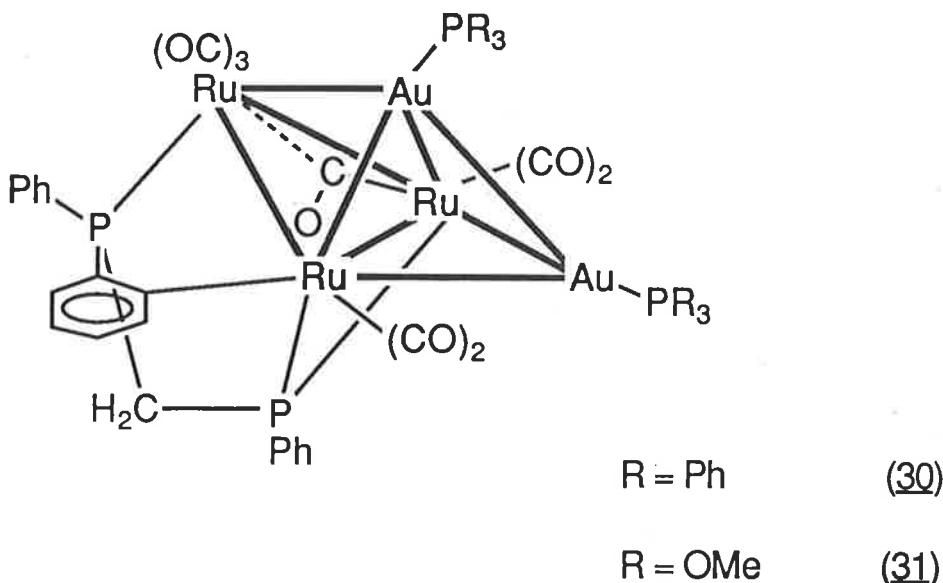
Preparation of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_8\{\text{Au}_2(\text{PR}_3)_2\}$

[R = Ph (30), OMe (31)]

Addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{X}]$ (X = Co(CO)₄, OAc or Cl) to $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (29) in tetrahydrofuran immediately gave a purple solution. Suitable work-up and crystallisation from dichloromethane/methanol afforded red-purple crystals of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (30) in high yield. Identification of (30) was made on the basis of microanalytical and spectroscopic data. The solution IR spectrum shows three bands in the $\nu(\text{CO})$ region while the ¹H NMR spectrum shows the CH₂ protons as two multiplets at δ2.83–2.95 and δ3.56–3.74, and the phenyl and benzyne protons are found as a multiplet between δ6.07–8.16. The FAB mass spectrum shows the expected peaks and a peak at *m/z* 1266 assigned to $[\text{M} - \text{CO} - \text{Au}(\text{PPh}_3)]^+$; the dominant peaks, once again, are $[\text{Au}(\text{PPh}_3)]^+$ and $[\text{Au}(\text{PPh}_3)_2]^+$. An interesting feature of this spectrum is the presence of a peak at *m/z* 2212 assigned to $[\text{M} + \text{Au}(\text{PPh}_3)]^+$. Ions of the general formula $[\text{M} + \text{Au}(\text{PR}_3)]^+$ (R = Ph, OMe) have been found in the spectra of several of the compounds prepared in this Chapter. They may be considered to be the isolobal analogues of $[\text{M} + \text{H}]^+$ ions, which are often

found in the FAB mass spectra of organic and organometallic compounds.³⁵

The reaction of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_9$ with $[\text{O}\{\text{Au}(\text{OMe})_3\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ similarly gave, after preparative TLC, red-purple crystals of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_8\{\text{Au}_2(\text{POMe})_3\}_2$ (31). The solution IR spectrum of (31) shows four bands in the terminal $\nu(\text{CO})$ region,



while the FAB mass spectrum shows an aggregation peak at m/z 1798 assigned to $[\text{M} + \text{Au}(\text{OMe})_3]^+$. Loss of the carbonyl ligands from this peak and from the weak molecular ion is observed, as well as the loss of $\text{P}(\text{OMe})_3$. Peaks at m/z 445 and 321 are assigned to $[\text{Au}(\text{POMe})_3]_2^+$ and $[\text{Au}(\text{POMe})_3]^+$, respectively, the latter being the base peak. The ^1H NMR spectrum of (31) shows two multiplets at δ 2.98-3.10 and δ 3.61-3.75 assigned to the CH_2 protons, while the phenyl and C_6H_4 protons are found from δ 6.03-8.12. Doublets at δ 3.55 [$J(\text{PH}) = 13.6\text{Hz}$] and δ 3.83 [$J(\text{PH}) = 13.3\text{Hz}$] are assigned to methyls of the two $\text{Au}(\text{POMe})_3$ groups coupling with the phosphorus atoms.

Molecular Structure of Ru₃{μ₃-PPhCH₂PPh(C₆H₄)}(CO)₈-{Au₂[P(OMe)₃]₂}·CH₂Cl₂ (31)

The molecular structure of (31) is shown in Figure 5 (see also Table 3). The same trigonal bipyramidal Ru₃Au₂ core as found in (24) and (27) is present. It is formed by the loss of a semi-bridging CO from the parent complex (29)^{4,5} [Ru(1)-C(10) 1.963(5)° Å, Ru(2)-C(10) 2.543(5)° Å] with the concomitant addition of the two Au{P(OMe)₃} groups. The Ru₃ triangle in (31) is capped by an orthometallated PPhCH₂PPh(C₆H₄) ligand acting as a six-electron donor. The coordination of each ruthenium atom is completed by three CO groups on Ru(2) and Ru(3), and two on Ru(1). The Ru-Ru bonds range between 2.915(2)° Å and 3.054(2)° Å, the shortest bond [Ru(2)-Ru(3)] being semi-bridged by CO(3) [Ru(2)-C(3) 1.95(3)° Å, Ru(3)-C(3) 2.83(2)° Å]. As found in the parent complex, the bond from Ru(1)-Ru(2) is bridged by the phosphido fragment P(1), and cyclometallation of one of the phenyl rings on P(2) gives a conventional Ru-C σ-bond [Ru(1)-C(202) 2.10(1)° Å]. The Ru-Au bonds range from 2.742(1)-3.070(1)° Å while the Au-Au bond distance is 2.763(1)° Å, which is at the shorter end of the usual range observed.

Preparation of Ru₃(μ₃-R)₂(CO)₈{Au₂(PPh₃)₂} [R = S (33), NPh (35)]

The addition of [O{Au(PPh₃)₃}][BF₄]/[ppn][Co(CO)₄] to a solution of Ru₃(μ₃-S)₂(CO)₉ (32) in tetrahydrofuran resulted in immediate darkening of the solution. Preparative TLC gave eight coloured bands, the largest of which (orange, R_f = 0.50) was crystallised from dichloromethane/methanol to give red crystals of Ru₃(μ₃-S)₂(CO)₈{Au₂(PPh₃)₂} (33) in 69% yield. Analogous reactions in which [ppn][OAc] and [ppn][Cl] were used in place of [ppn][Co(CO)₄] also gave (33) but in

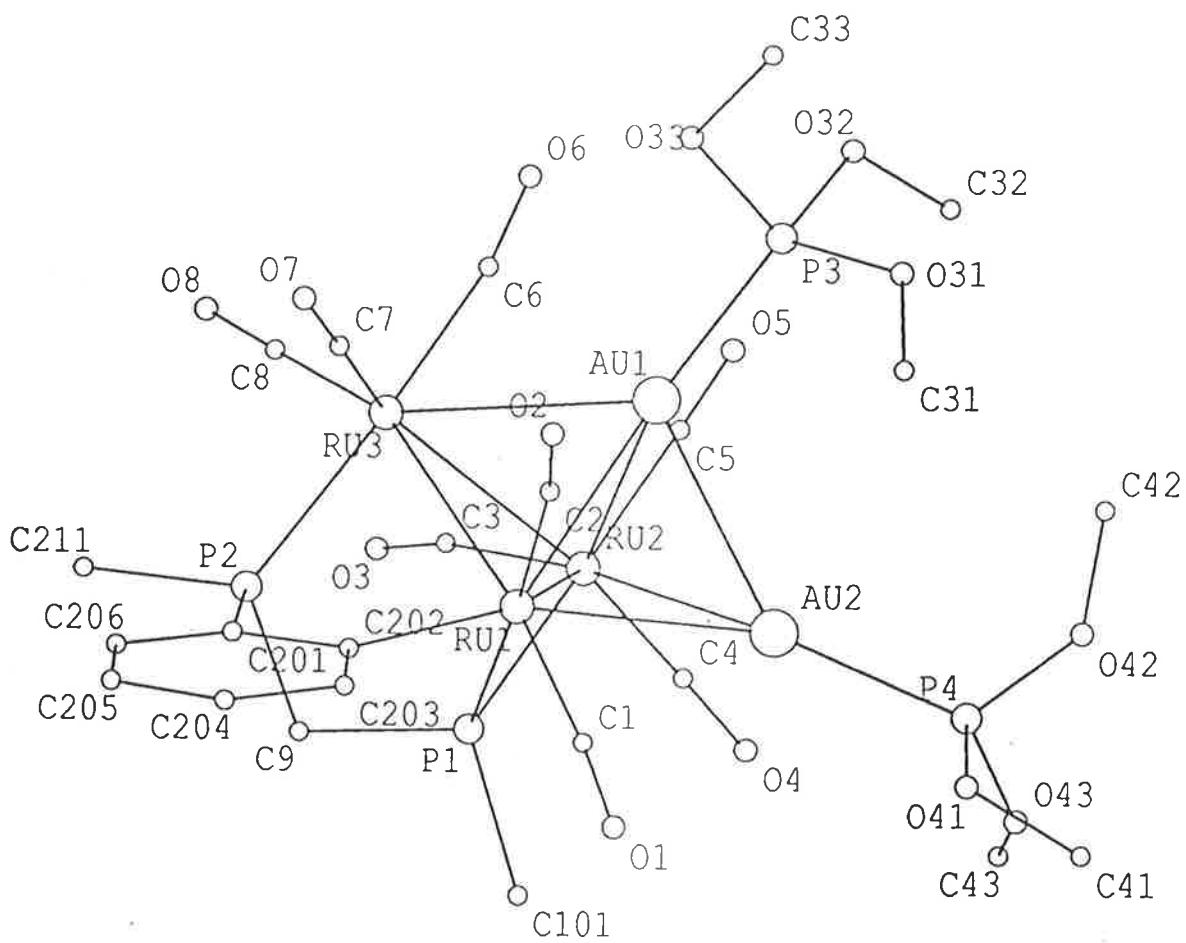


Figure 5 : PLUTO plot of the molecular structure of
 $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_8\{\text{Au}_2[\text{P}(\text{OMe})_3]_2\}\cdot\text{CH}_2\text{Cl}_2$ (31)
 (by E.R.T. Tiekink)

Note: phenyl groups have been omitted for
 reasons of clarity

Table 3: Selected interatomic parameters for (31)

Bond distances (Å)

Au(2)	-	Au(1)	2.763(1)	Ru(1)	-	Au(1)	2.742(1)
Ru(2)	-	Au(1)	2.874(1)	Ru(3)	-	Au(1)	3.070(1)
P(3)	-	Au(1)	2.253(5)	Ru(2)	-	Au(2)	2.845(1)
Ru(1)	-	Au(2)	2.900(1)	Ru(2)	-	Ru(1)	2.991(2)
P(4)	-	Au(2)	2.266(5)	P(1)	-	Ru(1)	2.316(4)
Ru(3)	-	Ru(1)	3.054(2)	Ru(3)	-	Ru(2)	2.915(2)
C(202)	-	Ru(1)	2.10 (1)	C(9)	-	P(1)	1.85 (1)
P(1)	-	Ru(2)	2.330(4)	C(9)	-	P(2)	1.81 (1)
P(2)	-	Ru(3)	2.386(4)	C(211)	-	P(2)	1.82 (1)
C(101)	-	P(1)	1.85 (1)	C(201)	-	P(2)	1.78 (1)

Bond angles (°)

Ru(1) - Au(1) - Au(2)	63.6(-)	Ru(2) - Au(1) - Au(2)	60.6(-)
Ru(2) - Au(1) - Ru(1)	64.3(-)	Ru(3) - Au(1) - Au(2)	111.0(-)
Ru(3) - Au(1) - Ru(1)	63.1(-)	Ru(3) - Au(1) - Ru(2)	58.6(-)
Ru(1) - Au(2) - Au(1)	57.9(-)	Ru(2) - Au(2) - Au(1)	61.7(-)
Ru(2) - Au(2) - Ru(1)	62.8(-)	Ru(2) - Ru(1) - Au(1)	60.0(-)
Au(2) - Ru(1) - Au(1)	58.6(-)	Ru(3) - Ru(1) - Au(1)	63.7(-)
Ru(2) - Ru(1) - Au(2)	57.7(-)	Ru(3) - Ru(1) - Ru(2)	57.6(-)
Ru(3) - Ru(1) - Au(2)	107.7(-)	Ru(1) - Ru(2) - Au(1)	55.7(-)
Au(2) - Ru(2) - Au(1)	57.8(-)	Ru(3) - Ru(2) - Au(1)	64.0(-)
Ru(1) - Ru(2) - Au(2)	59.5(-)	Ru(3) - Ru(2) - Ru(1)	62.3(-)
Ru(3) - Ru(2) - Au(2)	113.2(-)	Ru(2) - Ru(3) - Au(1)	57.3(-)
Ru(1) - Ru(3) - Au(1)	53.2(-)	C(9) - P(1) - Ru(1)	112.3(4)
Ru(2) - Ru(3) - Ru(1)	60.1(-)	C(203) - C(202) - Ru(1)	122 (1)
C(9) - P(1) - Ru(2)	115.8(5)	P(2) - C(9) - P(1)	102.7(7)
C(9) - P(2) - Ru(3)	113.2(5)	C(201) - C(202) - Ru(1)	121.0(9)

significantly lower yield (57% and 21%, respectively).

The reaction of $\text{Ru}_3(\mu_3\text{-NPh})_2(\text{CO})_9$, (34) with the oxonium reagent and $[\text{ppn}][\text{Co}(\text{CO})_4]$ in tetrahydrofuran similarly afforded orange crystals of $\text{Ru}_3(\mu_3\text{-NPh})_2(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (35) in 75% yield. Identification of both complexes was made on the basis of microanalytical and spectroscopic data. The solution IR spectrum of (33) shows six terminal $\nu(\text{CO})$ bands while the ^1H NMR spectrum shows the phenyl protons as a multiplet around $\delta 7.48$. The IR spectrum of (35) shows seven $\nu(\text{CO})$ bands. The phenyl protons resonate as a multiplet at $\delta 6.67\text{-}7.64$. The FAB mass spectra of (33) and (35) are very similar and show the expected peaks, as well as a peak assigned to $[\text{M} - 8\text{CO} - \text{Ph}]^+$; in both spectra the ion $[\text{Au}(\text{PPh}_3)]^+$ is dominant. Neither compound has so far given crystals suitable for X-ray structural analysis. The molecular structure of (34) shows an 'open' Ru_3 triangle, capped on both sides by a $\mu_3\text{-NPh}$ group.⁴⁶ Although (32) has not undergone an X-ray structural determination it is assumed to have a similar structure to $\text{Os}_3(\mu_3\text{-S})_2(\text{CO})_9$, which shows an open Os_3 triangle capped on both sides by a $\mu_3\text{-S}$ group.⁴⁷ The M_3R_2 core in (32) and (34) is thus based on a trigonal-bipyramidal arrangement, with the R groups occupying axial positions. It is possible that the Au atoms in complexes (33) and (35) are either situated apart from each other (e.g. Figure 6) or are bonded together (by analogy with the previous compounds discussed in this thesis).

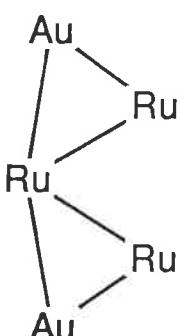


Figure 6

Preparation of Ru₆C(CO)₁₆{Au(PPh₃)₂} (36)

The reaction of Ru₆C(CO)₁₇ with [O{Au(PPh₃)₃}][BF₄]/[ppn]-[Co(CO)₄] in tetrahydrofuran gave red crystals of Ru₆C(CO)₁₆{Au(PPh₃)₂}·0.5CH₂Cl₂ (36) after crystallisation from dichloromethane/methanol. Identification was made on the basis of spectroscopic and microanalytical data. The solution IR spectrum shows four terminal ν(CO) bands and a bridging ν(CO) band. The FAB mass spectrum shows a molecular ion and a peak due to the loss of one carbonyl ligand. The other significant peaks are at *m/z* 1530 assigned to [M - Au(PPh₃) + H]⁺ and the usual peaks due to [Au(PPh₃)₂]⁺ and [Au(PPh₃)]⁺.

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This complex has been synthesised previously by Lewis *et al* from the reaction of [Ru₆C(CO)₁₆]²⁻ with AuCl(PPh₃); similarly prepared were Ru₆C(CO)₁₆{Au(PMePh₂)₂} (37), Ru₆C(CO)₁₆{Au(PEt₃)₂} (38), Ru₆C(CO)₁₆{Au(PMe₃)₂}, Ru₆C(CO)₁₆{Au(PEt₃)}{Au(PPh₃)} and Ru₆C(CO)₁₆{Au₂(dppe)}.

Molecular Structure of Ru₆C(CO)₁₆{Au(PPh₃)₂}·0.5CH₂Cl₂ (36)

A crystal of (36) which was suitable for X-ray analysis was obtained by recrystallisation from dichloromethane/methanol.

The molecular structure of Ru₆C(CO)₁₆{Au(PPh₃)₂} is shown in Fig. 7 (see Table 4). The most obvious feature is that there is no Au-Au interaction; the gold atoms are situated as far apart as possible, bridging opposite Ru-Ru edges of an octahedron of ruthenium atoms with the carbide atom C(1) lying at a crystallographic centre of symmetry. The bond Ru(1)-Ru(2) is bridged by the Au(PPh₃) ligand while the bond Ru(1)-Ru(2B) is bridged by a carbonyl ligand. The remaining carbonyls are terminal, two bonded to Ru(1) and Ru(2) and three to Ru(3).

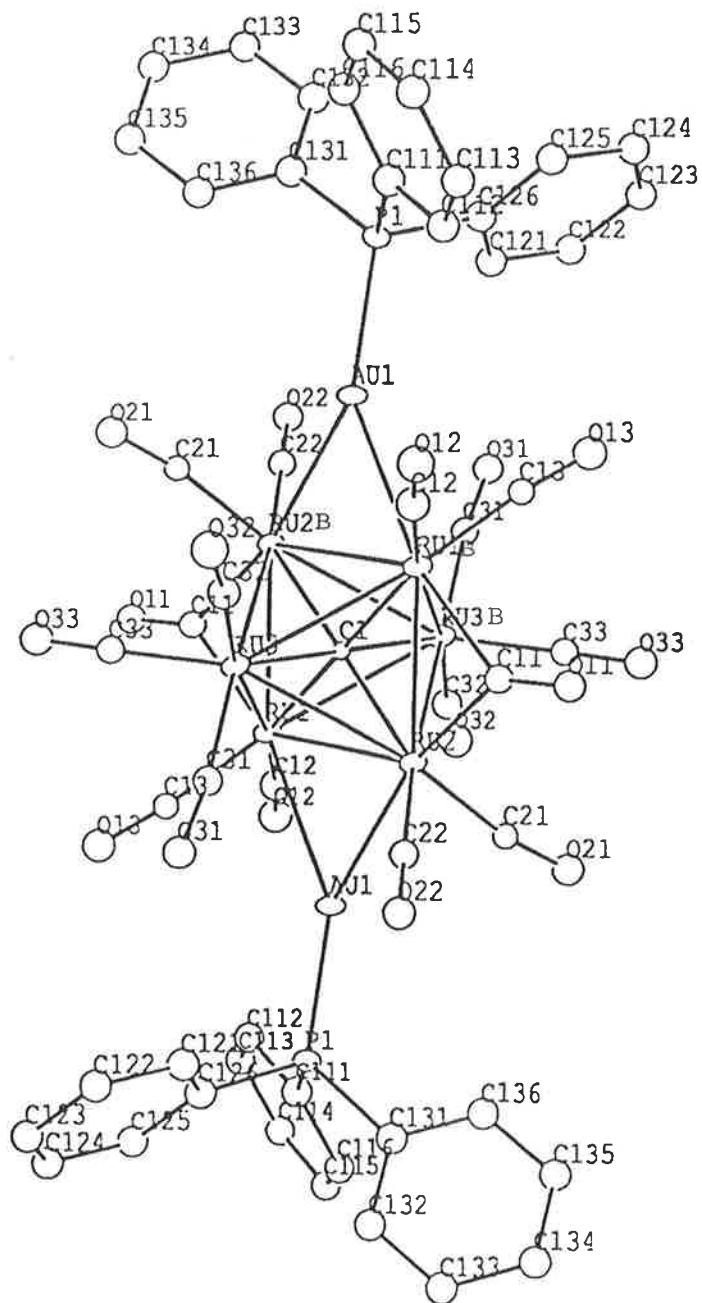


Figure 7: PLUTO plot of the molecular structure of
 $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PPh}_3)\}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (36)
 (by E. Horn and E.R.T. Tiekkink)

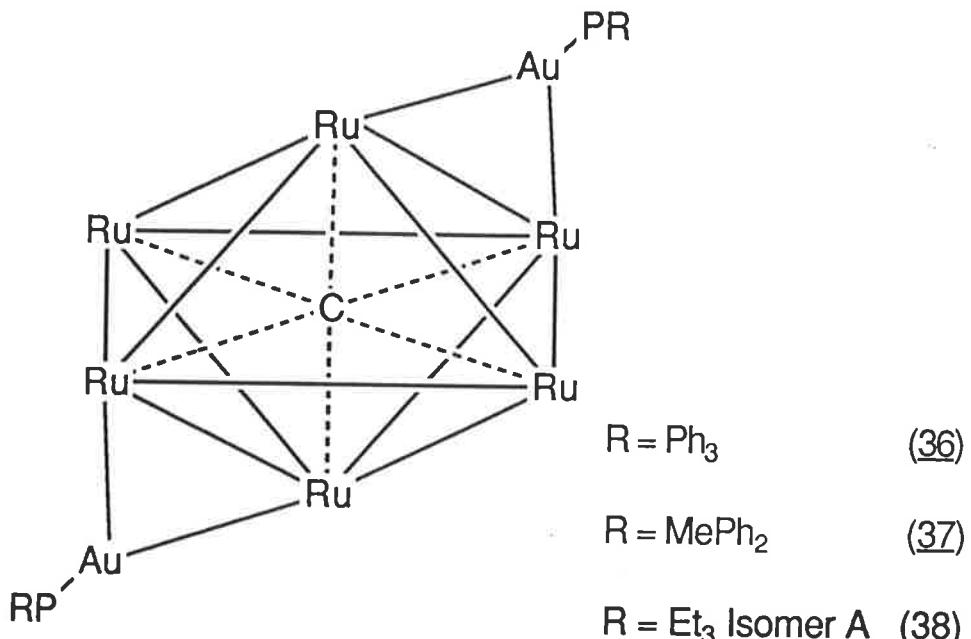
Table 4 : Selected interatomic parameters for (36)Bond distances (Å)

Ru(1) - Au(1)	2.787(2)	Ru(2) - Au(1)	2.753(2)
P(1) - Au(1)	2.281(6)	Ru(3) - Ru(1)	2.940(3)
Ru(2) - Ru(1)	3.050(3)	C(1) - Ru(2)	2.078(2)
C(1) - Ru(1)	2.076(2)	Ru(3) - Ru(2)	2.877(2)
C(1) - Ru(3)	2.023(2)		

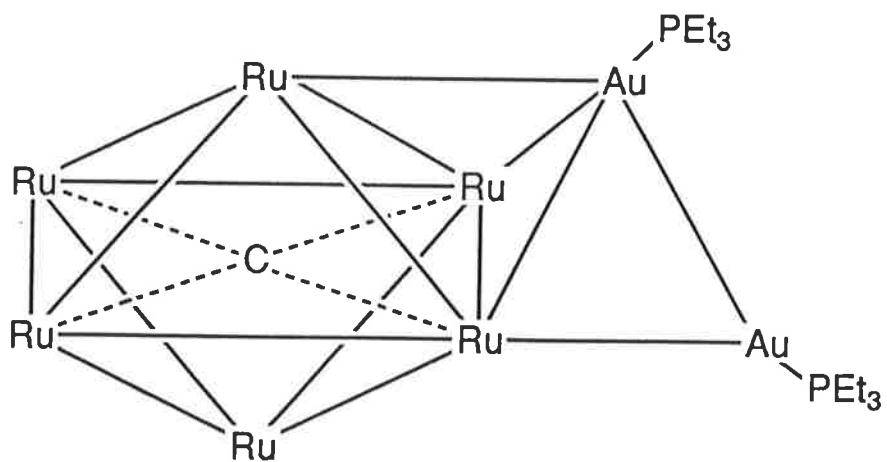
Bond angles (°)

Ru(2) - Au(1) - Ru(1)	66.8(1)	P(1) - Au(1) - Ru(1)	145.1(2)
Ru(2) - Ru(1) - Au(1)	56.1(1)	Ru(3) - Ru(1) - Au(1)	97.9(1)
Ru(3) - Ru(1) - Ru(2)	57.4(1)	C(1) - Ru(1) - Au(1)	98.8(1)
C(1) - Ru(1) - Ru(2)	42.8(1)	C(1) - Ru(1) - Ru(3)	43.5(1)
Ru(1) - Ru(2) - Au(1)	57.1(1)	Ru(1) - C(1) - Ru(1)	180.0(1)
Ru(3) - Ru(2) - Ru(1)	59.4(1)	Ru(3) - Ru(2) - Au(1)	100.3(1)
C(1) - Ru(2) - Ru(1)	42.7(1)	C(1) - Ru(2) - Au(1)	99.8(1)
Ru(2) - Ru(3) - Ru(1)	63.2(1)	C(1) - Ru(2) - Ru(3)	44.7(1)
C(1) - Ru(3) - Ru(2)	46.2(1)	Ru(2) - C(1) - Ru(2)	180.0(1)
Ru(2) - C(1) - Ru(1)	94.5(1)	C(1) - Ru(3) - Ru(1)	44.9(1)
Ru(3) - C(1) - Ru(2)	89.1(1)	Ru(3) - C(1) - Ru(3)	180.0(1)
		Ru(3) - C(1) - Ru(1)	91.6(1)

The Ru-Ru bond lengths range from $2.877(2)$ - $3.050(3)\text{\AA}$; the longest is Ru(1)-Ru(2). The Au-Ru bonds are unexceptional [Au(1)-Ru(1), Ru(2) $2.787(2)$, $2.753(2)\text{\AA}$]. This structure is very similar to that of $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PMePh}_2)\}_2$ (37) which has been determined previously.⁴⁸



It is worth noting that $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PEt}_3)\}_2$ (38) has been found to be fluxional in solution, being in equilibrium with the isomer containing an ' $\text{Au}_2(\text{PEt}_3)_2$ ' moiety capping an Ru_3 face [as found for the structure of $\text{Ru}_5\text{WC}(\text{CO})_{17}\{\text{Au}_2(\text{PEt}_3)_2\}$].⁴⁸



Preparation of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40)

The addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (39) in tetrahydrofuran gave an immediate colour change from yellow to orange. After chromatographic separation and crystallisation from dichloromethane/n-heptane, red-orange crystals of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})-(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40) were obtained in high yield, again demonstrating the replacement of a carbonyl ligand by the $\text{Au}_2(\text{PPh}_3)_2$ unit. This compound is analogous to $\text{Ru}_3(\text{CO})_8-(\mu_3-\text{C}\equiv\text{CBu}^t)\{\text{Au}_3(\text{PPh}_3)_3\}$ prepared in 3% yield from the reaction of $[\text{Ru}_3(\mu_3-\text{C}\equiv\text{CBu}^t)(\text{CO})_9]^-$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$,^{4,9} for which an X-ray structure was not reported.

Identification of (40) was made in the usual manner. The solution IR spectrum shows seven $\nu(\text{CO})$ bands, while the ^1H NMR spectrum shows the phenyl protons as a multiplet from $\delta 6.99-7.57$. The FAB mass spectrum shows peaks assigned to $[M]^+$ and $[M + \text{Au}(\text{PPh}_3)]^+$ which undergo the expected fragmentation via stepwise loss of carbonyl ligands, while the peak assigned to $[M - \text{CO}]^+$ fragments by loss of PPh_3 and $\text{Au}(\text{PPh}_3)$. As expected, the major peaks are $[\text{Au}(\text{PPh}_3)_2]^+$ and $[\text{Au}(\text{PPh}_3)]^+$.

Structure of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40)

In (40) there are eleven metal-metal bonds: three Au-Au, $2.809(2)-2.911(2)\text{\AA}$, five Au-Ru $2.674(2)-2.919(2)\text{\AA}$ and three Ru-Ru, $2.776(2)-2.971(3)\text{\AA}$ (Figure 8, see also Table 5). The Au atoms form a triangular system, but instead of the expected capped trigonal bipyramidal system, the arrangement of the six atoms is best described as a distorted capped square pyramid, with two basal golds and rutheniums and an apical ruthenium [Ru(1)] - the third gold atom caps on Au₂Ru face.

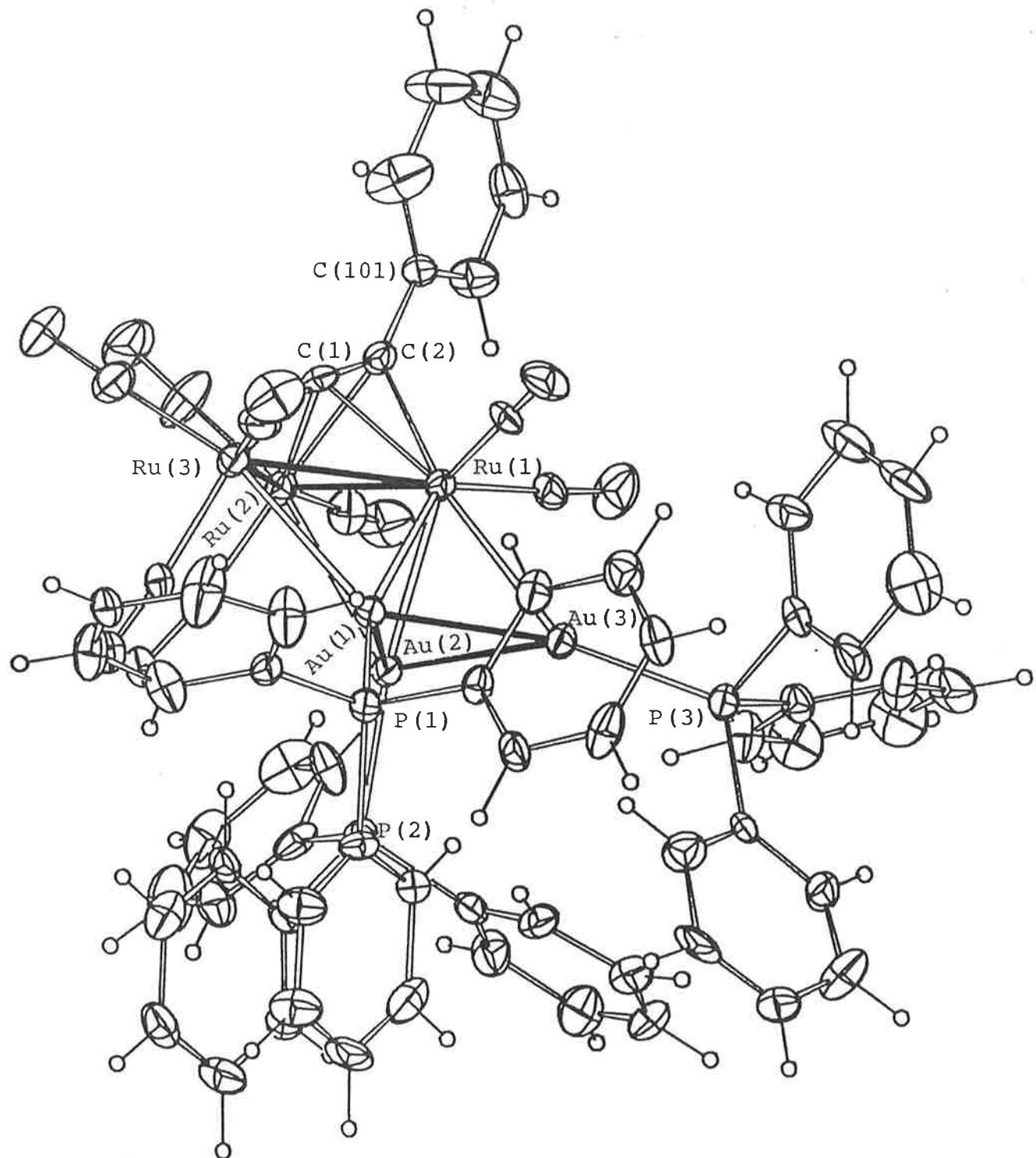


Figure 8: ORTEP plot of the molecular structure of
 $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\} \cdot 0.5\text{C}_7\text{H}_{16}$ (40)
 (by B.W. Skelton and A.H. White)

Table 5: Selected interatomic parameters for (40)

Bond distances (Å)

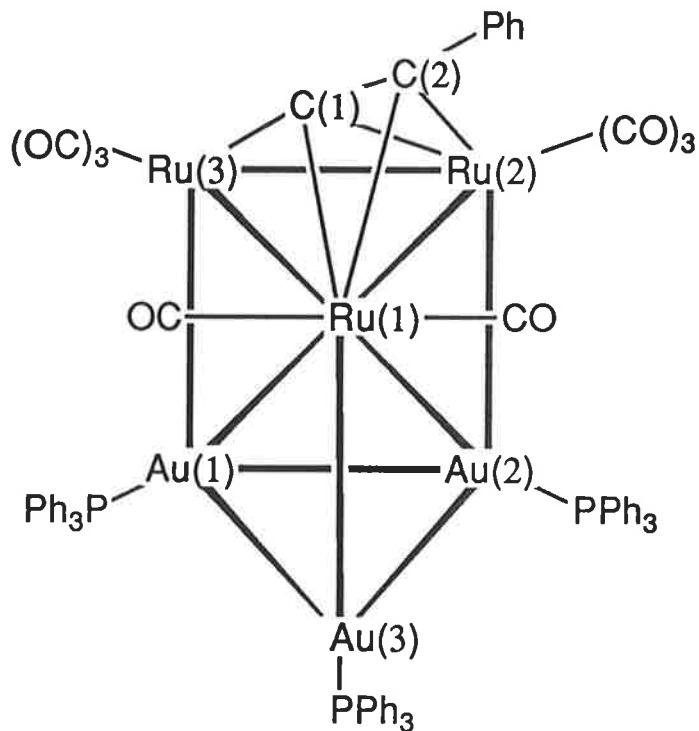
Au(1) -	Au(2)	2.911(2)	Ru(1) -	Ru(2)	2.776(2)
Au(1) -	Au(3)	2.809(2)	Ru(1) -	Ru(3)	2.971(3)
Au(1) -	Ru(1)	2.707(2)	Ru(1) -	C(1)	2.15 (1)
Au(1) -	Ru(3)	2.868(2)	Ru(1) -	C(2)	2.19 (1)
Au(1) -	P(1)	2.299(4)	Ru(2) -	Ru(3)	2.844(2)
Au(2) -	Au(3)	2.899(2)	Ru(2) -	C(1)	2.20 (2)
Au(2) -	Ru(1)	2.674(2)	Ru(2) -	C(2)	2.21 (2)
Au(2) -	Ru(2)	2.919(2)	Ru(3) -	C(1)	1.95 (1)
Au(2) -	P(2)	2.299(5)	C(1) -	C(2)	1.30 (2)
Au(3) -	Ru(1)	2.721(2)	C(2) -	C(101)	1.48 (2)
Au(3) -	P(3)	2.282(4)			

Bond angles (°)

Au(2) - Au(1) - Au(3)	60.87(5)	Ru(1) - Au(2) - Ru(2)	59.32(5)
Au(2) - Au(1) - Ru(1)	56.71(5)	Au(1) - Au(3) - Au(2)	61.30(5)
Au(2) - Au(1) - Ru(3)	85.44(6)	Au(1) - Au(3) - Ru(1)	58.60(6)
Au(3) - Au(1) - Ru(1)	59.07(5)	Au(2) - Au(3) - Ru(1)	56.73(5)
Au(3) - Au(1) - Ru(3)	123.24(6)	Au(1) - Ru(1) - Au(2)	65.49(5)
Ru(1) - Au(1) - Ru(3)	64.34(6)	Au(1) - Ru(1) - Au(3)	62.33(6)
Au(1) - Au(2) - Au(3)	57.83(5)	Au(1) - Ru(1) - Ru(2)	99.88(7)
Au(1) - Au(2) - Ru(1)	57.80(5)	Au(1) - Ru(1) - Ru(3)	60.45(5)
Au(1) - Au(2) - Ru(2)	92.10(6)	Au(2) - Ru(1) - Au(3)	64.99(5)
Au(3) - Au(2) - Ru(1)	58.28(5)	Au(2) - Ru(1) - Ru(2)	64.73(6)
Au(3) - Au(2) - Ru(2)	117.45(5)	Au(2) - Ru(1) - Ru(3)	87.79(7)
Au(3) - Ru(1) - Ru(2)	129.53(7)	Ru(1) - C(1) - Ru(2)	79.4 (5)
Au(3) - Ru(1) - Ru(3)	122.62(7)	Ru(3) - C(1) - C(2)	158 (1)
Ru(2) - Ru(1) - Ru(3)	59.20(6)	Ru(1) - C(2) - Ru(2)	78.1 (5)
C(1) - Ru(1) - C(2)	34.9 (5)	C(1) - C(2) - C(101)	140 (1)
Au(2) - Ru(2) - Ru(1)	55.94(5)	Au(2) - Ru(2) - Ru(3)	85.72(7)
Ru(1) - Ru(2) - Ru(3)	63.82(7)	C(1) - Ru(2) - C(2)	34.3 (5)
Au(1) - Ru(3) - Ru(1)	55.21(6)	Au(1) - Ru(3) - Ru(2)	94.59(7)
Ru(1) - Ru(3) - Ru(2)	56.98(6)		

The bond angles of the Ru_2Au_2 base range from $85.44(6)^\circ$ [$\text{Au}(2)-\text{Au}(1)-\text{Ru}(3)$] to $94.59(7)^\circ$ [$\text{Au}(1)-\text{Ru}(3)-\text{Ru}(2)$]. There are two longer bonds [$\text{Ru}(2)-\text{Au}(2)$ $2.919(2)\text{\AA}$ and $\text{Au}(1)-\text{Au}(2)$ $2.911(2)\text{\AA}$] and two shorter bonds [$\text{Ru}(3)-\text{Au}(1)$ $2.868(2)\text{\AA}$ and $\text{Ru}(3)-\text{Ru}(2)$ $2.844(2)\text{\AA}$]. The bond lengths from the base to $\text{Ru}(1)$ range from $2.674(2)\text{\AA}$ [$\text{Au}(2)$] to $2.971(3)$ [$\text{Ru}(3)$]. The bond length of $\text{Au}(3)$ to $\text{Ru}(1)$ is $2.721(2)\text{\AA}$. The $\text{Au}-\text{Ru}(1)$ bonds [$2.674(2)-2.721(2)\text{\AA}$] are significantly shorter than the $\text{Au}-\text{Ru}$ bonds not involving $\text{Ru}(1)$ [$2.868(2)\text{\AA}$ and $2.919(2)\text{\AA}$].

The phenyl acetylide ligand in (40) interacts with all three Ru atoms, via a σ -bond with $\text{Ru}(3)$ [$\text{C}(1)-\text{Ru}(3)$ $1.95(1)\text{\AA}$] and two π -bonds with $\text{Ru}(2)$ and $\text{Ru}(1)$ [$\text{C}(1)-\text{Ru}(1)$, $\text{Ru}(2)$ $2.15(1)$, $2.20(2)\text{\AA}$, $\text{C}(2)-\text{Ru}(1)$, $\text{Ru}(2)$ $2.19(1)$, $2.21(2)\text{\AA}$].



(40)

This type of structure with a distorted Ru_3Au_2 square pyramid has previously been found in the structure of the bicapped square pyramidal metal framework of $\text{Ru}_4(\mu\text{-H})(\text{CO})_{12}$ - $(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\{\text{Au}_3(\text{PPh}_3)_3\}$ (41)⁵⁰, which is capped on two adjacent triangular faces of the square pyramid by a $\text{Ru}(\text{CO})_3$ and a $\text{Au}(\text{PPh}_3)$ unit.

The number of heteronuclear clusters containing three AuL fragments is much lower than those with one or two. Apart from the above-mentioned clusters there are only four other Ru_3 or Ru_4 complexes with three $\text{Au}(\text{PPh}_3)$ units (all face capping) which have undergone X-ray structural determination and which show either (a) an open arrangement of the Au_3P_3 sub-units $[\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9\{\text{Au}_3(\text{PPh}_3)_3\}$ (42)²⁹, $\text{Ru}_4(\mu\text{-H})(\text{CO})_{12}\{-\text{Au}_3(\text{PPh}_3)_3\}$ (43)^{51,52} and $\text{CoRu}_3(\text{CO})_{12}\{\text{Au}_3(\text{PPh}_3)_3\}$ (44)²⁷] or (b) a closed triangular arrangement for $\text{Ru}_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8\{-\text{Au}_3(\text{PPh}_3)_3\}$ (45)⁵³ similar to that observed for (40), but showing an overall capped trigonal bipyramidal geometry of the metals, instead of a distorted capped square pyramidal geometry. Bonding types (a) and (b) are shown in Figure 9.

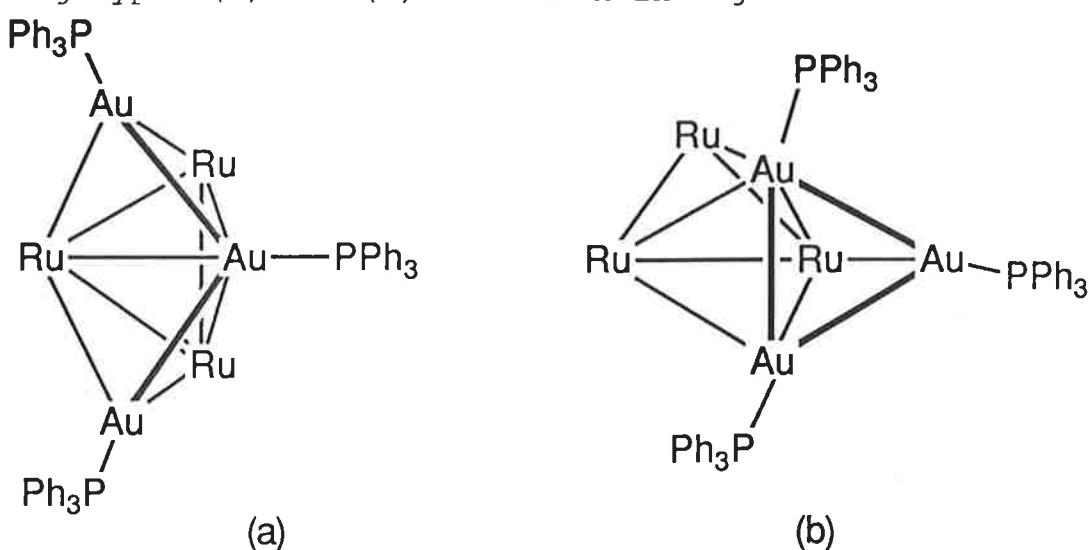


Figure 9 : Projections of Au_3P_3 sub-units onto the capped triangular Ru_3 faces

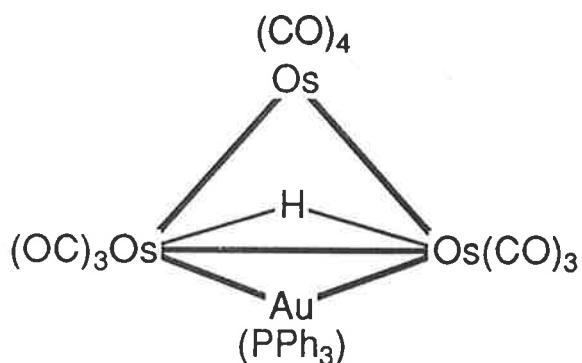
The energy difference between the acyclic and cyclic structures of H_3^+ attached to metals is calculated to be small,^{5,4} and it is possible that a similar small energy difference exists between the two forms of $[\text{Au}_3(\text{PR}_3)_3]^+$. The structure which is adopted by any particular complex probably depends on the steric constraints and the number of types of interactions with other metal atoms.

Addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to Osmium and Ruthenium Hydrido Clusters

Addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to a solution of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ in tetrahydrofuran resulted in a colour change from purple to green. Three main products were separated by TLC and crystallised. Several other unidentified complexes were present in trace amounts.

A green band ($R_f = 0.60$) was crystallised from dichloromethane/methanol to give $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}$ (7), in 15% yield, identified from its microanalytical and spectroscopic data. The FAB mass spectrum shows a strong $[\text{M}]^+$ peak and peaks corresponding to the stepwise loss of the carbonyl ligands. The major peaks are $[\text{Au}(\text{PPh}_3)_2]^+$ and $[\text{Au}(\text{PPh}_3)]^+$, the latter being the base peak. This complex was previously obtained from $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ and $\text{AuMe}(\text{PPh}_3)$ ^{5,5} and from the reaction of $[\text{ppn}][\text{Os}_3\text{H}(\text{CO})_{11}]$ with $\text{AuCl}(\text{PPh}_3)$.^{21,36} The yield from the latter reaction was enhanced by the inclusion of TlPF_6 (to remove Cl^- from the reaction mixture) (Scheme 3).^{21,36} Similarly (7) was synthesised by first isolating $\text{Os}_3\text{H}(\text{CO})_{11}\{-\{\text{Au}(\text{PPh}_3)\}$ and then heating to remove a carbonyl ligand (Scheme 3).³⁶

The molecular structure of (7)²¹ shows that the three osmium atoms define a distorted isosceles triangle, the short edge of which is bridged by the gold atom to give a butterfly arrangement. The hydride ligand was not located directly but was assumed also to bridge the short edge.



(7)

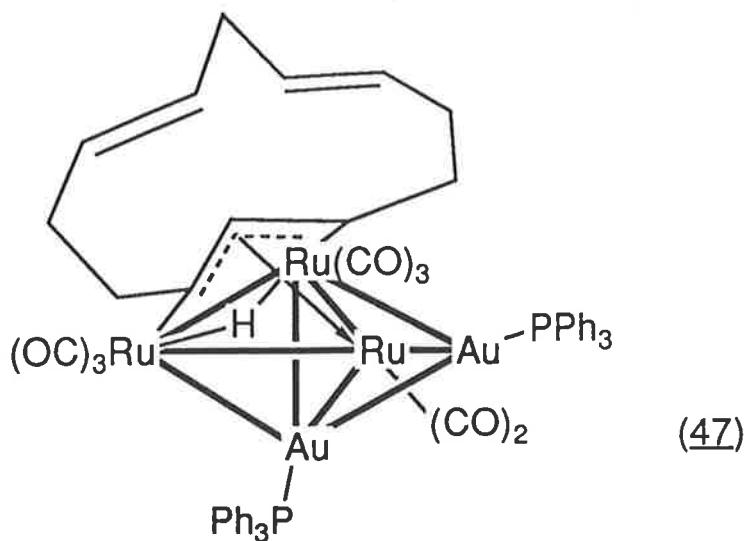
A green-yellow band ($R_f = 0.43$) was crystallised from dichloromethane/methanol to give green crystals of $\text{Os}_3(\text{CO})_{10} \cdot \{\text{Au}(\text{PPh}_3)\}_2$ (21) (16%), identified by comparison of its IR $\nu(\text{CO})$ spectrum with that of an authentic sample.

A yellow band ($R_f = 0.31$) was crystallised (dichloromethane/methanol) to give golden yellow crystals of a compound tentatively identified as $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{PPh}_3) \cdot \{\text{Au}(\text{PPh}_3)\}_2$ (46) (8%) on the basis of microanalytical and spectroscopic data. The FAB mass spectrum shows a strong peak at $[M]^+$, and aggregation peaks at $[M + \text{Au}(\text{PPh}_3)]^+$ and $[M + \text{Au}]^+$. Very strong peaks at m/z 1468 and m/z 1704 are assigned to $[M - \text{Au}(\text{PPh}_3) - \text{Ph} - 2\text{H}]^+$ and $[M - 8\text{CO} - \text{Ph} - \text{H}]^+$, respectively. The peaks due to $[\text{Au}(\text{PPh}_3)_2]^+$ and $[\text{Au}(\text{PPh}_3)]^+$ are again dominant. The solution IR spectrum shows one strong band in the $\nu(\text{CO})$ region with six weaker bands.

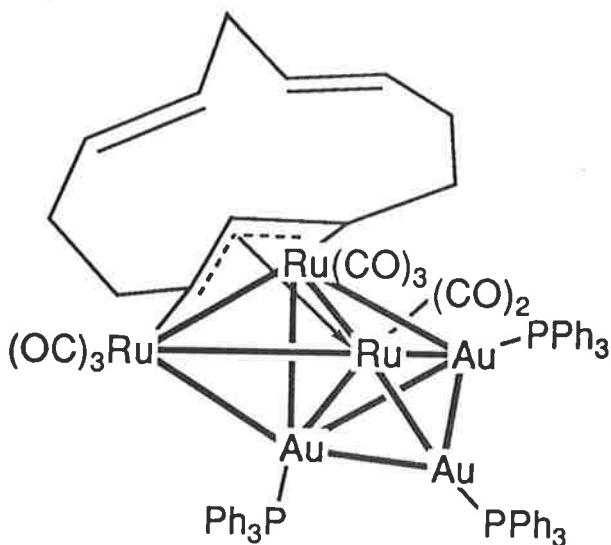
The ^1H NMR spectrum contains two distinct metal hydride resonances at δ -17.04 [t, $J(\text{PH}) = 15\text{Hz}$] and -7.01 [d, $J(\text{PH}) = 12\text{Hz}$], while the phenyl protons are seen as a multiplet from δ 7.16-7.47. At present the molecular structure of this compound is unknown.

An immediate colour change from yellow to purple resulted on addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to a solution of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9$ in tetrahydrofuran. Preparative TLC gave two major fractions.

A red band ($R_f = 0.60$) was crystallised (acetone) to give red-brown $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (47) (60%), identified by the usual methods. The solution IR spectrum of (47) shows five bands in the $\nu(\text{CO})$ region while the FAB mass spectrum shows the expected peaks. The dominant peaks are $[\text{Au}(\text{PPh}_3)]^+$ and $[\text{Au}(\text{PPh}_3)_2]^+$, the base peak. The ^1H NMR spectrum of (47) shows a doublet at δ -21.15 assigned to the metal bonded hydrogen, a multiplet from δ 1.71-5.80 assigned to protons of the C_{12} ring while the phenyl protons are seen as a multiplet from δ 7.18-7.48. The allylic CH proton is seen as a doublet at δ 6.39 [$J(\text{HH}) = 2.3\text{Hz}$], due to coupling between this proton and the metal hydride.



The other major coloured band (purple, $R_f = 0.52$) was crystallised (dichloromethane/methanol) affording purple crystals of the known complex $\text{Ru}_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (45) (29%), identified by comparison of its solution IR and FAB mass spectra with those previously obtained.^{5,3} This compound had been synthesised in 29% yield from the reaction of $[\text{Ru}_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9]^-$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]^{5,3}$. The structure of (45) shows the capped trigonal bipyramidal geometry, formed conceptually by the addition of an $\text{Au}(\text{PPh}_3)$ to an Ru_2Au face of an Ru_3Au tetrahedron, followed by capping of an RuAu_2 face of the resulting trigonal bipyramid.



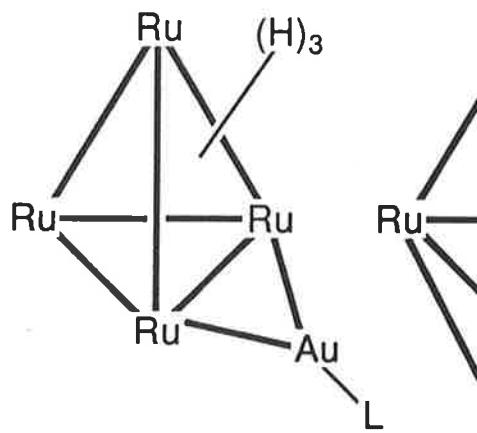
(45)

The reaction of $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]^-$ $[\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ in tetrahydrofuran yielded, after preparative TLC, a small amount of the starting cluster (9%) and three major products, $\text{Ru}_4(\mu_3\text{-H})(\mu\text{-H})_2(\text{CO})_{12}\{\text{Au}(\text{PPh}_3)\}$ (48) (3%), $\text{Ru}_4(\mu_3\text{-H})(\mu\text{-H})(\text{CO})_{12}\{\text{Au}_2(\text{PPh}_3)_2\}$ (9) (33%) and $\text{Ru}_4(\mu\text{-H})(\text{CO})_{12}\{\text{Au}_3(\text{PPh}_3)_3\}$ (43) (2%), in order of decreasing R_f on the silica plate. All were identified by comparison of their solution IR spectra with those of authentic samples, and from their FAB mass spectra. The FAB mass spectrum of (48) shows a weak molecular ion at m/z 1204 and peaks corresponding to the loss of one, two and three carbonyl ligands; other peaks are assigned to $[\text{M} - \text{nCO} - 2\text{H}]^+$ ($n = 4 - 9$). Similarly the FAB mass spectrum of (9) shows peaks at $[\text{M}]^+$, $[\text{M} - \text{CO}]^+$ and $[\text{M} - \text{nCO} - 2\text{H}]^+$ ($n = 2 - 12$), while the spectrum of the Au_3Ru_4 compound shows peaks corresponding to the molecular ion and the loss of three, five and six carbonyl ligands. Peaks at $[\text{Au}(\text{PPh}_3)_2]^+$ and $[\text{Au}(\text{PPh}_3)]^+$ again dominate all three spectra.

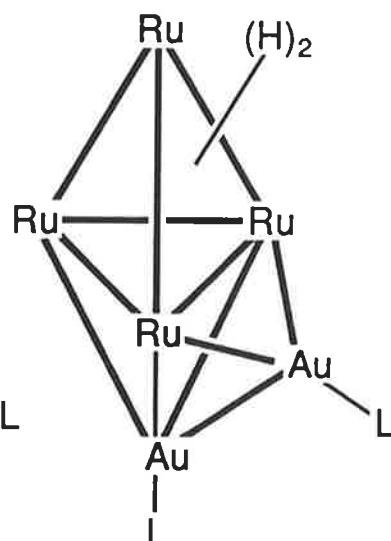
A previous reaction in which $[\text{Ru}_4(\mu\text{-H})_3(\text{CO})_{12}]^-$ and $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ were stirred together for four hours in tetrahydrofuran afforded the same products, although the yields were significantly different.⁵¹ In that study, (48) was isolated in 10% yield, while (9) and (43) were present in 3% and 15% yields, respectively. The gold oxonium reagent when reacted in conjunction with $[\text{ppn}][\text{Co}(\text{CO})_4]$ therefore provided a much higher yield of the bis-gold complex, but much less of the tri-gold complex.

The structures of all three of these compounds have been determined previously. The X-Ray structure of (48), shows that the gold bridges an edge according to the isolobal analogy with the H derivative.⁵⁶ The positions of the hydride atoms differ

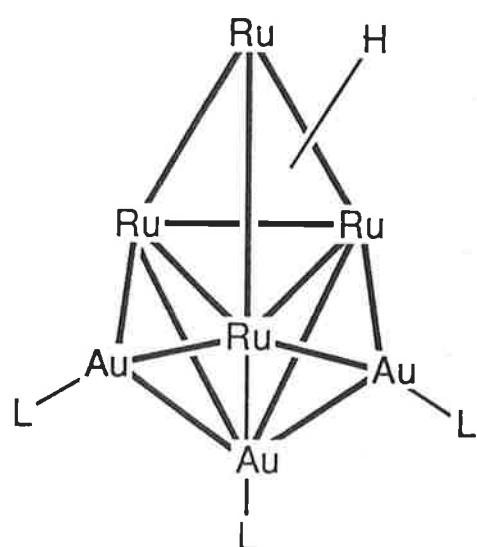
from those observed in $[\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}]$,⁵⁷ however, with two edge-bridging and one capping an Ru_3 face. The second gold atom in $\text{Ru}_4(\mu_3\text{-H})(\mu\text{-H})(\text{CO})_{12}\{\text{Au}_2(\text{PPh}_3)_2\}$ caps a AuRu_3 face therefore giving Au-Au bonding,²² while the third gold atom in (43) then caps a AuRu_2 face.^{51,52} The hydrides were not located in (9) and (43) but in (9) one is thought to be edge-bridging and the other triply-bridging an AuRu_2 face of the cluster, while in (43) the disposition of the carbonyl groups indicates that the hydride is edge-bridging.⁵¹



(48)



(9)



(43)

$^{31}\text{P}\{\text{H}\}$ NMR spectra of some gold-containing mixed metal clusters

The $^{31}\text{P}\{\text{H}\}$ NMR data obtained for some of the clusters synthesised in this Chapter are shown in Table 6. The chemical shifts for Au-P groups which are bonded to a Ru atom are found from δ 56.7-67.1 at 295K. This is similar to data previously obtained [e.g. δ 62.8 for $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-S})(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (49)⁵⁸, δ 64.4 for $\text{Ru}_3(\mu_3\text{-S})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (25)⁵⁸, δ 68.7 for the AuPPh_3 group of $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (50)⁵⁹ and δ 58.7 for $\text{Ru}_4(\mu_3\text{-H})(\mu\text{-H})(\text{CO})_{12}\{\text{Au}_2(\text{PPh}_3)_2\}$ (9)²²] for AuPPh_3 bonded to Ru atoms. The presence of only one signal, where two is expected on symmetry grounds, is explained by dynamic behaviour involving site exchange between structurally inequivalent sites, which is frequently observed in solution.

X-ray diffraction studies of $\text{Ru}_3(\mu_3\text{-S})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}(\text{L})$ [$\text{L} = \text{CO}$ (25), PPh_3 (51)]^{39, 58}, for example, show that both clusters adopt a trigonal bipyramidal geometry, with one gold atom occupying an equatorial site and the other an axial position. However, although there are two geometrically distinct gold sites in the ground state structures of (25) and (51), only a single resonance due to the $\text{Au}(\text{PPh}_3)$ groups was visible in the $^{31}\text{P}\{\text{H}\}$ NMR spectra of the clusters even at 183K.⁵⁸ It was postulated that the metal atom cores of both compounds rearrange in solution with concomitant site exchange of CO groups. The metal atoms undergo a Berry-type mechanism involving a square pyramidal intermediate (Scheme 4). The Scheme shows the scission of Au-Ru bonds which evidently requires little energy.

Table 6

³¹P{¹H} NMR data for some mixed metal clusters obtained in this work

<u>Complex</u>	(a), (b)	<u>δAuPPh₃ or δAuPPh₂</u>	<u>Other peaks</u>
		295K	Low Temperature
Ru ₃ (μ ₃ -C≡CPh)(CO) ₉ {Au(PPh ₃)}	(39)	62.5	-
{Ru ₃ (μ ₃ -C≡CPh)(CO) ₉ Au} ₂ dppe	(54)	60.7	-
Ru ₃ (μ ₃ -NPh)(CO) ₉ {Au ₂ (PPh ₃) ₂ }	(24)	64.5	<u>205K:</u> no change
Ru ₃ (μ ₃ -C ₆ H ₄)(μ-PPh ₂) ₂ (CO) ₆ {Au ₂ (PPh ₃) ₂ }	(27)	61.6, 67.1	-
Ru ₃ {μ ₃ -PPhCH ₂ PPh(C ₆ H ₄)}(CO) ₈ {Au ₂ (PPh ₃) ₂ }	(30)	62.9, 63.3	-
Ru ₃ (μ ₃ -S) ₂ (CO) ₈ {Au ₂ (PPh ₃) ₂ }	(33)	64.7	-
Ru ₃ (μ ₃ -NPh) ₂ (CO) ₈ {Au ₂ (PPh ₃) ₂ }	(35)	63.1	-
Ru ₃ (μ-H)(μ ₃ -C ₁₂ H ₁₅)(CO) ₈ {Au ₂ (PPh ₃) ₂ }	(47)	58.3	-
Ru ₃ (μ ₃ -C≡CPh)(CO) ₈ {Au ₃ (PPh ₃) ₃ }	(40)	56.7 ^(c)	<u>255K:</u> 51.7, 56.7, 65.3
Ru ₃ (μ ₃ -C ₁₂ H ₁₅)(CO) ₈ {Au ₃ (PPh ₃) ₃ }	(45)	60.3 ^(c)	<u>245K:</u> 46.2, 61.7, 64.5
Os ₃ (CO) ₁₀ {Au(PPh ₃) ₂ }	(21)	81.3	-

(a) Solvent CH₂Cl₂(b) External reference 0.1M HCl/0.01M H₃PO₄ in D₂O (δ0.8)

(c) Broad signal

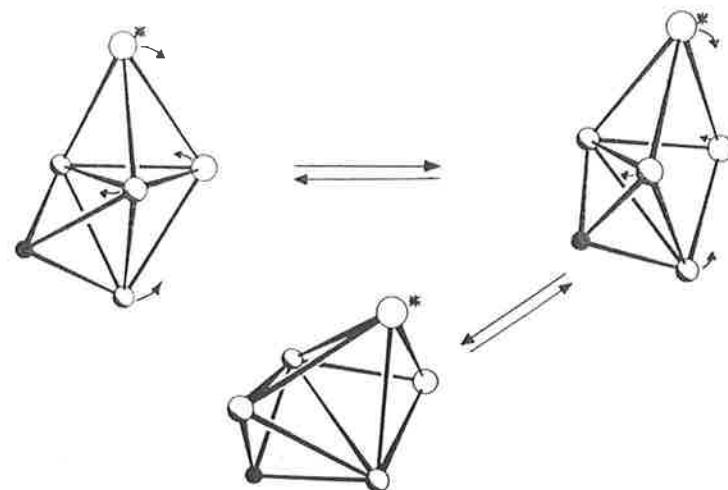
(d) PPh₂(e) doublet, *J*(PP)=96Hz, terminal P

(f) doublet, bridging P

1ω

ω

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Scheme 4: Interconversion of trigonal bipyramidal and square pyramidal forms of (25) or (51) leading to exchange between gold sites: a restricted Berry *pseudo*-rotation. Filled circle is S, shaded circles Ru, and circles are Au atoms.⁵⁸

Similarly, the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\text{-}\{\text{Au}_2(\text{PPh}_3)_2\}$ (24), which has the same core as (25) and (51), shows only one signal even when cooled to 205K.

The spectrum of $\text{Ru}_3(\mu_3\text{-C}\equiv\text{CPH})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40), which adopts a capped distorted square pyramidal geometry with two distinct basal gold atoms and a capping gold atom, similarly shows only one signal at 295K. This signal is broad, which suggests a higher free energy of activation for fluxional behaviour to occur in this compound. Indeed at 255K three singlets are observed, consistent with the three different $\text{Au}(\text{PPh}_3)$ environments observed in the solid state structure of (40).

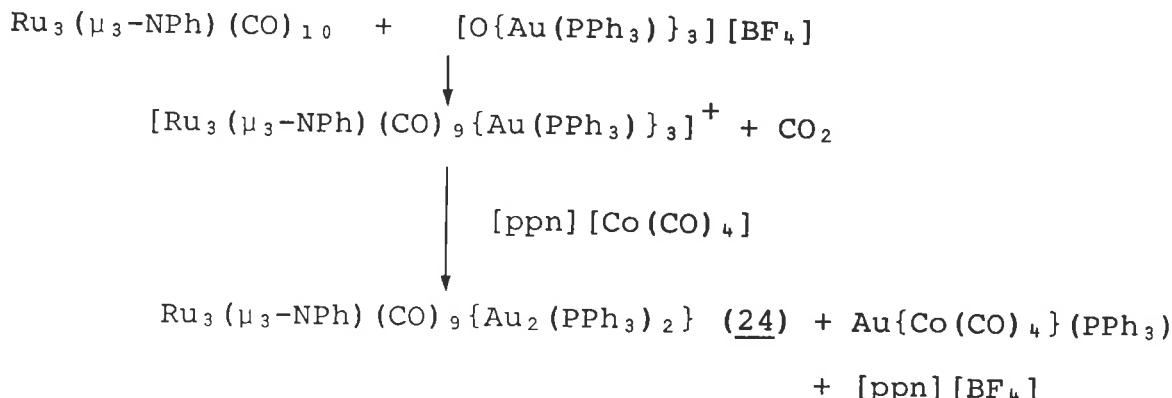
Similarly, the $^{31}\text{P}\{\text{H}\}$ spectrum of $\text{Ru}_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8\text{-}\{\text{Au}_3(\text{PPh}_3)_3\}$ (45), which adopts a capped trigonal bipyramidal geometry, shows one broad signal at 295K but three singlets at 245K.

Signals at δ 61.6 and 67.1 are observed for the Au-P

groups of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (27) showing that the $\text{Au}(\text{PPh}_3)$ moieties are held rigidly in solution. Signals at δ 104.0 and 191.2 are assigned to the two PPh_2 groups. Lack of fluxionality is also observed in the spectrum of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (30) with peaks observed at δ 62.9 and 63.3. Doublet signals at δ 0.7 and 152.1 are assigned to the terminal phosphorus and the bridging phosphorus of the $\text{PPhCH}_2\text{PPhC}_6\text{H}_4$ unit, with reference to ^{31}P data of the starting material, $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$.⁶⁰

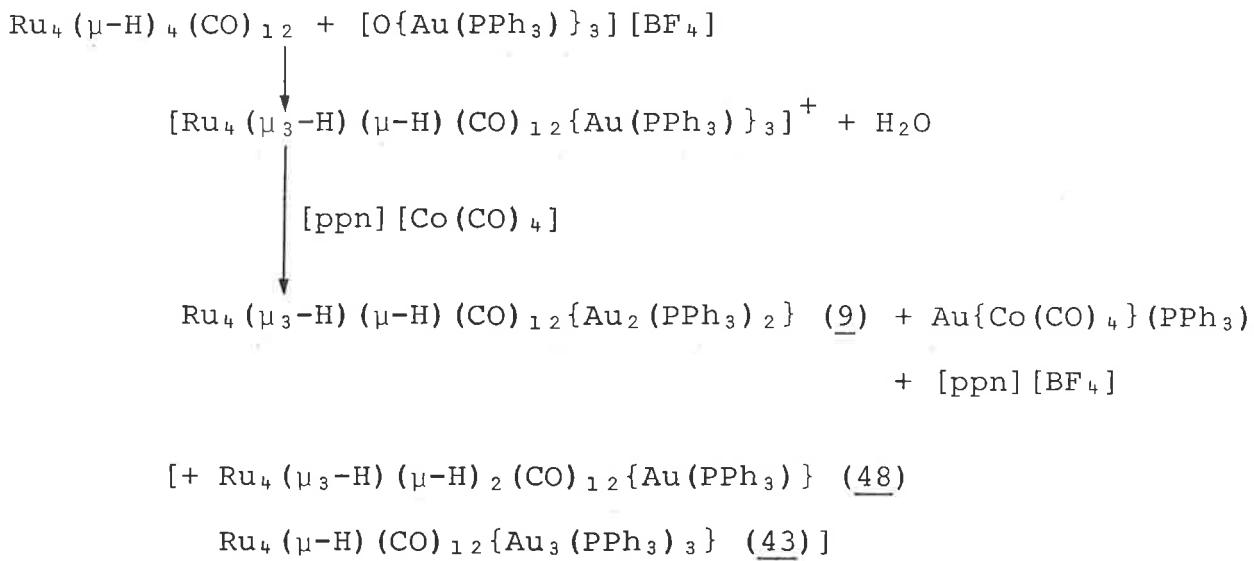
Postulated reaction mechanism

The addition of $[O\{Au(PR_3)\}_3][BF_4]$ [R = Ph (10), OMe (19)]/[ppn][X] [X = Co(CO)₄ (15), OAc, Cl] to neutral clusters in general leads to the loss of a carbonyl ligand, which is replaced by two Au(PR₃) ligands. In contrast, the addition of [ppn][Co(CO)₄] to the oxonium salt in tetrahydrofuran gave an orange solution[#], which did not then react with Os₃(CO)₁₂ to give Os₃(CO)₁₁{Au₂(PPh₃)₂} (17), i.e. a different result to adding the two reagents to the cluster. This suggests that a tri-gold adduct forms initially which then readily loses a [Au(PPh₃)]⁺ in the presence of [ppn][X] to form Au(PPh₃)X. Therefore the cluster undergoes a net reaction with '{Au(PPh₃)₂O}', the oxygen of which is assumed to be liberated with the departing carbonyl ligand as carbon dioxide (e.g. Scheme 5).

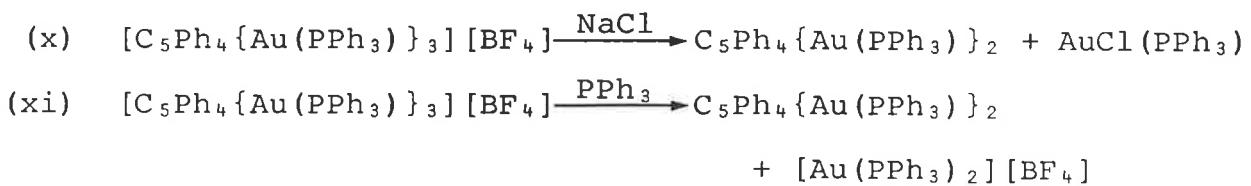
Scheme 5

A similar reaction may occur in the addition of (10) and (15) to metal hydride complexes, in which the hydrides are replaced by Au(PPh₃) moieties, and liberated with the oxygen from the oxonium salt as H₂O (e.g. Scheme 6).

[#]Attempts to characterise this orange solution have not been successful so far.

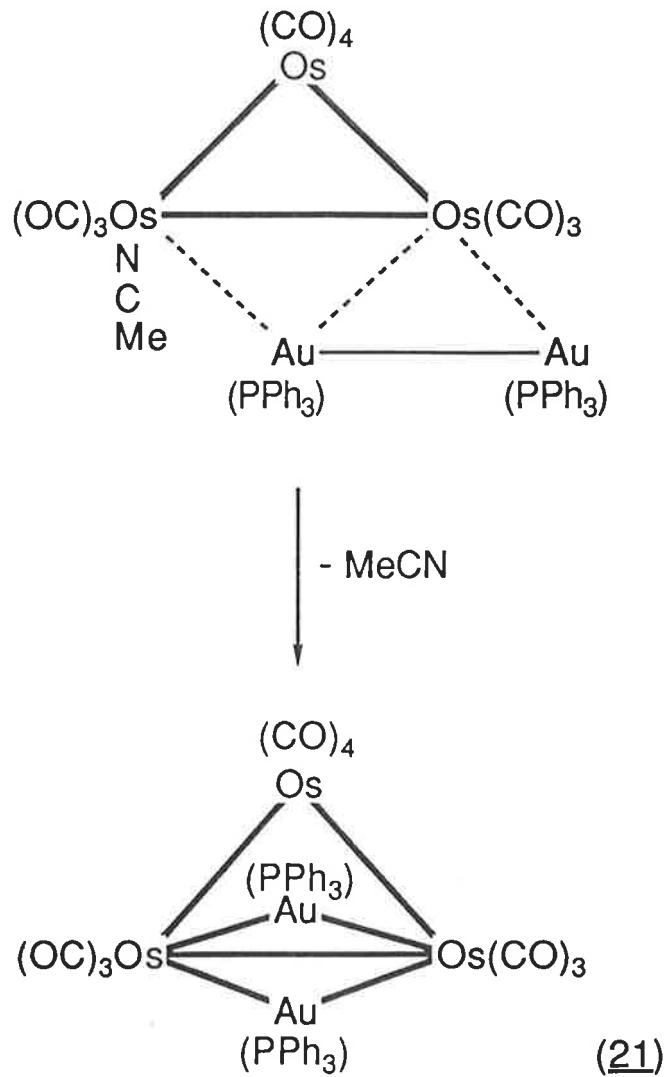
Scheme 6

If the initial products in these reactions are tri-gold adducts, which subsequently lose a $[\text{Au}(\text{PPh}_3)]^+$ moiety in the presence of nucleophiles, they can be considered to mimic the behaviour of tri-nuclear complexes, such as $[\text{C}_5\text{Ph}_4\text{-}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$, which lose $[\text{Au}(\text{PPh}_3)]^+$ under the action of various nucleophilic agents [e.g. Equations (x) and (xi)].^{25,26}



The reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]-[\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ resulted in the anomalous loss of the acetonitrile ligand, as well as the expected loss of a carbonyl ligand. The mechanism of the resulting formation of $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ (21) is not obvious at this stage, although the acetonitrile ligand in $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ is labile and therefore is suitable for substitution reactions.⁶¹ It is possible that initial formation of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})\{\text{Au}_2(\text{PPh}_3)_2\}$ is rapidly

followed by the loss of the acetonitrile ligand to give $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ (21) (Scheme 7).



Scheme 7

CONCLUSION

Reactions between neutral clusters and $[O\{Au(PR_3)\}_3]^-$ $[BF_4]$ ($R = Ph, OMe$) / $[ppn][X]$ [$X = Co(CO)_4, OAc, Cl$] in most cases afforded good yields of clusters derived from the starting cluster by the loss of one carbonyl ligand and the addition of two $Au(PPh_3)$ groups, the other products being $Au(PPh_3)X$ and $[ppn][BF_4]$.

A comparison of yields obtained from a limited number of similar reactions in which different $[ppn]^+$ salts were employed (Table 7), shows that $[ppn][Co(CO)_4]$ and $[ppn][OAc]$ were more successful than $[ppn][Cl]$; more comparative experiments are necessary, however, to determine if this is a general trend.

Table 7 : % Yield from $[ppn]^+$ salts used

	$Co(CO)_4$	OAc	Cl
$Os_3(CO)_{11}\{Au_2(PPh_3)_2\}$ (17)	70%	71%	54%
$Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_8\{Au_2(PPh_3)_2\}$ (30)	79%	71%	75%
$Ru_3(\mu_3-S)_2(CO)_8\{Au_2(PPh_3)_2\}$ (33)	69%	57%	21%

Using this method di-gold clusters were prepared in which (a) no Au-Au interaction is present as seen in the complex, $Ru_6C(CO)_{16}\{Au(PPh_3)\}_2$, (b) the gold atoms are sited close together but with a Au-Au separation too long for there

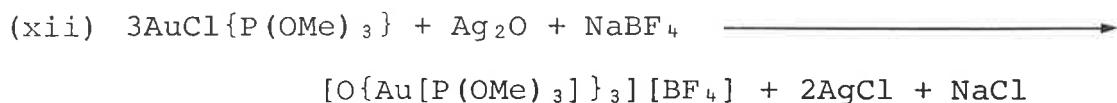
to be appreciable Au-Au bonding as in $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ or predominantly (c) a Au-Au bond exists [e.g. $\text{Ru}_3(\mu_3\text{-NPh})-(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ and the tri-gold cluster $\text{Ru}_3(\mu_3\text{-C}\equiv\text{CPh})-(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$]. It appears therefore to be a useful method for introducing ' $\{\text{Au}(\text{PPh}_3)\}_2$ ' into clusters under mild conditions, without the requirement that the cluster be a dianion or a multihydride complex. The cluster must, however, be capable of facile CO loss.

The addition of $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ to hydrido clusters gave more complex reactions with replacement of a carbonyl ligand and/or one or more metal bonded hydrogens by $\text{Au}(\text{PPh}_3)$ moieties - once again the formation of a di-gold cluster is favoured.

The isolobal analogy linking H and $\text{Au}(\text{PR}_3)$ does not appear to be useful in predicting structures of the corresponding hydride compound when there are two or more $\text{Au}(\text{PR}_3)$ fragments present, because of the tendency towards the formation of gold-gold bonds. However, the di-gold clusters prepared by this method may be useful models for the initial attack of H_2 on a cluster.

APPENDIXPreparation of $[O\{Au(P(OMe)_3)\}_3][BF_4]$ (19)

The new oxonium reagent $[O\{Au(P(OMe)_3)\}_3][BF_4]$ (19) was prepared from the reaction of $AuCl\{P(OMe)_3\}$ (52), freshly prepared silver oxide and sodium tetrafluoroborate in acetone [Equation (xii)], an analogous reaction to that used for the preparation of $[O\{Au(PPh_3)\}_3][BF_4]$.²³



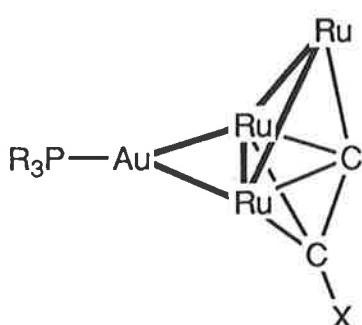
Identification of (19) was by microanalytical and spectroscopic data. The IR spectrum shows a broad band assigned to $[BF_4]^-$ at $1010-1080 \text{ cm}^{-1}$ while a strong $\nu(C-O)$ band is found at 1190 cm^{-1} . The 1H NMR spectrum shows a doublet [$J(PH)=13.4 \text{ Hz}$] assigned to the OMe protons at 63.82. The FAB mass spectrum of (19) shows $[O\{Au(P(OMe)_3)\}_3]^+$ as the base peak, fragmentation occurring via loss of $P(OMe)_3$ or $Au\{P(OMe)_3\}$ groups. Other significant peaks in the spectrum at m/z 445 and 321 were assigned to $[Au\{P(OMe)_3\}_2]^+$ and $[Au\{P(OMe)_3\}]^+$, respectively.

Preparation of $Ru_3(\mu_3-C\equiv CPh)(CO)_9\{Au(PR_3)\}$ [R = Ph (39), C_6H_4Me-p (53)] and $\{Ru_3(\mu_3-C\equiv CPh)(CO)_9Au\}_2dppe$ (54)

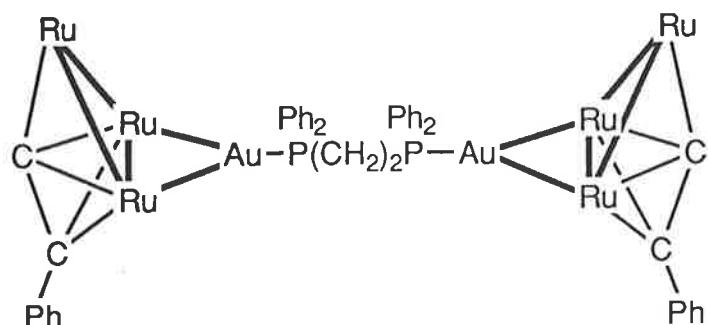
$Ru_3(\mu_3-C\equiv CPh)(CO)_9\{Au(PPh_3)\}$ (39), $Ru_3(\mu_3-C\equiv CPh)(CO)_9-\{Au[P(C_6H_4Me-p)_3]\}$ (53) and $\{Ru(\mu_3-C\equiv CPh)(CO)_9Au\}_2dppe$ (54) were prepared by adding a catalytic amount of trimethylamine oxide to a mixture of $Ru_3(CO)_{12}$ and $Au(C\equiv CPh)(PR_3)$ or $\{Au(C\equiv CPh)\}_{2-}dppe$ [mole ratio 1:1 for (39) and (53), 2:1 for (54)] in dichloromethane. Work up was by radial chromatography for (39) and (53), and by preparative thin layer chromatography

for (54). The solution IR spectra of the three complexes are very similar, (39) and (53) showing six $\nu(\text{CO})$ bands while (54) shows five $\nu(\text{CO})$ bands. The ^1H NMR spectrum of (39) shows the phenyl protons as a multiplet at δ 7.22-7.57, while that of (53) shows the phenyl protons at δ 7.20-7.55 and the methyl protons as a singlet at δ 2.40. The spectrum of the dppe derivative shows the CH_2 protons as a singlet at δ 2.74 and the aromatic protons as a multiplet at δ 7.23-7.57. The FAB mass spectra of (39) and (53) contain molecular ions, and peaks corresponding to the stepwise loss of the nine carbonyl ligands. The base peaks are $[\text{Au}(\text{PPh}_3)]^+$ and $[\text{Au}\{\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3\}]^+$, respectively. The FAB mass spectrum of (54) shows strong peaks only at $[\text{M}]^+$, $[\text{M} - 5\text{CO}]^+$ and $[\text{M} - 6\text{CO}]^+$.

These three compounds are analogues of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CBu}^\ddagger)(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}^{14}$ (5), which was synthesised by adding $\text{AuCl}(\text{PPh}_3)$ to the anionic complex $[\text{Ru}_3(\mu_3-\text{C}\equiv\text{CBu}^\ddagger)(\text{CO})_9]^-$ [formed by stirring a suspension of sodium hydride in a tetrahydrofuran solution of $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{C}\equiv\text{CBu}^\ddagger)(\text{CO})_9$ (3)]. The X-ray structure of (5) was determined and shown to consist of a butterfly arrangement, with the Au atom on a wingtip. The t-butylacetylidyne ligand interacts with all three Ru atoms, via one σ -bond and two π -bonds.¹⁴



$\text{R} = \text{Ph}$ $\text{X} = \text{Ph}$ (39)
 $\text{R} = \text{C}_6\text{H}_4\text{Me}$ $\text{X} = \text{Ph}$ (53)
 $\text{R} = \text{Ph}$ $\text{X} = \text{Bu}^\ddagger$ (5)



(54)

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1.

Starting Materials

The complexes $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3\text{[BF}_4\text{]}]$,^{2 3} $[\text{ppn}]\text{[Co(CO)}_4\text{]}$,^{6 2} $[\text{ppn}]\text{[OAc]}$,^{6 3} $[\text{ppn}]\text{[Cl]}$,^{6 2} $\text{Os}_3(\text{CO})_{12}$,^{6 4} $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$,^{6 1} $\text{Ru}_3(\mu_3-\text{NPh})(\text{CO})_{10}$,^{4 0} $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{PPh}_2)_2(\text{CO})_7$,^{6 5} $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_3\text{Me})\{\mu-\text{P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_7$,^{6 5} $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}-(\text{C}_6\text{H}_4)\}(\text{CO})_9$,^{4 5} $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_9$,^{6 6} $\text{Ru}_3(\mu_3-\text{NPh})_2(\text{CO})_9$,^{6 7} $\text{Ru}_6\text{C}(\text{CO})_{17}$,^{6 8} $\text{Os}_3(\mu-\text{H})_2(\text{CO})_{10}$,^{6 9} $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{C}_{12}\text{H}_{15})(\text{CO})_9$,^{7 0} $\text{Ru}_4(\mu-\text{H})_4(\text{CO})_{12}$,^{7 1} $\text{Au}(\text{C}\equiv\text{CPH})(\text{PPh}_3)$ ^{7 2} and $\text{Au}(\text{C}\equiv\text{CPH})-\{\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3\}$ ^{7 2} were prepared by literature methods. The preparation of $\{\text{Au}(\text{C}\equiv\text{CPH})\}_2\text{dppe}$ was via the same method used for preparing $\text{Au}(\text{C}\equiv\text{CPH})(\text{PPh}_3)$.^{7 2} $\text{AuCl}\{\text{P}(\text{OMe})_3\}$ and $[\text{O}\{\text{Au}(\text{P}(\text{OMe})_3)\}_3]\text{[BF}_4\text{]}$ were synthesised as described below. The preparation of $\text{AuCl}\{\text{P}(\text{OMe})_3\}$, is a modification of a general method reported in the literature.^{7 3}

Reactions of Osmium and Ruthenium Clusters with

$[\text{O}\{\text{Au}(\text{PR}_3)\}_3]\text{[BF}_4\text{]}$ (R = Ph, OMe) in the presence of $[\text{ppn}]^+$ salts

(a) Preparation of $\text{Os}_3(\text{CO})_{11}\{\text{Au}_2(\text{PPh}_3)_2\}$ (17)

(i) From $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]\text{[BF}_4\text{]}/[\text{ppn}]\text{[Co(CO)}_4\text{]}$ - To a stirred solution of $\text{Os}_3(\text{CO})_{12}$ (22 mg, 0.024 mmol) in thf (10 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]\text{[BF}_4\text{]}$ (36 mg, 0.024 mmol) and $[\text{ppn}]\text{[Co(CO)}_4\text{]}$ (17 mg, 0.024 mmol), all reactants dissolving within 5 min giving a colour change from pale yellow to orange. After stirring at room temperature for 15 min the solvent was removed *in vacuo*. Diethyl ether (15 ml) was added and the volume reduced; after cooling (-15°C), the resulting white precipitate was filtered off

and identified (IR, FAB MS) as $[\text{ppn}][\text{BF}_4]$ (12 mg, 80%).

The filtrate was evaporated to dryness (rotary evaporator) and purified by preparative TLC (acetone/X4 3:7) which showed two major bands. Band 1 (colourless, $R_f = 0.54$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give white crystals identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ (13 mg, 86%). Infrared (cyclohexane): $\nu(\text{CO})$ 2055s, 1990s, 1960vs cm^{-1} [lit:⁷⁴ $\nu(\text{CO})$ (CS_2) 2054s, 1988s, 1957s cm^{-1}]. FAB MS: 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 28; 630, $[\text{M}]^+$, 2; 602, $[\text{M} - \text{CO}]^+$, 30; 574, $[\text{M} - 2\text{CO}]^+$, 14; 546, $[\text{M} - 3\text{CO}]^+$, 24; 518, $[\text{M} - 4\text{CO}]^+$, 34; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100. Band 2 (orange, $R_f = 0.49$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give $\text{Os}_3(\text{CO})_{11}\{\text{Au}_2(\text{PPh}_3)_2\}$ (17) (30 mg, 70%) as an orange powder, m.p. 155–156°C (dec.). (Found: C, 31.28; H, 1.71; $\text{C}_{47}\text{H}_{30}\text{Au}_2\text{O}_{11}\text{Os}_3\text{P}_2$ requires C, 31.41; H, 1.68%). Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2097m, 2048s, 2015vs, 1997sh, 1978w, 1966w, 1930sh, 1918w cm^{-1} [lit.³⁶: $\nu(\text{CO})$ (CH_2Cl_2) 2111m, 2067m, 2031s, 2020sh, 2000m, 1978sh, 1955sh, 1931sh cm^{-1}]. ^1H NMR: $\delta(\text{CDCl}_3)$ 7.30 (m, Ph). FAB MS: 1798, $[\text{M}]^+$, 4; 1770, $[\text{M} - \text{CO}]^+$, 2; 1742, $[\text{M} - 2\text{CO}]^+$, 3; 1714, $[\text{M} - 3\text{CO}]^+$, 1; 1658, $[\text{M} - 5\text{CO}]^+$, 2; 1630, $[\text{M} - 6\text{CO}]^+$, 2; 1602, $[\text{M} - 7\text{CO}]^+$, 3; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 44.

(ii) $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{OAc}]$ – A similar reaction in which $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (26 mg, 0.018 mmol) and $[\text{ppn}][\text{OAc}]$ (10 mg, 0.017 mmol) were added to $\text{Os}_3(\text{CO})_{12}$ (15 mg, 0.017 mmol) in THF (10 ml), was stirred for 10 min and then evaporated to dryness *in vacuo*. Preparative TLC (acetone/X4 3:7) showed two bands. Band 1 (orange, $R_f = 0.56$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange crystals of $\text{Os}_3(\text{CO})_{11}\{\text{Au}_2(\text{PPh}_3)_2\}$ (17) (21 mg, 71%) identified by comparison

of its IR ν (CO) spectrum with that of the sample prepared above. Band 2 (colourless, $R_f = 0.48$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give white crystals of $\text{AuOAc}(\text{PPh}_3)$ (comparison of IR spectrum (Nujol) with that of an authentic sample).

(iii) From $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Cl}]$ - Similarly $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (26 mg, 0.018 mmol) and $[\text{ppn}][\text{Cl}]$ (10 mg, 0.017 mmol) were added to $\text{Os}_3(\text{CO})_{12}$ (15 mg, 0.017 mmol) in THF (10 ml). After stirring for 10 min, and evaporation of the solvent *in vacuo*, preparative TLC (acetone/X4 3:7) showed three bands. Band 1 (yellow, $R_f = 0.83$) (trace) was identified as unreacted $\text{Os}_3(\text{CO})_{12}$ [IR ν (CO) spectrum]; band 2 (orange, $R_f = 0.48$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give $\text{Os}_3(\text{CO})_{11}\{-\text{Au}_2(\text{PPh}_3)_2\}$ (17) (16 mg, 54%), identified by comparison of its IR ν (CO) spectrum with that of the sample prepared in (a) (i); band 3 (colourless, $R_f = 0.42$) was crystallised from $\text{CHCl}_3/\text{EtOH}$ to give white crystals of $\text{AuCl}(\text{PPh}_3)$ [comparison of IR spectrum (Nujol) with that of an authentic sample].

(b) Preparation of $\text{Os}_3(\text{CO})_{11}\{\text{Au}_2[\text{P}(\text{OMe})_3]_2\}$ (20)

As in (a) above, to a stirred solution of $\text{Os}_3(\text{CO})_{12}$ (29 mg, 0.032 mmol) in THF (15 ml) were added $[\text{O}\{\text{Au}[\text{P}(\text{OMe})_3]\}_3][\text{BF}_4]$ (34 mg, 0.032 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (23 mg, 0.032 mmol) giving an immediate colour change from pale yellow to orange. After evaporation to dryness *in vacuo* preparative TLC (acetone/X4 3:7) showed one major coloured band (orange, $R_f = 0.50$), which was extracted and crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange crystals of $\text{Os}_3(\text{CO})_{11}\{\text{Au}_2[\text{P}(\text{OMe})_3]_2\}$ (20) (26 mg, 53%) m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 13.52; H, 1.20; $\text{C}_{17}\text{H}_{18}\text{Au}_2\text{O}_{17}\text{Os}_3\text{P}_2$ requires C, 13.43; H, 1.19%). Infrared (CH_2Cl_2) ν (CO): 2101m, 2051s, 2019vs, 2003sh, 1979w, 1969w,

1936sh, 1922w cm^{-1} . ^1H NMR δ (CDCl_3) 3.79 [d, $J(\text{PH}) = 13.5\text{Hz}$, OMe]. FAB MS: 1520, $[M]^+$, 15; 1492, $[M - \text{CO}]^+$, 9; 1464, $[M - 2\text{CO}]^+$, 25; 1436, $[M - 3\text{CO}]^+$, 39; 1408, $[M - 4\text{CO}]^+$, 14; 1380, $[M - 5\text{CO}]^+$, 11; 1352, $[M - 6\text{CO}]^+$, 15; 1324, $[M - 7\text{CO}]^+$, 21; 445, $[\text{Au}\{\text{P(OMe)}_3\}_2]^+$, 100.

(c) Preparation of $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ (21)

Similarly, to a stirred solution of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ (42 mg, 0.046 mmol) in thf (17 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]^-$ $[\text{BF}_4]$ (68 mg, 0.046 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (32 mg, 0.045 mmol). The colour of the solution changed immediately from yellow to yellow-green. All reactants had dissolved after approximately 15 min. The reaction mixture was stirred at room temperature for 1.5 h, at which time the solution was dark green. After evaporation to dryness (*in vacuo*), preparative TLC (acetone/X4 3:7) showed seven bands and a red-brown baseline. Band 2 (colourless, $R_f = 0.63$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ [IR $\nu(\text{CO})$ spectrum and spot TLC]. Band 3 (green, $R_f = 0.57$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give dark green crystals of $\text{Os}_3(\text{CO})_{10} - \{\text{Au}(\text{PPh}_3)\}_2$ (21) (33 mg, 51%) m.p. 204–207°C (dec.). Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2070w, 2017s, 1982m, 1955w, 1944m cm^{-1} [lit.³⁶: $\nu(\text{CO})$ (CH_2Cl_2) 2067w, 2012s, 1977m, 1965w, 1937m cm^{-1}]. FAB MS: 1770, $[M]^+$, 7; 1742, $[M - \text{CO}]^+$, 10; 1714, $[M - 2\text{CO}]^+$, 3; 1686, $[M - 3\text{CO}]^+$, 2; 1658, $[M - 4\text{CO}]^+$, 7; 1630, $[M - 5\text{CO}]^+$, 4; 1602, $[M - 6\text{CO}]^+$, 10; 1255, $[M - 2\text{CO} - \text{Au}(\text{PPh}_3)]^+$, 10; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 41. The remaining bands were present in trace amounts.

(d) Preparation of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24)

To a stirred solution of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_{10}$ (40 mg, 0.059 mmol) in thf (15 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (89 mg, 0.060 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (42 mg, 0.059 mmol). After a reaction time of 15 min the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed six bands and a baseline. Band 2 (colourless, $R_f = 0.59$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ [IR $\nu(\text{CO})$ spectrum and spot TLC]. The major band (red, $R_f = 0.46$) was extracted and crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give dark red crystals of $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_9\{\text{Au}_2(\text{PPh}_3)_2\}$ (24) (60 mg, 65%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 39.02; H, 2.26; N, 0.90; $\text{C}_{51}\text{H}_{35}\text{Au}_2\text{NO}_9\text{P}_2\text{Ru}_3$ requires C, 39.14; H, 2.25; N, 0.90%). Infrared (cyclohexane): $\nu(\text{CO})$ 2052w, 2028vs, 2014vs, 1980(sh), 1972m, 1960s, 1952(sh) cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 7.31 (m, Ph). FAB MS: 1566, $[\text{M}]^+$, 63; 1538, $[\text{M} - \text{CO}]^+$, 37; 1510, $[\text{M} - 2\text{CO}]^+$, 43; 1482, $[\text{M} - 3\text{CO}]^+$, 25; 1454, $[\text{M} - 4\text{CO}]^+$, 37; 1426, $[\text{M} - 5\text{CO}]^+$, 100; 1398, $[\text{M} - 6\text{CO}]^+$, 25; 1370, $[\text{M} - 7\text{CO}]^+$, 55; 1342, $[\text{M} - 8\text{CO}]^+$, 72; 1328, $[\text{M} - 8\text{CO} - \text{N}]^+$, 41; 1314, $[\text{M} - 9\text{CO}]^+$, 61; 1237, $[\text{M} - 9\text{CO} - \text{Ph}]^+$, 50; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 50.

(e) Preparation of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6 -$ $\{\text{Au}_2(\text{PPh}_3)_2\}$ (27)

To a stirred solution of $\text{Ru}_3(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-PPh}_2)_2(\text{CO})_6 -$ (14 mg, 0.015 mmol) in thf (7 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (22 mg, 0.015 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (10 mg, 0.014 mmol). After a reaction time of 5 min the mixture was evaporated to dryness *in vacuo*. Preparative TLC (acetone/X4 3:7) showed five bands. Band 2 (colourless, $R_f = 0.56$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ [IR $\nu(\text{CO})$

spectrum and spot TLC]. Band 3 (purple, $R_F = 0.50$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$, to give dark purple crystals of $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{PPh}_2)_2(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (27) (18 mg, 70%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 47.47; H, 3.37; $\text{C}_{72}\text{H}_{54}\text{Au}_2\text{O}_6\text{P}_4\text{Ru}_3$ requires C, 47.10; H, 2.96%). Infrared (cyclohexane): $\nu(\text{CO})$ 1979vs(br), 1946m, 1927m(br) cm^{-1} . FAB MS: 1837, $[\text{M}]^+$, 5; 1809, $[\text{M} - \text{CO}]^+$, 28; 1781, $[\text{M} - 2\text{CO}]^+$, 6; 1753, $[\text{M} - 3\text{CO}]^+$, 3; 1725, $[\text{M} - 4\text{CO}]^+$, 9; 1697, $[\text{M} - 5\text{CO}]^+$, 17; 1669, $[\text{M} - 6\text{CO}]^+$, 4; 1547, $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 3; 1519, $[\text{M} - 2\text{CO} - \text{PPh}_3]^+$, 4; 1491, $[\text{M} - 3\text{CO} - \text{PPh}_3]^+$, 8; 1463, $[\text{M} - 4\text{CO} - \text{PPh}_3]^+$, 22; 1435, $[\text{M} - 5\text{CO} - \text{PPh}_3]^+$, 25; 1407, $[\text{M} - 6\text{CO} - \text{PPh}_3]^+$, 35; 1330, $[\text{M} - 6\text{CO} - \text{PPh}_3 - \text{Ph}]^+$, 24; 1252, $[\text{M} - 6\text{CO} - \text{PPh}_3 - 2\text{Ph} - \text{H}]^+$, 13; 1133, $[\text{M} - 6\text{CO} - \text{Au}(\text{PPh}_3) - \text{Ph}]^+$, 35; 1056, $[\text{M} - 6\text{CO} - \text{Au}(\text{PPh}_3) - 2\text{Ph}]^+$, 27; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 88. The remaining bands were present in trace amounts and were not identified.

(f) Preparation of $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_3\text{Me})\{\mu-\text{P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_6-\{\text{Au}_2(\text{PPh}_3)_2\}$ (28)

In a similar reaction $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (36 mg, 0.024 mmol) and [ppn] $[\text{Co}(\text{CO})_4]$ (17 mg, 0.024 mmol) were added to a solution of $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_3\text{Me})\{\mu-\text{P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2(\text{CO})_7$ (25 mg, 0.025 mmol) in thf (10 ml). After stirring at room temperature for 5 min the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed six bands. Band 2 (colourless, $R_F = 0.61$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ (spot TLC), while Band 3 (purple, $R_F = 0.54$) was extracted and crystallised from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ to give purple crystals of $\text{Ru}_3(\mu_3-\text{C}_6\text{H}_3\text{Me})\{\mu-\text{P}(\text{C}_6\text{H}_4\text{Me}-m)_2\}_2-(\text{CO})_6\{\text{Au}_2(\text{PPh}_3)_2\}$ (28) (33 mg, 72%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 48.80; H, 3.59; $\text{C}_{77}\text{H}_{64}\text{Au}_2\text{O}_6\text{P}_4\text{Ru}_3$ requires C,

48.51; H, 3.38%). Infrared (cyclohexane): ν (CO) 1977vs(br), 1945m, 1927m(br) cm^{-1} . ^1H NMR: δ (CDCl_3) 1.87 (s, 3H, $\text{C}_6\text{H}_3\text{Me}$), 2.13 (s, 6H, $\text{C}_6\text{H}_4\text{Me}-m$), 2.18 (s, 6H, $\text{C}_6\text{H}_4\text{Me}-m$), 6.06-7.62 (m, 49H, $\text{C}_6\text{H}_4\text{Me}-m$ + $\text{C}_6\text{H}_3\text{Me}$ + Ph). FAB MS: 1907, $[M]^+$, 2; 1879, $[M - \text{CO}]^+$, 5; 1617, $[M - \text{CO} - \text{PPh}_3]^+$, 2; 1533, $[M - 4\text{CO} - \text{PPh}_3]^+$, 3; 1477, $[M - 6\text{CO} - \text{PPh}_3]^+$, 10; 1386, $[M - 6\text{CO} - \text{PPh}_3 - \text{C}_6\text{H}_4\text{Me}]^+$, 4; 1189, $[M - 6\text{CO} - \text{Au}(\text{PPh}_3) - \text{C}_6\text{H}_4\text{Me}]^+$, 7; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 38.

(g) Preparation of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_8-$

$\{\text{Au}_2(\text{PPh}_3)_2\}$ (30)

(i) From $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ / [ppn] $[\text{Co}(\text{CO})_4]$ - To a stirred solution of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_9$ (29 mg, 0.034 mmol) in thf (10 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (52 mg, 0.035 mmol) and [ppn] $[\text{Co}(\text{CO})_4]$ (26 mg, 0.037 mmol), immediately giving a purple solution. After stirring at room temperature for 15 min the solvent was removed (rotary evaporator). Preparative TLC (acetone/X4 3:7) showed three bands. Band 1 (colourless, $R_f = 0.67$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ [IR $\nu(\text{CO})$ spectrum and spot TLC]. Band 3 (purple, $R_f = 0.53$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_8-\{\text{Au}_2(\text{PPh}_3)_2\}$ (30) (47 mg, 79%) m.p. 198-200°C. (Found: C, 42.72; H, 2.64; $\text{C}_{63}\text{H}_{46}\text{Au}_2\text{O}_8\text{P}_4\text{Ru}_3$ requires C, 43.19; H, 2.65%). Infrared (CH_2Cl_2): ν (CO) 2033m, 1980vs(br), 1925m (br) cm^{-1} . ^1H NMR: δ (CDCl_3) 2.83-2.95, 3.56-3.74 (2 x m, 2H, CH_2), 6.07-8.16 (m, 44H, Ph + C_6H_4). FAB MS: 2212, $[M + \text{Au}(\text{PPh}_3)]^+$, 3; 1753, $[M]^+$, 3; 1725, $[M - \text{CO}]^+$, 3; 1697, $[M - 2\text{CO}]^+$, 2; 1669, $[M - 3\text{CO}]^+$, 6; 1641, $[M - 4\text{CO}]^+$, 3; 1613, $[M - 5\text{CO}]^+$, 2; 1585, $[M - 6\text{CO}]^+$, 3; 1557, $[M - 7\text{CO}]^+$,

3; 1529, $[M - 8CO]^+$, 4; 1266, $[M - CO - Au(PPh_3)]^+$, 6; 721, $[Au(PPh_3)_2]^+$, 100; 459, $[Au(PPh_3)]^+$, 65. The remaining bands were present in trace amounts and were not identified.

(ii) From $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][OAc]$ - A similar reaction of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ (23 mg, 0.027 mmol) with $[O\{Au(PPh_3)\}_3][BF_4]$ (40 mg, 0.027 mmol) and $[ppn][OAc]$ (16 mg, 0.027 mmol) in thf (8 ml) was stirred for 15 min, then evaporated to dryness *in vacuo*. Preparative TLC (acetone/X4 3:7) showed four bands. Band 3 (colourless, $R_f = 0.39$) was identified as $AuOAc(PPh_3)$ (spot TLC). Band 4 (purple, $R_f = 0.37$) was crystallised from $CH_2Cl_2/MeOH$ to give feathery purple crystals of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9\{Au_2(PPh_3)_2\}$ (30) (33 mg, 71%) identified by comparison of its IR $\nu(CO)$ spectrum with that of the sample prepared above. The remaining bands were present in trace amounts and were not identified.

(iii) From $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Cl]$ - Similarly $[O\{Au(PPh_3)\}_3][BF_4]$ (57 mg, 0.039 mmol) and $[ppn][Cl]$ (22 mg, 0.038 mmol) were added to $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ (33 mg, 0.038 mmol) in thf (15 ml). After stirring for 10 min, and evaporation of the solvent *in vacuo*, preparative TLC (acetone/X4 3:7) showed six bands. Band 2 (red, $R_f = 0.82$) was identified as unreacted $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ [IR $\nu(CO)$ spectrum] (5 mg, 15%). Band 5 (colourless, $R_f = 0.64$) was identified as $AuCl(PPh_3)$ (spot TLC) while band 6 (purple, $R_f = 0.54$) was crystallised from $CH_2Cl_2/MeOH$ to give (30) (50 mg, 75%), identified by comparison of its IR $\nu(CO)$ spectrum with that of the sample prepared in (g) (i). The remaining bands were present in trace amounts and were not identified.

(h) Preparation of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh(C}_6\text{H}_4\text{)}\}(\text{CO})_8$ -{ $\text{Au}_2[\text{P(OMe)}_3]_2$ } (31)

To a stirred solution of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh(C}_6\text{H}_4\text{)}\}(\text{CO})_9$ (40 mg, 0.046 mmol) in thf (12 ml) were added $[\text{O}\{\text{Au}[\text{P(OMe)}_3]\}_3]$ - $[\text{BF}_4]$ (51 mg, 0.048 mmol) and [ppn] $[\text{Co}(\text{CO})_4]$ (34 mg, 0.048 mmol). After stirring at room temperature for 5 min, the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) of a CH_2Cl_2 extract showed one major coloured band (purple, $R_f = 0.39$) which was extracted and crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red-purple crystals of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh(C}_6\text{H}_4\text{)}\}(\text{CO})_8\{\text{Au}_2[\text{P(OMe)}_3]_2\}$ (31) (51 mg, 75%) m.p. 200–203°C. (Found: C, 26.80; H, 2.32; $\text{C}_{33}\text{H}_{34}\text{Au}_2\text{O}_{14}\text{P}_4\text{Ru}_3$ requires C, 26.86; H, 2.32%). Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2030m, 1986vs, 1977vs, 1934w(br) cm^{-1} . $^1\text{H NMR}$: $\delta(\text{CDCl}_3)$ 2.98–3.10, 3.61–3.75 (2 x m, 2H, CH_2), 3.55 [d, $J(\text{PH}) = 13.6\text{Hz}$, 9H, OMe], 3.83 [d, $J(\text{PH}) = 13.3\text{Hz}$, 9H, OMe], 6.03–8.12 (m, 14H, Ph + C_6H_4). FAB MS: 1798, $[\text{M} + \text{AuP(OMe)}_3]^+ \equiv [\text{M}']^+$, 3; 1770, $[\text{M}' - \text{CO}]^+$, 2; 1742, $[\text{M}' - 2\text{CO}]^+$, 5; 1714, $[\text{M}' - 3\text{CO}]^+$, 7; 1686, $[\text{M}' - 4\text{CO}]^+$, 5; 1658, $[\text{M}' - 5\text{CO}]^+$, 2; 1646, $[\text{M}' - \text{CO} - \text{P(OMe)}_3]^+$, 1; 1618, $[\text{M}' - 2\text{CO} - \text{P(OMe)}_3]^+$, 2; 1590, $[\text{M}' - 3\text{CO} - \text{P(OMe)}_3]^+$, 3; 1562, $[\text{M}' - 4\text{CO} - \text{P(OMe)}_3]^+$, 3; 1534, $[\text{M}' - 5\text{CO} - \text{P(OMe)}_3]^+$, 6; 1506, $[\text{M}' - 6\text{CO} - \text{P(OMe)}_3]^+$, 3; 1477, $[\text{M}]^+$, 5; 1449, $[\text{M} - \text{CO}]^+$, 7; 1421, $[\text{M} - 2\text{CO}]^+$, 6; 1393, $[\text{M} - 3\text{CO}]^+$, 53; 1365, $[\text{M} - 4\text{CO}]^+$, 20; 1353, $[\text{M} - \text{P(OMe)}_3]^+$, 5; 1337, $[\text{M} - 5\text{CO}]^+$, 15; 1325, $[\text{M} - \text{CO} - \text{P(OMe)}_3]^+$, 5; 1309, $[\text{M} - 6\text{CO}]^+$, 22; 1297, $[\text{M} - 2\text{CO} - \text{P(OMe)}_3]^+$, 5; 1281, $[\text{M} - 7\text{CO}]^+$, 11; 1269, $[\text{M} - 3\text{CO} - \text{P(OMe)}_3]^+$, 9; 1253, $[\text{M} - 8\text{CO}]^+$, 6; 1241, $[\text{M} - 4\text{CO} - \text{P(OMe)}_3]^+$, 8; 1213, $[\text{M} - 5\text{CO} - \text{P(OMe)}_3]^+$, 12; 1185, $[\text{M} - 6\text{CO} - \text{P(OMe)}_3]^+$, 14; 1156,

$[M - \text{Au}(\text{OMe})_3]^+$, 11; 1128, $[M - \text{CO} - \text{Au}(\text{OMe})_3]^+$, 14; 445, $[\text{Au}(\text{OMe})_3]_2^+$, 43; 321, $[\text{Au}(\text{OMe})_3]^+$, 100.

(i) Preparation of $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (33)

(i) From $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$ - As in (a), to a stirred solution of $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_9$ (30 mg, 0.048 mmol) in THF (10 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (72 mg, 0.049 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (35 mg, 0.049 mmol), producing an immediate darkening of the solution. After stirring at room temperature for 5 min the reaction mixture was evaporated to dryness (vacuum line). Preparative TLC (acetone/X4 3:7) showed nine bands, seven of which were present in trace amounts and not identified. Band 2 (colourless, $R_f = 0.61$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ (spot TLC). Band 3 (orange, $R_f = 0.50$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_8 - \{\text{Au}_2(\text{PPh}_3)_2\}$ (33) (50 mg, 69%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 34.97; H, 2.01; $\text{C}_{44}\text{H}_{30}\text{Au}_2\text{O}_8\text{P}_2\text{Ru}_3\text{S}_2$ requires C, 35.00; H, 2.00%). Infrared (cyclohexane): $\nu(\text{CO})$ 2073s, 2053vs, 2005s, 1990vs, 1974m, 1924m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 7.48 (m, Ph). FAB MS: 1511, $[M]^+$, 6; 1483, $[M - \text{CO}]^+$, 13; 1455, $[M - 2\text{CO}]^+$, 1; 1427, $[M - 3\text{CO}]^+$, 2; 1399, $[M - 4\text{CO}]^+$, 23; 1371, $[M - 5\text{CO}]^+$, 1; 1343, $[M - 6\text{CO}]^+$, 3; 1315, $[M - 7\text{CO}]^+$, 6; 1287, $[M - 8\text{CO}]^+$, 21; 1210, $[M - 8\text{CO} - \text{Ph}]^+$, 6; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 57; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100.

(ii) From $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{OAc}]$ - A similar reaction of $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_9$ (30 mg, 0.048 mmol) with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (84 mg, 0.051 mmol) and $[\text{ppn}][\text{OAc}]$ (31 mg, 0.052 mmol) in THF (15 ml) was stirred for 5 min then evaporated to dryness *in vacuo*. Preparative TLC showed one major coloured band (orange, $R_f = 0.59$) which was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of (33)

(41 mg, 57%) identified by comparison of its IR $\nu(\text{CO})$ spectrum with that of the sample prepared above.

(iii) $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}][\text{Cl}]$ - Similarly a reaction of $\text{Ru}_3(\mu_3-\text{S})_2(\text{CO})_9$ (36 mg, 0.058 mmol) with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (86 mg, 0.058 mmol) and $[\text{ppn}][\text{Cl}]$ (33 mg, 0.057 mmol) in thf (13 ml) was stirred for 10 min then evaporated to dryness *in vacuo*. Preparative TLC (acetone/X4 3:7) showed four bands and a brown-red baseline. Band 2 (orange, $R_f = 0.55$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give (33) (18 mg, 21%) identified by comparison of its IR $\nu(\text{CO})$ spectrum with that as prepared above.

(j) Preparation of $\text{Ru}_3(\mu_3-\text{NPh})_2(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (35)

To a stirred solution of $\text{Ru}_3(\mu_3-\text{NPh})_2(\text{CO})_9$ (42 mg, 0.057 mmol) in thf (15 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (84 mg, 0.057 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (40 mg, 0.056 mmol). After stirring at room temperature for 5 min, the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed two major bands and a brown baseline. Band 1 (colourless, $R_f = 0.67$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ (spot TLC). Band 2 (orange, $R_f = 0.55$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange crystals of $\text{Ru}_3(\mu_3-\text{NPh})_2(\text{CO})_8-\{\text{Au}_2(\text{PPh}_3)_2\}$ (35) (69 mg, 75%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 41.6; H, 2.8; N, 2.0; $\text{C}_{56}\text{H}_{40}\text{Au}_2\text{N}_2\text{O}_8\text{P}_2\text{Ru}_3$ requires C, 41.3; H, 2.5; N, 1.7%). Infrared (cyclohexane): $\nu(\text{CO})$ 2066s, 2049vs, 1993vs, 1988vs, 1972m, 1966s, 1912m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 6.67-7.64 (m, Ph). FAB MS: 1629, $[\text{M}]^+$, 1; 1601, $[\text{M} - \text{CO}]^+$, 8; 1573, $[\text{M} - 2\text{CO}]^+$, 7; 1517, $[\text{M} - 4\text{CO}]^+$, 6; 1489, $[\text{M} - 5\text{CO}]^+$, 3; 1461, $[\text{M} - 6\text{CO}]^+$, 5; 1433, $[\text{M} - 7\text{CO}]^+$, 4; 1405, $[\text{M} - 8\text{CO}]^+$, 18; 1328, $[\text{M} - 8\text{CO} - \text{Ph}]^+$, 5; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 63; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100.

(k) Preparation of $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PPh}_3)\}_2$ (36)

To a stirred solution of $\text{Ru}_6\text{C}(\text{CO})_{17}$ (35 mg, 0.032 mmol) in THF (15 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (47 mg, 0.032 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (23 mg, 0.032 mmol). After stirring for 10 min the solvent was removed *in vacuo*. Crystallisation from CH_2Cl_2 (14 ml) / MeOH (2 ml) gave a red-purple solid which was recrystallised from CH_2Cl_2 (25 ml) / MeOH (3 ml) to give red crystals of $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{Au}(\text{PPh}_3)\}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (36) (30 mg, 47%) m.p. 278–280°C. (Found: C, 31.35; H, 1.50; $\text{C}_{53}\text{H}_{30}\text{Au}_2\text{P}_2\text{Ru}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 31.69; H, 1.54%). Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2067w, 2049s, 2017vs, 1965w, 1822m(br) cm^{-1} . FAB MS: 1988, $[\text{M}]^+$, 19; 1960, $[\text{M} - \text{CO}]^+$, 3; 1530, $[\text{M} - \text{AuPPh}_3 + \text{H}]^+$, 3; 1409, -, 6; 1071, $[\text{M} - 2\text{AuPPh}_3 + \text{H}]^+$, 15; 950, -, 13; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 94; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100.

(l) Preparation of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40)

To a stirred solution of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (50 mg, 0.045 mmol) in THF (15 ml) were added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3] \cdot [\text{BF}_4]$ (67 mg, 0.045 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (32 mg, 0.045 mmol) immediately changing the colour of the solution from yellow to orange. After stirring at room temperature for 10 min the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed four bands. Band 2 (colourless, $R_f = 0.53$) was identified as $\text{AuCo}(\text{CO})_4(\text{PPh}_3)$ (spot TLC). Band 3 (orange, $R_f = 0.47$) was crystallised from $\text{CH}_2\text{Cl}_2/n\text{-heptane}$ to give orange crystals of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_8\{\text{Au}_3(\text{PPh}_3)_3\}$ (40) (67 mg, 75%) m.p. >150°C (dec.). (Found: C, 42.35; H, 2.82; $\text{C}_{70}\text{H}_{50}\text{Au}_3\text{O}_8\text{P}_3\text{Ru}_3$ requires C, 41.91; H, 2.51%). Infrared (cyclohexane): $\nu(\text{CO})$ 2047vs, 2020vs, 1981s, 1968(sh),

1965s, 1950(sh), 1914w cm^{-1} . ^1H NMR: δ (CDCl_3) 6.99-7.57 (m, Ph). FAB MS: 2466, $[M + \text{Au}(\text{PPh}_3)]^+ \equiv [M']^+$, 1; 2438, $[M' - \text{CO}]^+$, 1; 2410, $[M' - 2\text{CO}]^+$, 3; 2092, $[M' - \text{PPh}_3 - 4\text{CO}]^+$, 1; 2064, $[M' - \text{PPh}_3 - 5\text{CO}]^+$, 2; 2036, $[M' - \text{PPh}_3 - 6\text{CO}]^+$, 2; 2007, $[M]^+$, 3; 1979, $[M - \text{CO}]^+$, 4; 1895, $[M - 4\text{CO}]^+$, 8; 1839, $[M - 6\text{CO}]^+$, 4; 1811, $[M - 7\text{CO}]^+$, 3; 1783, $[M - 8\text{CO}]^+$, 3; 1745, $[M - \text{PPh}_3]^+$, 3; 1717, $[M - \text{PPh}_3 - \text{CO}]^+$, 4; 1548, $[M - \text{Au}(\text{PPh}_3)]^+$, 5; 1520, $[M - \text{Au}(\text{PPh}_3) - \text{CO}]^+$, 19; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 92.

(m) Reaction of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3]^-$
 $[\text{BF}_4]/[\text{ppn}][\text{Co}(\text{CO})_4]$

Similarly $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (110 mg, 0.0743 mmol) and $[\text{ppn}][\text{Co}(\text{CO})_4]$ (53 mg, 0.075 mmol) were added to a solution of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (63 mg, 0.074 mmol) in THF (20 ml) giving an immediate colour change from purple to green-brown. After stirring for 7 min the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed seven bands and a brown baseline. Band 1 (green, $R_f = 0.60$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give dark green crystals of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}$ (7) (15 mg, 15%). (Found: C, 24.80; H, 1.32; $\text{C}_{28}\text{H}_{16}\text{AuO}_{10}\text{Os}_3\text{P}$ requires C, 25.65; H, 1.23%). Infrared (n-hexane): $\nu(\text{CO})$ 2090w, 2047vs, 2041s, 2008s, 1997s, 1980s cm^{-1} . [lit.²¹: $\nu(\text{CO})$ (n-hexane) 2090w, 2047s, 2040m, 2008s, 1996m, 1977m cm^{-1}]. FAB MS: 1312, $[M]^+$, 66; 1284, $[M - \text{CO}]^+$, 11; 1256, $[M - 2\text{CO}]^+$, 10; 1228, $[M - 3\text{CO}]^+$, 8; 1200, $[M - 4\text{CO}]^+$, 23; 1172, $[M - 5\text{CO}]^+$, 8; 1144, $[M - 6\text{CO}]^+$, 31; 1116, $[M - 7\text{CO}]^+$, 12; 1087, $[M - 8\text{CO} - \text{H}]^+$, 18; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 81; 459, $[\text{Au}(\text{PPh}_3)]^+$, 100. Band 3 (green-yellow, $R_f = 0.43$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give green crystals of $\text{Os}_3(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}_2$ (21) (21 mg, 16%)

[IR ν (CO) spectrum and spot TLC]. Band 5 (yellow, $R_f = 0.31$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give golden yellow crystals of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{PPh}_3)\{\text{Au}(\text{PPh}_3)\}_2$ (46) (12 mg, 8%). (Found: C, 37.14; H, 2.44; $\text{C}_{63}\text{H}_{47}\text{Au}_2\text{O}_9\text{Os}_3\text{P}_3$ requires C, 37.73; H, 2.36%). Infrared (cyclohexane): ν (CO) 2075vw, 2043w, 1998vs, 1991(sh), 1962w(br), 1923w, 1918w cm^{-1} . ^1H NMR: δ (CDCl_3) -17.04 [t, $J(\text{PH}) = 15\text{Hz}$, 1H, Ru-H], -7.01 [d, $J(\text{PH}) = 12\text{Hz}$, 1H, Ru-H], 7.16-7.47 (m, 45H, Ph). FAB-MS: 2465, $[\text{M} + \text{Au}(\text{PPh}_3)]^+$, 1; 2203, $[\text{M} + \text{Au}]^+$, 2; 2006 $[\text{M}]^+$, 4; 1978, $[\text{M} - \text{CO}]^+$, 1; 1950, $[\text{M} - 2\text{CO}]^+$, 1; 1928, $[\text{M} - \text{Ph} - \text{H}]^+$, 2; 1922, $[\text{M} - 3\text{CO}]^+$, 1; 1866, $[\text{M} - 5\text{CO}]^+$, 1; 1844, $[\text{M} - 3\text{CO} - \text{Ph} - \text{H}]^+$, 2; 1704, $[\text{M} - 8\text{CO} - \text{Ph} - \text{H}]^+$, 13; 1468, $[\text{M} - \text{Au}(\text{PPh}_3) - \text{Ph} - 2\text{H}]^+$, 49; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 69. The remaining bands were present in trace amounts and were not identified.

(n) Reaction of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9$ with $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]/[\text{ppn}]\text{[Co}(\text{CO})_4]$

To a stirred solution of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9$ (42 mg, 0.059 mmol) in thf (15 ml) was added $[\text{O}\{\text{Au}(\text{PPh}_3)\}_3][\text{BF}_4]$ (87 mg, 0.059 mmol) and $[\text{ppn}]\text{[Co}(\text{CO})_4]$ (42 mg, 0.059 mmol). The colour of the solution changed from yellow to purple within 2 min. After stirring for 5 min the solvent was removed *in vacuo*. Preparative TLC (acetone/X4 3:7) showed four bands. Band 1 (yellow, $R_f = 0.90$) was identified as $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9$ [IR ν (CO) spectrum] (3 mg, 7%). Band 2 (colourless, $R_f = 0.68$) was identified as $\text{AuCo}(\text{CO})_4\text{-}(\text{PPh}_3)$ [IR ν (CO) spectrum]. Band 3 (red-brown, $R_f = 0.64$) was crystallised from acetone to give red-brown crystals of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8\{\text{Au}_2(\text{PPh}_3)_2\}$ (47) (57 mg, 60%) m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 41.66; H, 2.91; $\text{C}_{56}\text{H}_{46}\text{Au}_2\text{O}_8\text{P}_2\text{Ru}_3$ requires

C, 41.88; H, 2.89%). Infrared (cyclohexane): ν (CO) 2058m, 2040s, 1988vs, 1981(sh), 1966m, 1915w cm^{-1} . ^1H NMR: δ (CDCl₃) -21.15 [d, J (HH) = 2.3Hz, 1H, Ru-H], 1.71-5.80 (m, 14H, C₁₂ ring protons), 6.39 [d, J (HH) = 2.3Hz, 1H, allylic CH], 7.18-7.48 (m, 30H, Ph). FAB MS: 1607, $[M]^+$, 3; 1579, $[M - \text{CO}]^+$, 10; 1551, $[M - 2\text{CO}]^+$, 4; 1522, $[M - 3\text{CO} - \text{H}]^+$, 11; 1494, $[M - 4\text{CO} - \text{H}]^+$, 23; 1466, $[M - 5\text{CO} - \text{H}]^+$, 8; 1438, $[M - 6\text{CO} - \text{H}]^+$, 13; 1410, $[M - 7\text{CO} - \text{H}]^+$, 20; 1382, $[M - 8\text{CO} - \text{H}]^+$, 10; 1251, $[M - 7\text{CO} - \text{C}_{12}\text{H}_{15} - \text{H}]^+$, 7; 1223, $[M - 8\text{CO} - \text{C}_{12}\text{H}_{15} - \text{H}]^+$, 6; 1148, $[M - \text{Au}(\text{PPh}_3)]^+$, 8; 1120, $[M - \text{CO-Au}(\text{PPh}_3)]^+$, 10; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 100; 459, $[\text{Au}(\text{PPh}_3)]^+$, 48. Band 4 (purple, R_f = 0.52) was crystallised from CH₂Cl₂/MeOH to give thin purple needles of Ru₃(μ_3 -C₁₂H₁₅)-(CO)₈{Au₃(PPh₃)₃} (45) (35 mg, 29%). Infrared (cyclohexane): ν (CO) 2037s, 1975vs, 1954w, 1919m cm^{-1} [lit.⁵³: ν (CO) (cyclohexane) 2040m, 1974vs, 1957(sh), 1918m cm^{-1}].

(o) Reaction of Ru₄(μ -H)₄(CO)₁₂ with [O{Au(PPh₃)₃}]-[BF₄]/[ppn][Co(CO)₄]

To a stirred solution of Ru₄(μ -H)₄(CO)₁₂ (60 mg, 0.081 mmol) in THF (20 ml) were added [O{Au(PPh₃)₃}][BF₄] (119 mg, 0.0804 mmol) and [ppn][Co(CO)₄] (57 mg, 0.080 mmol) giving a dark red solution. After stirring for 0.5 h the solvent was removed *in vacuo*. Preparative TLC (benzene/X4 1:1) showed six bands and a brown baseline. Band 1 (yellow, R_f = 0.93) was identified as Ru₄(μ -H)₄(CO)₁₂ (5 mg, 9%) [IR ν (CO) spectrum]. Band 3 (orange, R_f = 0.77) was crystallised from Et₂O/petroleum spirit to give deep red crystals of Ru₄(μ_3 -H)(μ -H)₂(CO)₁₂{Au (PPh₃)₃} (48) (3 mg, 3%). Infrared (hexane): ν (CO) 2090m, 2063vs, 2050s, 2030vs, 2012s, 2001m, 1980w, 1965w, 1958w cm^{-1} [lit.⁵¹: ν (CO) (hexane) 2092s, 2084w, 2066vs, 2052s, 2039(sh), 2032vs, 2015m, 2003(sh), 1982m, 1979m, 1960m, 1900w cm^{-1}].

FAB MS: 1204, $[M]^+$, 3; 1176, $[M - CO]^+$, 4; 1148, $[M - 2CO]^+$, 5; 1120, $[M - 3CO]^+$, 9; 1090, $[M - 4CO - 2H]^+$, 9; 1062, $[M - 5CO - 2H]^+$, 8; 1034, $[M - 6CO - 2H]^+$, 22; 1006, $[M - 7CO - 2H]^+$, 9; 978, $[M - 8CO - 2H]^+$, 12; 950, $[M - 9CO - 2H]^+$, 12; 721, $[Au(PPh_3)_2]^+$, 34; 459, $[Au(PPh_3)]^+$, 100. Band 5 (red-brown, $R_f = 0.39$) was crystallised from $CH_2Cl_2/n\text{-hexane}$ to give purple-red crystals of $Ru_4(\mu_3\text{-H})(\mu\text{-H})(CO)_{12}\{Au_2(PPh_3)_2\}$ (9) (44 mg, 33%). Infrared (CH_2Cl_2): $\nu(CO)$ 2071s, 2043m, 2033s, 2023vs, 2008s, 1990m, 1977m, 1959(sh) cm^{-1} [lit.: $\nu(CO)$ (CH_2Cl_2) 2070s, 2043m, 2033s, 2022vs, 2006s, 1988m, 1975m, 1956(sh), 1914(sh) cm^{-1}]. FAB MS: 1662, $[M]^+$, 4; 1634, $[M - CO]^+$, 3, 1604, $[M - 2CO - 2H]^+$, 7; 1576, $[M - 3CO - 2H]^+$, 6; 1548, $[M - 4CO - 2H]^+$, 6; 1520, $[M - 5CO - 2H]^+$, 13; 1492, $[M - 6CO - 2H]^+$, 5; 1464, $[M - 7CO - 2H]^+$, 5; 1436, $[M - 8CO - 2H]^+$, 5; 1408, $[M - 9CO - 2H]^+$, 8; 1380, $[M - 10CO - 2H]^+$, 6; 1352, $[M - 11CO - 2H]^+$, 7; 1324, $[M - 12CO - 2H]^+$, 5; 721, $[Au(PPh_3)_2]^+$, 100; 459, $[Au(PPh_3)]^+$, 97. Band 6 (green, $R_f = 0.20$) was crystallised from $CH_2Cl_2/MeOH$ to give green crystals of $Ru_4(\mu\text{-H})(CO)_{12}\{Au_3(PPh_3)_3\}$ (43) (4 mg, 2%). Infrared (CH_2Cl_2): $\nu(CO)$ 2053s, 2012vs, 2009vs, 1989s, 1967m, 1953m, 1919w cm^{-1} [lit.^{5,2}: $\nu(CO)$ (CH_2Cl_2) 2053vs, 2013(sh), 2007vs, 1989s, 1967w, 1951m, 1920w cm^{-1}]. FAB MS: 2120, $[M]^+$, 3; 2036, $[M - 3CO]^+$, 1; 1980, $[M - 5CO]^+$, 1; 1952, $[M - 6CO]^+$, 1; 721, $[Au(PPh_3)_2]^+$, 100; 459, $[Au(PPh_3)]^+$, 92. The remaining bands were present in trace amounts and were not identified.

Preparation of $[O\{Au(P(OMe)_3)\}_3][BF_4]$ (19)

(a) Preparation of $AuCl\{P(OMe)_3\}$ (52)

Au metal (2.01 g, 10.2 mmol) was dissolved in aqua regia (20 ml) in an evaporating dish, and then taken to dryness on a steam bath. The residue was then dissolved in HCl (10 ml) and again taken to dryness on the steam bath, redissolved in H₂O (20 ml) and then filtered by gravity and the solution cooled in ice. Thiodiglycol (6 g, 49 mmol) was added via a dropping funnel over 1 h to give a clear solution. To this solution was added a solution of P(OMe)₃ (1.28 g, 10.3 mmol) in CHCl₃ (10 ml) via a dropping funnel over 20 min. The layers were separated - the water layer was washed with CHCl₃ (2 x 10 ml). The combined organic extracts were added to EtOH (100 ml) and evaporated (rotary evaporator) to approximately 10 ml to give AuCl{P(OMe)₃} (52) as a white powder (2.05 g, 56%) m.p. 98-101°C. Infrared (Nujol): $\nu(C-O)$ 1180 cm⁻¹. ¹H NMR: δ (CDCl₃) 3.76 [d, $J(PH) = 14.0$ Hz, OMe]. FAB MS: 677, $[\{Au(P(OMe)_3)\}_2Cl]^+$, 36; 445, $[Au\{P(OMe)_3\}_2]^+$, 12; 321, $[Au\{P(OMe)_3\}]^+$, 100.

(b) Preparation of $[O\{Au(P(OMe)_3)\}_3][BF_4]$ (19)

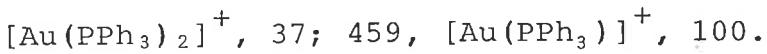
Silver oxide was prepared by adding a solution of NaOH (0.45 g, 11 mmol) in H₂O (10 ml) to a solution of silver nitrate (1.88 g, 11.1 mmol) in H₂O (10 ml). The brown precipitate was removed by filtration, then washed with water (2 x 5 ml), ethanol (2 x 5 ml), and acetone (2 x 5 ml) and then air dried. The freshly prepared solid silver oxide was added to a round-bottomed, 250 ml flask containing a stirred solution of AuCl{P(OMe)₃} in acetone (100 ml) (1.50 g, 4.21 mmol); this was followed by the addition of NaBF₄ (1.88 g, 17.1 mmol). The mixture was stirred rapidly for 1 h. The solvent was removed

(rotary evaporator), and the solid residue extracted with chloroform (3×15 ml). The combined extracts were filtered into freshly distilled Et_2O (150 ml) giving an off-white precipitate of $[\text{O}\{\text{Au}(\text{POMe})_3\}_3][\text{BF}_4]$ (19) which was collected and air-dried (597 mg, 40%).

(Found: C, 10.21; H, 2.56; $\text{C}_9\text{H}_{27}\text{Au}_3\text{BF}_4\text{O}_{10}\text{P}_3$ requires C, 10.14; H, 2.55%). Infrared (Nujol): $\nu(\text{C}-\text{O}) 1190 \text{ cm}^{-1}$; $\nu(\text{B}-\text{F}) 1010-1080 \text{ (br)} \text{ cm}^{-1}$. ^1H NMR: $\delta(\text{CDCl}_3)$ 3.82 [d, $J(\text{PH}) = 13.4 \text{ Hz}$, OMe]. FAB MS: 979, $[\text{M}]^+$ $\equiv [\text{O}\{\text{Au}(\text{POMe})_3\}_3]^+$, 100; 855, $[\text{M} - \text{P}(\text{OMe})_3]^+$, 7; 839, $[\text{M} - \text{P}(\text{OMe})_3 - \text{O}]^+$, 11; 659, $[\text{M} - \text{Au}\{\text{P}(\text{OMe})_3\} + \text{H}]^+$, 22; 445, $[\text{Au}\{\text{P}(\text{OMe})_3\}_2]^+$, 31; 321, $[\text{Au}\{\text{P}(\text{OMe})_3\}]^+$, 69.

Preparation of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (39)

To a solution of $\text{Ru}_3(\text{CO})_{12}$ (135 mg, 0.211 mmol) and $\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$ (119 mg, 0.212 mmol) in CH_2Cl_2 (60 ml) was added Me_3NO (25 mg, 0.33 mmol). The reaction mixture was stirred for 15 min then evaporated to dryness (vacuum line). Radial chromatography (loaded with acetone/X4 1:2, ca 2 ml) was then performed. Elution with X4 gave firstly $\text{Ru}_3(\text{CO})_{12}$ (15 mg, 11%), then an orange band which was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange-yellow crystals of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})-(\text{CO})_9\{\text{Au}(\text{PPh}_3)\}$ (39) (156 mg, 66%) m.p. $> 150^\circ\text{C}$ (dec.). (Found: C, 37.16; H, 1.79; $\text{C}_{35}\text{H}_{20}\text{AuO}_9\text{PRu}_3$ requires C, 37.68; H, 1.81%). Infrared (cyclohexane): $\nu(\text{CO}) 2073\text{w}, 2039\text{vs}, 1996\text{s}, 1990\text{w}, 1979\text{(sh)}, 1966 \text{ cm}^{-1}$. ^1H NMR: $\delta(\text{CDCl}_3)$ 7.22-7.57 (m, 20H, Ph). FAB MS: 1117, $[\text{M}]^+$, 12; 1089, $[\text{M} - \text{CO}]^+$, 7; 1061, $[\text{M} - 2\text{CO}]^+$, 4; 1033, $[\text{M} - 3\text{CO}]^+$, 20; 1005, $[\text{M} - 4\text{CO}]^+$, 16; 977, $[\text{M} - 5\text{CO}]^+$, 45; 949, $[\text{M} - 6\text{CO}]^+$, 15; 921, $[\text{M} - 7\text{CO}]^+$, 26; 893, $[\text{M} - 8\text{CO}]^+$, 26; 865, $[\text{M} - 9\text{CO}]^+$, 24; 788, $[\text{M} - 9\text{CO} - \text{Ph}]^+$, 20; 721,



Preparation of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\{\text{Au}[\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3]\}$ (53)

A similar reaction of $\text{Ru}_3(\text{CO})_{12}$ (37 mg, 0.058 mmol), $\text{Au}(\text{C}\equiv\text{CPh})\{\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3\}$ (35 mg, 0.058 mmol) and Me_3NO (6 mg, 0.08 mmol) in thf (10 ml) yielded yellow-orange crystals of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\{\text{Au}[\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3]\}$ (53) (39 mg, 58%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 39.19; H, 2.24; $\text{C}_{38}\text{H}_{26}\text{AuO}_9\text{PRu}_3$ requires C, 39.42; H, 2.26%). Infrared (cyclohexane) 2072w, 2038vs, 1996s, 1991(sh), 1978(sh), 1965 cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.40 (s, 9H, Me), 7.20-7.55 (m, 17H, Ph). FAB MS: 1539, - , 31; 1159, $[\text{M}]^+$, 50; 1131, $[\text{M} - \text{CO}]^+$, 8; 1103, $[\text{M} - 2\text{CO}]^+$, 4; 1075, $[\text{M} - 3\text{CO}]^+$, 28; 1047, $[\text{M} - 4\text{CO}]^+$, 23; 1019, $[\text{M} - 5\text{CO}]^+$, 46; 991, $[\text{M} - 6\text{CO}]^+$, 15; 963, $[\text{M} - 7\text{CO}]^+$, 27; 935, $[\text{M} - 8\text{CO}]^+$, 23; 907, $[\text{M} - 9\text{CO}]^+$, 22; 805, $[\text{Au}[\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3]]_2^+$, 38; 501, $[\text{Au}[\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3]]^+$, 100; 460, - , 46.

Preparation of $\{\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\text{Au}\}_2\text{dppe}$ (54)

To a stirred solution of $\text{Ru}_3(\text{CO})_{12}$ (100 mg, 0.156 mmol) and $\{\text{Au}(\text{C}\equiv\text{CPh})\}_2\text{dppe}$ (119 mg, 0.120 mmol) in CH_2Cl_2 (40 ml) was added Me_3NO (25 mg, 0.75 mmol). After stirring at room temperature for 0.5 h, preparative TLC (acetone/X4 2.5:7.5) showed eight bands and a brown baseline. The major coloured band (yellow-orange, $R_f = 0.77$) was extracted and crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give yellow-orange crystals of $\{\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\text{CO})_9\text{Au}\}_2\text{dppe}$ (54) (84 mg, 51%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 33.74; H, 1.59; $\text{C}_{60}\text{H}_{34}\text{Au}_2\text{O}_{18}\text{P}_2\text{Ru}_6$ requires C, 34.23; H, 1.63%). Infrared (cyclohexane): $\nu(\text{CO})$ 2073w, 2041w, 1996s, 1988(sh), 1962w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.74 (s, 4H, CH_2), 7.23-7.57 (m, 30H, Ph). FAB MS: 2106, $[\text{M}]^+$, 45; 1966, $[\text{M} - 5\text{CO}]^+$, 23; 1938, $[\text{M} - 6\text{CO}]^+$, 72; 1392, - , 100.

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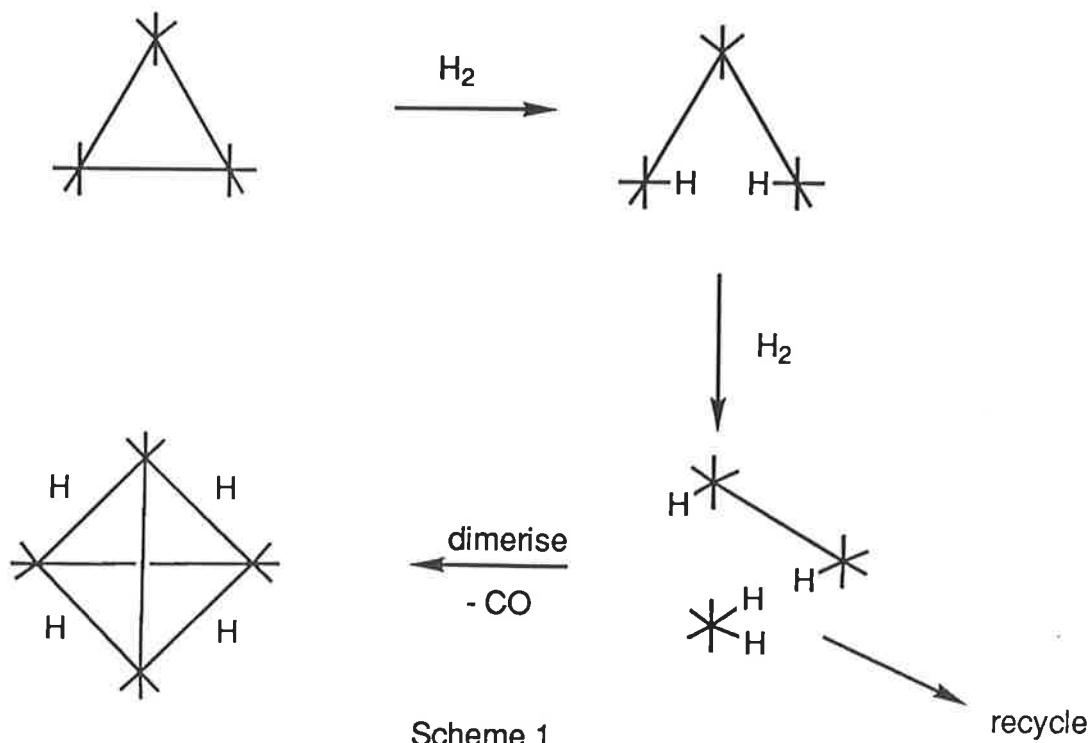
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CHAPTER THREE

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REACTIVITY OF $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ AND RELATED COMPLEXES	
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INTRODUCTION

Transition-metal clusters have been the focus of considerable attention because of their potential use in homogeneous catalysis.¹⁻⁶ However, their possible degradation under the reaction conditions is an obstacle to proving cluster catalysis, e.g. under hydrogen, Ru₃(CO)₁₂ readily gives Ru₄(μ-H)₄(CO)₁₂;⁷ the conversion is assumed to proceed by addition of H₂ 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.

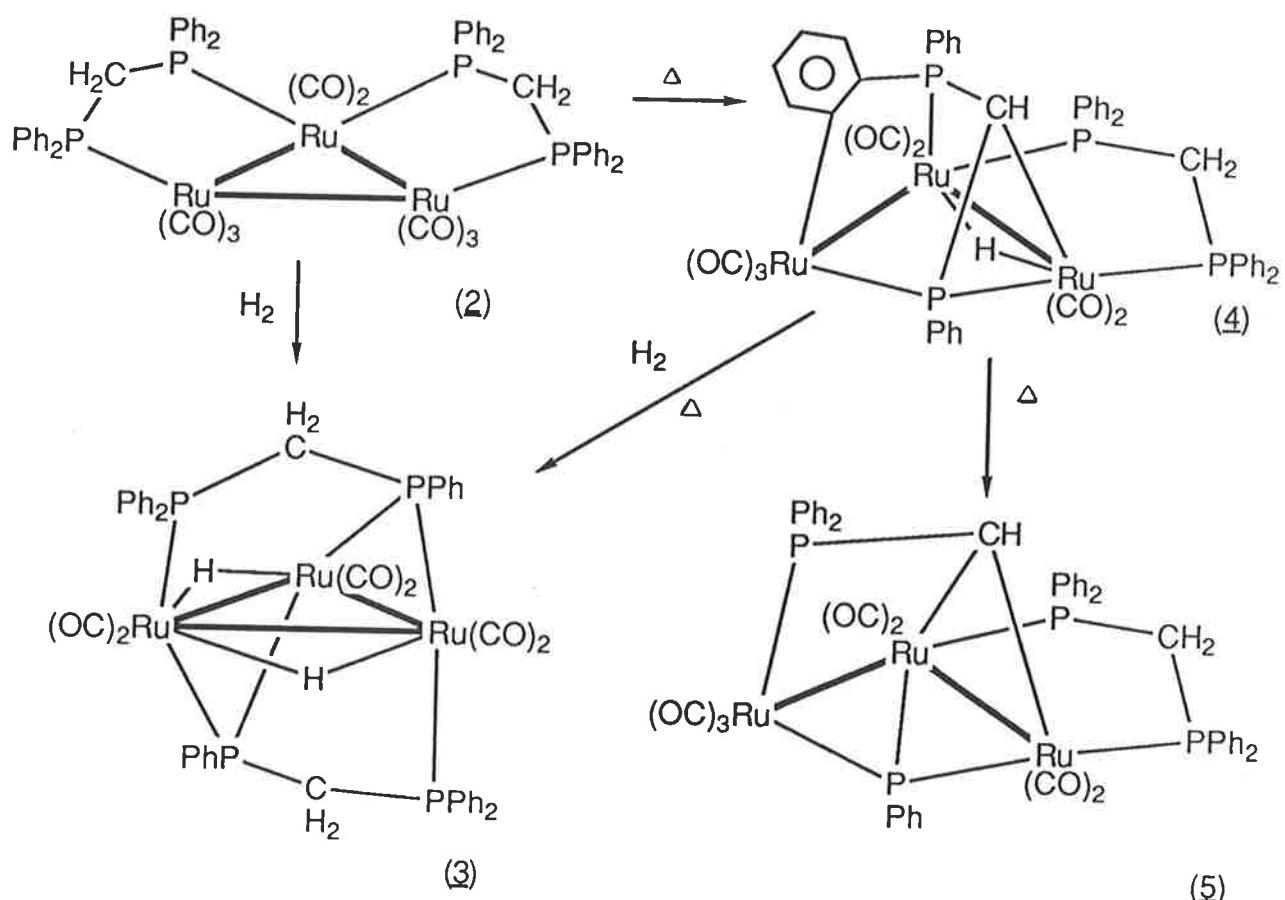
Scheme 1

Hydrogenation of complexes $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$ [$\text{L} = \text{PMe}_3$, PPh_3 , $\text{PPh}(\text{OMe})_2$, $\text{P}(\text{OMe})_3$] ($n = 1-3$) under mild conditions (80°C , 20 atm, 2 h), afforded $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-m}(\text{L})_m$ [where $m = (0-4)$ is not related to n].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, $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_8(\text{L})_4$, even when the trinuclear complex contained one ligand on each metal atom.

With the advent of mild synthetic routes⁹ to derivatives of $\text{Ru}_3(\text{CO})_{12}$ containing tertiary phosphine, phosphite and arsine ligands, considerable interest in their chemistry has ensued. Extension of these studies to complexes containing bidentate ligands in which the ligand bridges a metal-metal bond, in the hope that cluster degradation under more severe reaction conditions might be prevented, has uncovered an interesting area of chemistry. The thermal reaction between bis(diphenylphosphino)methane (dppm) and $\text{Ru}_3(\text{CO})_{12}$ in tetrahydrofuran was first described in 1977,¹⁰ when the fluxional properties of the resulting $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) were also reported. 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 $\text{Fe}_2(\text{CO})_9$ and $\{\text{RuCl}_2(p\text{-cymene})\}_2$ (dppm) in refluxing benzene.¹¹ Meanwhile, the reaction between dppm and $\text{Ru}_3(\text{CO})_{12}$ in xylene at $80-85^\circ\text{C}$ had been found to give $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ (2).¹²

The hydrogenation of $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ (2) at 85°C gave the trinuclear dihydrido cluster $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PPhCH}_2\text{PPh}_2\}_2(\text{CO})_6$ (3) in high yield.¹³ [Under the same conditions, $\text{Ru}_3(\mu\text{-dpam})_2\text{-}$

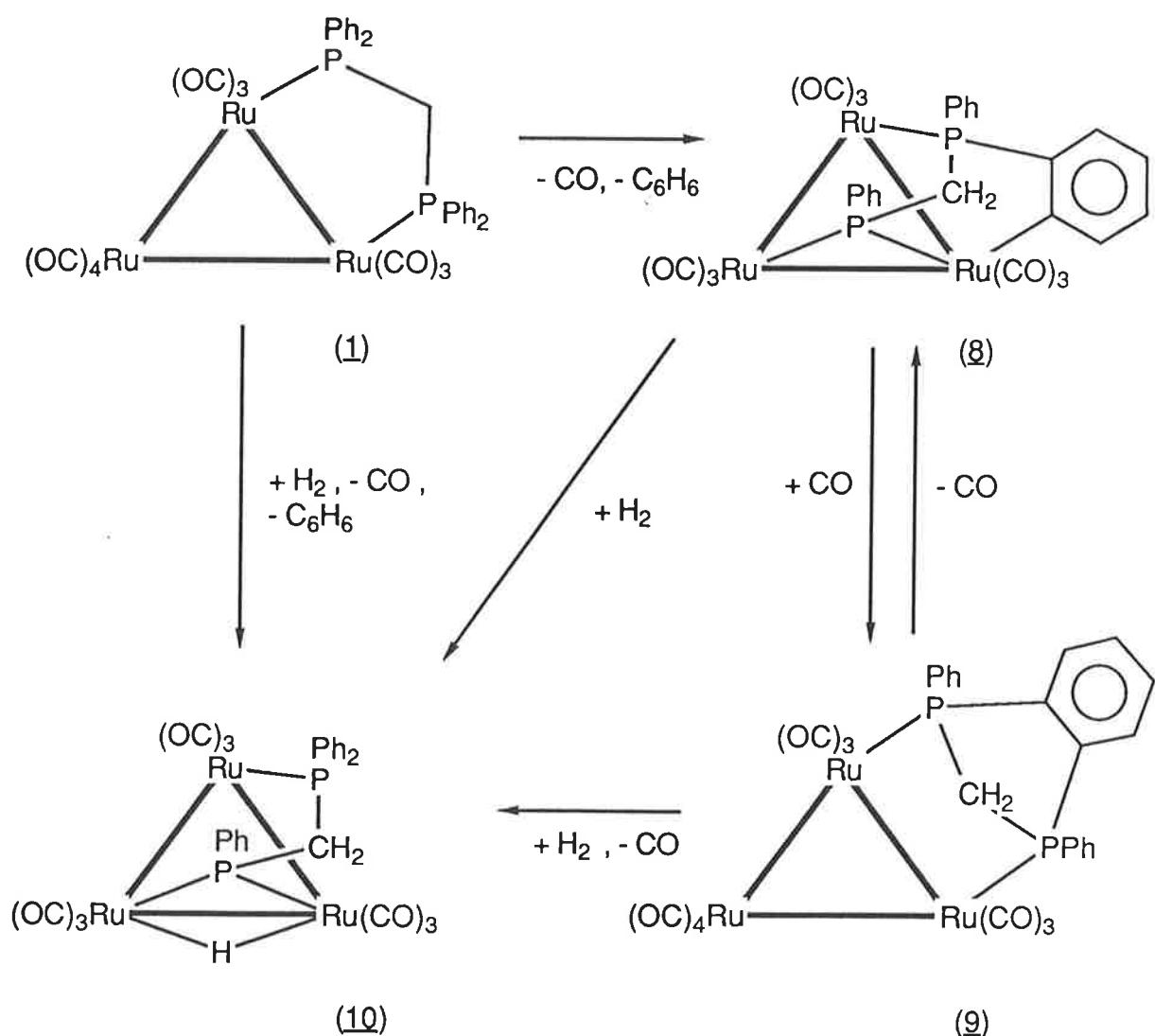
$(CO)_8$ ($d_{pam} = Ph_2AsCH_2AsPh_2$) gave the intermediate monohydride $Ru_3(\mu-H)\{\mu-AsPhCH_2AsPh_2\}(\mu-d_{pam})(CO)_7$, which further reacts with H_2 at $120^\circ C$, yielding the dihydrido cluster complex $Ru_3(\mu-H)_2\{\mu-AsPhCH_2AsPh_2\}_2(CO)_6$.¹³ Pyrolysis of $Ru_3(\mu-dppm)_2(CO)_8$ (2) gave $Ru_3(\mu-H)-\{\mu_3-PPhCHPPh(C_6H_4)\}(\mu-dppm)(CO)_7$ (4), which was subsequently converted into $Ru_3(\mu_3-PPh)(\mu_3-CHPPh_2)(\mu-dppm)(CO)_7$ (5).¹⁴ In the presence of H_2 , (4) gave $Ru_3(\mu-H)_2\{\mu_3-PPhCH_2PPh_2\}_2(CO)_6$ (3).¹⁴ These reactions are shown in Scheme 2.



Scheme 2

Complex (2) was reacted with iodine in toluene ($75^\circ C$, 2 h) to give a mixture of $Ru_2(\mu-I)_2(\mu-dppm)(CO)_4$ (6) and $RuI_2(dppm)-(\mu-CO)_2$ (7).¹⁵

The chemistry of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) has also been extensively studied. Bonnet *et al* showed that the pyrolysis of (1) gave $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$, (8). Thermolysis of (8) in the presence of CO yielded $\text{Ru}_3\{\mu\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_{10}$ (9) in high yield. When (9) was refluxed in cyclohexane under N_2 , (8) was formed. Reacting (1), (8) or (9) with H_2 gave $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9$, (10) (see Scheme 3).¹⁶ In contrast the hydrogenation of $\text{Os}_3(\mu\text{-dppm})(\text{CO})_{10}$ afforded $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$.⁸



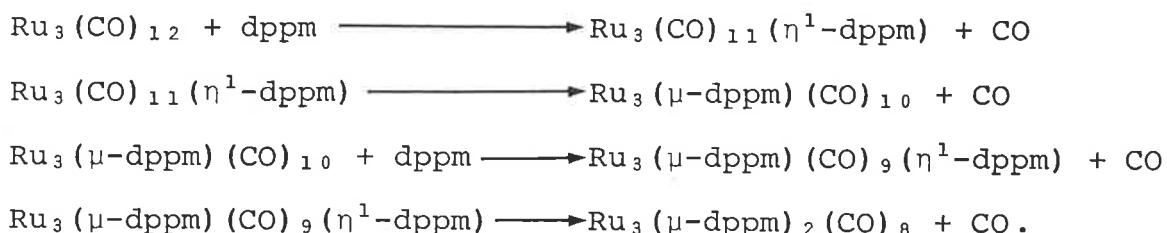
Scheme 3

Bonnet *et al* also reacted $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) with thiophenol in toluene at 85°C to give $\text{Ru}_3(\mu\text{-H})-(\mu\text{-SPh})(\mu\text{-dppm})(\text{CO})_8$ (11). Prolonged heating under the same conditions gave the sulphido complex $\text{Ru}_3(\mu_3\text{-S})(\mu\text{-dppm})(\text{CO})_8$ in 95% yield.¹⁷ With hydrogen, this complex gave $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-dppm})(\text{CO})_7$.¹⁷ This sequence of reactions was repeated with $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ leading directly to $\text{Ru}_3(\mu_3\text{-S})(\mu\text{-dppm})_2(\text{CO})_6$ in 80% yield; the latter compound was reacted with hydrogen to give $\text{Ru}_3-(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-dppm})_2(\text{CO})_5$.¹⁷

The substitution chemistry of (1) has been investigated by Smith *et al.*¹⁸ They described the preparation of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{PPh}_3)$ (12) and $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9-\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3\}$, together with the silica-supported cluster $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiOSi}\equiv)$ and the polymer supported cluster $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{Ph}_2\text{PCH}_2\text{-polymer})$.

Similar results were obtained with $\text{Os}_3(\mu\text{-dppm})(\text{CO})_{10}$.¹⁸

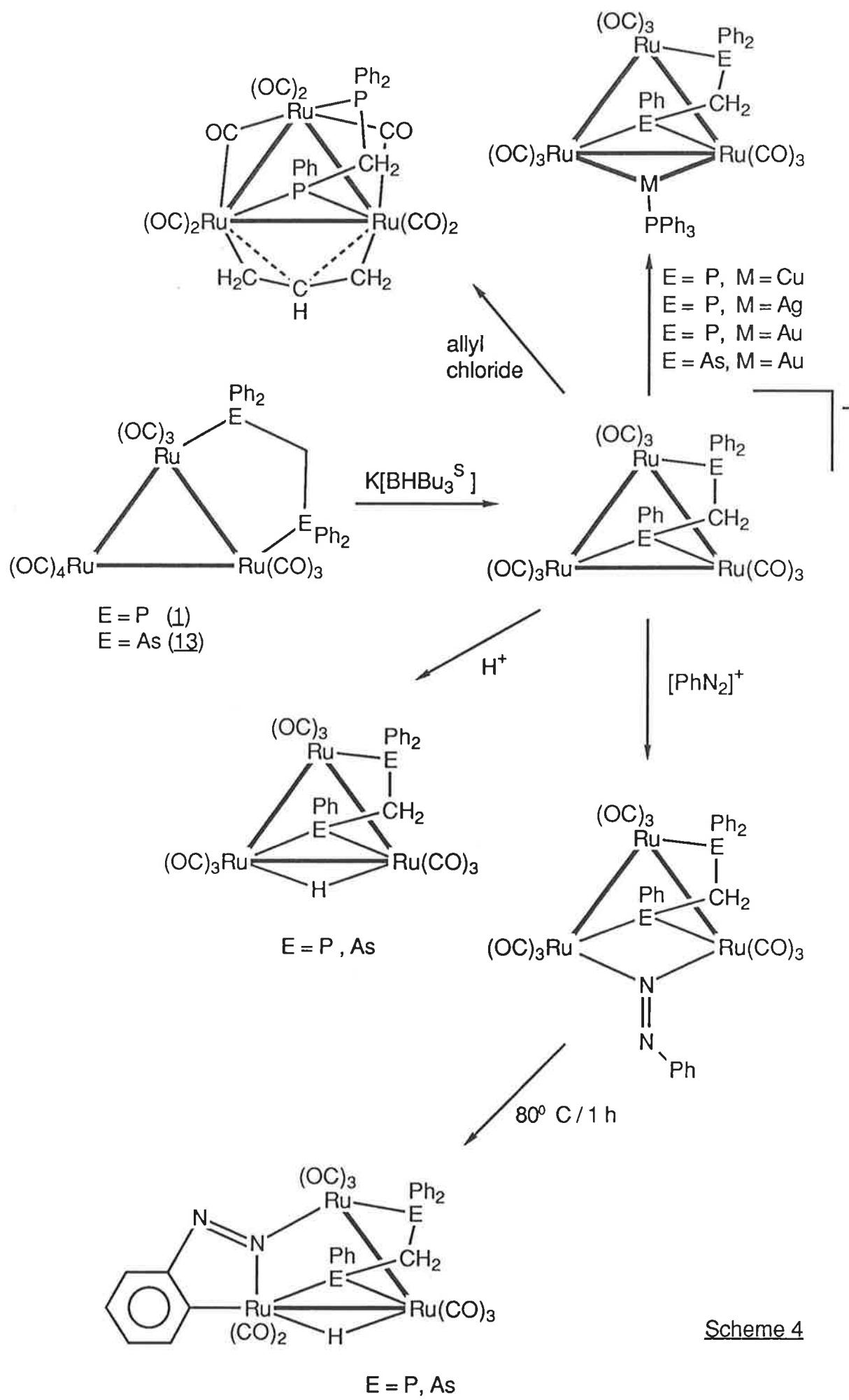
In 1985 Poë *et al*¹⁹ showed that the reaction of dppm with $\text{Ru}_3(\text{CO})_{12}$ proceeded *via* $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\eta^1\text{-dppm})$ to form $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$; the kinetics of the three reactions in benzene were determined, allowing the following reaction sequence to be proposed:



In addition, the kinetics of the substitution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with several P-donor and As-donor nucleophiles in benzene to form $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{L})$ were studied.^{20,21}

The chemistry of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) [and $\text{Ru}_3(\mu\text{-dpam})(\text{CO})_{10}$ (13)] has also been extensively studied by Bruce and co-workers. As found concurrently by Bonnet,¹⁶ the major reaction products obtained from $\text{Ru}_3(\mu\text{-Ph}_2\text{ECH}_2\text{EPH}_2)(\text{CO})_{10}$ [$E = \text{P}$ (1), As (13)] and hydrogen were the dephenylated complexes $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-EPHCH}_2\text{EPH}_2)(\text{CO})_9$, (10) and (14), respectively.⁸ These complexes were also formed by sequential addition of H^- and H^+ to the same precursors. Oxidative addition of H_2 to the Ru_3 complexes is followed by P-C bond cleavage and elimination of benzene; the μ_3 -bridging ligands preventing both break-up and condensation of the clusters as expected. Cleavage of a second P-C bond occurred after prolonged reaction to give $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPH})(\text{CO})_8(\text{PMPh}_2)$. This unusual reaction is a net conversion of the dppm ligand to benzene, coordinated phenyl phosphinidene and PMPh_2 , mediated by the cluster.

Treatment of $\text{Ru}_3(\mu\text{-Ph}_2\text{ECH}_2\text{EPH}_2)(\text{CO})_{10}$ with $\text{K}[\text{HBBu}_3^{\text{S}}]$ gave the corresponding anions $[\text{Ru}_3(\mu_3\text{-EPHCH}_2\text{EPH}_2)(\text{CO})_9]^-$, which reacted with $[\text{PhN}_2][\text{PF}_6]$ to give $\text{Ru}_3(\mu_3\text{-EPHCH}_2\text{EPH}_2)(\mu\text{-N}_2\text{Ph})(\text{CO})_9$.²² These compounds were found to undergo facile cyclometallation reactions when heated (Scheme 4). Similarly the reaction between $[\text{Ru}_3(\mu_3\text{-PPHCH}_2\text{PPH}_2)(\text{CO})_9]^-$ and allyl chloride gave $\text{Ru}_3(\mu_3\text{-PPHCH}_2\text{PPH}_2)(\mu\text{-C}_3\text{H}_5)(\text{CO})_8$,²³ while the group IB metal containing clusters $\text{Ru}_3(\mu\text{-EPHCH}_2\text{EPH}_2)(\text{CO})_9\{\text{M}(\text{PPh}_3)\}$ ($E = \text{P}$, $M = \text{Cu}, \text{Ag}$ or Au ; $E = \text{As}$, $M = \text{Au}$) were prepared from $[\text{Ru}_3(\mu_3\text{-EPHCH}_2\text{EPH}_2)(\text{CO})_9]^-$ and sources of $[\text{M}(\text{PPh}_3)]^+$ (Scheme 4).²⁴ Structural studies demonstrated for the first time the variation in Ru-M ($M = \text{Cu}, \text{Ag}, \text{Cu}$) bond lengths down the Group.²⁴



In this Chapter, examination of the substitution chemistry of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1), which has been somewhat limited, is further explored (a) with acetylenes and (b) with other small molecules; the reactivity of several of the resultant clusters was investigated. The latter part of the Chapter details some related chemistry of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (8).

RESULTS AND DISCUSSION

Multisite cluster-bound acetylene derived ligands have been the focus of considerable interest because they may be regarded as models for chemisorption of alkynes on transition metal surfaces.²⁵⁻²⁷ The first half of this Chapter describes the addition of terminal acetylenes and $C_2(CO_2Me)_2$ to $Ru_3(\mu\text{-dppm})-(CO)_{10}$ (1).

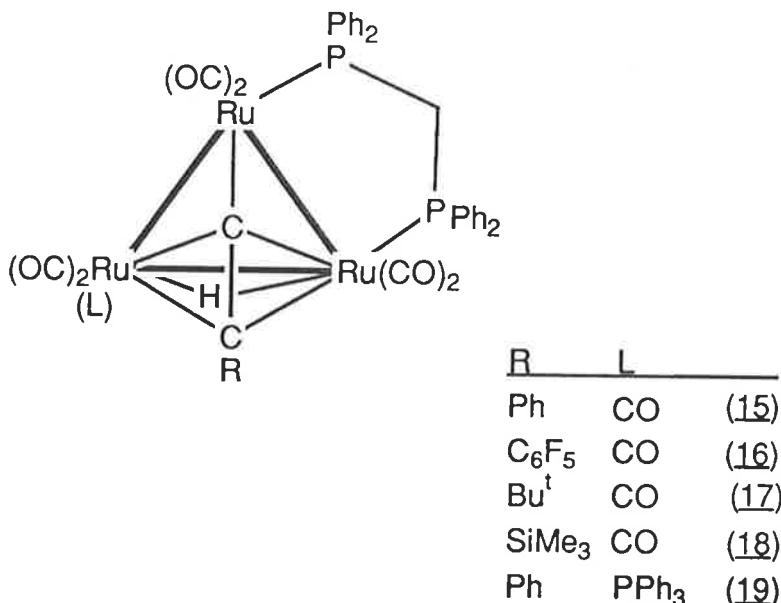
Preparation of $Ru_3(\mu\text{-H})(\mu_3\text{-C}\equiv CR)(\mu\text{-dppm})(CO)_7$

(R = Ph, C_6F_5 , Bu^t and $SiMe_3$)

The reaction of $HC\equiv CPh$ with $Ru_3(\mu\text{-dppm})(CO)_{10}$ (1) in refluxing tetrahydrofuran yielded, after evaporation to dryness and crystallisation from dichloromethane/methanol, yellow crystals of $Ru_3(\mu\text{-H})(\mu_3\text{-C}\equiv CPh)(\mu\text{-dppm})(CO)_7$, (15) in 92% yield, identified on the basis of spectroscopic and microanalytical data. The solution infrared spectrum of (15) contains seven $\nu(CO)$ bands, while the 1H NMR spectrum shows a hydride signal at δ -19.26 as a doublet [$J(PH) = 34Hz$]; a small signal is present at δ -19.25 (see discussion later). The two protons of the methylene bridge of the dppm ligand resonate as two doublets of triplets at δ 3.33 and 4.31 [$J(HH) = 14Hz$, $J(PH) = 12Hz$ and 11Hz]. A multiplet at δ 6.42-7.89 is assigned to the phenyl protons. The FAB mass spectrum of (15) shows the molecular ion at m/z 987 as the base peak, peaks corresponding to the stepwise loss of the seven carbonyl groups, and peaks corresponding to $[m - nCO - Ph - H]^+$ ($n = 5-7$).

In similar reactions $Ru_3(\mu\text{-dppm})(CO)_{10}$ reacted with $HC\equiv CR$ (R = C_6F_5 , Bu^t and $SiMe_3$) to give $Ru_3(\mu\text{-H})(\mu_3\text{-C}\equiv CR)-(\mu\text{-dppm})(CO)_7$ [R = C_6F_5 (16), Bu^t (17) and $SiMe_3$, (18)] ,

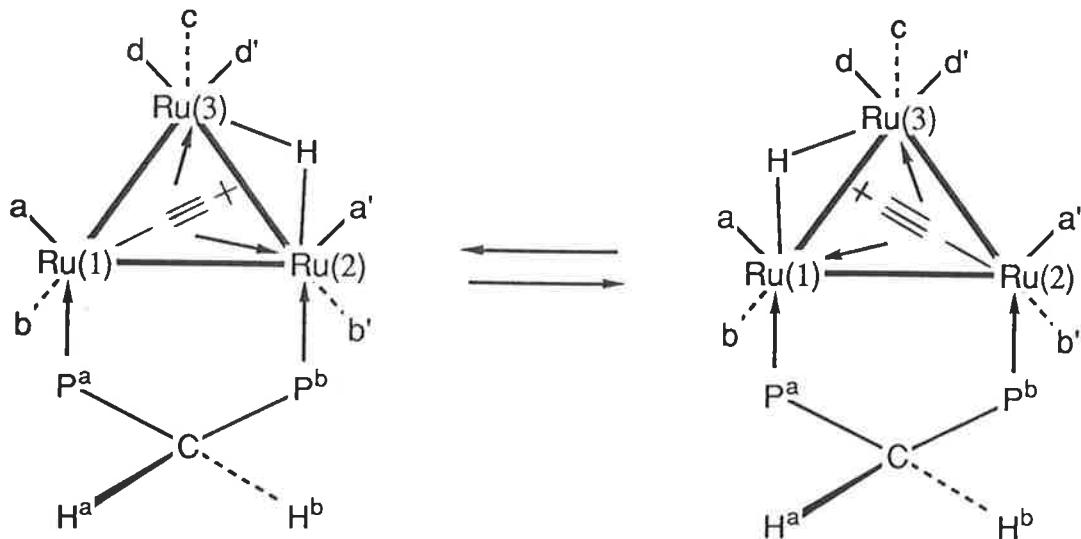
while the reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1), $\text{HC}\equiv\text{CPh}$ and PPh_3 in refluxing THF over 18 h afforded $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})-(\mu\text{-dppm})(\text{CO})_6(\text{PPh}_3)$ (19) in high yield, in which it is assumed (for steric reasons) that the PPh_3 ligand is located on the Ru atom not bonded to the dppm ligand.



All of the compounds were obtained in good yield by crystallisation of the reaction mixture. The spectroscopic properties of these complexes are as expected (see Experimental section) [although because of the low solubility of (19) an informative ^1H NMR spectrum was not able to be obtained; it is clear that the methylene protons are found around δ 3.32 and 4.31 (presumably as the usual two doublets of triplets) and the phenyl groups resonate at a multiplet from δ 6.31-7.74]. The hydride regions of the ^1H NMR spectra, however, are worthy of comment. Whereas (16) and (18) show doublets at δ -19.41 [$J(\text{PH}) = 33\text{Hz}$] and δ -19.99 [$J(\text{PH}) = 34\text{Hz}$], respectively, and (15), as mentioned, shows a doublet with a small signal at δ -19.25, the

spectrum of (17) shows a third peak forming at 295K to give a triplet [$J(\text{PH}) = 17\text{Hz}$]. In a recent report it has been shown that (17) can be obtained in 50% yield from a short reflux of $\text{Ru}_3(\mu\text{-H})(\mu\text{-C}\equiv\text{CBu}^t)(\text{CO})_9$, with dppm and Me_3NO in hexane, followed by preparative thin layer chromatography.²⁹ Infrared and room temperature ^1H NMR data are similar to those obtained in this study; variable temperature ^1H , ^{13}C and ^{31}P NMR spectra of (17) were also reported.²⁹ The two P atoms, which exhibit a well resolved ^{31}P AB pattern at 233K, became equivalent at 313K, giving a single peak. The hydride is strongly coupled to only the adjacent phosphorus, giving a doublet at 233K [ABX system: $^2J(\text{AX}) = 33$, $^4J(\text{BX}) = 0\text{Hz}$]. As the temperature is increased and $[\delta(\text{A}) - \delta(\text{B})] \rightarrow 0$, the doublet tends to a triplet (A_2X system at 313K), the observed splitting being $\frac{1}{2}[J(\text{AX}) + J(\text{BX})]$. The two protons of the methylene bridge of the diphosphine are inequivalent over the range of temperatures examined, suggesting that the diphosphine is rigidly anchored to one side of the cluster. The presence of the bridging ligand blocks the axial-equatorial CO site exchange at Ru(1) (σ -bound to the acetylide) but promotes a new concentration independent fluxional behaviour ($\Delta G^\ddagger = 57.8 \text{ kJ/mol}$, obtained from the ^{31}P coalescence), namely acetylide rotation and concomitant hydride transfer as depicted in Scheme 5.²⁹ This process equalises (see Scheme 5) P^{a} and P^{b} , Ru(1) and Ru(2), the carbonyls a and a' , b and b' , d and d' , but not H^{a} and H^{b} , and so leads to racemisation of the cluster on the NMR time scale. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows seven doublets at 233K corresponding to the seven different carbonyls of the rigid system. These collapse to four broad peaks at 273K (intensity ratio 2:2:2:1),

consistent with the proposed mechanism.²⁹



Scheme 5²⁹

[Recent work by the same authors details investigations into the reactions of the cluster $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CBu}^t)(\text{CO})_9$ with the bidentate ligands $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2$ ($\text{E} = \text{P, dppe; As, dppae}$) in the presence of Me_3NO , to give two isomers of the complex $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CBu}^t)(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2)(\text{CO})_7$. In the first isomer, the ligand chelates the ruthenium atom opposite to the bridging hydride (1,1-derivative), whereas, in the second, it bridges a hydride-free edge (1,2-derivative).]³⁰

Structure of Ru₃(μ-H)(μ₃-C≡CC₆F₅)(μ-dppm)(CO)₇ (16)

An X-ray diffraction study was performed on complex (16) - the molecular structure is shown in Figure 1 (see also Table 1). It shows an almost equilateral triangle of Ru atoms [Ru-Ru distances 2.797(2)-2.811(2)°Å] with seven terminal carbonyl groups; two attached to Ru(1) and Ru(2), three bonded to Ru(3). The C₂C₆F₅ ligand interacts in a σ-fashion with Ru(1) [Ru(1)-C(2') 1.927(4)°Å] and in a π-fashion with Ru(2) [Ru(2)-C(1'), C(2') 2.227(5), 2.198(4)°Å] and Ru(3) [Ru(3)-C(1'), C(2') 2.246(4), 2.216(4)°Å]. The dppm ligand bridges the Ru(1)-Ru(2) edge. The metal bonded hydrogen was not located although it is assumed to bridge the Ru(2)-Ru(3) edge [therefore interacting with only P(2) as found in the ¹H NMR spectrum at 295K, to give the expected high value for J(PH) through two bonds] where the hydride atom has been located in the neutron diffraction study of Ru₃(μ-H)(μ₃-C≡CBu^t)³¹(CO)₉ and in the X-ray analysis of Ru₃(μ-H)(μ₃-C≡CBu^t)(μ-dppm)(CO)₇ (17).²⁹ In both of these compounds the Ru-Ru edge which is bridged by the hydride is the longest, which is due to the usual observed M-M bond lengthening caused by the presence of a μ-H atom. However in this study Ru(2)-Ru(3) is the shortest bond at 2.797(2)°Å; the other two Ru-Ru bonds are 2.811(2)°Å and 2.810(2)°Å. This is possibly because of a C≡C(1) Ru-Ru interaction which counteracts the H-bridge lengthening effect and which depends on the substituent on the alkyne. Similar observations have been made in Os₃(μ-H)(μ₃-C≡CCF₃)(CO)₉,³² where the supposedly H-bridged bond is shorter at 2.828(1)°Å than the unbridged bonds [av. 2.873(1)°Å] and also

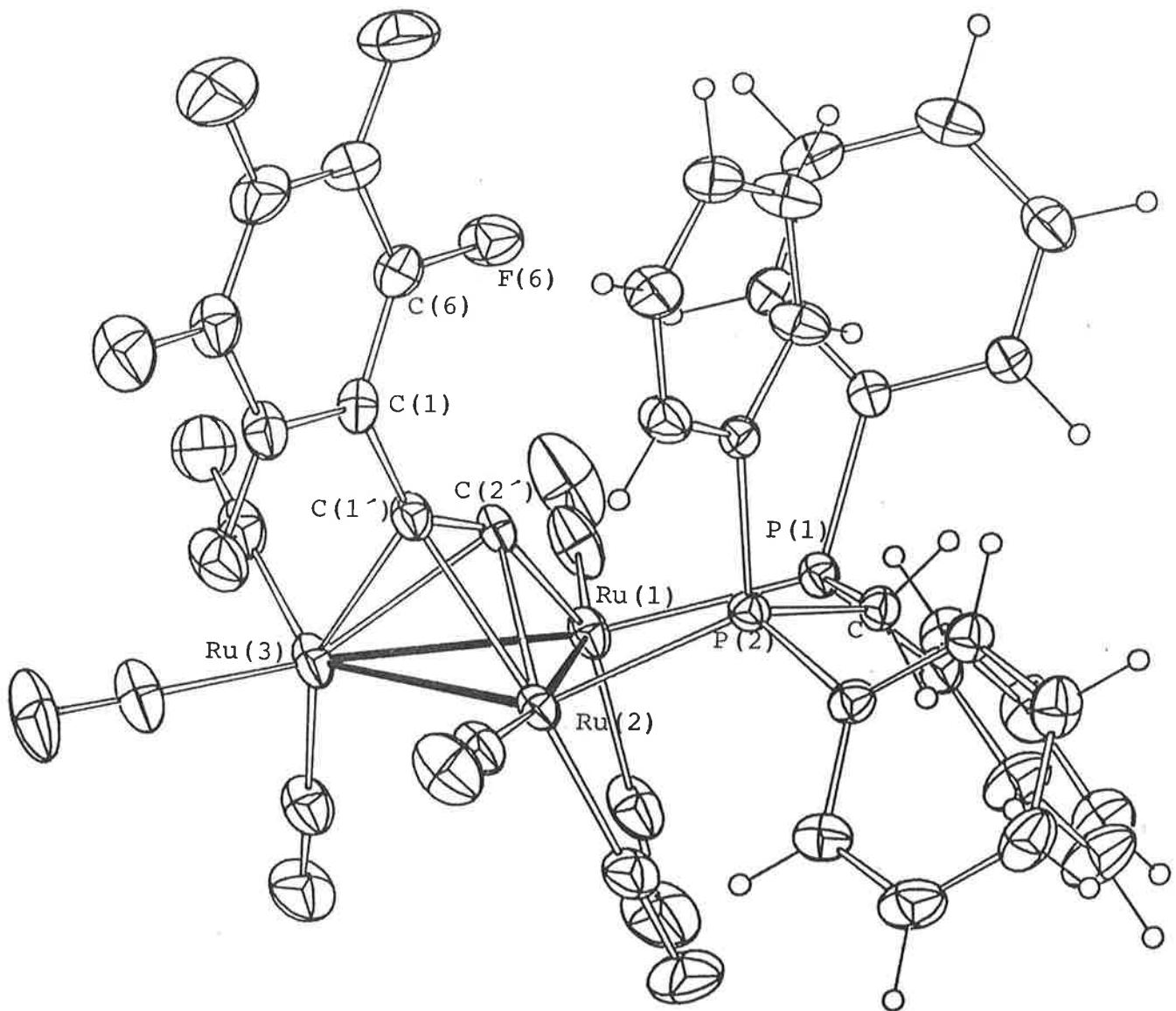


Figure 1: ORTEP plot of the molecular structure of
 $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CC}_6\text{F}_5)(\mu\text{-dppm})(\text{CO})_7$, (16)
 (by B.W. Skelton and A.H. White)

Table 1: Selected interatomic parameters for (16)

Bond distances (Å)

Ru(1) - Ru(2)	2.811(2)	C(1') - C(2')	1.320(5)
Ru(1) - Ru(3)	2.810(2)	C(1') - C(1)	1.451(6)
Ru(1) - C(2')	1.927(4)	Ru(1) - P(1)	2.274(2)
Ru(2) - Ru(3)	2.797(2)	Ru(2) - P(2)	2.304(2)
Ru(2) - C(1')	2.227(5)	P(1) - C	1.840(4)
Ru(2) - C(2')	2.198(4)	P(2) - C	1.828(4)
Ru(3) - C(1')	2.246(4)		
Ru(3) - C(2')	2.216(4)		

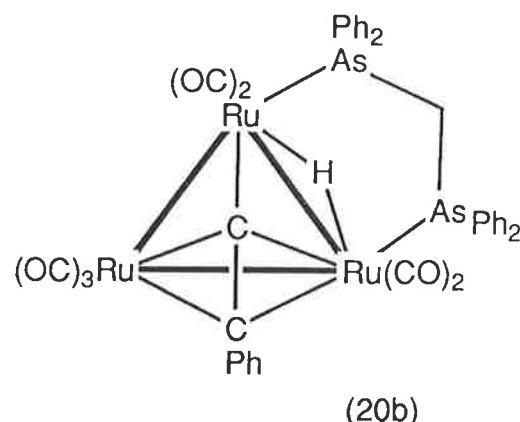
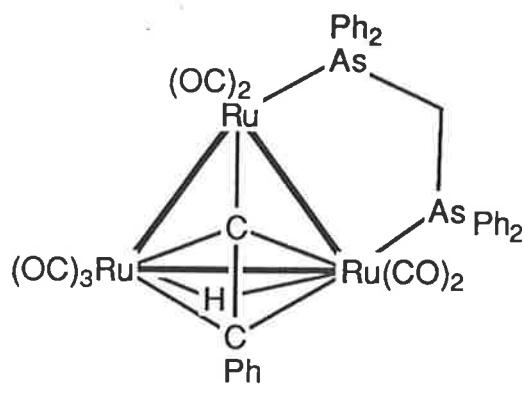
Bond angles (°)

Ru(2) - Ru(1) - Ru(3)	59.69(5)	Ru(1) - Ru(3) - Ru(2)	60.18(5)
Ru(2) - Ru(1) - C(2')	51.2(1)	Ru(1) - Ru(3) - C(1')	76.5(1)
Ru(3) - Ru(1) - C(2')	51.8(1)	Ru(1) - Ru(3) - C(2')	43.1(1)
Ru(1) - Ru(2) - Ru(3)	60.13(5)	Ru(2) - Ru(3) - C(1')	51.0(1)
Ru(1) - Ru(2) - C(1')	76.8(1)	Ru(2) - Ru(3) - C(2')	50.4(1)
Ru(1) - Ru(2) - C(2')	43.1(1)	C(1') - Ru(3) - C(2')	34.4(1)
Ru(3) - Ru(2) - C(1')	51.6(0)	C(1') - Ru(2) - C(2')	34.7(1)
Ru(3) - Ru(2) - C(2')	50.95(9)	Ru(1) - P(1) - C(0)	112.6(1)

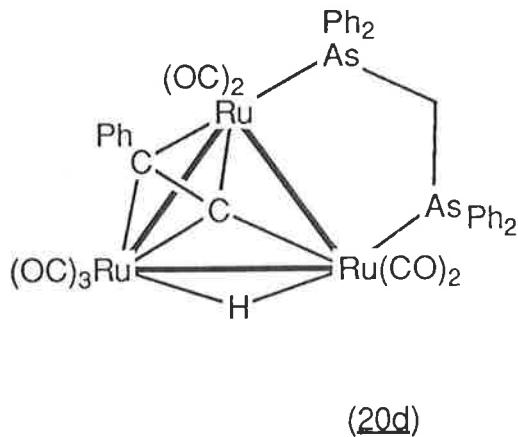
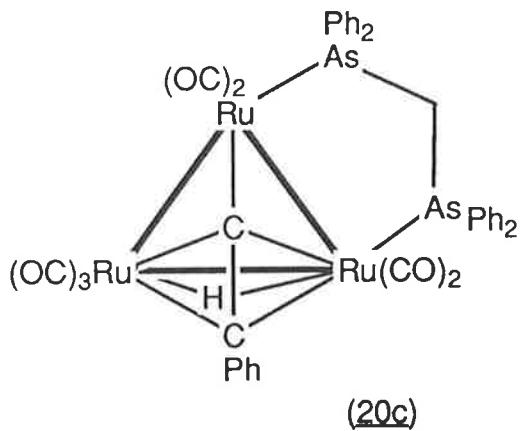
in $\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CSiMe}_3)(\text{CO})_9$ ^{3,3} where the H-bridged bond [2.833(1) Å] is shorter than the other two [2.843(1) and 2.846(1) Å].

Preparation of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dpam})(\text{CO})_7$ (20)

The reaction of $\text{Ru}_3(\mu\text{-dpam})(\text{CO})_{10}$ (13) and $\text{HC}\equiv\text{CPh}$ in refluxing THF readily afforded $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dpam})(\text{CO})_7$ (20) as an orange-yellow powder in 76% yield, identified by microanalytical and spectroscopic methods. The FAB mass spectrum shows a molecular ion and peaks corresponding to $[M - n\text{CO}]^+$ ($n = 1\text{-}7$) and $[M - n\text{CO} - \text{Ph} - \text{H}]^+$ ($n = 5\text{-}7$). The peak assigned to $[M - 7\text{CO} - \text{Ph} - \text{H}]^+$ is the base peak. The ¹H NMR spectrum of (20) is particularly interesting. Instead of the expected one hydride peak and two doublets (due to coupling of the inequivalent methylene hydrogens), there are two hydride peaks ($\delta = 20.01$ and -19.89) and two sets of doublets at $\delta = 2.01$ and 2.50 [$J(\text{HH}) = 11\text{Hz}$] and $\delta = 3.05$ and 3.99 [$J(\text{HH}) = 12\text{Hz}$]. The phenyl protons resonate as a multiplet from $\delta = 6.71$ – 7.47 . The ¹H NMR data suggest the presence of two isomers (ratio 1:1) which do not interconvert on the NMR time scale at 295K. Positioning of the hydride on the side of the Ru triangle bridged by the dpam ligand, as well as that postulated for the dppm ligand would give the required isomers (20a) and (20b).



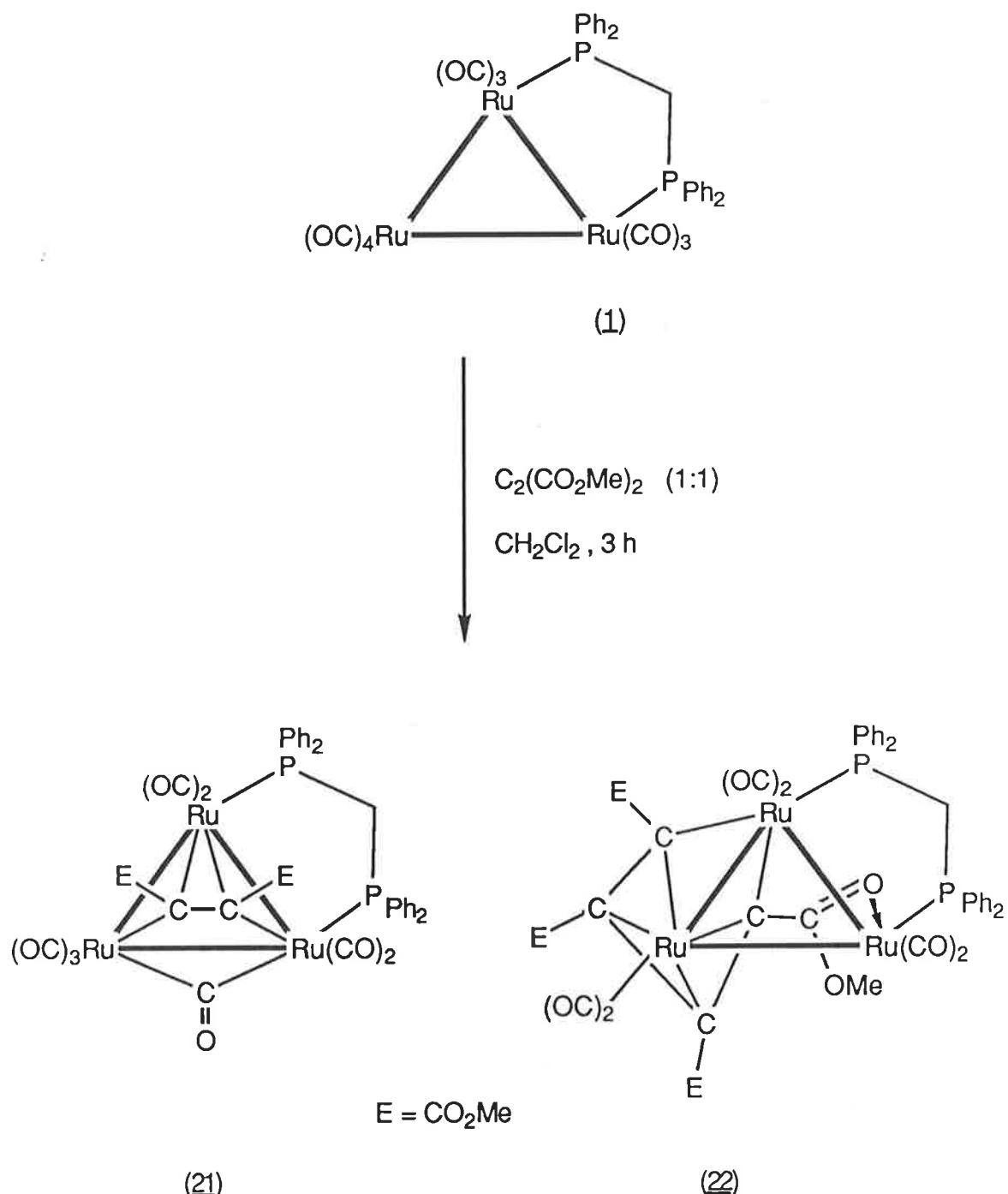
Another possibility is that the C₂Ph ligand may be positioned in two different positions relative to the hydride [(20c) and (20d)].



Reactivity of Ru₃(μ-dppm)(CO)₁₀ (1) with C₂(CO₂Me)₂

The reaction of Ru₃(μ-dppm)(CO)₁₀ (1) with C₂(CO₂Me)₂ was found to give various products depending on the stoichiometries and conditions employed. Refluxing a 1:1 mixture in dichloromethane for 3 hours followed by preparative TLC and crystallisation yielded (1), purple crystals of Ru₃{μ₃-C₂(CO₂Me)₂} (μ-dppm)(μ-CO)(CO)₇ (21) and olive-green crystals of Ru₃{μ₃-C₄(CO₂Me)₄} (μ-dppm)(CO)₆ (22) (approximately 30% of each) (Scheme 6). Similar results were obtained in refluxing tetrahydrofuran over much shorter reaction times (less than 1 hour).

The mono-substituted cluster (21), which was crystallised from dichloromethane/n-hexane, was identified by the usual methods. The solution IR spectrum contains ν(CO) bands consistent with the presence of both terminal and bridging



Scheme 6

carbonyl ligands. The ^1H NMR spectrum contains two singlets at δ 3.39 and 3.61 assigned to the OMe protons while the CH_2 protons are seen as two multiplets (ABXY pattern) at δ 4.85 and 5.50. The aromatic multiplet is observed at δ 7.37. The FAB mass spectrum supports the formulation of this compound as $\text{Ru}_3\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7$, showing a peak at m/z 1054 assigned to $[\text{M} - \text{H}]^+$, and peaks formed by the competitive loss of CO, OMe and $\text{C}_2(\text{CO}_2\text{Me})_2$.

The other product, $\text{Ru}_3\{\mu_3-\text{C}_4(\text{CO}_2\text{Me})_4\}(\mu-\text{dppm})(\text{CO})_6$ (22) was also readily synthesised by reacting (1) with >2 equivalents of $\text{C}_2(\text{CO}_2\text{Me})_2$ (72%) or by further reacting the isolated mono-substituted cluster (21) with $\text{C}_2(\text{CO}_2\text{Me})_2$ (79%) (Scheme 7); in both cases isolation of (22) was achieved by evaporation of the reaction mixture followed by crystallisation from dichloromethane/methanol. Microanalytical and spectroscopic data showed the presence of two $\text{C}_2(\text{CO}_2\text{Me})_2$ ligands. The solution IR spectrum of (22) shows six $\nu(\text{CO})$ bands, while the ^1H NMR spectrum shows four singlet peaks at δ 2.97, 3.78, 3.79 and 3.80 assigned to the four CO_2Me groups, and the two protons of the methylene group as two doublets of triplets at δ 4.73 and 5.32 [$J(\text{HH}) = 15\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$]. The phenyl protons are present as a multiplet at δ 7.06–7.91. The FAB mass spectrum shows the molecular ion at m/z 1141 and peaks corresponding to the stepwise loss of the six carbonyl groups (the peak assigned to $[\text{M} - 5\text{CO}]^+$ is the base peak). Peaks at m/z 943 and 915 are assigned to $[\text{M} - \text{C}_2(\text{CO}_2\text{Me})_2 - n\text{CO}]$ ($n = 2, 3$), while the peak at m/z 857 is assigned to $[\text{M} - 2\{\text{C}_2(\text{CO}_2\text{Me})_2\}]^+$.

An X-ray diffraction study of (22) was performed to determine the mode of attachment of the two $\text{C}_2(\text{CO}_2\text{Me})_2$ ligands to the cluster (Figure 2). It shows a triangle of Ru atoms with six

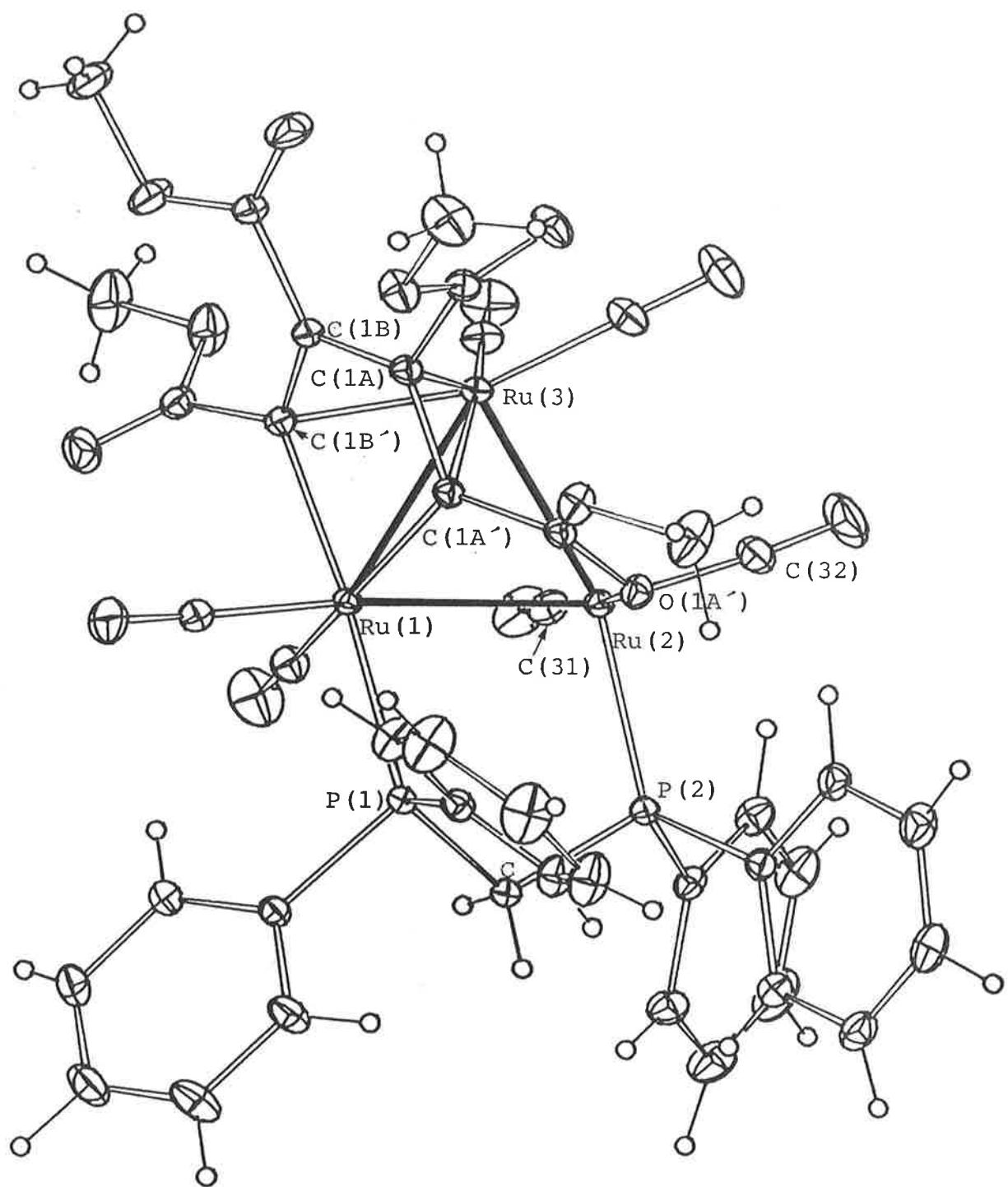


Figure 2: ORTEP plot of the molecular structure of
 $\text{Ru}_3\{\mu_3\text{-C}_4(\text{CO}_2\text{Me})_4\}(\mu\text{-dppm})(\text{CO})_6$ (22)
 (by B.W. Skelton and A.H. White)

Table 2: Selected interatomic parameters for (22)Bond distances (Å)

Ru(1) - Ru(2)	2.8631(6)	Ru(2) - O(1A')	2.1876(14)
Ru(1) - Ru(3)	2.7388(4)	Ru(2) - P(2)	2.3155(6)
Ru(1) - C(1A')	2.1154(19)	Ru(3) - C(1A)	2.2506(18)
Ru(1) - C(1B')	2.1181(15)	Ru(3) - C(1A')	2.2194(14)
Ru(1) - P(1)	2.3686(5)	Ru(3) - C(1B)	2.2917(17)
Ru(2) - Ru(3)	2.6977(5)	Ru(3) - C(1B')	2.1747(16)
C(1A) - C(1A')	1.4164(24)	P(1) - C	1.8404(18)
C(1A) - C(1B)	1.4427(20)	P(2) - C	1.8366(17)
C(1B) - C(1B')	1.4167(29)		

Bond angles (°)

Ru(2) - Ru(1) - Ru(3)	57.52(1)	Ru(1) - Ru(3) - Ru(2)	63.55(1)
Ru(1) - Ru(2) - Ru(3)	58.92(1)	P(1) - C - P(2)	113.20
Ru(3) - Ru(2) - O(1A')	87.92(4)	O(1A') - Ru(2) - P(2)	89.98(4)
O(1A') - Ru(2) - C(31)	172.87(7)	O(1A') - Ru(2) - C(32)	93.78(9)
Ru(1) - Ru(2) - O(1A')	85.68(3)		

Table 3: Selected interatomic parameters for (27)Bond distances (Å)

Ru(1) - Ru(2)	2.835(1)	Ru(3) - C(3)	2.038(4)
Ru(1) - Ru(3)	2.9760(9)	P(1) - C	1.827(4)
Ru(2) - Ru(3)	2.7491(8)	C - P(2)	1.830(4)
Ru(1) - P(1)	2.332(1)	C(2) - C(3)	1.397(6)
Ru(1) - C(2)	2.121(5)	Ru(2) - P(2)	2.351(1)
Ru(2) - C(2)	2.216(4)	Ru(2) - C(3)	2.239(5)

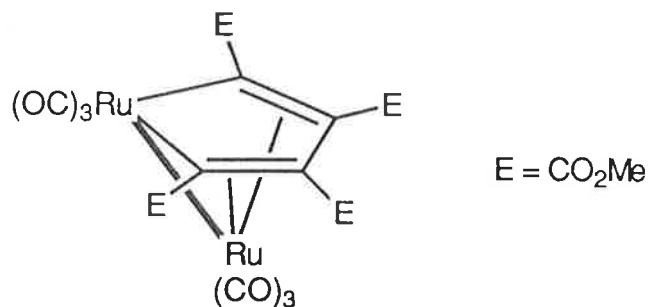
Bond angles (°)

Ru(2) - Ru(1) - Ru(3)	56.40(2)	Ru(1) - Ru(3) - Ru(2)	59.21(2)
Ru(1) - Ru(1) - Ru(3)	64.38(3)	P(1) - C - P(2)	116.8(2)
Ru(1) - P(1) - C	114.0(2)	C(1) - C(2) - C(3)	121.7(4)
Ru(2) - P(2) - C	111.9(1)	C(2) - C(3) - C(4)	118.5(3)

terminal carbonyl groups, two on each Ru atom. The dppm ligand bridges the Ru(1)-Ru(2) bond. A $C_4(CO_2Me)_4$ ligand formed by linkage of two $C_2(CO_2Me)_2$ molecules interacts with the cluster via two σ -bonds to Ru(1) and the diene to Ru(3), i.e. as a 6e donor. One of the carbomethoxy ligands bonds to Ru(2) via an ester CO group [$Ru(2)-O(1A')$ $2.1876(14)\text{\AA}$]. The cluster is thus electron precise (48e). This interaction explains the observation in the 1H NMR spectrum that one of the OMe groups resonates at $\delta 2.97$. The Ru-Ru bond lengths range from $2.6977(5)$ - $2.8631(6)\text{\AA}$ [the longest bond is Ru(1)-Ru(2) which is bridged by the dppm ligand]. In the parent complex (1) the Ru-Ru bond lengths range from $2.834(1)$ - $2.860(1)\text{\AA}$ and the bond bridged by the dppm ligand is the shortest.¹¹

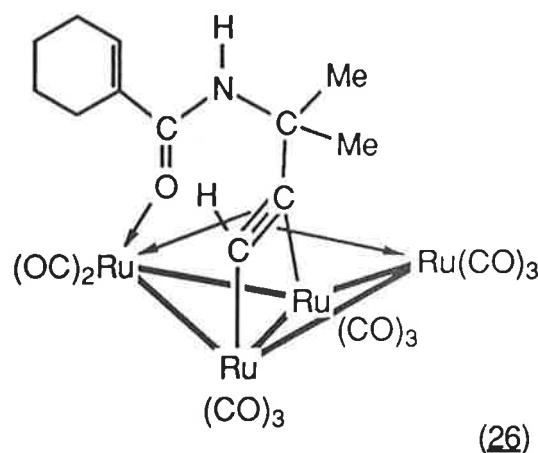
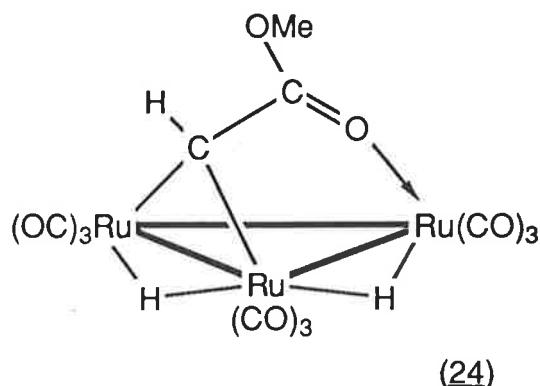
The formation of the $C_4(CO_2Me)_4$ ligand in (22) is not unusual. Transition-metal clusters, when reacted with excess alkyne, often promote the formation of products where C-C bond formation has occurred to give larger, co-ordinated organic groups.^{25, 34}

Dimerisation of $C_2(CO_2Me)_2$ had been observed in the reaction of $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$ in refluxing tetrahydrofuran which gave $Ru_2\{\mu-C_4(CO_2Me)_4\}(CO)_6$ (23) (13%) as the major product. The only other identified product was $Ru_3\{C_2(CO_2Me)_2\}_4(CO)_7$ (4%). The structure determination of (23) showed a tetra-substituted tricarbonyl ruthenacyclopentadiene ligand π -bonded to the second $Ru(CO)_3$ group.³⁵



(23)

The interaction of one cluster metal with an oxygen atom of an organic CO group, is also not uncommon in ruthenium cluster chemistry. Examples of this include $Ru_3(\mu-H)_2-\{\mu_3-\eta^2-CHC(O)OMe\}(CO)_9$ (24),³⁶ the "raft" cluster $Ru_6(\mu-H)(\mu_3-H)- (C_6H_4O)(CO)_{16}$ (25)³⁷ (where the phenoxy ligand is coordinated to three of the Ru atoms in an edge-bridged butterfly arrangement and the oxygen atom bridges two metal centres) and the recently reported butterfly cluster $Ru_4(\mu_4-\eta^2-HC\equiv CMe_2NHCOC_6H_9)-(CO)_{11}$ (26).³⁸

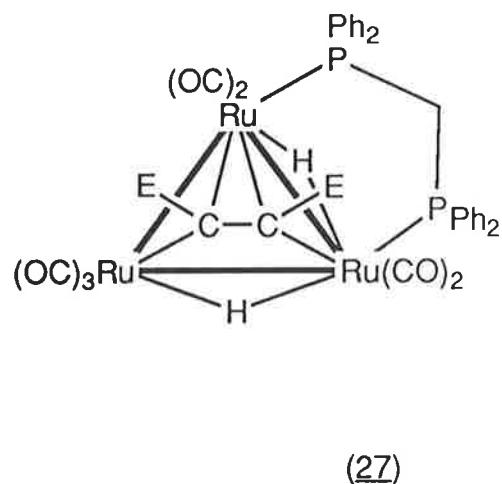
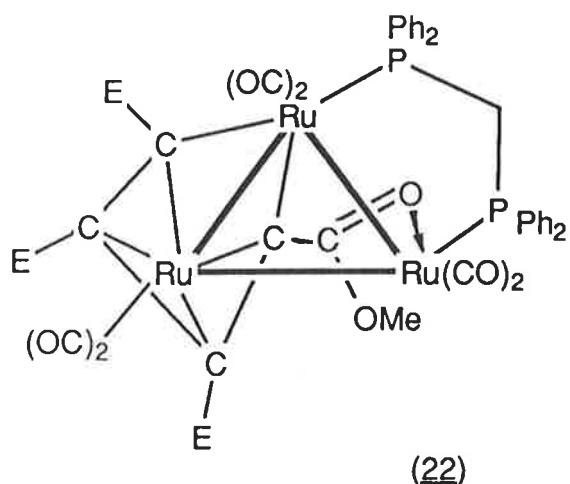
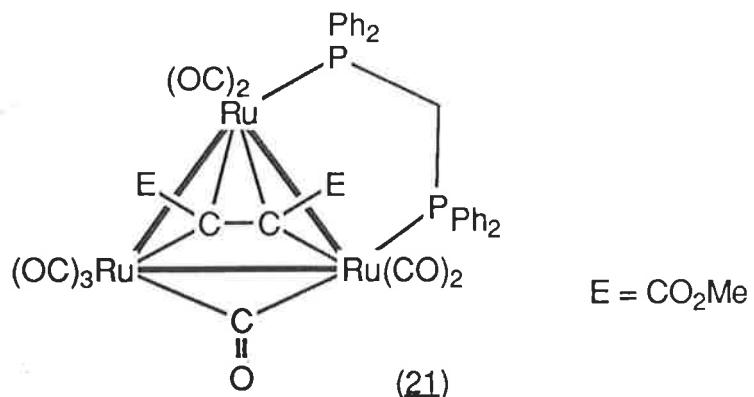


The reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) and $\text{C}_2(\text{CO}_2\text{Me})_2$ (1:1) in tetrahydrofuran over 18 hours gave a complex mixture of products which was separated by preparative TLC. An orange-red band ($R_f = 0.57$) was identified as $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$, (8) (18%), while bands with $R_f = 0.40$ and 0.16 were identified as (21) (1%) and (22) (19%), respectively.

A yellow band ($R_f = 0.44$) was crystallised from dichloromethane/methanol to give orange crystals of $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_7$, (27) (1%). This compound was also prepared by the hydrogenation of a refluxing dichloromethane solution of (21) in 77% yield. Identification was made using microanalytical and spectroscopic data. The FAB mass spectrum shows a molecular ion at m/z 1029 and peaks due to the competitive loss of OMe, CO and CO_2Me groups. The solution infrared spectrum shows only terminal $\nu(\text{CO})$ bands and, apart from the absence of a bridging $\nu(\text{CO})$ band, is similar to that of (21). The ^1H NMR spectrum shows two distinct hydride signals (a doublet at δ -19.22 [$J(\text{PH}) = 39\text{Hz}$] and a triplet at δ -14.89 [$J(\text{PH}) = 14\text{Hz}$]). The CO_2Me protons are seen as two singlet resonances at δ 3.46 and 3.76, while the methylene protons are found at δ 3.56 and 4.49 as multiplets (ABXY pattern). The phenyl protons are seen as a multiplet from δ 6.96-7.54.

Molecular structure of $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_7$, (27)

An X-ray diffraction study of (27) was undertaken and shows (Figure 3, see also Table 3) a triangle of Ru atoms with seven terminal carbonyl groups, two each on Ru(1) and Ru(2), which are bridged by the dppm ligand, and three on Ru(3). The $\text{C}_2(\text{CO}_2\text{Me})_2$ ligand interacts with all three Ru atoms via two σ -bonds and one π -bond to Ru(2),



Scheme 7

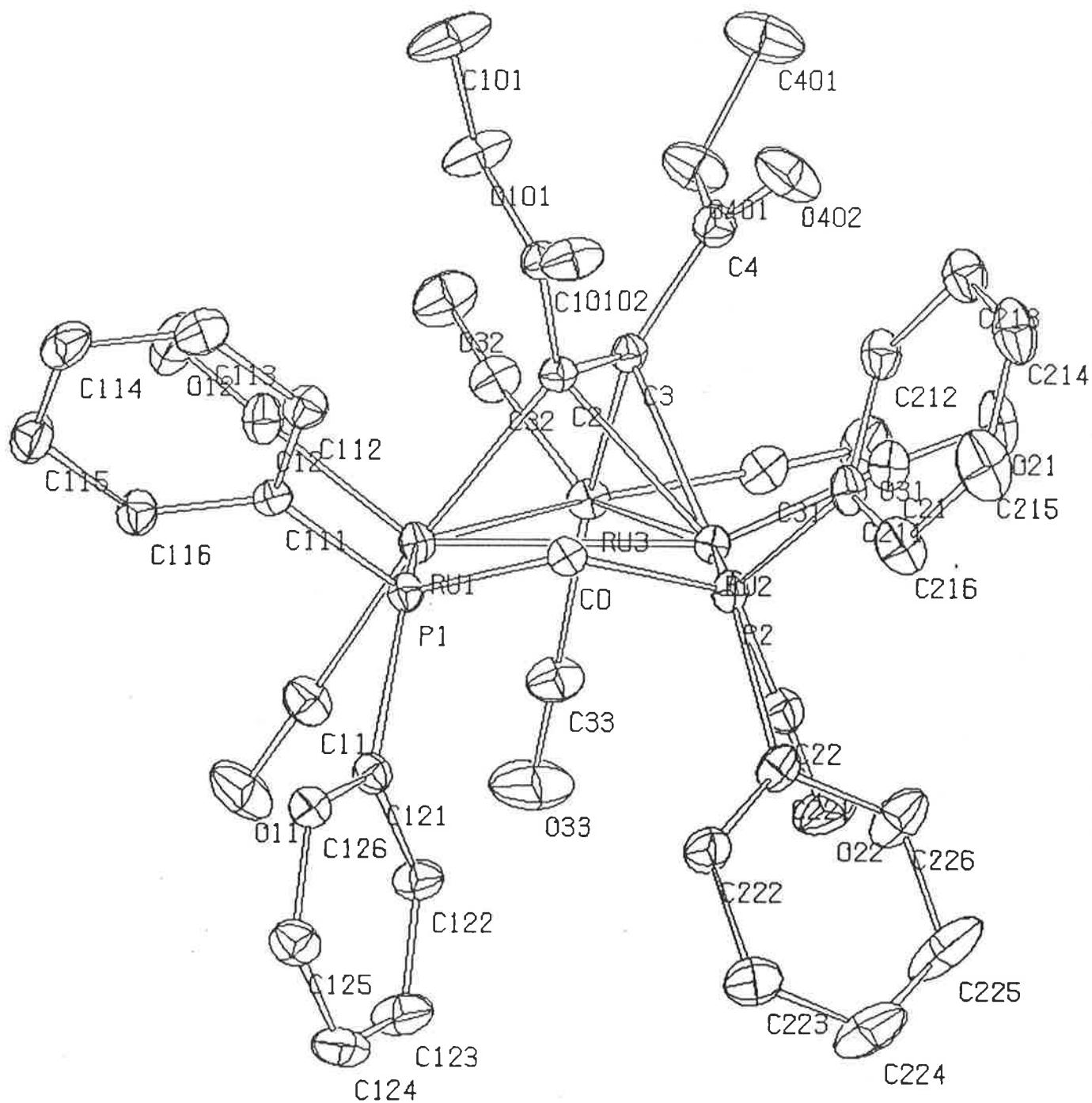


Figure 3: ORTEP plot of the molecular structure of
 $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_7$, (27)
 (by B.W. Skelton and A.H. White)

($2\sigma + \pi$ or $\mu_3-\eta^2$), a bonding mode which is commonly found in homo- and heterometallic alkyne clusters.^{25, 26} This mode of bonding brings the C-C bond nearly parallel to one edge of the cluster (from which the notation $\mu_3-\eta^2(||)$ is derived for this bonding). A formal electron count shows that the $\mu_3-\eta^2$ ligand acts as a 4e donor to the electron precise (48e) cluster. [It seems logical to assume that the $C_2(CO_2Me)_2$ ligand in (21) is bonded to the three metal atoms in a similar manner.] The Ru-Ru bond lengths in (27) range from 2.7491(8)-2.9760(9) \AA . Although the hydrides were not located, the 1H NMR spectrum shows one hydride coupled with two phosphorus atoms to give a triplet, suggesting that there is a hydride bridging the same bond as the dppm ligand. The other hydride bridges one of the other two Ru-Ru bonds, presumably Ru(1)-Ru(3) which is the longest bond.

Tetranuclear complexes

Two other products were isolated in low yield from the above reaction and found to be Ru_4 clusters. An orange-yellow band ($R_f = 0.47$) was crystallised from dichloromethane/methanol to give orange-red crystals of a compound identified as $Ru_4(\mu_3-H)\{\mu_4-C_2(CO_2Me)_2\}\{\mu-PPh(C_6H_4)CH_2PPh_2\}(CO)_9$, (28) (1%) after an X-ray structural determination was undertaken (Figure 4).

The structure is best described as a butterfly arrangement of the four ruthenium atoms, capped by the $C_2(CO_2Me)_2$ ligand. A metal hydride caps the Ru(1), Ru(2), Ru(3) face, while a five-electron orthometallated $Ph_2PCH_2P(C_6H_4)Ph$ fragment (derived from the dppm ligand by the loss of the H atom) bridges the Ru(1)-Ru(2) edge. The coordination of the four ruthenium atoms is completed by nine carbonyl ligands; three bonded to Ru(4)

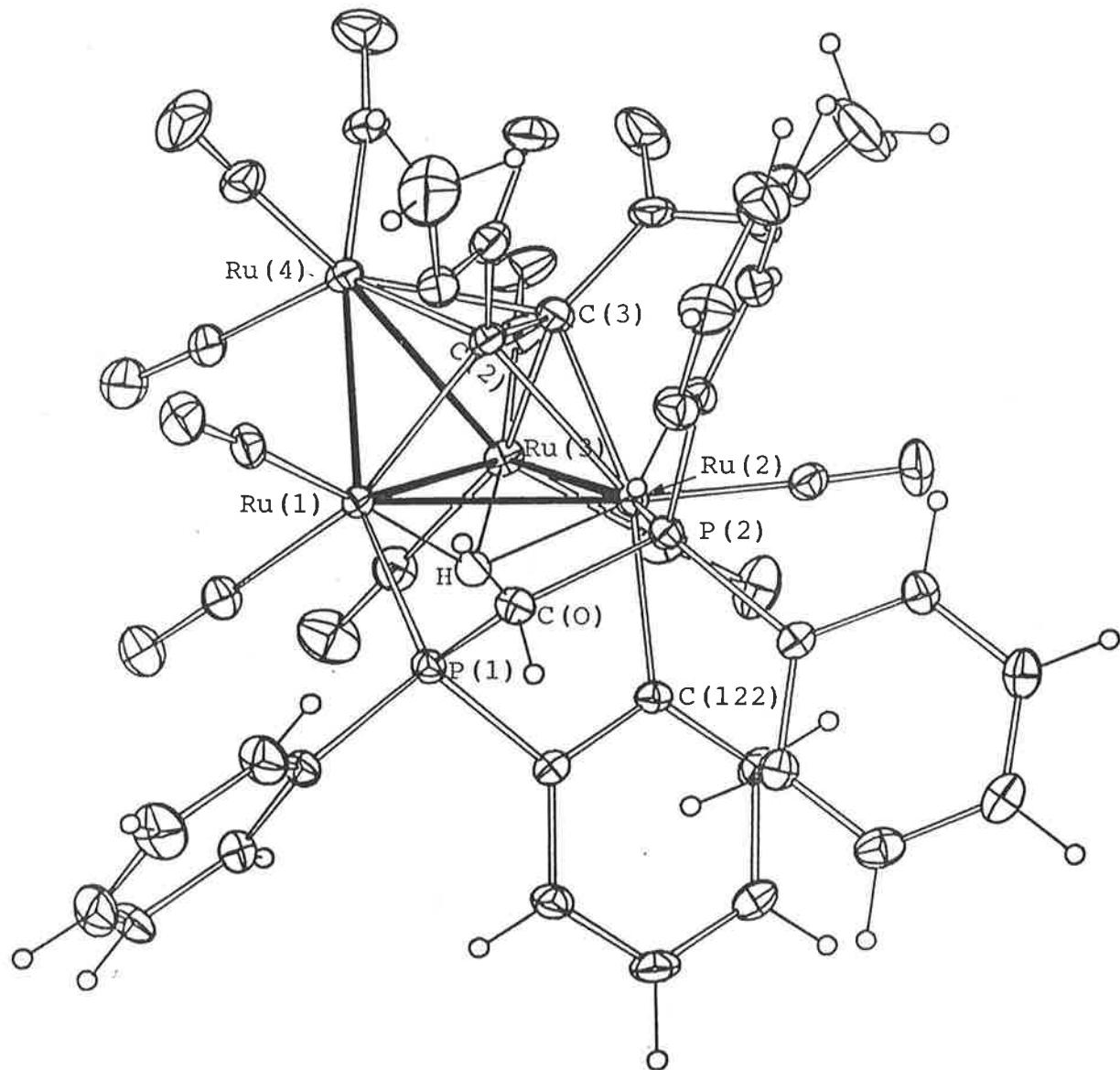


Figure 4 : ORTEP plot of the molecular structure of
 $\text{Ru}_4(\mu_3\text{-H})\{\mu_4\text{-C}_2(\text{CO}_2\text{Me})_2\}\{\mu\text{-Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}\}(\text{CO})_9$,
(28) (by B.W. Skelton and A.H. White)

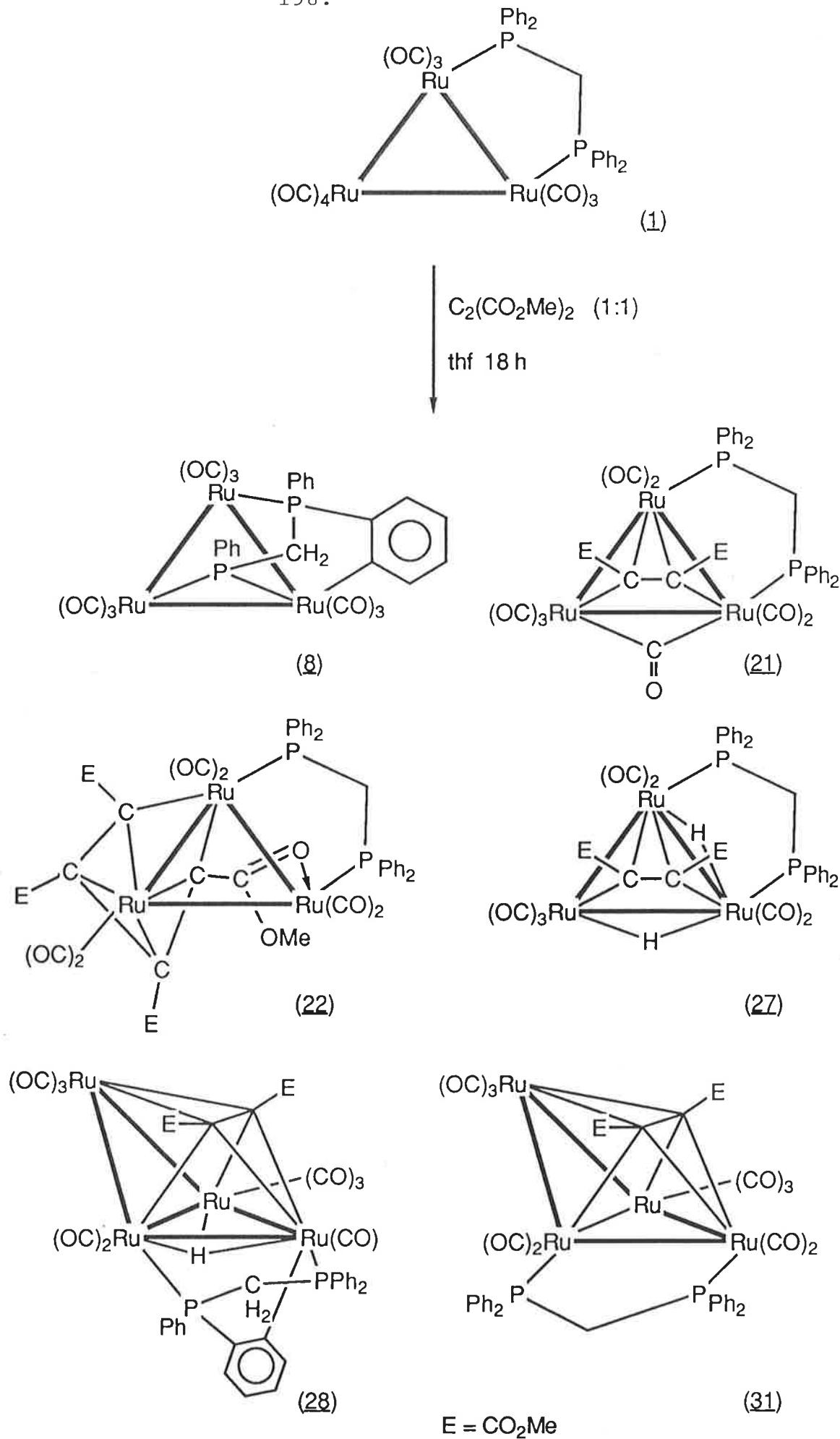
Table 4: Selected interatomic parameters for (28)
and related complexes

Bond distances (Å)

	(28)	(29)	(30)
Ru(1) - Ru(2)	2.807(1)	2.728(1)	2.74(1)
Ru(1) - Ru(3)	2.942(1)	2.880(1)	2.85(1)
Ru(1) - Ru(4)	2.723(1)	2.710(1)	2.71(1)
Ru(2) - Ru(3)	2.851(1)	2.710(1)	2.71(1)
Ru(3) - Ru(4)	2.739(1)	2.728(1)	2.74(1)
Ru(1) - C(2)	2.146(8)	2.16(1)	2.16(1)
Ru(2) - C(2)	2.230(7)	2.24(1)	2.25(1)
Ru(4) - C(2)	2.257(7)	2.27(1)	2.24(1)
Ru(2) - C(3)	2.317(8)	2.27(1)	2.26(1)
Ru(3) - C(3)	2.139(7)	2.16(1)	2.16(1)
Ru(4) - C(3)	2.218(8)	2.24(1)	2.24(1)
C(2) - C(3)	1.44(1)	1.45(1)	1.46(2)
Ru(1) - P(1)	2.309(2)		
Ru(2) - C(122)	2.073(7)		
Ru(2) - P(2)	2.268(2)		
P(1) - C(0)	1.834(8)		
C(0) - P(2)	1.830(8)		

Bond Angles (°)

Ru(2) - Ru(1) - Ru(3)	59.41(3)	Ru(2) - Ru(3) - Ru(4)	91.31(4)
Ru(2) - Ru(1) - Ru(4)	92.61(4)	Ru(1) - Ru(4) - Ru(3)	65.20(3)
Ru(3) - Ru(1) - Ru(4)	57.67(3)	C(2) - Ru(4) - C(3)	37.6(3)
Ru(1) - Ru(2) - Ru(3)	62.66(3)	Ru(1) - P(1) - C(0)	111.4(2)
Ru(1) - Ru(2) - C(122)	95.8(2)	P(1) - C(0) - P(2)	106.2(4)
Ru(3) - Ru(2) - C(122)	101.2(2)	Ru(2) - P(2) - C(0)	105.1(2)
C(2) - Ru(2) - C(3)	36.9(3)	Ru(2) - C(2) - Ru(4)	126.0(3)
Ru(1) - Ru(3) - Ru(2)	57.93(3)	Ru(2) - C(3) - Ru(4)	123.7(3)
Ru(1) - Ru(3) - Ru(4)	57.14(3)		

**Scheme 8**

and Ru(3), two bonded to Ru(1) and one bonded to Ru(2).

The mode of attachment of $\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}$ is via two conventional two-electron bonds from P(1)-Ru(1) and P(2)-Ru(2). Further attachment to the cluster is achieved by cyclometallation of one of the phenyl rings on P(1) to give a Ru-C σ -bond [Ru(2)-C(122) $2.073(7)\text{\AA}$].

The $\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}$ ligand had previously been observed in the unsaturated cluster $\text{Os}_3\{\mu_3-\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}\}(\mu-\text{H})(\text{CO})_8$ formed by thermolysis of $\text{Os}_3(\mu\text{-dppm})(\text{CO})_{10}$ in refluxing toluene;³⁹ the metallated phenyl group in this compound, however, adopts a bridging position between two Os atoms.³⁹

The bonding of the $\text{C}_2(\text{CO}_2\text{Me})_2$ ligand to the cluster can be described as $\mu_4-\eta^2$ ($2\sigma, 2\pi$); coordination to the two "hinge" metal atoms is via σ -bonds and to the two "wingtip" metal atoms via π -bonds. This can be considered as derived from $2\sigma + \pi$, $\mu_3-\eta^2$ complexes upon addition of a $\text{M}(\text{CO})_n$ fragment on one side of the cluster. This is the most common bonding of alkynes to butterfly clusters.^{25, 26}

Other complexes of this type include $\text{Ru}_4(\mu_4-\eta^2-\text{C}_2\text{Me}_2)(\text{CO})_{12}$ ⁴¹ (29) and $\text{Ru}_4(\mu_4-\eta^2-\text{C}_2\text{Ph}_2)(\text{CO})_{12}$ (30).⁴² Selected bond lengths and angles for (28) are shown in Table 4, and where appropriate, corresponding values of (29) and (30) are listed. As found previously, the Ru-Ru bonds of the Ru_4 butterfly embrace a set of four wing edges, which in (28) range from $2.723(1)$ - $2.851(1)$ \AA , and a longer "hinge" bond of $2.942(1)$ \AA . The major differences between (28) and complexes (29) and (30), are that the hinge bond [Ru(1)-Ru(3)], Ru(1)-Ru(2) [which is bridged by the $\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}$ ligand] and Ru(2)-Ru(3), i.e. the three bonds that define the face capped by the metal hydride, are all significantly longer in (28). The alkyne C(2)-C(3) bond

[1.44(1) \AA] 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. [Spectroscopic data obtained for complex (28) are in accord with the crystallographically determined structure. The solution IR spectrum shows eight terminal $\nu(\text{CO})$ bands, while the FAB mass spectrum shows a peak at m/z 1183 (identified as $[\text{M} - \text{H}]^+$), which degrades via the loss of CO ligands and $\text{C}_2(\text{CO}_2\text{Me})_2$.] A purple band at $R_F = 0.43$, was crystallised from dichloromethane/methanol to give purple crystals of $\text{Ru}_4\{\mu_4-\text{C}_2(\text{CO}_2\text{Me})_2\}-(\mu\text{-dppm})(\text{CO})_{10}$ (31) in 2% yield, the final product isolated from the reaction of (1) and $\text{C}_2(\text{CO}_2\text{Me})_2$ in tetrahydrofuran over eighteen hours. Although no crystals suitable for an X-ray structural determination of this compound were obtained, spectroscopic data and the X-ray study of (28), which is probably derived from (31), support the view that (31) also contains a butterfly arrangement of the four ruthenium atoms, capped by the $\text{C}_2(\text{CO}_2\text{Me})_2$ ligand and bridged on one edge by a dppm ligand. Two carbonyl ligands are bonded to the rutheniums on this edge and three each to the other two ruthenium atoms. The solution IR spectrum of (31) shows eight terminal $\nu(\text{CO})$ bands, while the FAB mass spectrum shows a peak at m/z 1212 due to the molecular ion and peaks due to the competitive loss of OMe and the carbonyl ligands. The ^1H NMR spectrum shows two singlets at δ 3.03 and 3.79 assigned to the OMe protons, two doublets of triplets at δ 4.75 and 4.97 [$J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$] due to the methylene protons, and the aromatic protons as a multiplet from δ 6.92-7.83.

Preparation of Ru₃(μ₃-C≡CPh)(μ-dppm)(CO)₇{Au(PR₃)}

[R = Ph (32) or C₆H₄Me-p (33)]

A reaction of Ru₃(μ-dppm)(CO)₁₀ with Au(C≡CPh)(PPh₃) in refluxing tetrahydrofuran afforded, after crystallisation from dichloromethane/methanol, orange crystals of Ru₃(μ₃-C≡CPh)- (μ-dppm)(CO)₇{Au(PPh₃)} (32) in excellent yield. Identification was made on the basis of spectroscopic data. The FAB mass spectrum shows, in addition to the expected molecular ion, an ion at *m/z* 1904 which is assigned to [M + Au(PPh₃)]⁺. Peaks are found due to the stepwise loss of the carbonyl ligands ([M - 3CO]⁺ is the base peak), while peaks at *m/z* 1227, 1199 and 1171 are assigned to [M - nCO - Ph - H]⁺ (n = 5-7). Other significant peaks are found at *m/z* 459 and 721, assigned to [Au(PPh₃)]⁺ and [Au(PPh₃)₂]⁺, respectively. The solution infrared spectrum shows six bands in the terminal ν(CO) region, while the ¹H NMR spectrum shows the phenyl protons as a multiplet from δ6.34-7.94 and the characteristic resonances of the CH₂ group of the dppm ligand as two doublets of triplets at δ3.34 and 4.25 [J(HH) = 14Hz, J(PH) = 11Hz].

Likewise, the reaction of (1) with Au(C≡CPh){P(C₆H₄Me-p)₃} yielded orange crystals of Ru₃(μ₃-C≡CPh)(μ-dppm)(CO)₇-[Au{P(C₆H₄Me-p)₃}] (33). The spectroscopic data are similar to that obtained for (32); the ¹H NMR shows the phenyl protons from δ6.38-8.54, the methylene protons at δ3.34 and 4.25 [J(HH) = 14Hz, J(PH) = 11Hz] and the methyl groups as a singlet at δ2.39.

Structure of Ru₃(μ₃-C≡CPh)(μ-dppm)(CO)₇[Au{P(C₆H₄Me-p)₃}] (33)

An X-ray study of (33) (see Figure 5, also Table 5) shows a triangle of ruthenium atoms, with three carbonyl groups bonded to Ru(1) and two each to Ru(2) and Ru(3). The C₂Ph ligand is bonded in a σ-manner to Ru(3) [C(3)-Ru(3) 1.953(16) Å] and a π-manner to

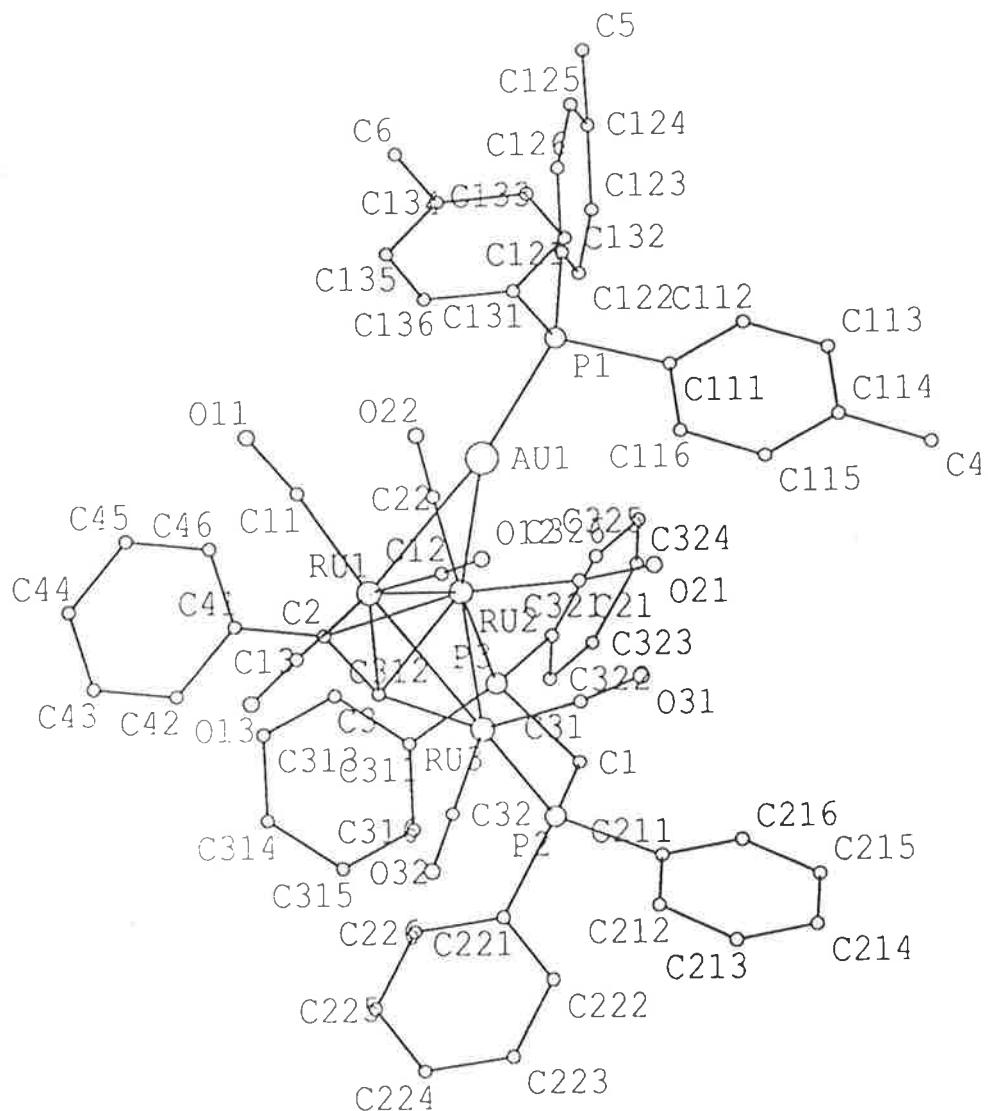


Figure 5: PLUTO plot of the molecular structure of
 $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPh})(\mu-\text{dppm})(\text{CO})_7\{\text{Au}[\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3]\}$ (33)
 (by E. Horn and E.R.T. Tieckink)

Table 5 : Selected interatomic parameters for (33)

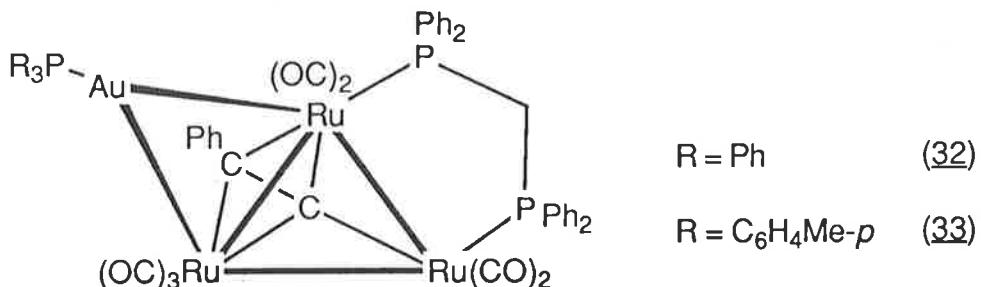
Bond distances (Å)

Ru(1) - Au(1)	2.773(2)	Ru(2) - Au(1)	2.743(1)
Ru(3) - Ru(1)	2.812(2)	Ru(2) - Ru(1)	2.826(2)
C(3) - Ru(1)	2.236(15)	C(2) - Ru(1)	2.227(17)
Ru(3) - Ru(2)	2.826(2)	P(3) - Ru(2)	2.326(5)
C(2) - Ru(2)	2.242(17)	C(3) - Ru(2)	2.199(15)
P(2) - Ru(3)	2.297(4)	C(3) - Ru(3)	1.953(16)
C(1) - P(3)	1.834(15)	C(1) - P(2)	1.859(16)
C(3) - C(2)	1.306(21)	C(41) - C(2)	1.472(19)

Bond angles (°)

Ru(2) - Au(1) - Ru(1)	61.6(1)	Ru(3) - Ru(1) - Au(1)	96.6(1)
Ru(2) - Ru(1) - Au(1)	58.7(1)	Ru(3) - Ru(1) - Ru(2)	60.2(1)
Ru(3) - Ru(2) - Au(1)	97.0(1)	Ru(1) - Ru(2) - Au(1)	59.7(1)
Ru(3) - Ru(2) - Ru(1)	59.7(1)	Ru(2) - C(2) - Ru(1)	78.4(6)
Ru(2) - C(3) - Ru(1)	79.2(5)	Ru(2) - Ru(3) - Ru(1)	60.2(1)
P(3) - C(1) - P(2)	114.0(9)	C(41) - C(2) - C(3)	141.1(15)
C(2) - C(3) - Ru(3)	151.71(13)		

Ru(1) [Ru(1)-C(2), C(3) 2.227(17), 2.236(15) \AA] and Ru(2) - C(2), C(3) 2.242(17), 2.199(15) \AA]. The dppm ligand bridges the Ru(2)-Ru(3) edge, while the Au{P(C₆H₄Me-*p*)₃} group bridges the Ru(1)-Ru(2) edge. This compound therefore is seen to have a structure analogous to that of (16) described above (apart from the obvious replacement of the Ph for a C₆F₅ on the C₂ ligand), with the Au{P(C₆H₄Me-*p*)₃} unit replacing the hydride, the two isolobal with each other (see Introduction of Chapter 2). Complexes (32) and (33) are related to those described in Chapter 2 [Ru₃(μ₃-C≡CPh)(CO)₉{Au(PR₃)}, R = Ph, C₆H₄Me-*p*)] by the addition of dppm and the loss of two carbonyl ligands.



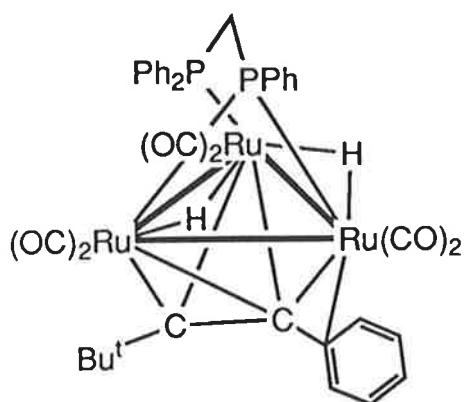
Reactions of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CR})(\mu\text{-dppm})(\text{CO})_7$, ($\text{R} = \text{Bu}^t, \text{Ph}$)

Pyrolysis of a toluene solution of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CBu}^t)$ -
 $(\mu\text{-dppm})(\text{CO})_7$, (17) for 60 hours afforded $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-Bu}^t\text{C}_2\text{Ph})$ -
 $\{\mu_3\text{-PhPCH}_2\text{PPh}_2\}(\text{CO})_6$ (34) in 41% yield identified by X-ray
 crystallography.

The structure of (34) is shown in Figure 6 (see also Table 6). It consists of a triangle of Ru atoms [2.721(2)-2.889(2) \AA] with six terminal carbonyl groups, two on each of the Ru atoms. A five-electron $\text{PhPCH}_2\text{PPh}_2$ ligand [derived from dppm via the loss of a phenyl fragment and previously found in $\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{PPhCH}_2\text{PPh}_2)_2(\text{CO})_6$ and $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{PPhCH}_2\text{PPh}_2)(\text{CO})_9$ ^{8, 13, 14, 16, 22-24} and its derivatives] sits on one face of the Ru_3 triangle so that P(2) is bonded to Ru(3) and P(1) bridges Ru(1)

and Ru(2). A $\text{Bu}^t\text{C}_2\text{Ph}$ ligand on the reverse face of the Ru_3 triangle interacts with all three Ru atoms. Coordination is completed by two hydrides which bridge Ru(1)-Ru(3) and Ru(2)-Ru(3).

The $\text{Bu}^t\text{C}_2\text{Ph}$ ligand, which is formed by the unusual migration of the phenyl group lost from dppm to the C_2Bu^t of (17), interacts with the metal triangle via two bonds to both Ru(3) and Ru(1) and one σ -bond to Ru(2). The bonds from C(1)-Ru(1) and from C(2)-Ru(3) are $2.037(7)$ and $2.155(6)\text{\AA}^\circ$, respectively, while the bonds from C(1)-Ru(3) and C(2)-Ru(3) are considerably longer [$2.416(7)$ and $2.416(6)\text{\AA}^\circ$]. These bond lengths indicate that the ligand lies in a very distorted manner across the Ru(1)-Ru(3) bond. The σ -bond from C(2)-Ru(2) is $2.254(6)\text{\AA}^\circ$. Additional electron density is donated to the cluster from the phenyl ring of the $\text{Bu}^t\text{C}_2\text{Ph}$ ligand, which interacts with Ru(2) through C(201) [$2.401(7)\text{\AA}^\circ$].



(34)

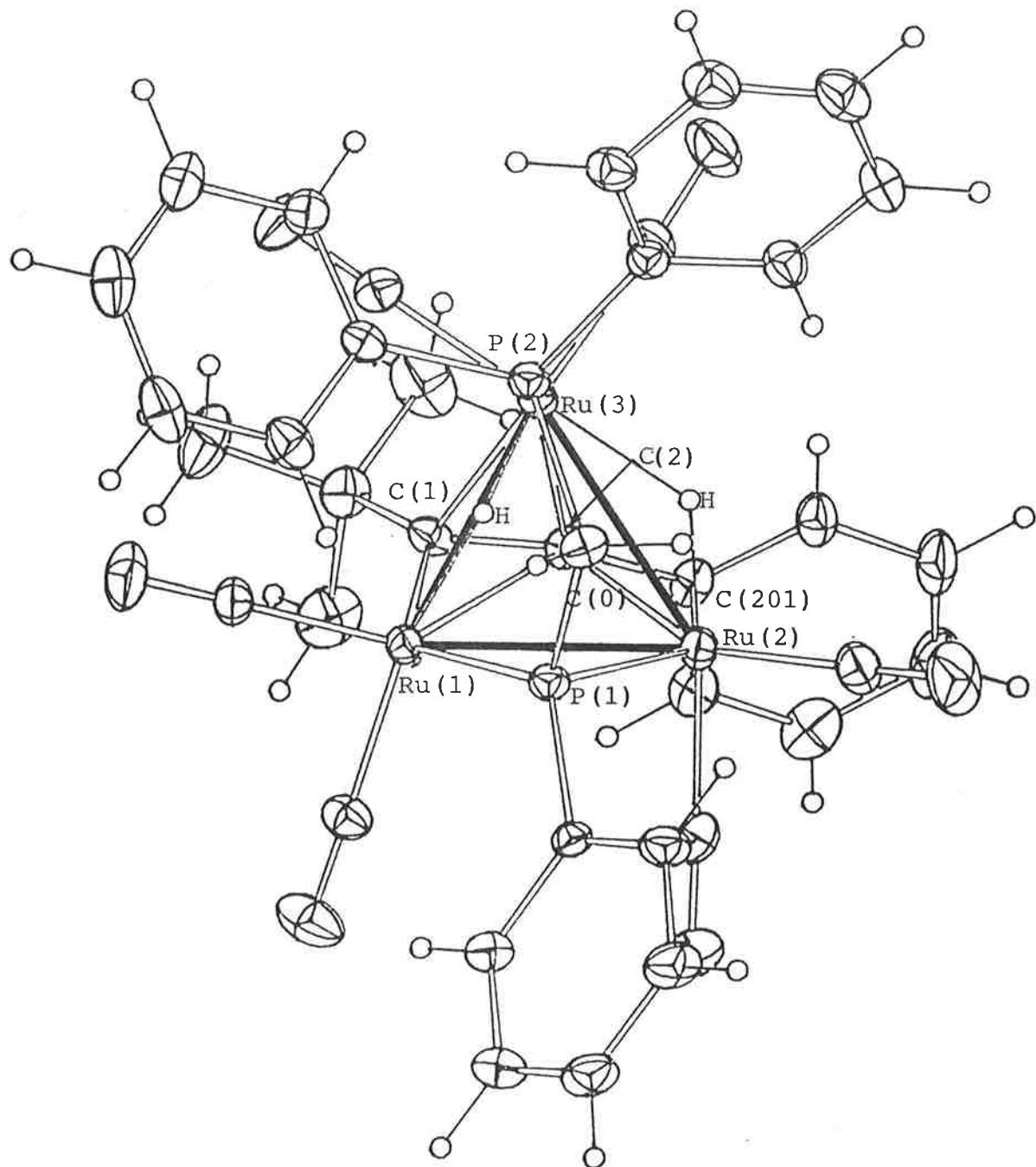


Figure 6: ORTEP plot of the molecular structure of
 $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-Bu}^t\text{C}_2\text{Ph})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_6$ (34)
(by B.W. Skelton and A.H. White)

Table 6: Selected interatomic parameters for (34)Bond distances (Å)

Ru(1) - Ru(2)	2.865(2)	Ru(3) - C(1)	2.416(7)
Ru(1) - Ru(3)	2.721(2)	Ru(3) - C(2)	2.155(6)
Ru(1) - P(1)	2.298(2)	Ru(1) - C(1)	2.037(7)
Ru(1) - C(2)	2.416(6)	P(1) - C(0)	1.843(7)
C(0) - P(2)	1.840(7)	Ru(2) - Ru(3)	2.889(2)
C(1) - C(2)	1.330(9)	Ru(2) - P(1)	2.317(2)
Ru(2) - C(2)	2.254(6)	Ru(2) - C(201)	2.401(7)
Ru(3) - P(2)	2.318(2)		

Bond angles (°)

Ru(2) - Ru(1) - Ru(3)	62.22(4)	Ru(1) - Ru(3) - Ru(2)	61.33(5)
Ru(1) - Ru(2) - Ru(3)	56.44(2)	Ru(1) - Ru(2) - C(201)	88.2(2)
Ru(3) - Ru(2) - C(201)	76.2(2)	C(101) - C(1) - C(2)	130.8(6)
C(1) - C(2) - C(201)	141.6(6)	Ru(1) - P(1) - C(0)	121.4(2)
Ru(2) - P(1) - C(0)	102.4(3)	P(1) - C(0) - P(2)	108.2(3)
Ru(3) - P(2) - C(0)	107.9(2)		

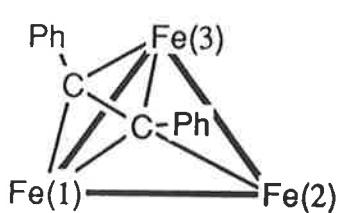
Table 7: Selected interatomic parameters for (37)Bond distances (Å)

I - Ru(1)	2.7646(9)	Ru(2) - C(2)	2.231(8)
I - Ru(2)	2.804(1)	Ru(2) - C(1)	2.367(7)
Ru(1) - Ru(2)	2.713(1)	P(1) - C	1.851(9)
Ru(1) - P(1)	2.276(2)	C - P(2)	1.858(6)
Ru(1) - C(2)	2.021(6)	C(2) - C(1)	1.251(9)
Ru(2) - P(2)	2.288(2)		

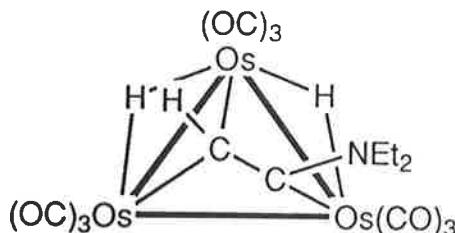
Bond angles (°)

Ru(1) - I - Ru(1)	58.31(3)	I - Ru(1) - Ru(2)	61.58(3)
Ru(1) - Ru(2) - P(2)	95.27(6)	Ru(2) - Ru(1) - P(1)	95.02(6)
Ru(1) - Ru(2) - C(2)	47.0(2)	Ru(2) - Ru(1) - C(2)	53.9(2)
Ru(1) - Ru(2) - C(1)	78.2(2)	I - Ru(2) - Ru(1)	60.11(3)
Ru(1) - C(2) - Ru(2)	79.1(2)	Ru(1) - C(2) - C(1)	153.9(6)
Ru(2) - C(2) - C(1)	80.3(5)	Ru(2) - C(1) - C(2)	68.3(4)
		C(2) - C(1) - C(101)	154.9(8)

Consideration of the $\text{Bu}^t\text{C}_2\text{Ph}$ ligand as a 5 electron donor gives an electron precise (48e) cluster. The bonding of this ligand in (34) may be regarded as intermediate between a μ_3 -(η^2 - \perp) interaction and the common μ_3 -(η^2 -||) interaction found in the molecular structure of (27). The former bonding type is far less common for alkynes than for acetylides; the only examples of trimetallic clusters possessing the μ_3 - \perp mode are the 46e clusters $\text{Fe}_3(\mu_3\text{-C}_2\text{Ph}_2)(\text{CO})_9$ (35), $\overset{4}{\text{Ru}}\overset{2}{\text{Fe}}_2(\mu_3\text{-C}_2\text{Ph}_2)-(\text{CO})_9$, $\overset{4}{\text{Os}}_3(\mu_3\text{-C}_2\text{Ph}_2)(\mu\text{-dppm})(\text{CO})_7$, $\overset{4}{\text{W}}_2\overset{4}{\text{Fe}}\{\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me}-p)_2\}-\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\overset{4}{\text{Fe}}\{\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me}-p)_2\}(\text{O})\text{Cp}_2(\text{CO})_5$. In (35), for example, the bonds to $\text{Fe}(1)$ and $\text{Fe}(3)$ are of similar length [2.098(15), 1.947(16), 2.048(16) and 1.945(15) $\overset{\circ}{\text{A}}$], i.e. the PhC_2Ph ligand is perpendicular to the $\text{Fe}(1)\text{-Fe}(3)$ bond.



(35)

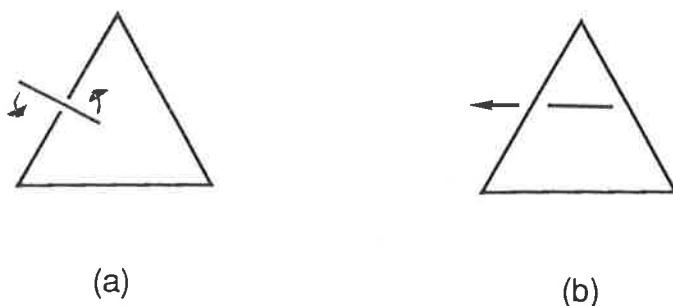


(36)

A recent paper, however, discusses the bonding in the 48e cluster $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-HC}_2\text{NET}_2)(\text{CO})_9$ (36) in which it is considered that the coordination of the HC_2NET_2 ligand is μ_3 -(\perp), although this differs significantly from the 46e clusters with the μ_3 -(\perp) alkyne mode in that the ligand is shifted away from the \perp edge.⁴⁷

It can be seen that the alkyne bonding in (34) could be thought of as distorted μ_3 -(η^2 - \perp) (twisting of the alkyne ligand) [Scheme 9(a)] or alternatively, slippage of a μ_3 -(η^2 -||) bonded

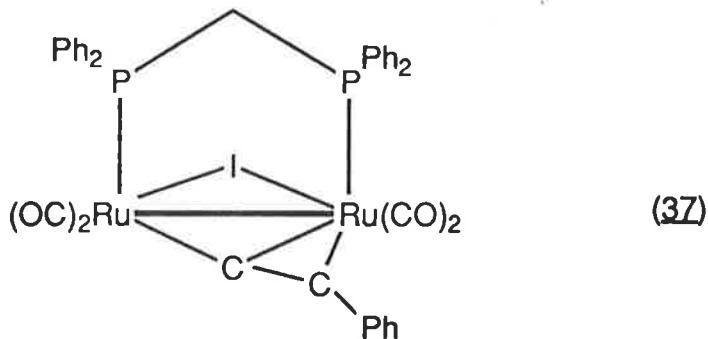
alkyne ligand would give a similar bonding pattern [Scheme 9(b)].



Scheme 9

The spectroscopic data obtained for (34) is in agreement with the crystallographically determined structure. The solution infrared spectrum shows only terminal $\nu(\text{CO})$ bands, while the FAB mass spectrum shows a peak at m/z 939 ($[M - \text{H}]^+$), which fragments via loss of H, the carbonyl ligands, $\text{PhPCH}_2\text{PPh}_2$ and PhC_2Bu^t . The base peak at m/z 531 is assigned to $[M - \text{H} - \text{C}_2\text{Ph} - \text{PhPCH}_2\text{PPh}_2]^+$. The ^1H NMR spectrum shows two signals in the hydride region. A multiplet (seven peaks) from δ -17.63-17.50 is assumed to be two doublets of doublets (with overlap of the two middle peaks) due to coupling of one of the metal-hydrides with the other, and with two inequivalent phosphorus nuclei. A seven peak signal around δ -17.01 is also thought to be two overlapping doublets of doublets [$J(\text{HH}) = 17\text{Hz}$, $J(\text{PH}) = 10\text{Hz}$, $J(\text{PH}) = 6\text{Hz}$]. The CH_2 group of the $\text{PPhCH}_2\text{PPh}_2$ ligand resonates as a multiplet from δ 4.06-4.53, while the phenyl protons are found from δ 7.16-7.77. A doublet at δ 5.69 [$J(\text{PH}) = 7\text{Hz}$] is tentatively assigned to a proton adjacent to the phenyl carbon bonded to Ru(2).

The dropwise addition of iodine to a solution of $\text{Ru}_3(\mu\text{-H})(\mu_5\text{-C}\equiv\text{CPh})(\text{CO})_7(\mu\text{-dppm})$ (15) in tetrahydrofuran resulted in a colour change of yellow through to orange. After stirring at room temperature for one hour, preparative TLC showed six bands and a brown baseline. A red band ($R_f = 0.44$) was crystallised from dichloromethane/methanol to give red crystals of $\text{Ru}_2(\mu\text{-I})(\mu\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_4$ (37) (34%) identified by the usual spectroscopic methods. The solution IR spectrum of (37) shows six bands in the terminal $\nu(\text{CO})$ region. The ^1H NMR spectrum shows the CH_2 protons as two doublets of triplets at δ 3.63 and 4.73 [$J(\text{HH}) = 13\text{Hz}$, $J(\text{PH}) = 12\text{Hz}$], while the phenyl hydrogens are found as a multiplet from δ 6.89-7.54. The FAB mass spectrum of (37) shows a peak at m/z 928 ($[\text{M}]^+$), then strong peaks corresponding to $[\text{M} - n\text{CO}]^+$ ($n = 1, 3, 4$) and $[\text{M} - n\text{CO} - \text{I}]^+$ ($n = 2-4$); $[\text{M} - 3\text{CO}]^+$ is the base peak.



Structure of $\text{Ru}_2(\mu\text{-I})(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})(\text{CO})_4$ (37)

An X-ray diffraction study of (37) was undertaken to determine the structure, which is shown in Figure 7 (see also Table 7). The Ru atoms are bonded together [Ru(1)-Ru(2) 2.713(1) \AA]. The dppm ligand bridges this bond, as does the $\mu\text{-I}$ ligand [Ru(1)-I 2.7646(9) \AA , Ru(2)-I 2.804(1) \AA]. Two terminal CO ligands are bonded to each Ru atom. Coordination is completed by the $\mu\text{-C}_2\text{Ph}$ ligand which is π -bonded to Ru(2) [Ru(2)-C(2) 2.231(8) \AA , Ru(2)-C(1) 2.367(7) \AA] and σ -bonded to Ru(1) [Ru(1)-C(2) 2.021(6) \AA]. This σ - π acetylidyne interaction is similar to that found in $\text{Ru}_2(\mu_2\text{-C}\equiv\text{CR})(\mu\text{-PPPh}_2)(\text{CO})_6$ ($\text{R} = \text{Ph}, \text{Bu}^\text{t}, \text{Pr}^\text{i}$) synthesised by Carty *et al.*^{4,8}

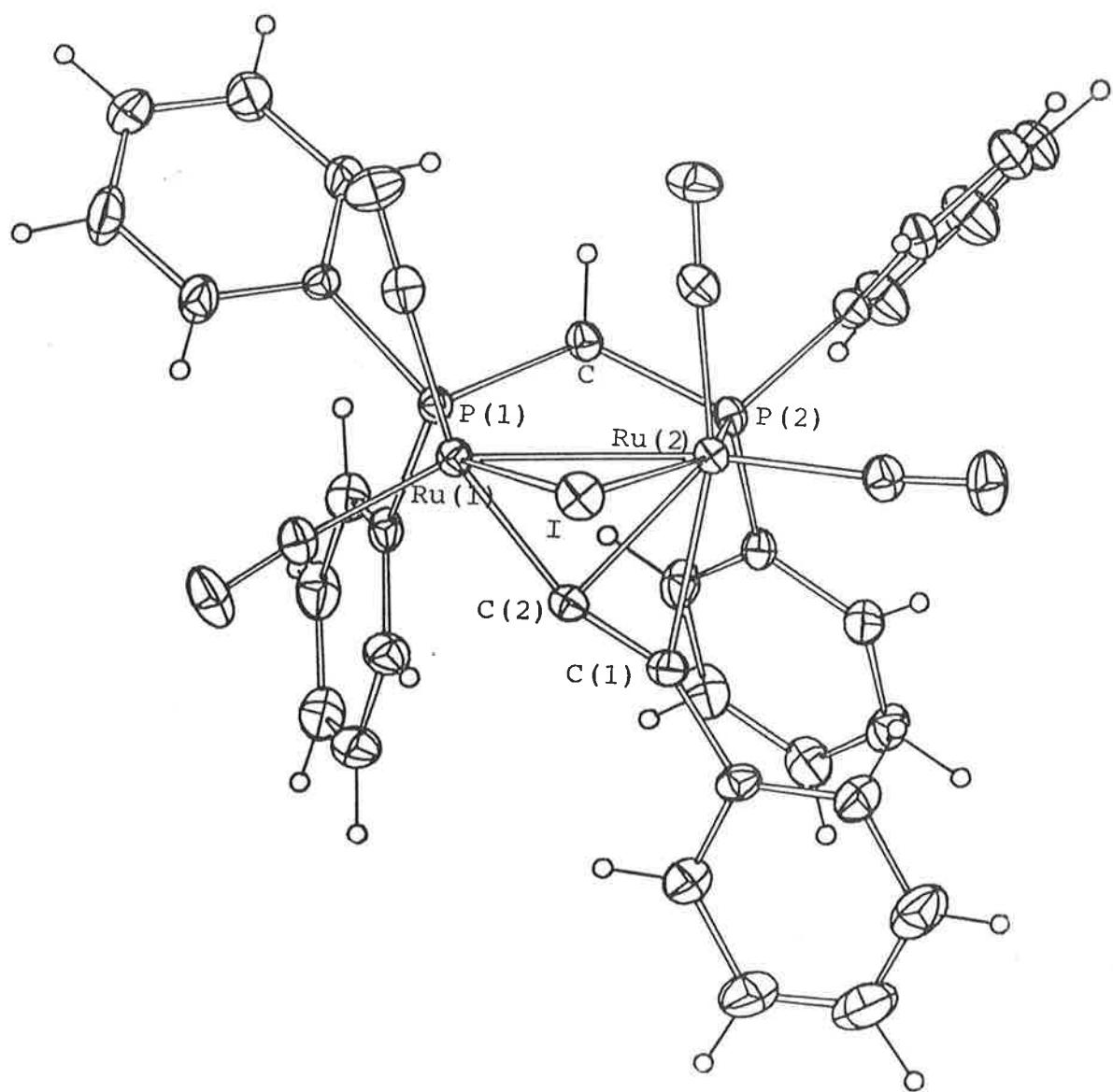


Figure 7: ORTEP plot of the molecular structure of
 $\text{Ru}_2(\mu\text{-I})(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})(\text{CO})_4$ (37)
(by B.W. Skelton and A.H. White)

The second half of this Chapter discusses the results of some reactions of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) with various small molecules.

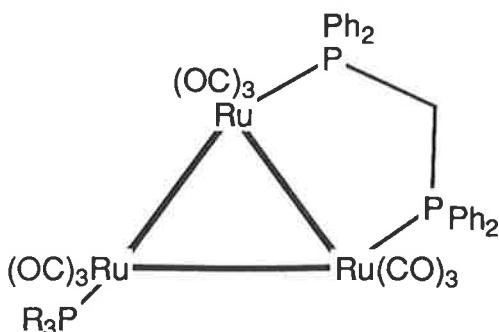
Preparation of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{PR}_3)$ R = OMe (38), Ph (12)

Reactions of (1) with PR_3 (R = OMe, Ph) in tetrahydrofuran were initiated by the dropwise addition of a sodium diphenylketethyl solution, which has been shown to electronically induce specific carbonyl substitution, in $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ and other clusters, using a wide range of ligands.^{9(a), 49}

The addition produced an immediate darkening of the solution and reactions proceeded readily to give good yields of $\text{Ru}_3(\mu\text{-dppm})-(\text{CO})_9(\text{PR}_3)$ [R = OMe (38) and Ph (12)].

The solution IR spectra of these red complexes show only terminal $\nu(\text{CO})$ bands. The ^1H NMR spectrum of (38) shows a doublet at $\delta 3.62$ [$J(\text{PH}) = 12\text{Hz}$] assigned to the OMe protons, a triplet at $\delta 4.22$ [$J(\text{PH}) = 10\text{Hz}$] assigned to the methylene protons and the aromatic protons as a multiplet from $\delta 7.31-7.42$. The ^1H NMR spectra of (12) shows a triplet at $\delta 4.16$ [$J(\text{PH}) = 10\text{Hz}$] (CH_2 protons) and the aromatic multiplet around $\delta 7.34$.

The substitution pattern is assumed to be the same as that found for the parent carbonyl, $\text{Ru}_3(\text{CO})_{12}$, in which tertiary phosphines and phosphites go into equatorial sites, as found in many such derivatives that have been studied; the PR_3 ligand^{9(a), 49} will be bonded to the uncomplexed metal atom.



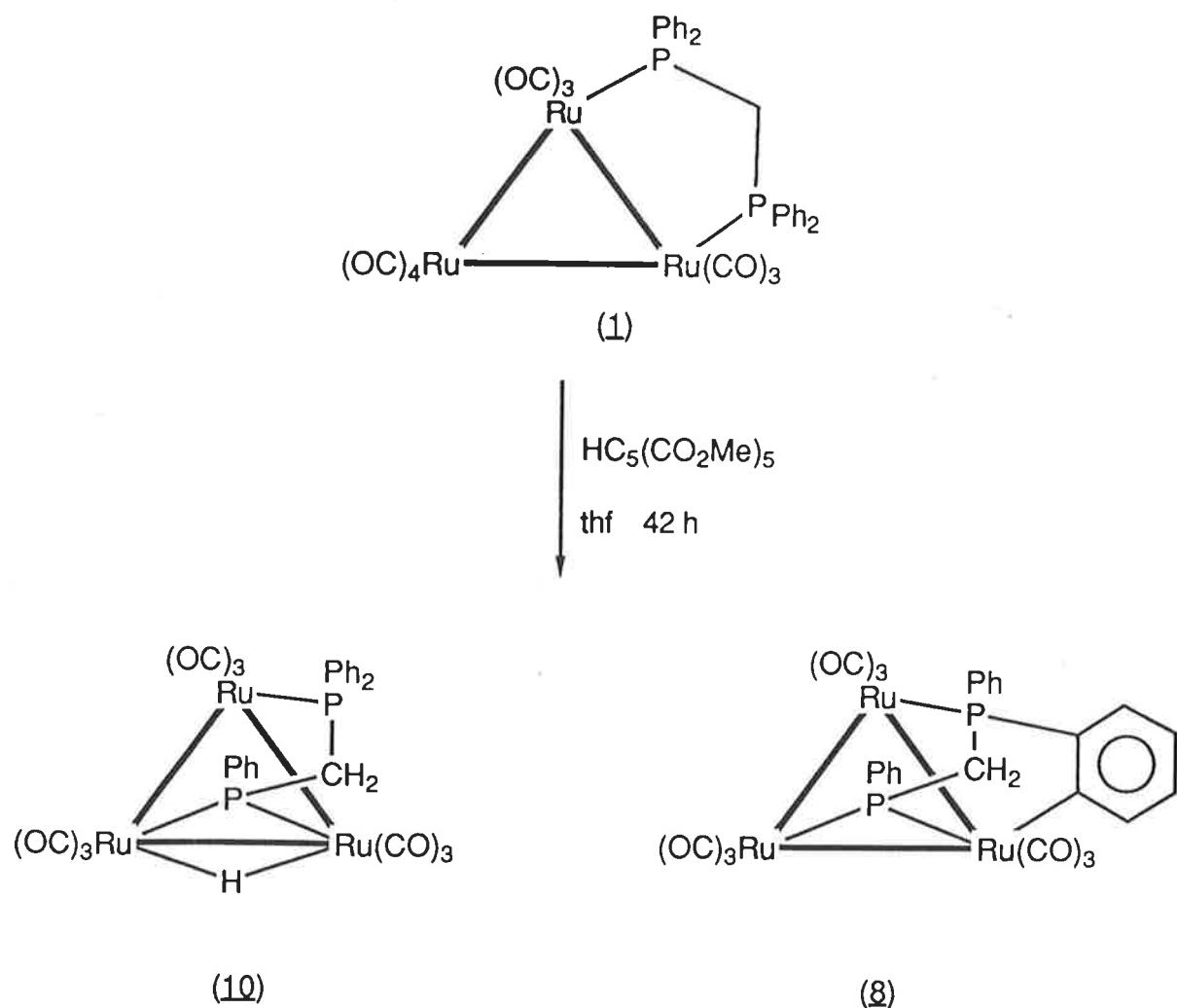
R = Ph (12)

R = OMe (38)

Complex (12) was synthesised by reacting $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with PPh_3 in refluxing tetrahydrofuran over two hours¹⁸, while reactions of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with (i) $\text{P}(\text{OMe})_3$ and (ii) PPh_3 in 1,2 dichloroethane at 50°C have been studied kinetically.^{20,21}

Reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with $\text{HC}_5(\text{CO}_2\text{Me})_5$

The reaction of (1) with $\text{HC}_5(\text{CO}_2\text{Me})_5$ ¹⁷ in refluxing tetrahydrofuran afforded, after preparative TLC, $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$, (8) in 40% yield and $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9$, (10) in 26% yield. Identification of these compounds was made on the basis of spectroscopic and TLC comparison with authentic samples. Isolation of (10) from this reaction suggests that protonation of (1), and elimination of $\text{C}_6\text{H}_5\text{C}_5(\text{CO}_2\text{Me})_5$, has occurred. This fragment, however, was not isolated.



Scheme 10

Complex (8) was also isolated by thermolysis of (1) in refluxing cyclohexane,^{16, 51} while (10) had previously been synthesised by the hydrogenation of (1) in refluxing cyclohexane,⁸ or (1) in toluene at 90°C,¹⁶ or alternatively, by sequentially treating (1) with K[BHBu₃^S] and H₃PO₄.²⁴

The molecular structure of complex (8), which is shown in Figure 8 (see also Table 8), consists of a triangular Ru core capped by a six-electron-donor orthometallated PPhCH₂PPh-(C₆H₄) ligand. The coordination of each ruthenium atom is completed by three CO groups. The Ru-Ru bonds range between 2.8250(7) and 2.8962(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 PPhCH₂PPh(C₆H₄) ligand resembles to some extent the dephenylated PPhCH₂PPh₂ ligands found earlier in Ru₃(μ-η³-C₃H₅)(μ₃-PPhCH₂PPh₂)(CO)₈,²³ Ru₃(μ-H)₂-²³(μ₃-PPhCH₂PPh₂)₂(CO)₆^{13, 14} and MRu₃(μ₃-PPhCH₂PPh₂)(CO)₉(PPh₃) (M = Cu, Ag and Au).²⁴ 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.

Preparation of Ru₃(μ-Cl)(μ-dppm)(CO)₈{Au(PPh₃)} (39)

The reaction of Ru₃(μ-dppm)(CO)₁₀ with AuCl(PPh₃) in refluxing tetrahydrofuran proceeded readily to afford Ru₃(μ-Cl)-(μ-dppm)(CO)₈{Au(PPh₃)} (39) in high yield. Identification was confirmed by microanalytical and analytical data. The solution infrared spectrum shows only terminal ν(CO) bands, while the ¹H NMR spectrum shows two doublets of triplets at δ4.26 and 4.66

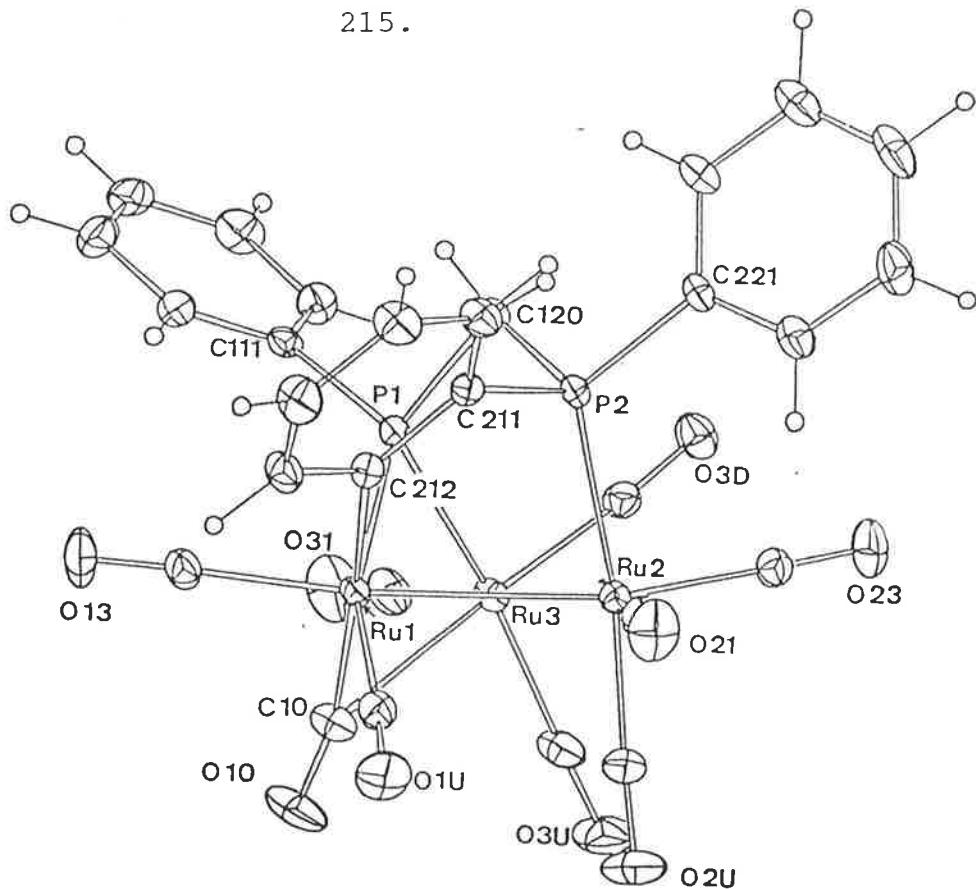


Figure 8 : ORTEP plot of the molecular structure of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (8) (by B.W. Skelton and A.H. White)

Table 8: Selected interatomic parameters for (8)

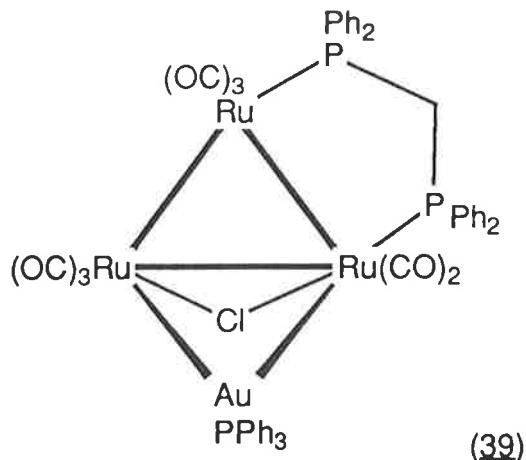
Bond distances (Å)

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)		

Bond 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)

[$J(HH) = 15\text{Hz}$, $J(PH) = 11\text{Hz}$, 10Hz] assigned to the two protons of the methylene group, and the phenyl protons as a multiplet from $\delta 7.06$ - 7.61 . The FAB mass spectrum shows a molecular ion and peaks corresponding to the sequential loss of the carbonyl ligands. A peak at m/z 1106 is assigned to $[M - 8\text{CO} - \text{Ph}]^+$. Peaks assigned to $[\text{Au}(\text{PPh}_3)_n]^+$ ($n = 1, 2$) are, as expected (see Chapter 2), dominant. This compound is assumed to have a structure analogous to that of $\text{Ru}_3(\mu\text{-Cl})(\text{CO})_{10}\{\text{Au}(\text{PPh}_3)\}$ prepared by Bonnet *et al* from $\text{Ru}_3(\text{CO})_{12}$ and $\text{AuCl}(\text{PPh}_3)$ in refluxing dichloromethane over 18 hours (55%), the structure of which shows a butterfly cluster with the gold atom occupying one of the wingtips. The Cl atom bridges the same bond as the $\text{Au}(\text{PPh}_3)$ unit.⁵²



Formation of Binuclear Ruthenium dppm compounds

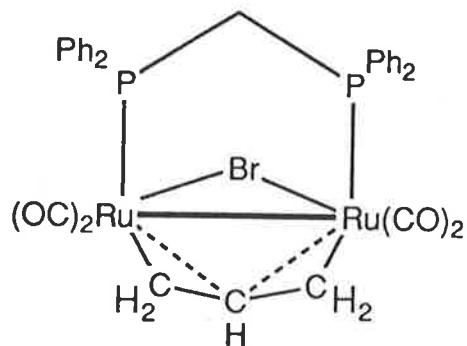
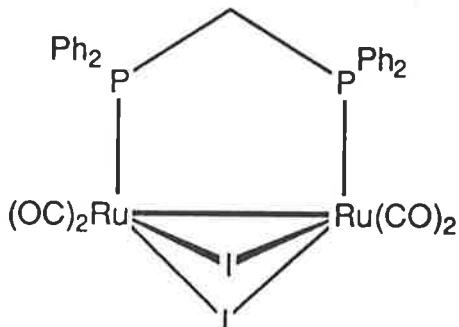
Ligands such as dppm have been used extensively because of their ability to form bridged binuclear complexes with various metals.⁵³

A number of binuclear ruthenium dppm complexes have recently been prepared;^{15, 54} in this study, the addition of small molecules to (1) has yielded further examples.

Formation of Binuclear Ruthenium dppm compounds

A reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and I_2 in refluxing tetrahydrofuran afforded $\text{Ru}_2(\mu\text{-I})_2(\mu\text{-dppm})(\text{CO})_4$ (6) in 46% yield after preparative TLC. This was identified by FAB mass spectroscopy and by comparing its solution IR spectrum with that reported in the literature. The FAB mass spectrum shows a molecular ion and peaks assigned to $[\text{M} - n\text{CO}]^+$ ($n = 1, 3$ and 4).

This compound has been isolated previously in 12% yield from the reaction of $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ (2) with I_2 in toluene.¹⁵ The molecular structure of (6) consists of two Ru centres which are bridged by the dppm ligand and two iodine atoms, with two carbonyl ligands on each Ru atom. One iodine atom is *cis* to both P atoms while the other is *trans*.¹⁵



(6)

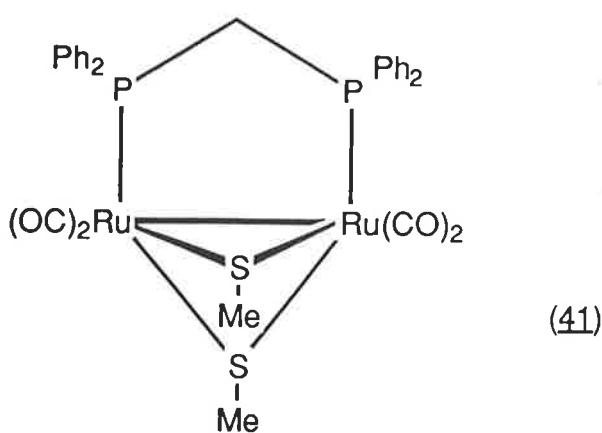
(40)

The reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and allyl bromide in refluxing tetrahydrofuran yielded, after preparative TLC and crystallisation from boiling methanol, orange-yellow crystals of $\text{Ru}_2(\mu\text{-Br})(\mu\text{-C}_3\text{H}_5)(\mu\text{-dppm})(\text{CO})_4$ (40) in 50% yield. The solution IR spectrum shows the usual four bands in the terminal $\nu(\text{CO})$ region, while the ^1H NMR spectrum shows the C_3H_5 and CH_2 protons as a multiplet from $\delta 1.33\text{-}4.96$ and the phenyl protons as a multiplet around $\delta 7.06$. The FAB mass spectrum shows a molecular ion and peaks assigned to $[\text{M} - \text{nCO}]^+$ ($n = 1\text{-}4$), $[\text{M} - \text{nCO} - \text{C}_3\text{H}_5]^+$ ($n = 2, 4$) and $[\text{M} - 4\text{CO} - \text{C}_3\text{H}_5 - \text{Br} + \text{H}]^+$.

The peak at m/z 708 ($[M - 4CO]^+$) is the base peak. A suggested structure for (40) is shown above. The C_3H_5 ligand and Br both donate 3e to give a 34e Ru_2 species.

The reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (1) with Me_2S_2 in tetrahydrofuran gave a mixture of products which were separated by preparative TLC. Two of these were crystallised and identified.

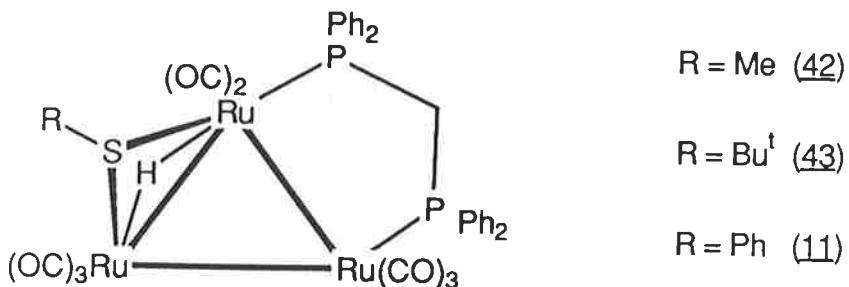
A yellow band ($R_f = 0.73$) was crystallised from dichloro-methane/methanol to give yellow crystals of $Ru_2(\mu\text{-SMe})_2(\mu\text{-dppm}) - (CO)_4$ (41) in 30% yield, identified using microanalytical and spectroscopic data. The solution IR spectrum shows the expected four bands in the $\nu(CO)$ region, while the FAB mass spectrum shows a molecular ion and peaks corresponding to the loss of the four carbonyl ligands. The 1H NMR spectrum shows a singlet peak at $\delta 1.94$ assigned to a methyl group in a *cis* position relative to the phosphorus atom, while the other methyl group which is in a *trans* position resonates at $\delta 2.54$ as a triplet [$J(PH) = 3.5\text{Hz}$]. The methylene protons are found at $\delta 3.46$ and 3.87 as two doublets of triplets [$J(HH) = 14\text{Hz}$, $J(PH) = 10\text{Hz}$] and the phenyl protons are found from $\delta 7.11-7.54$.



An orange band at $R_f = 0.66$ was crystallised from $CH_2Cl_2/MeOH$ to give red crystals of $Ru_3(\mu\text{-H})(\mu\text{-SMe})(\mu\text{-dppm})(CO)_8$ (42), in 8% yield, identified by the usual methods. The solution IR

spectrum of (42) shows seven $\nu(\text{CO})$ bands, while the ^1H NMR spectrum shows a doublet of doublets at δ -14.71 assigned to the metal hydride coupling with the phosphorus atoms two [$^2J(\text{PH}) = 35.4\text{Hz}$] and three bonds away [$^3J(\text{PH}) = 3.30\text{Hz}$]. The CH_2 protons are present as two multiplets (ABXY pattern) around δ 4.21 and 4.62, while the phenyl protons are found from δ 7.22-7.58. The FAB mass spectrum shows strong peaks at $[M]^+$ and $[M - n\text{CO}]^+$ ($n = 1-4$); $[M - \text{CO}]^+$ is the base peak.

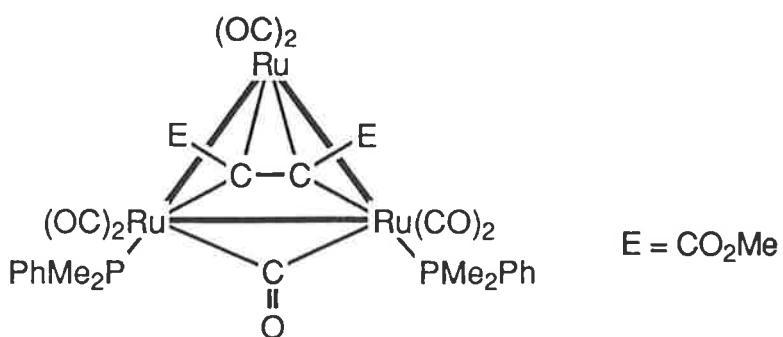
This compound is an analogue of $\text{Ru}_3(\mu-\text{H})(\mu-\text{SBu}^\ddagger)(\mu-\text{dppm})-(\text{CO})_8$ (43), prepared by the sodium diphenylketetyl-catalysed addition of dppm to $\text{Ru}_3(\mu-\text{H})(\mu_3-\text{SBu}^\ddagger)(\text{CO})_9$,⁵⁵ and $\text{Ru}_3(\mu-\text{H})-(\mu-\text{SPh})(\mu-\text{dppm})(\text{CO})_8$ (11) prepared by adding thiophenol to $\text{Ru}_3(\mu-\text{dppm})(\text{CO})_{10}$.¹⁷ Both (43)⁵⁶ and (11)¹⁷ have undergone X-ray structural determinations which show a triangle of Ru atoms. One edge of the triangle is bridged by the dppm ligand, while another edge is bridged by the SR group and the hydride, which is approximately *trans* to the phosphorus bonded to the same Ru atom.



Reaction of $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$ with $\text{C}_2(\text{CO}_2\text{Me})_2$

Preparative TLC of the resultant mixture from a short reflux of $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$ and $\text{C}_2(\text{CO}_2\text{Me})_2$ in tetrahydrofuran, showed a complex mixture of products as well as some unreacted $\text{Ru}_3(\text{CO})_{10}-(\text{PMe}_2\text{Ph})_2$. A red band ($R_F = 0.68$) was crystallised from dichloro-methane/methanol to give red needles of $\text{Ru}_3\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{CO})-$

$(CO)_7(PMe_2Ph)_2$ (44). The solution IR spectrum shows four terminal $\nu(CO)$ bands and a bridging $\nu(CO)$ band at 1802 cm^{-1} (with a shoulder at 1811 cm^{-1}). The 1H NMR spectrum of (44) shows the methyl protons as a doublet at $\delta 1.92$ [$J(PH) = 9.5\text{ Hz}$]. The OMe protons resonate as a singlet at $\delta 3.51$, while the phenyl protons are present as a multiplet around $\delta 7.43$. The FAB mass spectrum of (44) shows a peak assigned to $[M - H]^+$ which fragments via the stepwise loss of the carbonyl ligands ($[M - H - 4CO]^+$ is the base peak). Further fragmentation gives peaks assigned to $[M - nCO - OMe]^+$ ($n = 7, 8$). An X-ray diffraction study of (44) was performed to determine the mode of attachment of the $C_2(CO_2Me)_2$ ligand to the cluster. A molecule of (44) is shown in Figure 9 (see also Table 9). The three Ru atoms form a triangle with the Ru(1)-Ru(3) and Ru(2)-Ru(3) edges being of similar length [2.717(1) and $2.7204(9)\text{\AA}$, respectively] while Ru(1)-Ru(2) is longer at $2.817(1)\text{\AA}$. Two terminal CO ligands are bonded to Ru(1) and Ru(2) while three are bonded to Ru(3); the remaining μ -CO ligand bridges Ru(1)-Ru(2) [Ru(1)-C(12) $2.149(6)\text{\AA}$, Ru(2)-C(12) $2.110(6)\text{\AA}$]. One PMe₂Ph ligand is attached to both Ru(1) and Ru(2). The Ru₃ triangle is capped by the $C_2(CO_2Me)_2$ ligand which interacts in



(44)

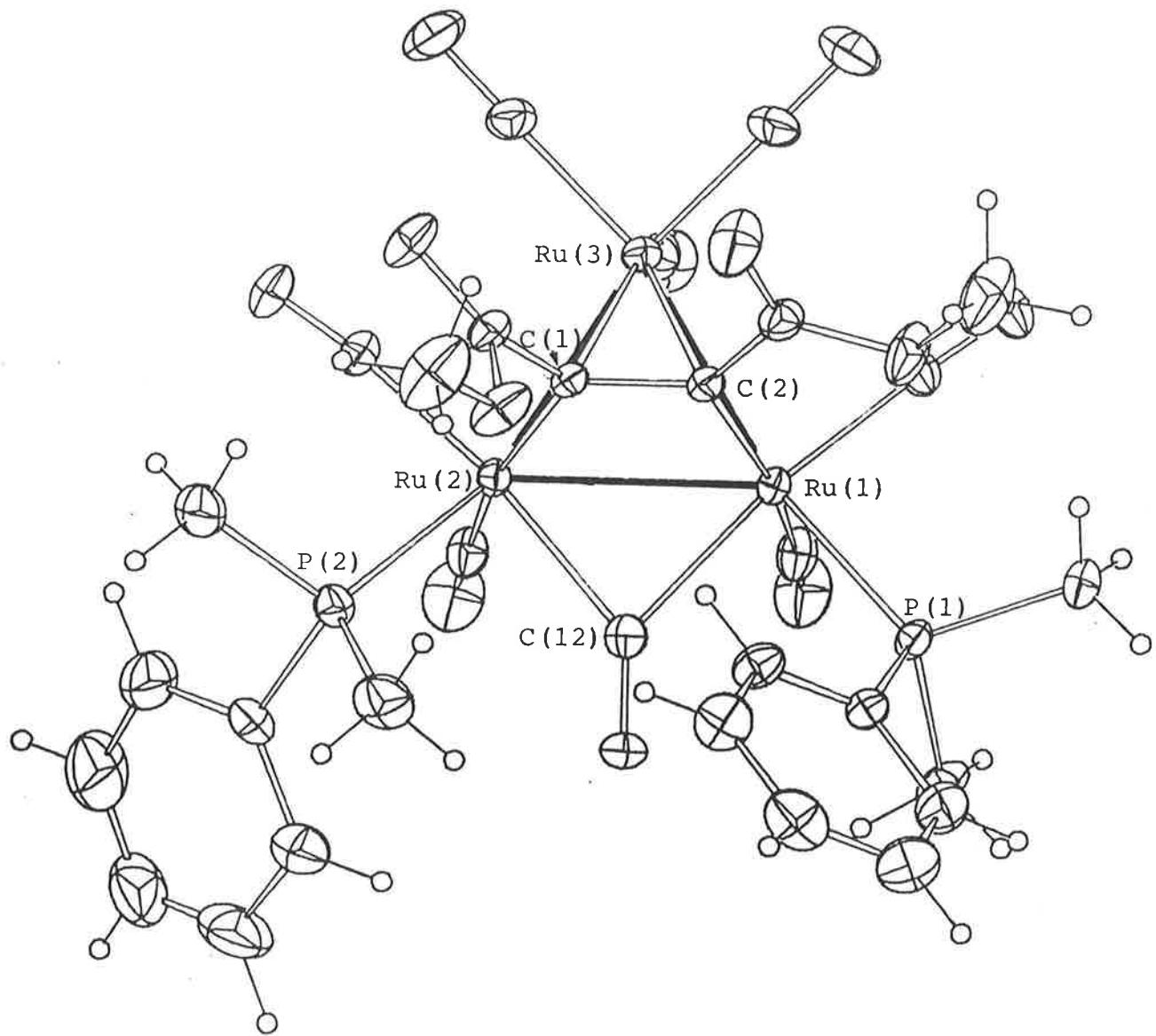


Figure 9: ORTEP plot of the molecular structure of
 $\text{Ru}_3\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{CO})(\text{CO})_7(\text{PMe}_2\text{Ph})_2$ (44)
 (by B.W. Skelton and A.H. White)

Table 9: Selected interatomic parameters for (44)

Bond distances (Å)

Ru(1) - Ru(2)	2.8174(12)	Ru(2) - Ru(3)	2.7204(9)
Ru(1) - Ru(3)	2.7174(14)	Ru(2) - P(2)	2.3455(18)
Ru(1) - P(1)	2.3476(18)	Ru(2) - C(12)	2.1099(64)
Ru(1) - C(12)	2.1494(62)	Ru(2) - C(1)	2.0865(53)
Ru(1) - C(2)	2.0854(55)	Ru(3) - C(1)	2.2251(53)
C(1) - C(2)	1.3788(74)	Ru(3) - C(2)	2.2352(57)

Bond angles (°)

Ru(2) - Ru(1) - Ru(3)	58.85(3)	C(1) - Ru(3) - C(2)	36.01(19)
Ru(1) - Ru(2) - Ru(3)	58.74(2)	Ru(2) - C(1) - Ru(3)	78.17(18)
Ru(1) - Ru(3) - Ru(2)	62.41(2)	Ru(1) - C(2) - Ru(3)	77.86(20)
Ru(2) - C(1) - C(2)	110.53(38)	Ru(1) - C(12) - Ru(2)	82.82(22)
Ru(1) - C(2) - C(1)	109.81(39)		

a σ -fashion with Ru(1) and Ru(2) [Ru(1)-C(2) 2.0854(55) and Ru(2)-C(1) 2.0865(53) \AA] and in a π -fashion with Ru(3) [Ru(3)-C(1) 2.2251(53) \AA and Ru(3)-C(2) 2.2352(57) \AA]. It is, therefore, acting as a 4e donor in the same bonding mode [$2\sigma + \pi$ or $\mu_3-\eta^2(||)$] as found in the molecular structure of (27) and postulated for (21).

A bright yellow product isolated from a yellow band ($R_f = 0.26$) was tentatively identified as $\text{Ru}_3\{\text{C}_2(\text{CO}_2\text{Me})_2\}_3-(\text{CO})_6(\text{PMe}_2\text{Ph})_2$ (45) on the basis of FAB mass spectral evidence, which shows a peak at m/z 1175 ($[M]^+$), which fragments via the competitive loss of the carbonyl ligands, $\text{C}_2(\text{CO}_2\text{Me})_2$ and OMe groups. The ^1H NMR spectrum shows a complex set of resonances from δ 1.85-2.10 (assigned to the Me protons) and from δ 3.40-3.73 (OMe protons), while the phenyl protons are found from δ 7.26-7.78.

Reactions of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_9$ (8)

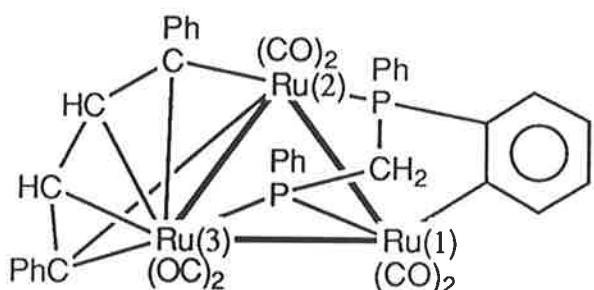
The reaction of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\text{(CO)}_9$ (8) with excess $\text{HC}\equiv\text{CPh}$ in refluxing tetrahydrofuran over nine hours yielded $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\mu-\text{C}_4\text{H}_2\text{Ph}_2)(\text{CO})_6$ (46) (31%) identified by X-ray crystallography. The structural determination however, although sufficient to obtain a basic molecular structure, was not of sufficient quality for a detailed analysis. The structure obtained shows a triangle of Ru atoms, with two carbonyl ligands attached to each Ru. The Ru_3 core is capped by a six-electron donor orthometallated $\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)$ ligand as observed in the precursor (8), while a $\mu-\text{C}_4\text{H}_2\text{Ph}_2$ ligand (with terminal phenyl groups), formed by the dimerisation of $\text{HC}\equiv\text{CPh}$, bridges the Ru(2)-Ru(3) bond. This ligand is tilted away from Ru(2) so that only the two terminal carbons interact with Ru(2); all four carbons interact with Ru(3). This ligand acts as a 6e donor

therefore giving an electron precise (48e) cluster.

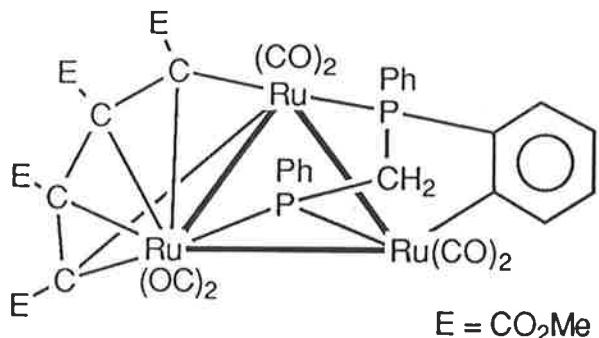
Spectroscopic data obtained for (46) supports the crystallographically determined structure. The solution infrared spectrum shows six terminal $\nu(\text{CO})$ bands while the FAB mass spectrum shows a molecular ion at m/z 983 which fragments via sequential loss of the six carbonyl ligands; $[\text{M} - 4\text{CO}]^+$ is the base peak. A peak at m/z 735 is assigned to $[\text{M} - 6\text{CO} - \text{C}_6\text{H}_6 - 2\text{H}]^+$. The ^1H NMR spectrum of (46) shows the CH_2 protons as a multiplet (ABXY pattern) centred on δ 2.97, while a complex set of resonances found from δ 5.88-7.70 are assigned to the CH_2 , phenyl and C_6H_4 protons.

The reaction of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (8) with $\text{C}_2(\text{CO}_2\text{Me})_2$ in tetrahydrofuran yielded, after workup by radial chromatography, dark green crystals of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}-\{\mu-\text{C}_4(\text{CO}_2\text{Me})_4\}(\text{CO})_6$ (47) (21%) identified from microanalytical and spectroscopic data. The solution IR spectrum shows six terminal $\nu(\text{CO})$ bands, while the Nujol spectrum also shows several strong $\nu(\text{C=O})$ and $\nu(\text{C-O})$ bands between $1700-1730\text{ cm}^{-1}$ and $1170-1240\text{ cm}^{-1}$, respectively. The ^1H NMR spectrum shows a multiplet from δ 2.49-3.06 (ABXY pattern) assigned to the CH_2 group, four singlets (δ 3.45, 3.63, 3.88 and 3.91) assigned to the OMe protons and a multiplet from δ 6.29-8.04 assigned to the phenyl and C_6H_4 protons. The FAB mass spectrum shows a molecular ion, and peaks corresponding to $[\text{M} - n\text{CO}]^+$ ($n = 1-6$) and $[\text{M} - n\text{CO} - \text{C}_2(\text{CO}_2\text{Me})_2]^+$ ($n = 0-2$). It would seem likely that the mode of bonding in this compound would be similar to that observed in $\text{Ru}_3\{\mu_4-\text{C}_4(\text{CO}_2\text{Me})_4\}(\mu-\text{dppm})(\text{CO})_6$ (22) which was prepared from the reaction of $\text{Ru}_4(\mu-\text{dppm})(\text{CO})_{10}$ and $\text{C}_2(\text{CO}_2\text{Me})_2$. However, whereas dppm is a 4e donor the $\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)$ ligand is a 6e donor so the $\text{C}_4(\text{CO}_2\text{Me})_4$ ligand needs to donate only 6e to give an electron precise (48e) Ru_3

cluster. It is therefore likely that the ester CO - Ru interaction found in the molecular structure of (22) is not present in the structure of (47). This is supported by the lack of an OMe resonance significantly further upfield than the other three OMe resonances, as observed in the ^1H NMR spectrum of (22) (δ 2.97, 3.78, 3.79 and 3.80). This ligand is therefore believed to be bonded to the cluster in a similar way to that observed in the molecular structure of (46).



(46)



(47)

CONCLUSION

Reactions of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with terminal acetylenes afforded high yields of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CR})(\mu\text{-dppm})(\text{CO})_7$, ($\text{R} = \text{Ph}, \text{C}_6\text{F}_5, \text{Bu}^t$ and SiMe_3). Pyrolysis of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CBu}^t)(\mu\text{-dppm})(\text{CO})_7$, yielded $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-Bu}^t\text{C}_2\text{Ph})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_6$, in which an unusual phenyl transfer from the dppm ligand to the acetylide has occurred to give a PhC_2Bu^t ligand bonded to the cluster in a manner intermediate between $\mu_3\text{-}\eta^2\text{-}(\parallel)$ and $\mu_3\text{-}\eta^2\text{-}(\perp)$. The reaction of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPH})(\mu\text{-dppm})(\text{CO})_7$ with I_2 gave $\text{Ru}_2(\mu\text{-I})(\mu\text{-C}\equiv\text{CPH})(\mu\text{-dppm})(\text{CO})_4$.

The reactivity of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with $\text{C}_2(\text{CO}_2\text{Me})_2$ was also studied. Good to high yields of clusters containing one or two $\text{C}_2(\text{CO}_2\text{Me})_2$ groups were obtained depending on the conditions used. The reaction of $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$ with $\text{C}_2(\text{CO}_2\text{Me})_2$ gave a large number of products, suggesting that the dppm ligand may lead to some degree of specificity of reaction. Under more forceful conditions two tetranuclear clusters were obtained from the reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with $\text{C}_2(\text{CO}_2\text{Me})_2$; $\text{Ru}_4\{\mu_4\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_{10}$ and $\text{Ru}_4(\mu_3\text{-H})\{\mu_4\text{-C}_2(\text{CO}_2\text{Me})_2\}\{\mu\text{-PPh}(\text{C}_6\text{H}_4)\text{CH}_2\text{PPh}_2\}(\text{CO})_9$. In both clusters the bonding of the alkyne is $\mu_4\text{-}\eta^2(\sigma\text{-}\pi\text{-}\sigma\text{-}\pi)$.

The reactivity of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ was investigated with other small molecules. Under conditions in which cluster fragmentation occurred, the bridging dppm ligand proved to be a stabilising force in the isolation of a number of Ru_2 compounds such as $\text{Ru}_2(\mu\text{-C}_3\text{H}_5)(\mu\text{-Br})(\mu\text{-dppm})(\text{CO})_4$ and $\text{Ru}_2(\mu\text{-SMe})_2-(\mu\text{-dppm})(\text{CO})_4$.

EXPERIMENTAL

General experimental conditions are as outlined in Chapter 1.

Starting Materials

The complexes $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$, $\text{Ru}_3(\mu\text{-dpam})(\text{CO})_{10}$,^{9(a)} $\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$,^{5b} $\text{Au}(\text{C}\equiv\text{CPh})\{\text{P}(\text{C}_6\text{H}_4\text{Me}-p)_3\}$,^{5b} $\text{HC}_5(\text{CO}_2\text{Me})_5$,^{5c} $\text{AuCl}(\text{PPh}_3)$,^{5d} $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2$,^{9(a)} $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$,^{5e} and sodium diphenylketyl solutions were prepared by literature methods.

Reactions of $\text{Ru}_3(\mu\text{-Ph}_2\text{ECH}_2\text{EPh}_2)(\text{CO})_{10}$ [E = P (1), As (13)] with $\text{HC}\equiv\text{CR}$ (R = Ph, C_6F_5 , Bu^t , SiMe_3)

(a) Preparation of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (15)

To a stirred solution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (350 mg, 0.362 mmol) in thf (25 ml) was added $\text{HC}\equiv\text{CPh}$ (60 mg, 0.59 mmol). The reaction mixture was refluxed for 1 h 40 min at which time the reaction was adjudged complete [the disappearance of the $\nu(\text{CO})$ band of (1) at 2079 cm^{-1} was monitored]. After evaporation to dryness (rotary evaporator), crystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yielded $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (15) as a yellow powder (329 mg, 92%), m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 48.67; H, 2.87; $\text{C}_{40}\text{H}_{28}\text{O}_7\text{P}_2\text{Ru}_3$ requires C, 48.74; H, 2.86%). Infrared (cyclohexane): $\nu(\text{CO})$ 2065s, 2011vs, 2003vs, 1994(sh), 1985m, 1958m, 1940w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ -19.26 [d, $J(\text{PH})$ = 34Hz, 1H, Ru-H]^{*}, 3.33 [dt, $J(\text{HH})$ = 14Hz, $J(\text{PH})$ = 12Hz, 1H, CH_2], 4.31 [dt, $J(\text{HH})$ = 14Hz, $J(\text{PH})$ = 11Hz, 1H, CH_2], 6.42-7.89 (m, 25H, Ph). FAB MS: 987, $[\text{M}]^+$, 100; 959, $[\text{M} - \text{CO}]^+$, 21; 931, $[\text{M} - 2\text{CO}]^+$, 7; 903, $[\text{M} - 3\text{CO}]^+$, 18;

*Note: A small signal is present at δ -19.25 at 295K.

875, $[M - 4CO]^+$, 77; 847, $[M - 5CO]^+$, 62; 819, $[M - 6CO]^+$, 50; 791, $[M - 7CO]^+$, 94; 769, $[M - 5CO - Ph - H]^+$, 39; 741, $[M - 6CO - Ph - H]^+$, 16; 713, $[M - 7CO - Ph - H]^+$, 64.

(b) Preparation of Ru₃(μ-H)(μ₃-C≡C₆F₅)(μ-dppm)(CO)₇ (16)

Following the method in (a) above, a stirred solution of Ru₃(μ-dppm)(CO)₁₀ (249 mg, 0.257 mmol) and HC≡CC₆F₅ (75 mg, 0.39 mmol) in THF (25 ml) was refluxed for 1.5 h. After evaporation to dryness (rotary evaporator), crystallisation from CH₂Cl₂/MeOH gave orange crystals of Ru₃(μ-H)(μ₃-C≡CC₆F₅)(μ-dppm)(CO)₇ (16) (214 mg, 77%), m.p. >200°C (dec.). (Found: C, 44.65; H, 2.18; C₄₀H₂₃F₅O₇P₂Ru₃ requires C, 44.66; H, 2.16%). Infrared (cyclohexane): ν(CO) 2070s, 2018(sh), 2013vs, 2002m, 1992m, 1965m, 1947w cm⁻¹. ¹H NMR: δ(CDCl₃) -19.41 [d, J(PH) = 33Hz, 1H, Ru-H], 3.21 [dt, J(HH) = 14Hz, J(PH) = 12Hz, 1H, CH₂], 4.19 [dt, J(HH) = 14Hz, J(PH) = 11Hz, 1H, CH₂], 6.29-8.03 (m, 20H, Ph). FAB MS: 1077, $[M]^+$, 46; 1049, $[M - CO]^+$, 20; 1021, $[M - 2CO]^+$, 4; 993, $[M - 3CO]^+$, 52; 965, $[M - 4CO]^+$, 26; 937, $[M - 5CO]^+$, 39, 909, $[M - 6CO]^+$, 70; 881, $[M - 7CO]^+$, 100; 859, $[M - 5CO - Ph - H]^+$, 41; 831, $[M - 6CO - Ph - H]^+$, 15; 803, $[M - 7CO - Ph - H]^+$, 39.

(c) Preparation of Ru₃(μ-H)(μ₃-C≡CBu^t)(μ-dppm)(CO)₇ (17)

Following the method in (a) above, a stirred solution of Ru₃(μ-dppm)(CO)₁₀ (500 mg, 0.517 mmol) and HC≡CBu^t (60 mg, 0.73 mmol) in THF (20 ml) was refluxed for 9 h. After evaporation to dryness (rotary evaporator), crystallisation from CH₂Cl₂/MeOH afforded orange crystals of Ru₃(μ-H)(μ₃-C≡CBu^t)(μ-dppm)(CO)₇ · 0.5CH₂Cl₂ (17) (402 mg, 81%) m.p. 133-136°C. (Found: C, 45.68; H, 3.32; C₃₈H₃₂O₇P₂Ru₃ · 0.5CH₂Cl₂ requires C, 45.86; H, 3.30%). Infrared (cyclohexane): ν(CO)

2061s, 2008s, 1996vs, 1980m, 1967vw, 1955m, 1937w cm^{-1} .

^1H NMR: $\delta(\text{CDCl}_3)$ -19.86 [t, $J(\text{PH}) = 17\text{Hz}$, 1H, Ru-H], 0.95 (s, 9H, Me), 3.42 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 12\text{Hz}$, 1H, CH_2], 4.19 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 5.30 (s, 1H, 0.5 CH_2Cl_2), 7.35-7.57 (m, 20H, Ph). FAB MS: 967, $[M]^+$, 13; 939, $[M - \text{CO}]^+$, 11; 911, $[M - 2\text{CO}]^+$, 7; 883, $[M - 3\text{CO}]^+$, 61; 855, $[M - 4\text{CO}]^+$, 34; 827, $[M - 5\text{CO}]^+$, 72; 799, $[M - 6\text{CO}]^+$, 72; 777, $[M - 4\text{CO} - \text{Ph} - \text{H}]^+$, 100; 771, $[M - 7\text{CO}]^+$, 84; 749, $[M - 5\text{CO} - \text{Ph} - \text{H}]^+$, 80.

(d) Preparation of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CSiMe}_3)(\mu\text{-dppm})(\text{CO})_7$ (18)

Following the method in (a) above, a mixture of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (200 mg, 0.207 mmol) and $\text{HC}\equiv\text{CSiMe}_3$ (22 mg, 0.22 mmol) in thf (20 ml) was refluxed for 9 h. After evaporation to dryness (rotary evaporator), crystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave orange crystals of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CSiMe}_3) - (\mu\text{-dppm})(\text{CO})_7 \cdot 0.5\text{CH}_2\text{Cl}_2$ (18) (151 mg, 74%), m.p. 149-152°C. (Found: C, 44.05; H, 3.33; $\text{C}_{37}\text{H}_{32}\text{O}_7\text{P}_2\text{Ru}_3\text{Si} \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 43.97; H, 3.25%). Infrared (cyclohexane): $\nu(\text{CO})$ 2062s, 2008s, 1998vs, 1991(sh), 1981m, 1956m, 1938w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ -19.99 [d, $J(\text{PH}) = 34\text{Hz}$, 1H, Ru-H], 0.05 (s, 9H, Me), 3.38 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 12\text{Hz}$, 1H, CH_2], 4.29 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 5.30 (s, 1H, 0.5 CH_2Cl_2), 7.39 (m, 20H, Ph). FAB MS: 983, $[M]^+$, 22; 955, $[M - \text{CO}]^+$, 22; 899, $[M - 3\text{CO}]^+$, 51; 871, $[M - 4\text{CO}]^+$, 24; 843, $[M - 5\text{CO}]^+$, 32; 815, $[M - 6\text{CO}]^+$, 44; 793, $[M - 4\text{CO} - \text{Ph} - \text{H}]^+$, 72; 787, $[M - 7\text{CO}]^+$, 61; 765, $[M - 5\text{CO} - \text{Ph} - \text{H}]^+$, 100.

(e) Preparation of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})$ - $(\text{CO})_6(\text{PPh}_3)$. (19)

A mixture of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (151 mg, 0.156 mmol), PPh_3 (45 mg, 0.17 mmol) and $\text{HC}\equiv\text{CPh}$ (20 mg, 0.20 mmol) in thf (20 ml) was refluxed for 18 h. After evaporation to dryness, crystallisation from CH_2Cl_2 (6 ml)/MeOH (10 ml) yielded $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_6(\text{PPh}_3)\cdot0.5\text{CH}_2\text{Cl}_2$ (19) as a yellow powder. (130 mg, 68%) m.p. $>250^\circ\text{C}$. (Found: C, 54.92; H, 3.73; $\text{C}_{57}\text{H}_{43}\text{O}_6\text{P}_3\text{Ru}_3\cdot0.5\text{CH}_2\text{Cl}_2$ requires: C, 54.70; H, 3.51%). Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2072m, 2043vw, 2016vs, 1986s, 1968m, 1953m, 1915w(br) cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.32 (m, 1H, CH_2), 4.31 (m, 1H, CH_2), 5.30 (s, 1H, 0.5 CH_2Cl_2), 6.31-7.74 (m, 40H, Ph). FAB MS: 1221, $[M]^+$, 100; 1137, $[M - 3\text{CO}]^+$, 21; 1109, $[M - 4\text{CO}]^+$, 32; 1081, $[M - 5\text{CO}]^+$, 26; 1053, $[M - 6\text{CO}]^+$, 26; 1031, $[M - 4\text{CO} - \text{Ph} - \text{H}]^+$, 17; 1003, $[M - 5\text{CO} - \text{Ph} - \text{H}]^+$, 23; 975, $[M - 6\text{CO} - \text{Ph} - \text{H}]^+$, 38. No hydride signal was detected in ^1H NMR spectrum.

(f) Preparation of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dpam})(\text{CO})_7$ (20)

To a stirred solution of $\text{Ru}_3(\mu\text{-dpam})(\text{CO})_{10}$ (78 mg, 0.074 mmol) in thf (15 ml) was added $\text{HC}\equiv\text{CPh}$ (11 mg, 0.11 mmol). After heating at reflux for 1.5 h the reaction mixture had changed to orange-yellow and was adjudged to be complete (spot TLC). After evaporation to dryness (rotary evaporator), crystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yielded $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dpam})(\text{CO})_7$ (20) as an orange-yellow powder (60 mg, 76%), m.p. $>190^\circ\text{C}$ (dec.), melts 208-210°C. (Found: C, 43.86; H, 2.65; $\text{C}_{40}\text{H}_{28}\text{As}_2\text{O}_7\text{Ru}_3$ requires C, 44.75; H, 2.63%). Infrared (cyclohexane): $\nu(\text{CO})$ 2068m, 2062s, 2012vs, 2005(sh), 1992s, 1983m, 1958m, 1937w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ -20.01, -19.89 (2 x s, 1H, Ru-H) (isomers 1 and 2), 2.01 [d, $\jmath(\text{HH}) = 11\text{Hz}$, 0.5H, CH_2] (isomer 1), 2.50 [d, $\jmath(\text{HH}) = 11\text{Hz}$, 0.5H, CH_2] (isomer 1), 3.05 [d, $\jmath(\text{HH}) = 12\text{Hz}$, 0.5H, CH_2] (isomer 2), 3.99 [d, $\jmath(\text{HH}) =$

12Hz, 0.5H, CH₂] (isomer 2), 6.71-7.47 (m, 25H, Ph). FAB MS: 1075, [M]⁺, 72; 1047, [M - CO]⁺, 13; 1019, [M - 2CO]⁺, 5; 991, [M - 3CO]⁺, 20; 963, [M - 4CO]⁺, 15; 935, [M - 5CO]⁺, 20; 907, [M - 6CO]⁺, 33; 879, [M - 7CO]⁺, 52; 857, [M - 5CO - Ph - H]⁺, 38; 829, [M - 6CO - Ph - H]⁺, 46; 801, [M - 7CO - Ph - H]⁺, 100.

Reaction of Ru₃(μ-dppm)(CO)₁₀ with C₂(CO₂Me)₂ (1:1.1)

A mixture of Ru₃(μ-dppm)(CO)₁₀ (243 mg, 0.251 mmol) and C₂(CO₂Me)₂ (40 mg, 0.28 mmol) in CH₂Cl₂ (15 ml) was refluxed for 3 h. After evaporation to dryness (rotary evaporator), preparative TLC (acetone/X4 3:7) showed seven bands. Band 2 (red, R_f = 0.55) was identified as unreacted Ru₃(μ-dppm)(CO)₁₀ (1) (70 mg, 29%) [IR ν(CO) spectrum and spot TLC]. Band 3 (purple, R_f = 0.45) was crystallised from CH₂Cl₂/n-hexane to give purple crystals of Ru₃{μ₃-C₂(CO₂Me)₂} (μ-dppm) (μ-CO)-(CO)₇ (21) (80 mg, 30%) m.p. 205-207°C. (Found: C, 44.78; H, 2.94; C₃₉H₂₈O₁₂P₂Ru₃ requires: C, 44.45; H, 2.68%).

Infrared (cyclohexane) 2070vs, 2041s, 2016vs, 2002vs, 1978m, 1858w(br), 1855m cm⁻¹. ¹H NMR: δ(CDCl₃) 3.39, 3.61 (2 x s, 2 x 3H, 2 x OMe), 4.85 (m, ABXY pattern, 1H, CH₂), 5.50 (m, ABXY pattern, 1H, CH₂), 7.37 (m, 20H, Ph). FAB MS: 1054, [M - H]⁺, 9; 1026, [M - CO - H]⁺, 63; 996, [M - CO - OMe]⁺, 14; 968, [M - 2CO - OMe]⁺, 62; 943, [M - 4CO]⁺, 68; 915, [M - 5CO]⁺, 89, 887, [M - 6CO]⁺, 100; 859, [M - 7CO]⁺, 89; 829, [M - C₂(CO₂Me)₂ - 3CO]⁺, 61; 801, [M - C₂(CO₂Me)₂ - 4CO]⁺, 47; 772, [M - C₂(CO₂Me)₂ - 5CO - H]⁺, 59. Band 5 (olive-green, R_f = 0.18) was crystallised from CH₂Cl₂/MeOH to give green crystals of Ru₃{μ₃-C₄(CO₂Me)₄} (μ-dppm)(CO)₆ (22) (92 mg, 32%) m.p. 262-266°C. (Found: C, 45.31; H, 2.99; C₄₃H₃₄O₁₄P₂Ru₃ requires: C, 45.31; H, 3.01%). Infrared (CH₂Cl₂): ν(CO) 2034m, 2013vs, 1977(sh), 1969s, 1951m, 1930w cm⁻¹. Infrared

(Nujol): ν (C \equiv O) 2037s, 2008vs, 1978vs, 1971s, 1950vs, 1927m; ν (C=O) 1742m, 1738(sh), 1711s, 1705(sh); ν (C-O) 1261w, 1219m, 1211(sh), 1171w cm $^{-1}$. 1 H NMR: δ (CDCl $_3$) 2.97, 3.78, 3.79, 3.80 (4 x s, 4 x 3H, 4 x OMe), 4.73 [dt, J (HH) = 15Hz, J (PH) = 11Hz, 1H, CH $_2$], 5.32 [dt, J (HH) = 15Hz, J (PH) = 11Hz, 1H, CH $_2$], 7.06-7.91 (m, 20H, Ph). FAB MS: 1141, $[M]^+$, 47; 1113, $[M - CO]^+$, 45; 1085, $[M - 2CO]^+$, 89; 1057, $[M - 3CO]^+$, 83; 1029, $[M - 4CO]^+$, 99; 1001, $[M - 5CO]^+$, 100, 973, $[M - 6CO]^+$, 92, 943, $[M - C_2(CO_2Me)_2 - 2CO]^+$, 42; 915, $[M - C_2(CO_2Me)_2 - 3CO]^+$, 94; 857, $[M - 2\{C_2(CO_2Me)_2\}]^+$, 49.

Reaction of Ru₃(μ -dppm)(CO)₁₀ with C₂(CO₂Me)₂ (1:2.7)

Preparation of Ru₃{ μ_3 -C₄(CO₂Me)₄}(μ -dppm)(CO)₆ (22)

A mixture of Ru₃(μ -dppm)(CO)₁₀ (175 mg, 0.181 mmol) and C₂(CO₂Me)₂ (70 mg, 0.49 mmol) in THF (15 ml) was refluxed for 40 min at which time all of the Ru₃(μ -dppm)(CO)₁₀ had been consumed (spot TLC). After evaporation to dryness (rotary evaporator), crystallisation from CH₂Cl₂/MeOH yielded olive-green microcrystals of Ru₃{ μ_3 -C₄(CO₂Me)₄}(μ -dppm)(CO)₆ (22) (149 mg, 72%) identified by comparison of its IR ν (CO) spectrum with that of the sample prepared above.

Reaction of Ru₃{ μ_3 -C₂(CO₂Me)₂}(μ -dppm)(μ -CO)(CO)₇ with C₂(CO₂Me)₂

Preparation of Ru₃{ μ_3 -C₄(CO₂Me)₄}(μ -dppm)(CO)₆ (22)

A mixture of Ru₃{ μ_3 -C₂(CO₂Me)₂}(μ -dppm)(μ -CO)(CO)₇ (21) (31 mg, 0.029 mmol) and C₂(CO₂Me)₂ (10 mg, 0.070 mmol) in CH₂Cl₂ (15 ml) was refluxed for 4.5 h at which time spot TLC showed that no starting material remained. After evaporation to dryness (rotary evaporator) crystallisation from CH₂Cl₂/MeOH yielded green crystals of Ru₃{ μ_3 -C₄(CO₂Me)₄}(μ -dppm)(CO)₆ (22)

(26 mg, 79%) identified by comparison of its IR ν (CO) spectrum with that of an authentic sample.

Preparation of $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_7$ (27)

Hydrogen was passed through a solution of $\text{Ru}_3\{-\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\mu\text{-CO})(\text{CO})_7$ (21) (24 mg, 0.023 mmol) in refluxing CH_2Cl_2 (20 ml) for 6 h. After filtration through a cottonwool plug, evaporation to dryness and crystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yielded orange crystals of $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\text{CO})_7$ (27) (18 mg, 77%) $>180^\circ\text{C}$ (dec.). (Found: C, 44.12; H, 2.98; $\text{C}_{38}\text{H}_{30}\text{O}_{11}\text{P}_2\text{Ru}_3$ requires: C, 44.41; H, 2.94%). Infrared (cyclohexane) 2072vs, 2043s, 2019vs, 2004vs, 1998(sh), 1969w(br), 1966(sh) cm^{-1} . ^1H NMR: δ (CDCl_3) -19.22 [d, $J(\text{PH}) = 39\text{Hz}$, 1H, Ru-H], -14.89 [t, $J(\text{PH}) = 14\text{Hz}$, 1H, Ru-H], 3.46 (s, 3H, OMe), 3.56 (m, ABXY pattern, 1H, CH_2), 3.76 (s, 3H, OMe), 4.49 (m, ABXY pattern, 1H, CH_2), 6.96-7.54 (m, 20H, Ph). Minor peaks -20.76 [t, $J(\text{PH}) = 17\text{Hz}$, $\mu\text{-H}$], -15.78 [t, $J(\text{PH}) = 14\text{Hz}$, $\mu\text{-H}$], 3.29 (s, OMe), 4.67 (m, CH_2). FAB MS: 1029, $[\text{M}]^+$, 30; 998, $[\text{M} - \text{OMe}]^+$, 52; 972, $[\text{M} - \text{H} - 2\text{CO}]^+$, 35; 945, $[\text{M} - 3\text{CO}]^+$, 80; 917, $[\text{M} - 4\text{CO}]^+$, 100; 887, $[\text{M} - \text{C}_2(\text{CO}_2\text{Me})_2]^+$, 83; 859, $[\text{M} - \text{C}_2(\text{CO}_2\text{Me})_2 - \text{CO}]^+$, 64.

Reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with $\text{C}_2(\text{CO}_2\text{Me})_2$ (1:1) 18 hours

A mixture of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (182 mg, 0.188 mmol) and $\text{C}_2(\text{CO}_2\text{Me})_2$ (29 mg, 0.204 mmol) in THF (20 ml) was refluxed for 18 h. After evaporation to dryness (rotary evaporator) preparative TLC (acetone/X4 3:7) showed 10 bands, and a brown baseline. Band 1 (red, $R_f = 0.57$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (8) (29 mg, 18%) identified by comparison of its

IR $\nu(\text{CO})$ spectrum with that of an authentic sample. Band 4 (orange-yellow, $R_f = 0.47$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange-red crystals of $\text{Ru}_4(\mu_3-\text{H})\{\mu_4-\text{C}_2(\text{CO}_2\text{Me})_2\}-\{\mu-\text{PPh}(\text{C}_6\text{H}_4)\text{CH}_2\text{PPh}_2\}(\text{CO})_9$ (28) (1 mg, 1%). Infrared (cyclohexane): $\nu(\text{CO})$ 2077vs, 2044vs, 2028vs, 2016w, 2001m, 1988s, 1959w, 1948w cm^{-1} . FAB MS: 1183, $[\text{M} - \text{H}]^+ \equiv [\text{M}']^+$, 11; 1155, $[\text{M}' - \text{CO}]^+$, 28; 1127, $[\text{M}' - 2\text{CO}]^+$, 58; 1099, $[\text{M}' - 3\text{CO}]^+$, 78; 1071, $[\text{M}' - 4\text{CO}]^+$, 39; 1043, $[\text{M}' - 5\text{CO}]^+$, 100; 1041, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2]^+$, 86; 1015, $[\text{M}' - 6\text{CO}]^+$, 89; 1013, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2 - \text{CO}]^+$, 86, 987, $[\text{M}' - 7\text{CO}]^+$, 67; 985, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2 - 2\text{CO}]^+$, 56; 957, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2 - 3\text{CO}]^+$, 58; 929, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2 - 4\text{CO}]^+$, 53; 901, $[\text{M}' - \text{C}_2(\text{CO}_2\text{Me})_2 - 5\text{CO}]^+$, 39. Band 5 (yellow, $R_f = 0.44$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give orange crystals of $\text{Ru}_3(\mu-\text{H})_2\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{dppm})(\text{CO})_7$ (27) (1 mg, 1%) identified by comparison of its IR $\nu(\text{CO})$ spectrum with that of the sample prepared above. Band 6 (purple, $R_f = 0.43$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give purple crystals of $\text{Ru}_4\{\mu_4-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu-\text{dppm})(\text{CO})_{10}$ (31) (4 mg, 2%). Infrared (cyclohexane) 2071s, 2039vs, 2014vs, 2001s, 1999(sh), 1969w, 1963(sh), 1949w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.03, 3.79 (2 x S, 2 x 3H, 2 x OMe), 4.75 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 4.97 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 6.92-7.83 (m, 20H, Ph). FAB MS: 1212, $[\text{M}]^+$, 27, 1181, $[\text{M} - \text{OMe}]^+$, 17; 1156, $[\text{M} - 2\text{CO}]^+$, 29; 1128, $[\text{M} - 3\text{CO}]^+$, 100; 1100, $[\text{M} - 4\text{CO}]^+$, 96; 1072, $[\text{M} - 5\text{CO}]^+$, 23; 1044, $[\text{M} - 6\text{CO}]^+$, 100; 1016, $[\text{M} - 7\text{CO}]^+$, 92; 988, $[\text{M} - 8\text{CO}]^+$, 38; 986, $[\text{M} - \text{CO}_2\text{Me} - 3\text{CO}]^+$, 46; 960, $[\text{M} - 9\text{CO}]^+$, 35; 958, $[\text{M} - \text{CO}_2\text{Me} - 4\text{CO}]^+$; 932, $[\text{M} - 10\text{CO}]^+$, 35; 901, $[\text{M} - \text{OMe} - 10\text{CO}]^+$, 32; 872, $[\text{M} - \text{CO}_2\text{Me} - 7\text{CO} - 2\text{H}]^+$, 47. Band 7 (purple, $R_f = 0.40$) was crystallised

from CH_2Cl_2 /n-hexane to give purple crystals of $\text{Ru}_3\{\mu_3-\text{C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-dppm})(\mu\text{-CO})(\text{CO})_7$ (21) (2 mg, 1%) identified by comparison of its IR $\nu(\text{CO})$ spectrum with that of the sample prepared above. Band 10 (olive-green, $R_F = 0.16$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give green crystals of $\text{Ru}_3\{\mu_3-\text{C}_4(\text{CO}_2\text{Me})_4\}(\mu\text{-dppm})(\text{CO})_6$ (22) (40 mg, 19%) identified by comparison of its IR $\nu(\text{CO})$ spectrum with that of an authentic sample.

Preparation of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPH})(\mu\text{-dppm})(\text{CO})_7\{\text{Au}(\text{PPh}_3)\}$ (32)

To a stirred solution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (102 mg, 0.105 mmol) in THF (28 ml) was added $\text{Au}(\text{C}\equiv\text{CPH})(\text{PPh}_3)$ (59 mg, 0.11 mmol). After heating at reflux for 1.5 h, spot TLC (acetone/X4 3:7) showed that no starting material remained. After evaporation to dryness (rotary evaporator) crystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ afforded orange microcrystals of $\text{Ru}_3(\mu_3-\text{C}\equiv\text{CPH})-(\mu\text{-dppm})(\text{CO})_7\{\text{Au}(\text{PPh}_3)\} \cdot 1.5\text{CH}_2\text{Cl}_2$ (32) (147 mg, 89%) m.p.>190°C (dec.). (Found: C, 45.39; H, 2.75; $\text{C}_{58}\text{H}_{42}\text{AuO}_7\text{P}_3\text{Ru}_3 \cdot 1.5\text{CH}_2\text{Cl}_2$ requires C, 45.48; H, 2.89%). Infrared (cyclohexane): $\nu(\text{CO})$ 2034vs, 1990s, 1971vs, 1957m, 1940m, 1909w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.34 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 4.25 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 11\text{Hz}$, 1H, CH_2], 5.30 (s, 3H, $1.5\text{CH}_2\text{Cl}_2$), 6.34-7.94 (m, 40H, Ph). FAB MS: 1904, $[\text{M} + \text{Au}(\text{PPh}_3)]^+$, 11; 1876, $[\text{M} + \text{Au}(\text{PPh}_3) - \text{CO}]^+$, 20; 1445, $[\text{M}]^+$, 71; 1417, $[\text{M} - \text{CO}]^+$, 11; 1389, $[\text{M} - 2\text{CO}]^+$, 3; 1361, $[\text{M} - 3\text{CO}]^+$, 100; 1333, $[\text{M} - 4\text{CO}]^+$, 23; 1305, $[\text{M} - 5\text{CO}]^+$, 29; 1277, $[\text{M} - 6\text{CO}]^+$, 21; 1249, $[\text{M} - 7\text{CO}]^+$, 29; 1227, $[\text{M} - 5\text{CO} - \text{Ph} - \text{H}]^+$, 9; 1199, $[\text{M} - 6\text{CO} - \text{Ph} - \text{H}]^+$, 6; 1171, $[\text{M} - 7\text{CO} - \text{Ph} - \text{H}]^+$, 26; 986, $[\text{M} - \text{Au}(\text{PPh}_3)]^+$, 19; 721, $[\text{Au}(\text{PPh}_3)_2]^+$, 36; 459, $[\text{Au}(\text{PPh}_3)]^+$, 86.

Preparation of Ru₃(μ₃-C≡CPh)(μ-dppm)(CO)₇[Au{P(C₆H₄Me-p)₃}] (33)

A similar reaction using Ru₃(μ-dppm)(CO)₁₀ (74 mg, 0.076 mmol) and Au(C≡CPh){P(C₆H₄Me-p)₃} (46 mg, 0.076 mmol) in THF (20 ml) was refluxed for 0.5 h before evaporation to dryness (rotary evaporator). Crystallisation from CH₂Cl₂/MeOH yielded orange crystals of Ru₃(μ₃-C≡CPh)(μ-dppm)(CO)₇[Au{P(C₆H₄Me-p)₃}] · 0.5CH₂Cl₂ (33) (107 mg, 92%) m.p. >200°C (dec.). (Found: C, 48.38; H, 3.24; C₆₁H₄₈AuO₇P₃Ru₃ · 0.5CH₂Cl₂ requires C, 48.32; 3.23%).

Infrared (cyclohexane): ν (CO) 2034vs, 1990s, 1970vs, 1957m, 1939m, 1909w cm⁻¹. ¹H NMR: δ(CDCl₃) 2.39 (s, 9H, Me), 3.34 [dt, J (HH) = 14Hz, J (HP) = 11Hz, 1H, CH₂], 4.25 [dt, J (HH) = 14Hz, J (HP) = 11Hz, 1H, CH₂], 5.30 (s, 1H, 0.5CH₂Cl₂), 6.38-8.54 (m, 37H, Ph + C₆H₄). FAB MS: 1988, [M + Au{P(C₆H₄Me-p)₃}]⁺ ≡ [M']⁺, 1; 1960, [M' - CO]⁺, 17; 1932, [M' - 2CO]⁺, 1; 1487, [M]⁺, 9; 1459, [M - CO]⁺, 4, 1431, [M - 2CO]⁺, 3; 1403, [M - 3CO]⁺, 51; 1375, [M - 4CO]⁺, 18; 1347, [M - 5CO]⁺, 22; 1319, [M - 6CO]⁺, 20; 1291, [M - 7CO]⁺, 25; 1213, [M - 7CO - Ph - H]⁺, 21; 1199, [M - 7CO - C₆H₄Me - H]⁺, 9; 986, [M - Au{P(C₆H₄Me-p)₃}]⁺, 9; 805, [Au{P(C₆H₄Me-p)₃}]²⁺, 45; 501, [Au{P(C₆H₄Me-p)₃}]⁺, 100.

Reactions of Ru₃(μ-H)(μ₃-C≡CR)(μ-dppm)(CO)₇ (R = Bu^t, Ph)

(a) Pyrolysis of Ru₃(μ-H)(μ₃-C≡CBu^t)(μ-dppm)(CO)₇ (17) - A solution of Ru₃(μ-H)(μ₃-C≡CBu^t)(μ-dppm)(CO)₇ (17) (200 mg, 0.207 mmol) in toluene (50 ml) was refluxed for 60 h and then evaporated to dryness (rotary evaporator). Preparative TLC (acetone/X4 3:7) showed three bands and a brown baseline. The major band (orange, R_f = 0.69) was crystallised from CH₂Cl₂/MeOH to give red crystals of Ru₃(μ-H)₂(μ₃-PPh₂CH₂PPh₂)(μ₃-PhC₂Bu^t)(CO)₆ (34) (80 mg, 41%) m.p. >150°C (dec.). (Found: C, 47.08; H, 3.54; C₃₇H₃₃O₆P₂Ru₃ requires C, 47.34; H, 3.54%). Infrared (cyclohexane): ν (CO)

2034m, 2024vw, 2008vs, 1992m, 1977vs, 1954m(br), 1942(sh), 1921m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ -17.63 - (-17.50) [2 x dd (7 peaks), 1H, Ru-H], -17.01 [2 dd (7 peaks), $J(\text{HH}) = 17\text{Hz}$, $J(\text{PH}) = 10\text{Hz}$, $J(\text{PH}) = 6\text{Hz}$, 1H, Ru-H], 4.06-4.53 (m, 2H, CH_2), 5.69 [d, $J(\text{PH}) = 7\text{Hz}$, 1H], 7.16-7.77 (m, 20H, Ph). FAB MS: 939, $[\text{M} - \text{H}]^+$, 16; 910, $[\text{M} - 2\text{H} - \text{CO}]^+$, 10; 882, $[\text{M} - 2\text{H} - 2\text{CO}]^+$, 10; 854, $[\text{M} - 2\text{H} - 3\text{CO}]^+$, 50; 826, $[\text{M} - 2\text{H} - 4\text{CO}]^+$, 75; 798, $[\text{M} - 2\text{H} - 5\text{CO}]^+$, 42; 781, $[\text{M} - \text{H} - \text{PhC}_2\text{Bu}^t]^+$, 20; 770, $[\text{M} - 2\text{H} - 6\text{CO}]^+$, 62; 750, $[\text{M} - \text{H} - 4\text{CO} - \text{Ph}]^+$, 25; 691, -, 40; 634, $[\text{M} - \text{PhPCH}_2\text{PPh}_2 + \text{H}]^+$, 35; 611, $[\text{M} - 3\text{H} - 6\text{CO} - \text{PhC}_2\text{Bu}^t]^+$, 65; 531, $[\text{M} - \text{H} - \text{C}_2\text{Ph} - \text{PhPCH}_2\text{PPh}_2]^+$, 100.

(b) Reaction of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ with I_2 - To a stirred solution of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (130 mg, 0.132 mmol) in thf (15 ml) was added a solution of I_2 (36 mg, 0.14 mmol) in thf (17 ml) through a pressure equalising dropping funnel over a period of 30 min. The colour of the reaction mixture changed from yellow to yellow-orange, and then to orange. After stirring at room temperature for 1 h, the reaction mixture was evaporated to dryness *in vacuo*. Preparative TLC (acetone/X4 3:7) showed six bands and a brown baseline. Band 2 (red, $R_f = 0.44$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of $\text{Ru}_2(\mu\text{-I})(\mu\text{-C}_2\text{Ph})(\mu\text{-dppm})(\text{CO})_4 \overset{\Delta}{\underset{0.5\text{CH}_2\text{Cl}_2}{\longrightarrow}} (\text{37})$ (42 mg, 34%) m.p. $>180^\circ\text{C}$ (dec.). (Found: C, 45.86; H, 2.96; I, 12.12; $\text{C}_{37}\text{H}_{27}\text{IO}_4\text{P}_2\text{Ru}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 46.48; H, 2.91; I, 13.09%). Infrared (cyclohexane): $\nu(\text{CO})$ 2025s, 2002m, 1991s, 1969vs, 1954w, 1947w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 3.63 [dt, $J(\text{HH}) = 13\text{Hz}$, $J(\text{PH}) = 12\text{Hz}$, 1H, CH_2], 4.73 [dt, $J(\text{HH}) = 13\text{Hz}$, $J(\text{PH}) = 12\text{Hz}$, 1H, CH_2], 5.30 (s, 1H, $0.5\text{CH}_2\text{Cl}_2$), 6.89-7.54 (m, 25H, Ph). FAB MS: 928, $[\text{M}]^+$, 32; 900, $[\text{M} - \text{CO}]^+$ 46; 844, $[\text{M} - 3\text{CO}]^+$, 100; 816, $[\text{M} - 4\text{CO}]^+$, 40; 745, $[\text{M} - 2\text{CO} - \text{I}]^+$, 80; 717, $[\text{M} - 3\text{CO} - \text{I}]^+$, 46; 689, $[\text{M} - 4\text{CO} - \text{I}]^+$, 88. The other bands were present in trace amounts and were not identified.

Preparation of Ru₃(μ-dppm)(CO)₉(PR₃) (R = OMe, Ph)

(a) R = OMe - To a stirred solution of Ru₃(μ-dppm)(CO)₁₀ (65 mg, 0.067 mmol) and P(OMe)₃ (11 mg, 0.089 mmol) in thf (10 ml) was added 0.5 ml of Na[Ph₂CO] initiator solution. Preparative TLC (acetone/X4 3:7) showed one major band which was extracted and crystallised from CH₂Cl₂/MeOH to give red-orange crystals of Ru₃(μ-dppm)(CO)₉{P(OMe)₃} (38) (41 mg, 57 %) m.p. 196–199°C. (Found: C, 41.67; H, 2.82; C₃₇H₃₁O₁₂P₃Ru₃ requires C, 41.78; H, 2.94%). Infrared (cyclohexane): ν(CO) 2061w, 2000vs, 1985vs, 1974(sh), 1950w, 1935vw cm⁻¹. ¹H NMR: δ(CDCl₃) 3.62 [d, *J*(PH) = 12Hz, 9H, OMe], 4.22 [t, *J*(PH) = 10Hz, 2H, CH₂], 7.31–7.42 (m, 20H, Ph). FAB MS: 1065, [M]⁺, 25; 1037, [M – CO]⁺, 14; 1009, [M – 2CO]⁺, 51; 981, [M – 3CO]⁺, 33; 953, [M – 4CO]⁺, 92; 925, [M – 5CO]⁺, 79; 897, [M – 6CO]⁺, 100; 869, [M – 7CO]⁺, 83; 841, [M – 8CO]⁺, 50; 813, [M – 9CO]⁺, 44.

(b) R = Ph - In a similar reaction, to a solution of Ru₃-(μ-dppm)(CO)₁₀ (100 mg, 0.102 mmol) and PPh₃ (27 mg, 0.10 mmol) in thf (15 ml) was added 5 ml of Na[Ph₂CO] initiator solution, giving an immediate darkening of solution. After stirring at room temperature for 1.5 min evaporation to dryness and crystallisation from CH₂Cl₂/MeOH afforded red-orange crystals of Ru₃(μ-dppm)(CO)₉(PPh₃) (12) (62 mg, 51%) m.p. 205–207°C. Infrared (cyclohexane): ν(CO) 2055w, 1997vs, 1982vs, 1946w cm⁻¹ [lit.¹⁸: ν(CO) (CH₂Cl₂): 2052w, 1992s, 1975s, 1942m cm⁻¹]. ¹H NMR: δ(CDCl₃) 4.16 [t, *J*(PH) = 10Hz, 2H, CH₂], 7.34 (m, 35H, Ph). FAB MS: 1203, [M]⁺, 100; 1175, [M – CO]⁺, 12; 1147, [M – 2CO]⁺, 23; 1119, [M – 3CO]⁺, 8; 1091, [M – 4CO]⁺, 23; 1063, [M – 5CO]⁺, 46; 1035, [M – 6CO]⁺, 38; 1007, [M – 7CO]⁺, 62; 979, [M – 8CO]⁺, 38; 958, [M – 6CO – Ph]⁺, 54; 951, [M – 9CO]⁺, 46; 930, [M – 7CO – Ph]⁺, 50; 902, [M – 8CO – Ph]⁺, 36; 874, [M – 9CO – Ph]⁺, 98.

Reaction of Ru₃(μ-dppm)(CO)₁₀ with HC₅(CO₂Me)₅

A mixture of Ru₃(μ-dppm)(CO)₁₀ (292 mg, 0.301 mmol) and HC₅(CO₂Me)₅ (107 mg, 0.301 mmol) in thf (35 ml) was heated under gentle reflux for 42 h at which time the solvent was removed (rotary evaporator). Preparative TLC (X4) showed two major bands. Band 1 (yellow, $R_F = 0.40$) was identified as Ru₃(μ-H)(μ₃-PPhCH₂PPh₂)(CO)₉ (10) (68 mg, 26%) and band 2 (orange, $R_F = 0.30$) identified as Ru₃{μ₃-PPhCH₂PPh(C₆H₄)}(CO)₉ (8) (103 mg, 40%), both by comparison of IR ν(CO) spectra and spot TLC behaviour with those of authentic samples.

Reaction of Ru₃(μ-dppm)(CO)₁₀ with AuCl(PPh₃)

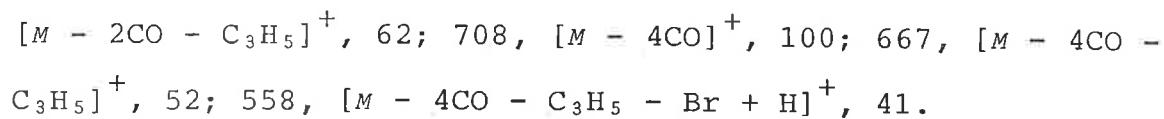
To a stirred solution of Ru₃(μ-dppm)(CO)₁₀ (100 mg, 0.103 mmol) in thf (25 ml) was added AuCl(PPh₃) (50 mg, 0.10 mmol). The reaction mixture was refluxed for 2.5 h at which time the reaction was adjudged complete [the disappearance of the ν(CO) band of (1) at 2079 cm⁻¹ was monitored]; the reaction mixture at this time was dark green. After evaporation to dryness, crystallisation from CH₂Cl₂/MeOH yielded dark green crystals of Ru₃(μ-Cl)(μ-dppm)(CO)₈{Au(PPh₃)} (39) (118 mg, 81%) m.p. 185–188°C. (Found: C, 43.78; H, 2.57; C₅₁H₃₇AuClO₈P₃Ru₃ requires: C, 43.56; H, 2.65%). Infrared (cyclohexane): 2050s, 2011m, 1985vs, 1975s, 1957m, 1905w cm⁻¹. ¹H NMR: δ(CDCl₃) 4.26 [dt, J (HH) = 15Hz, J (PH) = 11Hz, 1H, CH₂], 4.66 [dt, J (HH) = 15Hz, J (PH) = 10 Hz, 1H, CH₂], 7.06–7.61 (m, 35H, Ph). FAB MS: 1407, [M]⁺, 5; 1379, [M - CO]⁺, 6; 1351, [M - 2CO]⁺, 7; 1323, [M - 3CO]⁺, 13; 1295, [M - 4CO]⁺, 9; 1267, [M - 5CO]⁺, 14; 1239, [M - 6CO]⁺, 25; 1211, [M - 7CO]⁺, 10; 1183, [M - 8CO]⁺, 11; 1106, [M - 8CO - Ph]⁺, 23; 721, [Au(PPh₃)₂]⁺, 50; 459, [Au(PPh₃)]⁺, 100.

Reaction of Ru₃(μ₃-dppm)(CO)₁₀ with I₂

A mixture of Ru₃(μ-dppm)(CO)₁₀ (100 mg, 0.103 mmol) and I₂ (26 mg, 0.10 mmol) in thf (20 ml) was refluxed for approximately 4 h. After evaporation to dryness (rotary evaporator), preparative TLC (acetone/X4 3:7) showed six bands and a yellow baseline. Band 3 (yellow-orange, $R_f = 0.68$) was identified as Ru₃(μ-dppm)(CO)₁₀ (1) (11 mg, 11%) by its solution infrared spectrum. Band 4 (orange, $R_f = 0.65$) was crystallised from CH₂Cl₂/MeOH affording red-orange crystals of Ru₂(μ-I)₂(μ-dppm)(CO)₄ (6) (45 mg, 46%). Infrared (cyclohexane): ν (CO) 2024s, 2004vs, 1965s, 1951w cm⁻¹ [lit.¹⁵: ν (CO) 2025s, 2005vs, 1965s, 1952w cm⁻¹]. FAB MS: 954, [M]⁺, 54; 926, [M - CO]⁺, 95; 870, [M - 3CO]⁺, 100; 842, [M - 4CO]⁺, 56. The other four bands were present in trace amounts and were not identified.

Reaction of Ru₃(μ-dppm)(CO)₁₀ with allyl bromide

A mixture of Ru₃(μ-dppm)(CO)₁₀ (160 mg, 0.165 mmol) and allyl bromide (100 mg, 0.827 mmol) in thf (20 ml) was heated at reflux point for 0.75 h at which time all of the Ru₃(μ-dppm)-(CO)₁₀ had been consumed (spot TLC). The reaction mixture had changed to yellow-orange. After evaporation to dryness (rotary evaporator) preparative TLC (acetone/X4 3:7) showed one major coloured band (yellow, $R_f = 0.57$) which was crystallised from hot MeOH to give orange-yellow crystals of Ru₂(μ-Br)(μ-C₃H₅)-(μ-dppm)(CO)₄ (40) (68 mg, 50%) m.p. 199-201°C. (Found: C, 47.03; H, 3.16; Br, 9.70; C₃H₂BrO₄P₂Ru₂ requires C, 46.90; H, 3.32; Br, 9.75%). Infrared (cyclohexane): ν (CO) 2021m, 1996vs, 1949vs, 1932w cm⁻¹. ¹H NMR: δ(CDCl₃) 1.33-4.96 (m, 7H, C₃H₅+CH₂), 7.06 (m, 20H, Ph). FAB MS: 820, [M]⁺, 34; 792, [M - CO]⁺, 67; 764, [M - 2CO]⁺, 79; 736, [M - 3CO]⁺, 31; 723,



Reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with Me_2S_2

A mixture of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (203 mg, 0.210 mmol) and Me_2S_2 (30 mg, 0.32 mmol) in thf (15 ml) was refluxed for 3.5 h at which time the reaction was adjudged complete [the disappearance of the $\nu(\text{CO})$ band of (1) at 2079 cm^{-1} was monitored]. After evaporation to dryness *in vacuo*, preparative TLC (acetone/X4 3:7) showed seven bands and a brown baseline. Band 1 (yellow, $R_f = 0.73$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give yellow crystals of $\text{Ru}_2(\mu\text{-SMe})_2(\mu\text{-dppm})(\text{CO})_4 \cdot \text{CH}_2\text{Cl}_2$ (41) (50 mg, 30%) m.p. 236–238°C. (Found: C, 44.74; H, 3.58; $\text{C}_{31}\text{H}_{28}\text{O}_4\text{P}_2\text{Ru}_2\text{S}_2 \cdot \text{CH}_2\text{Cl}_2$ requires C, 45.30; H, 3.50%). Infrared (cyclohexane): $\nu(\text{CO})$ 2003m, 1984vs, 1944vs, 1934w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 1.94 (s, 3H, Me), 2.54 [t, $J(\text{PH}) = 3.5\text{Hz}$, 3H, Me], 3.46 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 10\text{Hz}$, 1H, CH_2], 3.87 [dt, $J(\text{HH}) = 14\text{Hz}$, $J(\text{PH}) = 5.30$ (s, 2H, CH_2Cl_2), 10Hz, 1H, CH_2]; 7.11–7.54 (m, 20H, Ph). FAB MS: 793, $[M]^+$, 18; 765, $[M - \text{CO}]^+$, 100; 737, $[M - 2\text{CO}]^+$, 5; 709, $[M - 3\text{CO}]^+$, 91; 681, $[M - 4\text{CO}]^+$, 44. Band 2 (orange, $R_f = 0.66$) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give red crystals of $\text{Ru}_3(\mu\text{-H})(\mu\text{-SMe})\text{-}(\mu\text{-dppm})(\text{CO})_8$ (42) (16 mg, 8%) m.p. >160°C (dec.). (Found: C, 42.47; H, 2.82; $\text{C}_{34}\text{H}_{26}\text{O}_8\text{P}_2\text{Ru}_3\text{S}$ requires C, 42.55; H, 2.73%). Infrared (cyclohexane): $\nu(\text{CO})$ 2067s, 2023m, 2000vs, 1983w, 1966m(br), 1953w, 1939w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ -14.71 [dd, $^2J(\text{PH}) = 35.4\text{Hz}$, $^3J(\text{PH}) = 3.3 \text{ Hz}$, 1H, Ru-H], 4.21 (m, ABXY pattern, 1H, CH_2), 4.62 (m, ABXY pattern, 1H, CH_2), 7.22–7.58 (m, 20H, Ph). FAB MS: 961, $[M]^+$, 7; 933, $[M - \text{CO}]^+$, 100; 905, $[M - 2\text{CO}]^+$, 59; 877, $[M - 3\text{CO}]^+$, 32; 849, $[M - 4\text{CO}]^+$, 33.

Reaction of Ru₃(CO)₁₀(PMe₂Ph)₂ with C₂(CO₂Me)₂

To a stirred solution of Ru₃(CO)₁₀(PMe₂Ph)₂ (200 mg, 0.233 mmol) in thf (25 ml) was added C₂(CO₂Me)₂ (1 ml of a 0.48M standard solution, 0.48 mmol). After a gentle reflux for 45 min the reaction mixture was evaporated to dryness (rotary evaporator). Preparative TLC (acetone/X4 3:7) showed fourteen bands. Band 1 (orange, R_f = 0.68) was identified as unreacted Ru₃(CO)₁₀(PMe₂Ph)₂ (34 mg, 17%) by comparison of its IR ν (CO) spectrum with that of an authentic sample. Band 3 (orange, R_f = 0.57) was crystallised from CH₂Cl₂/MeOH to give Ru₃{μ₃-C₂(CO₂Me)₂} (μ-CO)(CO)₇(PMe₂Ph)₂ (44) as red needles (25 mg, 11%), m.p. 154-157°C. (Found: C, 38.12; H, 2.96; C₃₀H₂₈O₁₂P₂Ru₃ requires: C, 38.10; H, 2.98%). Infrared (cyclohexane): ν (CO) 2064s, 2018vs, 1995m, 1884w, 1811(sh), 1802m cm⁻¹. Infrared (Nujol): ν (C≡O) 2064s, 2019vs, 2014vs, 1987m, 1981m, 1962m, 1807s; ν (C=O) 1707(sh), 1701m; ν (C-O) 1199m, 1190w, 1177m, 1162w cm⁻¹. ¹H NMR: δ(CDCl₃) 1.92 [d, J (PH) = 9.5Hz, 12H, Me], 3.51 (s, 6H, OMe), 7.43 (m, 10H, Ph). FAB MS: 946, [M - H]⁺, 4; 918, [M - H - CO]⁺, 21; 890, [M - H - 2CO]⁺, 32, 862, [M - H - 3CO]⁺, 21; 834, [M - H - 4CO]⁺, 100; 806, [M - H - 5CO]⁺, 68; 778, [M - H - 6CO]⁺, 71; 751, [M - 7CO]⁺, 75; 720, [M - 7CO - OMe]⁺, 37; 692, [M - 8CO - OMe]⁺, 39. Band 10 (yellow, R_f = 0.26) was crystallised from CH₂Cl₂/MeOH to give yellow crystals of Ru₃{C₂(CO₂Me)₂}₃(CO)₆(PMe₂Ph)₂ · CH₂Cl₂ (45) (4 mg, 1%). (Found: C, 37.51; H, 3.19; C₄₀H₄₀O₁₈P₂Ru₃ · CH₂Cl₂ requires C, 39.12; H, 3.36%). Infrared (CH₂Cl₂): ν (CO) 2043s, 2022s, 1987vs, 1975(sh), 1873w, 1864w cm⁻¹. ¹H NMR: δ(CDCl₃) 1.85-2.10 (7 peaks, 12H, 4 x Me), 3.40-3.73 (5 peaks, 18H, 6 x OMe), 5.29 (s, 2H, CH₂Cl₂), 7.26-7.78 (m, 10H, Ph). FAB MS: 1175, [M]⁺, 11; 1147, [M - CO]⁺,

100; 1116, $[M - CO - OMe]^+$, 83; 1091, $[M - 3CO]^+$, 39; 1063, $[M - 4CO]^+$, 56; 1033, $[M - C_2(CO_2Me)_2]^+$, 44; 1005, $[M - CO - C_2(CO_2Me)_2]^+$, 33; 977, $[M - 2CO - C_2(CO_2Me)_2]^+$, 39; 949, $[M - 3CO - C_2(CO_2Me)_2]^+$, 39; 918, $[M - 3CO - C_2(CO_2Me)_2 - OMe]^+$, 17; 890, $[M - 4CO - C_2(CO_2Me)_2 - OMe]^+$, 22. The other bands were present in trace amounts and were not identified.

Reaction of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ with $HC\equiv CPh$

To a stirred solution of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ (96 mg, 0.11 mmol) in thf (17 ml) was added $HC\equiv CPh$ (30 mg, 0.29 mmol). After heating at reflux for 9 h, the reaction mixture was evaporated to dryness (rotary evaporator). Preparative TLC (acetone/X4 2.5:7.5) showed seven bands and a brown baseline. Band 2 (orange, $R_f = 0.69$) was crystallised from $CH_2Cl_2/MeOH$ to give $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(\mu-C_4H_2Ph_2)(CO)_6$ (46) (34 mg, 31%) as an orange-red powder m.p. $>150^\circ C$ (dec.). (Found: C, 49.66; H, 2.89; $C_{41}H_{28}O_6P_2Ru_3$ requires: C, 50.16; H, 2.87%). Infrared (cyclohexane) 2041s, 2010s, 2000vs, 1970w, 1959s, 1945w cm^{-1} . 1H NMR: δ ($CDCl_3$) 2.97 (m, ABXY pattern, 2H, CH_2) 5.88-7.70 (m, 26H, 2 x $CH + 4 \times Ph + C_6H_4$). FAB MS: 983, $[M]^+$, 66; 955, $[M - CO]^+$, 89; 927, $[M - 2CO]^+$, 37; 899, $[M - 3CO]^+$, 32; 871, $[M - 4CO]^+$, 100; 843, $[M - 5CO]^+$, 32; 815, $[M - 6CO]^+$, 42; 735, $[M - 6CO - 2H - C_6H_6]^+$, 37.

Reaction of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ with $C_2(CO_2Me)_2$

To a stirred solution of $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(CO)_9$ (100 mg, 0.116 mmol) in thf (20 ml) was added $C_2(CO_2Me)_2$ (2 ml of a 0.26M solution in thf, 0.52 mmol). After heating at reflux for 2.25 h the reaction was adjudged complete [spot TLC (acetone/ $Et_2O/X4$ 2:2:6)] and the solvent was removed (rotary evaporator). Radial chromatography (acetone/X4 2:8)

of an acetone (1.5 ml) extract eluted four bands. Band 3 (green) was crystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ affording dark-green crystals of $\text{Ru}_3\{\mu_3-\text{PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}\{\mu-\text{C}_4(\text{CO}_2\text{Me})_4\}(\text{CO})_6$ (47) (26 mg, 21%) m.p. $>150^\circ\text{C}$ (dec.). (Found: C, 41.80; H, 2.62; $\text{C}_{37}\text{H}_{26}\text{O}_{14}\text{P}_2\text{Ru}_3$ requires C, 41.86; H, 2.66%). Infrared (cyclohexane): $\nu(\text{CO})$ 2066m, 2050vs, 2025s, 2009m, 1989w, 1977m cm^{-1} . Infrared (Nujol): $\nu(\text{C}\equiv\text{O})$ 2062m, 2046vs, 2020s, 2002s, 1992m, 1978s, 1969s; $\nu(\text{C}=\text{O})$ 1727m, 1722(sh), 1718m, 1708m, 1700(sh); $\nu(\text{C}-\text{O})$ 1238m, 1214m, 1205m, 1178m, 1172m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.49-3.06 (m, ABXY pattern, 2H, CH_2), 3.45, 3.63, 3.88, 3.91 (4 x s, 12H, 4 x OMe), 6.29-8.04 (m, 14H, Ph + C_6H_4). FAB MS: 1063, $[\text{M}]^+$, 7; 1035, $[\text{M} - \text{CO}]^+$, 26; 1007, $[\text{M} - 2\text{CO}]^+$, 16; 979, $[\text{M} - 3\text{CO}]^+$, 100; 951, $[\text{M} - 4\text{CO}]^+$, 34; 923, $[\text{M} - 5\text{CO}]^+$, 44; 921, $[\text{M} - \text{C}_2(\text{CO}_2\text{Me})_2]^+$, 44; 895, $[\text{M} - 6\text{CO}]^+$, 12; 893, $[\text{M} - \text{CO} - \text{C}_2(\text{CO}_2\text{Me})_2]^+$, 12; 865, $[\text{M} - 2\text{CO} - \text{C}_2(\text{CO}_2\text{Me})_2]^+$, 11. The other three bands and a further two bands eluted (acetone/X4 5:5) were not identified.

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