# SOME ASPECTS OF THE CHEMISTRY OF METAL CLUSTERS

by

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Glory be to Almighty Allah, Most Gracious,
Most Merciful, Who has gifted man with
intellect and reason so that man should explore
and understand himself and nature

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# SUMMARY

This thesis reports some of the chemistry of tri- and tetra-nuclear ruthenium cluster carbonyls. The first two chapters describe studies in the area of syntheses and reactions of clusters containing tertiary phosphines. This is followed by a chapter about the designed syntheses of heterometallic clusters containing gold while the final chapter looks at the reactions of trinuclear iron and ruthenium cluster carbonyls with azoarenes.

It has been shown that specific carbonyl substitution by phosphines, arsines or isocyanides ligands of triruthenium cluster carbonyls can be achieved using sodium benzophenone ketyl (BPK), [PPN][OAc] or [PPN][CN] as an initiator or electron transfer catalyst (ETC). Application of these reagents to the designed synthesis of $Ru_3(CO)_{12}$ derivatives has enabled a study of the reactivity of these complexes.

Chapter One describes the reactions of some substituted ruthenium cluster carbonyls with dihydrogen. Hydrogenation of complexes $Ru_3(CO)_{12-n}(L)_n$ (L = $PMe_3$, $PPh_3$, $PPh(OMe)_2$, $P(OMe)_3$; (n = 1-3) under mild conditions (80°C, 20 atm., 2h) afforded $Ru_4(\mu\text{-}H)_4(CO)_{12-m}(L)_m$ (where m is not related to n). In contrast, hydrogenation of $Ru_3$ (L-L)$(CO)_{10}$ [(L-L) = dppm or dpam] results in P-C or As-C bond cleavage to yield $\mu_3$-phosphido-phosphine or $\mu_3$-arsenido-arsine ligands and elimination of benzene. Further reactions of dihydrogen

with complexes containing the $\mu_3$-$PPhCH_2PPh_2$ ligand resulted in further P-C bond cleavage to give $\mu_3$-PPh and $PMePh_2$ ligands attached to the cluster in $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$. Hydrogenation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ and $Ru_3(\mu\text{-}H)(\mu_n\text{-}SBu^t)(\mu\text{-}dppm)(CO)_{10-n}$ ($n = 2,3$) resulted in S-C bond cleavage but not P-C bond cleavage and formation of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7(L_2)$ [$L_2 = (CO)_2$, $\mu$-dppm].

Chapter Two describes the syntheses of $Ru_3(\mu\text{-}dppf)_n(CO)_{12-2n}$ ($n = 1,2$) [dppf = 1,1'-diphenylphosphinoferrocene] and the hydrogenation of $Ru_3(\mu\text{-}dppf)(CO)_{10}$ to give $Ru_4(\mu\text{-}H)_4(\mu\text{-}dppf)(CO)_{10}$. The pyrolysis of $Ru_3(\mu\text{-}dppf)(CO)_{10}$ yields several novel complexes by P-C and C-H bond cleavage reactions. The complexes contain the following type of ligands:- $\mu$-vinyl [in $Ru_3(\mu\text{-}H)\{\mu_3\text{-}(\eta^1,\eta^2\text{-}C_6H_4)PPhFc'PPh_2\}(CO)_8$], cyclometallated phenyl [in $Ru_3\{\mu_3\text{-}(C_6H_4)PFc'PPh_2\}(\mu\text{-}CO)(CO)_8$] and benzyne complexes [in $Ru_3(\mu_3\text{-}C_6H_4)(\mu_2\text{-}PPh_2)(\mu_2\text{-}PPhFc)(CO)_7$ and $Ru_4(\mu\text{-}H)_2(\mu_4\text{-}PFc)(\mu_4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_{10}$].

Chapter Three focusses on the synthesis of mixed metal-gold clusters using the $\mu_3$-oxo-trigold (1+) derivative, $[O\{Au(PPh_3)\}_3][BF_4]$, which can be used to introduce up to three $Au(PPh_3)$ units directly onto the cluster. Complexes containing more than one gold atom in the metal cluster core were obtained from reactions of $[\{Au(PPh_3)\}_3O]^+$ with the anions derived from $Ru_3(\mu\text{-}H)(\mu\text{-}C_2Bu^t)(CO)_9$, $Ru_3(\mu\text{-}H)(\mu\text{-}C_{12}H_{15})(CO)_9$, $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$; these complexes were chosen with a view to examining further possible interaction of the gold atom(s) with the hydrocarbon or sulphur ligands. We have obtained and characterised the complexes $Ru_3Au(\mu\text{-}C_2Bu^t)(CO)_9(PPh_3)$, $Ru_3Au_2(\mu\text{-}C_2HBu^t)(CO)_9(PPh_3)_2$, $Ru_3Au_3(\mu\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$, $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$, $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$ and $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$. The digold-ruthenium complex structures show that they may model the initial attack of $H_2$ on the ruthenium cluster.

Chapter Four describes the reactions of $Ru_3(CO)_{12}$ and azoarenes, $C_6H_4RN{=}NC_6H_4R'$ [R=R' = H, *m*-$CH_3$; R = H, R' = *m*-$CH_3$, *m*-$CF_3$, *m*-F, *P*-F]. Trinuclear products obtained from the reactions between $M_3(CO)_{12}$ (M = Fe or Ru) and azobenzenes are shown to have the structure $M_3(\mu_3\text{-}NAr)_2(CO)_9$, rather than the *o*-semidine formulation proposed earlier. Other products from the reactions of $Ru_3(CO)_{12}$ include the cyclometallated complexes $Ru(C_6H_3RN{=}NC_6H_4R)_2(CO)_2$ (R = H, *m*-$CH_3$) and an uncharacterised dark brown powder.

# 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.

Omar bin Shawkataly

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# ABBREVIATIONS

In general

| | |
|---|---|
| Å | angstrom |
| Ar | aryl |
| atm | atmosphere |
| $Bu^s$ | *sec*-butyl |
| $Bu^t$ | *tert*-butyl |
| Bz | benzyl: $C_6H_5CH_2$ |
| C | Celcius |
| *ca* | circa |
| $C_5H_5$ | cyclopentadienyl |
| cm | centimetres |
| Cy | cyclohexyl |
| dec. | decomposed |
| dpam | bis(diphenylarsino)methane |
| dppm | bis(diphenylphosphino)methane |
| dppa | 1,2-bis(diphenylphosphino)ethyne |
| dpae | 1,2-bis(diphenylarsino)ethane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dmpm | bis(dimethylphosphino)methane |
| dppee | 1,1-bis(diphenylphosphino)ethene |
| dppf | 1,1'-bis(diphenylphosphino)ferrocene |
| ebdp | cis-1,2-bis(diphenylphosphino)ethene |
| Et | ethyl |
| ffars | tetrafluorocyclobutene-bis(dimethylarsine) |
| ffos | tetrafluocyclobutene-bis(diphenylphosphine) |
| $f_6fos$ | hexafluorocyclohexene-bis(diphenylphosphine) |
| g | grams |

| | |
|---|---|
| h | hours |
| Hz | hertz |
| i.e. | that is |
| IR | infrared |
| l | litres |
| lit. | literature |
| M | molecular ion |
| Me | methyl |
| Mg | milligrams |
| min | minutes |
| ml | millilitres |
| mmol | millimoles |
| m.p. | melting point |
| MHz | megahertz |
| NMR | nuclear magnetic resonance |
| Ph | phenyl |
| ppn | bis(triphenylphosphine)iminium $[N(PPh_3)_2]^+$ |
| $Pr^i$ | iso-propyl |
| R | alkyl |
| sec | seconds |
| sp | ortho-styryldiphenylphosphine |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |

For Infrared Spectroscopy

| | |
|---|---|
| br | broad |
| $cm^{-1}$ | wave numbers (reciprocal centimetres) |
| m | medium |
| s | strong |
| sh | shoulder |

| | |
|---|---|
| vs | very strong |
| vw | very weak |
| w | weak |

For NMR Spectroscopy

| | |
|---|---|
| d | doublet |
| dd | doublet of doublets |
| m | multiplet |
| q | quartet |
| s | singlet |
| t | triplet |

# CHAPTER 1

PAGE

## SYNTHESES AND REACTIONS OF TRIRUTHENIUM CLUSTERS CONTAINING TERTIARY PHOSPHINES

# SYNTHESES AND REACTIONS OF TRIRUTHENIUM CLUSTERS CONTAINING TERTIARY PHOSPHINES

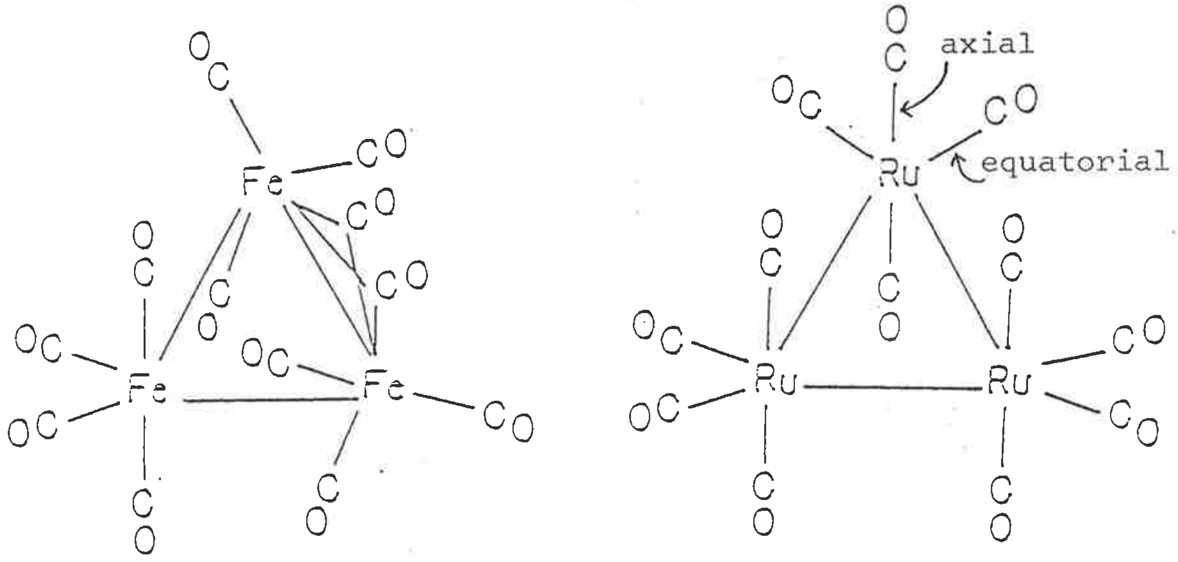
## 1. INTRODUCTION

### (i) Chemistry of Triruthenium Cluster Carbonyls

Metal cluster carbonyl chemistry, where a metal 'cluster' compound was defined by Cotton[1] as "those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster", was initiated by the discovery of dodecacarbonyltriiron ($Fe_3(CO)_{12}$)[2] in 1907 by heating non-aqueous suspensions of nonacarbonyldiiron ($Fe_2(CO)_9$). However, the precise nature of this dark green carbonyl was not unequivocally determined until the X-ray structure investigations by several research groups[3] which culminated in the final resolution of the disorder present in the solid-state structure by Dahl and Wei[4] in 1966.

The first ruthenium cluster carbonyl was obtained, but again not recognised as such, by Mond and co-workers[5] in 1910, as an orange crystalline solid from the reaction of ruthenium metal and carbon monoxide (400 atm, 300°C). The product was established as a ruthenium carbonyl, but it was not correctly characterised until it was formulated as $Ru_3(CO)_{12}$ by Corey and Dahl[6] on the basis of X-ray crystallography of the osmium analogue; for most of the intervening period, it was considered to be $Ru_2(CO)_9$.

The best current preparation of $Ru_3(CO)_{12}$ was reported by Bruce and co-workers in 1983[7]. It involves the carbonylation of 1% methanol solutions of hydrated ruthenium trichloride ($RuCl_3.xH_2O$) (50-60 atm CO, 125°C, 16h). Almost quantitative yields can be achieved when the mother liquors are recycled with fresh ruthenium trichloride. Dodecacarbonyltriruthenium has a slightly distorted equilateral triangle of metal atoms with all carbonyl ligands being terminally bonded[8] (see Fig. 1).



$Fe_3(CO)_{12}$ $Ru_3(CO)_{12}$

Figure 1

### (ii) Chemistry of $Ru_3$ derivatives containing Group 15 ligands

The chemistry of $Ru_3(CO)_{12}$ has been explored to a greater extent than any of its simple substituted derivatives[9]. An area of considerable current interest has been the synthesis and reactivity of derivatives of $Ru_3$ clusters containing Group 15 ligands, because of their possible application to catalysis.

(a) Monodentate Ligands

The complex $Ru_3(CO)_9(PPh_3)_3$[10] was reported in 1966 subsequently it was also reported that the thermal reaction of $P(Bu^n)_3$ and $PMe_2Bz$ with $Ru_3(CO)_{12}$ yield $Ru_3(CO)_9[P(Bu^n)_3]_3$[11] and $Ru_3(CO)_9(PMe_2Bz)_3$[12] respectively.

Before 1972, mono or disubstituted complexes of $Ru_3(CO)_{12}$ (1) had not been isolated. This was ascribed to their kinetic instability relative to the trisubstituted species[13]. Subsequently, Stone and co-workers[14] reported that complexes $Ru_3(CO)_{12-n}(PR_3)_n$ (n = 1-3) were formed in a small yield as byproducts from the preparation of platinum-ruthenium cluster complexes from reactions between $Ru_3(CO)_{12}$ and low-valent platinum complexes containing tertiary phosphines. It was also reported[15] that if chromatographic separation of the reaction products is employed, rather than crystallisation as had previously been used, mono and disubstituted trinuclear products can be isolated from the thermally induced reactions between $Ru_3(CO)_{12}$ and the tertiary phosphine, although the trisubstituted complexes predominate.

High temperatures are required for $Ru_3(CO)_{12}$ to react with various tertiary phosphines. The usual products from such reactions are $Ru_3(CO)_9(PR_3)_3$[10-17]. Poë and co-workers showed that mono and di-substituted complexes are obtainable if the reaction is performed under CO[18,19]. Mono and disubstituted species have also been obtained by using sterically demanding ligands such as tricyclohexylphosphine[25]. Trifluorophosphine is the only ligand at present known to displace more than four carbonyl ligands, the complex $Ru_3(CO)_7(PF_3)_5$ being reported as one of many related complexes found in the reaction between $Ru_3(CO)_{12}$ and $PF_3$[20]. The photochemical reaction of $Ru_3(CO)_{12}$ and $PPh_3$ was later found to produce $Ru_3(CO)_{11}(PPh_3)$ as well as mono- and trans-di-substituted mononuclear species. Crystallographic analysis of $Ru_3(CO)_{11}(PPh_3)$ shows that the $PPh_3$ ligand occupies an equatorial site (see Fig. 1)[27].

In general, the reaction of $Ru_3(CO)_{12}$ and group 15 ligands can give a mixture of products. However, the yields of mono and di-substituted species are usually low. For the thermal reactions, reasonable yields of cluster compounds are limited to the trisubstituted products.

## (b) 'Mild' Synthetic Routes

Reiger and co-workers first showed that specific carbonyl substitution in polynuclear carbonyl complexes can be electrochemically induced[21]. Since then several 'mild' routes to carbonyl substitution have been developed[22-26]. The first to be developed was by Bruce and co-workers[24] which uses sodium benzophenone ketyl (BPK) to induce specific carbonyl substitution of metal clusters. This substitution involves an electron transfer-catalysed (ETC) process. The proposed mechanism for the electron transfer process with $Ru_3(CO)_{12}$ is outlined in equations (1)-(3).

$$Ru_3(CO)_{12} + [Ph_2CO]^{\bar{\cdot}} \rightarrow [Ru_3(CO)_{12}]^{\bar{\cdot}} + Ph_2CO \qquad ...(1)$$

$$[Ru_3(CO)_{12}]^{\bar{\cdot}} + L \rightarrow [Ru_3(CO)_{11}L]^{\bar{\cdot}} + CO \qquad ...(2)$$

$$[Ru_3(CO)_{11}L]^{\bar{\cdot}} + Ru_3(CO)_{12} \rightarrow Ru_3(CO)_{11}L + [Ru_3(CO)_{12}]^{\bar{\cdot}} \qquad ...(3)$$

The process relies on the increased susceptibility of the radical anion of $Ru_3(CO)_{12}$ towards nucleophilic attack, as compared with the neutral parent cluster. It is likely that Ru-Ru bond cleavage occurs to generate a labile 17e metal centre; related mononuclear 17e carbonyls are known to be very readily substituted. The substituted cluster radical anion is less stable than that formed from the parent carbonyl and rapid electron transfer to unreacted $Ru_3(CO)_{12}$ establishes a cycle that is followed until either carbonyl or ligand is used up. An explanation involving fragmentation of the cluster, followed by substitution and reassembly of the fragments does not accord with the high degree of specificity and excellent yields which are characteristic of these BPK reactions.

Other methods of activating $Ru_3(CO)_{12}$ towards specific CO substitution have been described recently by Lavigne and Kaesz[23]. These include the use of a catalytic amount of [PPN][OAc] or [PPN][CN], which promotes substitution by tertiary phosphines, such as $PPh_3$, dppm or dppe, but not by trialkyl phosphites or $AsPh_3$[23]. Other $[PPN]^+$ salts show varying degrees of activity; rates of ligand substitution in $Ru_3(CO)_{12}$ were also enhanced by addition of methoxide ion[28,29], which formed the labile methoxycarbonyl complex $[Ru_3(CO_2Me)(CO)_{11}]^-$. Recently, the complex $[Fe(CO)_2(\eta^5-C_5H_5)]_2$ has been used to promote CO substitution in many complexes such as $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Ru_4(\mu-H)_4(CO)_{12}$, $Co_2(CO)_6(PhC_2Ph)$ and $Fe_3(CO)_8(PhC_2Ph)$[30]. The ETC substitution reactions are related to the now well-established ET-promoted reactions first recognised in organic chemistry[31], for which there exist several good reviews[32,33].

With the advent of mild synthetic routes to derivatives of $Ru_3(CO)_{12}$ containing tertiary phosphine, phosphite and arsine ligands[25], considerable interest in their chemistry has developed. X-ray studies of $Ru_3(CO)_{12-n}(L)_n$ [L = $PPh_3$, n = 1; L = $PCy_3$, n = 1; L = $P(OMe)_3$, n = 2; L = $PMe_3$, n = 3; L = $PPh(OMe)_2$, n = 4][27,34] have been reported. The latter is unusual in having the $Fe_3(CO)_{12}$-type structure (see Fig. 1) with two CO ligands bridging one of the Ru-Ru bonds. The X-ray studies of a range of derivatives containing bidentate tertiary phosphine or arsine ligands, $Ru_3(CO)_{12-2n}(LL)_n$ [LL = dppm, n = 1 or 2; LL = dppe, n = 1; LL = ffars, n = 1 or 2] have also been reported. In all cases the Group 15 atom was found to occupy an equatorial site as expected on steric grounds. Only with the isocyanide complexes $Ru_3(CO)_{12-n}(CNBu^t)_n$ (n = 1 or 2)[7] was axial coordination found for the non-CO ligands.

However, until recently, it had not been possible to compare a series of complexes related by progressive substitution of CO by the same ligand. This deficiency has now been redressed[38]. Before this study, the only examples of $Ru_3(CO)_{12}$ substituted by more than three tertiary phosphine or arsine ligands were $Ru_3(CO)_8(L)_4$ [L = $PF_3$, $PMe_3$, $PH_3$ and $PPh(OMe)_2$][15,20,25,37]. The only example that has been studied by X-ray methods is $Ru_3(\mu\text{-}CO)_2(CO)_6$-$[PPh(OMe)_2]_4$[34].

The syntheses of $Ru_3(CO)_8(L)_4$ [L = $P(OMe)_3$, $P(OPh)_3$] are reported here. X-ray studies of the complexes

$Ru_3(CO)_{12-n}(L)_n$ [L = $PPh(OMe)_2$, n = 1, 2 and 3; L = $P(OMe)_3$, n = 4; L = $AsPh_3$, n = 1; L = $AsMe_2Ph$, n = 3; L = $P(OPh)_3$, n = 4] were undertaken by White and co-workers[38]. These extra data allow more extensive comparisons to be made within a series and between P and As. The method utilised for the synthesis of $Ru_3(CO)_8(L)_4$ has now been extended to other phosphines and phosphites including $PMe_2Ph$, $PMe_2Bz$, $P(OCH_2CF_3)_3$ and $P(OEt)_3$[39].

### (c) Bidentate Ligands

Reactions of $Ru_3(CO)_{12}$ with bidentate tertiary phosphine and arsine ligands produce substituted clusters where the ligands preferentially bridge metal-metal bonds. An early report suggested the formation of $Ru_3(dppe)_3(CO)_6$, but this has not been confirmed[120]. However, recently Smith and co-workers have isolated and characterised spectroscopically the complexes $Ru_3(LL)_3(CO)_6$ [L = dppm, dppee][40,41]. Complexes of the types $Ru_3(LL)(CO)_{10}$ [where LL = dppm, dmpm, ebdp, dpam, dppee, dppe, dppf, dppp, ffars, ffos and $f_6$fos][30,40-47] and $Ru_3(LL)_2(CO)_8$ [where LL = dppm, dmpm, dpam, dppee, ffars, ffos and $f_6$fos][40-46] have been fully characterised.

In triruthenium clusters with bidentate phosphines or arsines, the ligands bridge two metal atoms in an equatorial plane. In the case of a bidentate ligand the bite angle has an influence on the metal-metal separation[48]; dppm is known to accommodate a wide range of metal-metal distances[49-51].

### (iii) Reactivity of $Ru_3(CO)_{12-n}(L)_n$

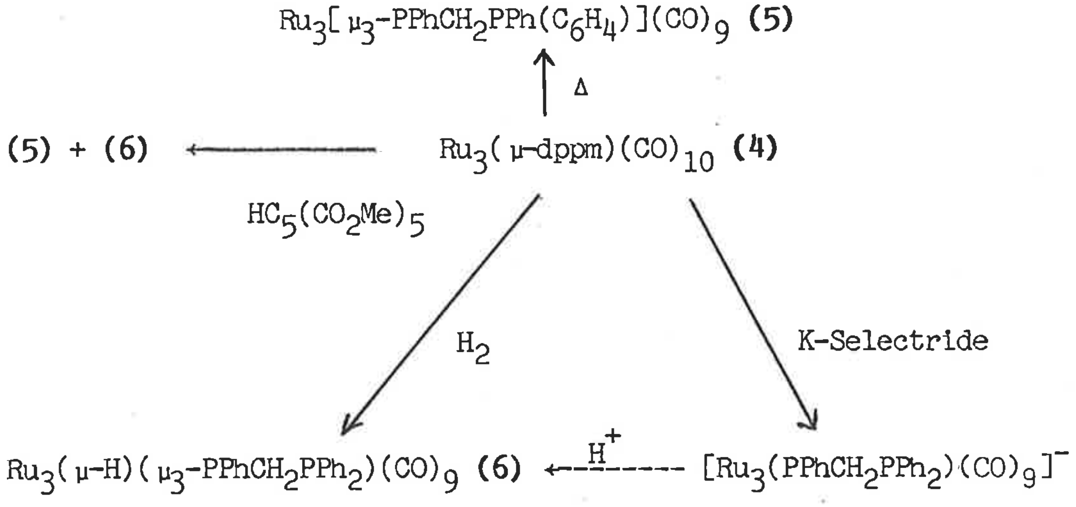
### (a) Monodentate ligands

The reactivity of triruthenium clusters containing tertiary phosphine has been studied to some extent. Hydrogenation of $Ru_3(CO)_{12-n}(L)_n$ [L = $P(OMe)_3$, $PPh_3$, $PMe_3$, $PPh(OMe)_2$; n = 1,2 and 3] has been studied, and some results are reported in this chapter. The pyrolysis of $Ru_3(CO)_9(PR_3)_3$ (R = Ph, p-tolyl, m-tolyl) gave several products, including the $\mu_3$-benzyne complexes. $Ru_3(C_6H_3X)[\mu P(C_6H_4X)]_2(CO)_7$ [X = H, m-Me, p-Me], with a preponderance of binuclear products[15]. Under pyrolytic conditions (refluxing decalin) $Ru_3(CO)_9[P(OPh)_3]_3$ and $Ru_3(CO)_9[P(OC_6H_4Me\text{-}p)_3]_3$ form the cyclo metallated mononuclear derivatives, $Ru(CO)_2\{(C_6H_4O)P(OPh)_2\}_2$ and $Ru(CO)_2\{(C_6H_3MeO)P\ (OC_6H_4Me)_2\}_2$, respectively[52]. The complex $Ru_3(CO)_9(PPh_3)_3$ reacts with $X_2$ (where X = Cl, Br, I) to yield $RuX_2(CO)_3(PPh_3)$, which on heating loses CO to give $\{Ru(\mu\text{-}X)X(CO)_2(PPh_3)\}_2$. The latter reacts with excess $PPh_3$ to yield $RuX_2(CO)_2\ (PPh_3)_2$[53,54]. Similar chemistry (when X = Cl) is observed with $Ru_3(CO)_9(PPh_3)_3$ and $Ru_3(CO)_{10}$-$(AsPh_3)_2$ in chloroform or carbon tetrachloride[17,53]. $Ru_3(CO)_9(PPh_3)_3$ also reacts with $RCO_2H$ (R = H, Me or Et)[55] or p-toluenesulphonyl azide[56] to give $Ru_2(CO)_4(RCO_2)_2(PPh_3)_2$ and $Ru\{N[(SO_2R)CON(SO_2R)]\}(CO)_2(PPh_3)_2$ (R = $C_6H_4Me\text{-}p$), respectively. Pyrolysis of $Ru_3(CO)_9(PPh_3)_3$ in the presence of oxygen results in the formation of an uncharacterised yellow precipitate[57].

Recently, Bonnet and co-workers found that the complex $Ru_3(CO)_{11}(PPh_2py)$ loses CO at ambient temperature (40°C) to yield an acyl complex $Ru_3[\mu-\eta^2-C(O)(C_6H_5)](\mu_3-\eta^2-P(C_6H_5)(C_5H_4N)](CO)_9$[58].

(b) Bidentate ligands

The chemistry of $Ru_3(\mu\text{-dppm})_2(CO)_8$ **(23)** has been studied in detail by Bonnet and co-workers. The pyrolysis of $Ru_3(\mu\text{-dppm})_2(CO)_8$ in xylene at 100°C had been found to give $Ru_3(\mu_3\text{-PPh})(\mu_3\text{-CHPPh})(dppm)(CO)_7$[45]. The hydrogenation of $Ru_3(\mu\text{-dppm})_2(CO)_8$ has also been studied (see section (iv)). Complex **(23)** reacts with iodine in toluene (75°C, 2h) to give $[Ru_2(\mu\text{-I})_2(\mu\text{-dppm})(CO)_4]$ and $RuI_2(CO)_2(dppm)$[59]. The complex $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** was extensively studied by Bruce and co-workers and an interesting spectrum of cluster chemistry was uncovered (see Scheme 1)[69,74,115-119].

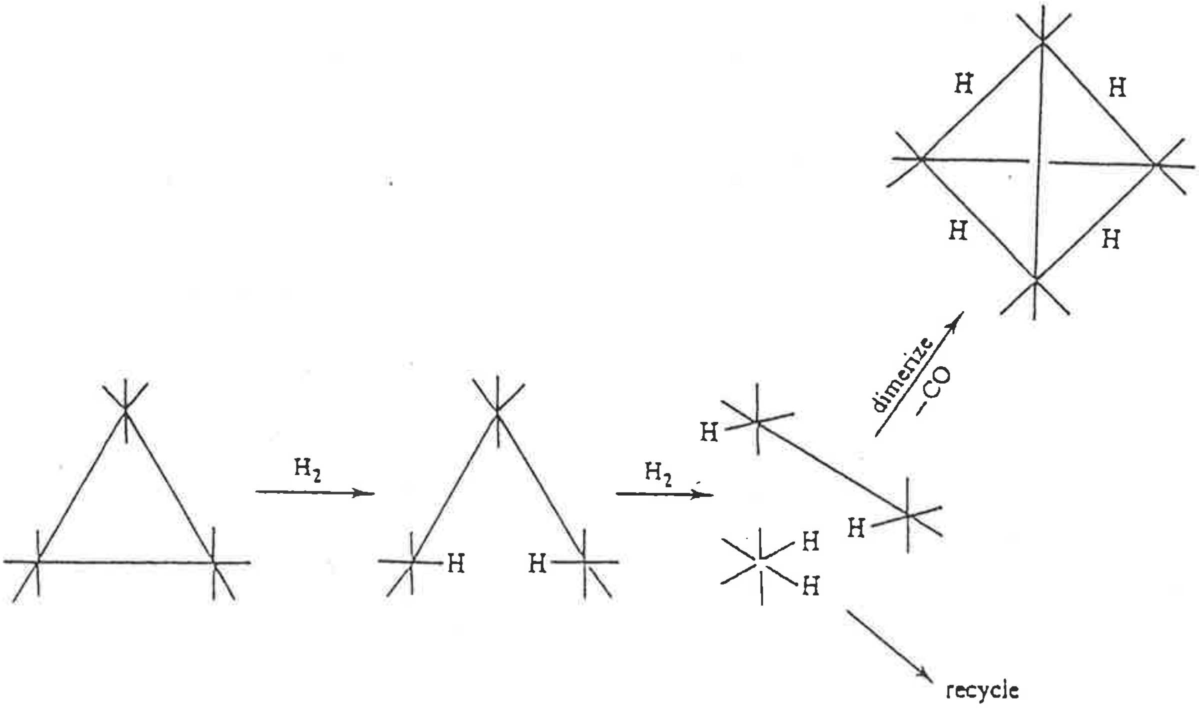


(Scheme 1)

### (iv) Reactions of some Substituted Ruthenium Cluster Carbonyls with Dihydrogen

The potential utility of transition metal cluster complexes in homogeneous catalysis has often been considered in recent years[60-65]. Metal clusters have often been postulated as catalysts in hydrogenation reactions. Hence it is useful to investigate the hydrogenation of metal clusters under catalytic conditions i.e. mild pressure and temperature. Under CO, or in the presence of many Lewis bases, the simpler clusters tend to fragment, while in the presence of hydrogen, several types of behaviour have been found. Thus, $Ru_3(CO)_{12}$ reacts readily in refluxing octane to give high yields of the tetranuclear derivative, $Ru_4(\mu\text{-}H)_4(CO)_{12}$ **(1)**, while the osmium analogue forms initially the unsaturated cluster hydride, $Os_3(\mu\text{-}H)_2(CO)_{10}$; prolonged treatment with hydrogen is required to generate $Os_4(\mu\text{-}H)_4(CO)_{12}$[66].

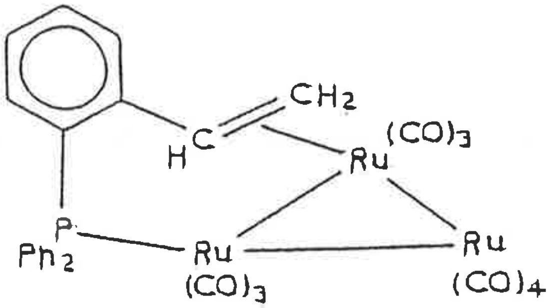
The conversion of $Ru_3(CO)_{12}$ to $Ru_4(\mu\text{-}H)_4(CO)_{12}$ **(1)** is assumed to proceed by addition of $H_2$ to the trinuclear cluster, resulting in cleavage of Ru-Ru bonds to produce dinuclear and mononuclear fragments which on aggregation give the tetranuclear hydrido cluster (Scheme 2). It would therefore be difficult to unambiguously assign any catalytic activity to the presence of the initial cluster species.



(Scheme 2)

When the Group 8 cluster carbonyls contain other Lewis bases as ligands, the additional possibility of reaction of the ligand, activated by coordination to the cluster, has to be recognised. Hydrogenation of $Ru_3(CO)_{11}(CNBu^t)$, for example, not only gave the series $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(CNBu^t)_n$ (n = 0-2), but also the formimidoyl complexes $Ru_3(\mu\text{-}H)$-$(\mu_3\text{-}HC{=}NBu^t)(CO)_9$ and $Ru_3(\mu\text{-}H)(\mu_3\text{-}HC{=}NBu^t)(CO)_8(CNBu^t)$[67]. The hydrogenation of benzonitrile in the presence of $M_3(CO)_{12}$ (M = Fe or Ru) is instructive in this regard, affording $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CHPh)(CO)_{10}$ and $Ru_3(\mu\text{-}H)(\mu\text{-}NHCH_2Ph)$-$(CO)_{10}$, together with $Ru_4(\mu\text{-}H)_4(CO)_{12}$ **(1)** and benzylamine[68]. The reaction of $Ru_3(CO)_{10}(sp)$ **(2)** with hydrogen (20 atm, 50°C, 2h) proceeded readily to give

$Ru_4(\mu\text{-}H)_4(CO)_{12}$ (1) and $Ru_4(\mu\text{-}H)_4(CO)_{11}(PPh_2C_6H_4Et\text{-}2)$ (3)[69].



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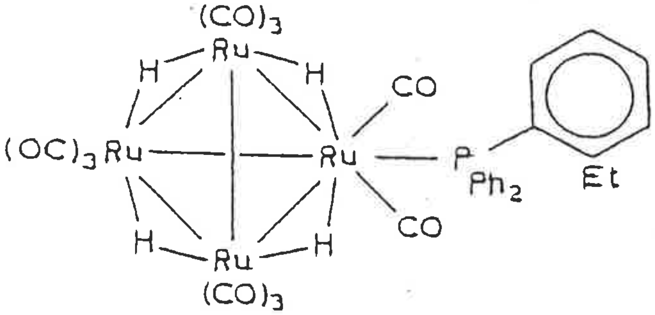
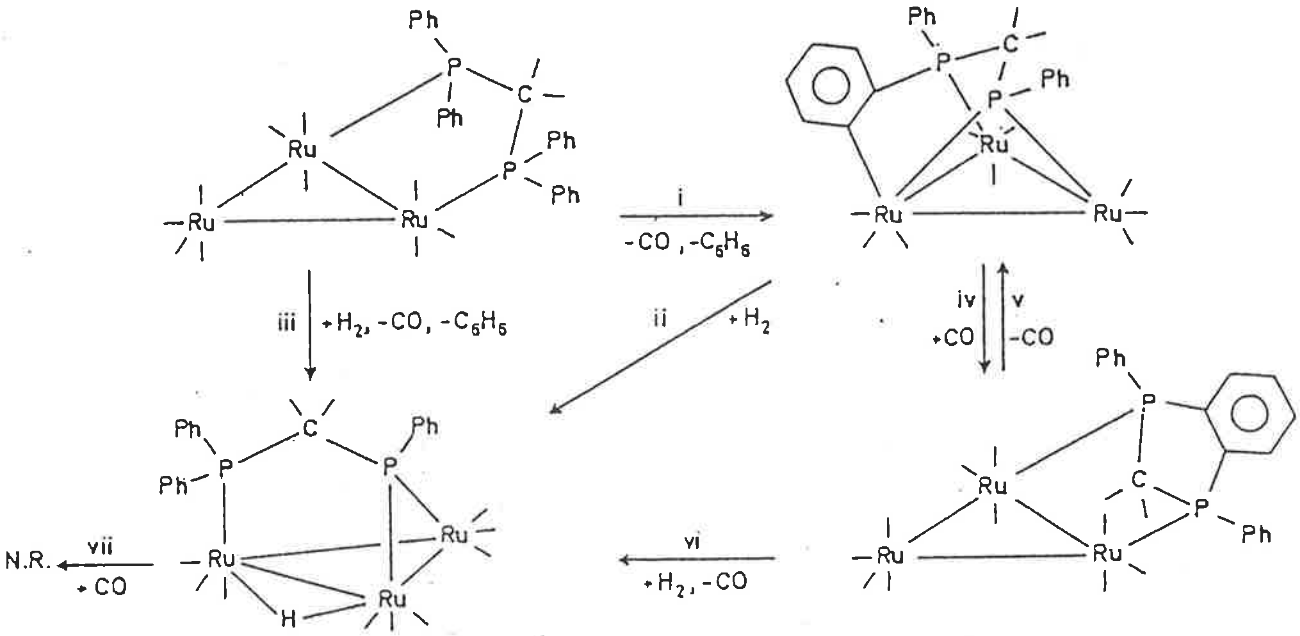


3

The reactivity of Group 15 ligands coordinated to Group 8 cluster carbonyls was clearly demonstrated in the reaction of $Os_3(CO)_{12}$ with $PPh_3$, from which a variety of trinuclear complexes formed by P-C bond cleavage reactions, and in one case, C-C bond formation, were isolated and characterised by X-ray crystallography[70,71]. A predominance of related but binuclear complexes was found in similar reactions of $Ru_3(CO)_{12}$[15,72]. The subject has been reviewed[73] and consideration of the results reported so far suggests that although the P-C bond cleavage reactions occur readily, elimination of the alkyl or aryl group so formed only takes place in the presence of hydride ligands when intra- or inter-molecular reductive elimination (of alkane or arene) can occur.

Bidentate ligands (LL) such as dppm or dpam have been used to bridge one or two of the Ru-Ru bonds in complexes such as $Ru_3(\mu\text{-LL})(CO)_{10}$ or $Ru_3(\mu\text{-LL})_2(CO)_8$. However, modification of the Group 15 ligand by loss of phenyl group (as benzene) is found in reactions with hydrogen, with concomitant capping of one or both sides of the $Ru_3$ triangle in the resulting complexes $Ru_3(\mu\text{-H})(\mu_3\text{-EPhCH}_2\text{EPh}_2)(CO)_9$ or $Ru_3(\mu\text{-H})_2(\mu_3\text{-EPhCH}_2\text{EPh}_2)_2(CO)_6$ (E = P or As)[44,74]. The cleavage of P-C, As-C and S-C bonds in reactions of metal cluster derivatives, and particularly on heating, has been reported many times[75]. Similarly, reaction of $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_9$ with $H_2$ afforded the phosphinidene cluster, $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_9$, with loss of benzene[76].

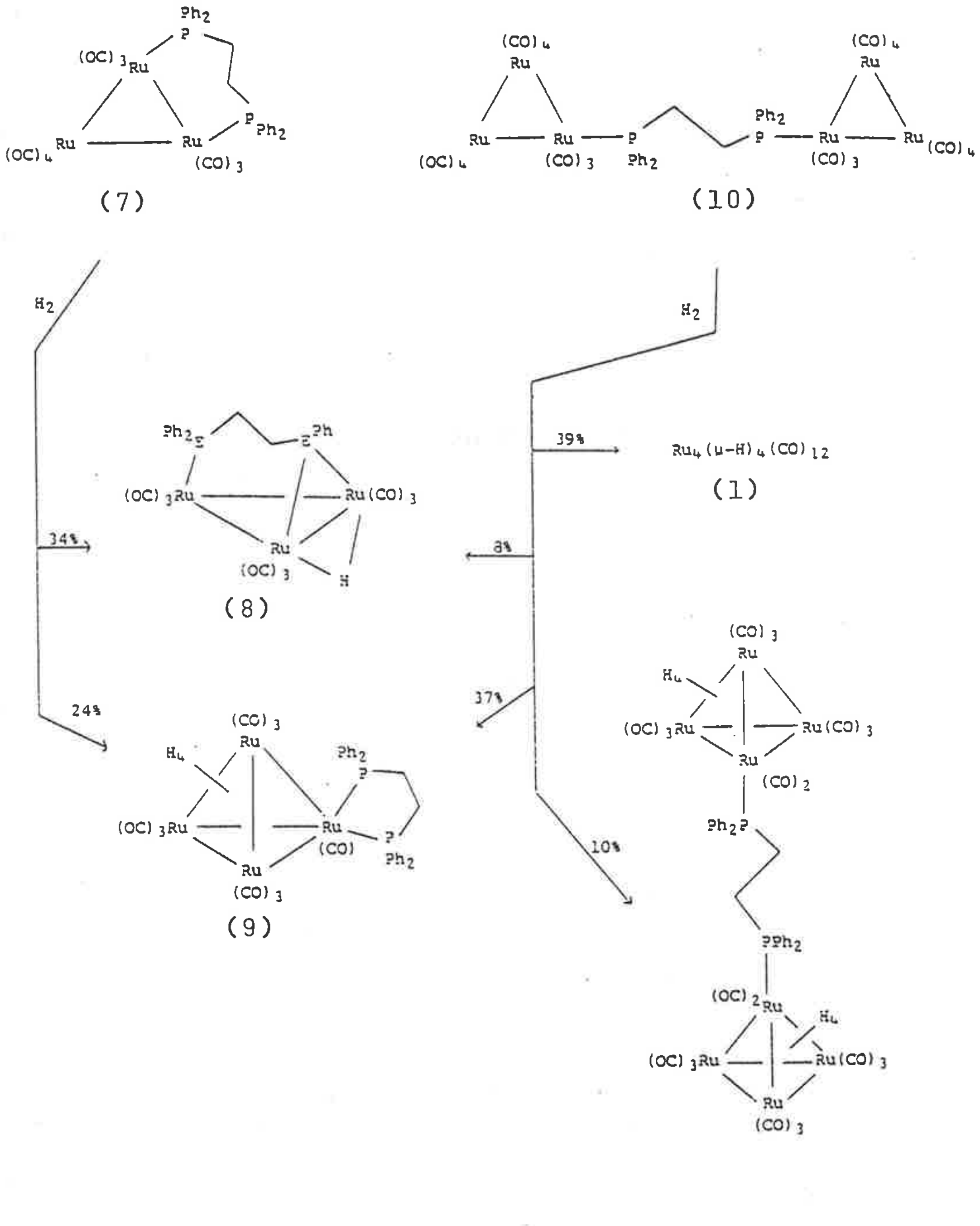
The chemistry of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** was also independently studied by Bonnet et al.[77]. The pyrolysis of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** yields $Ru_3(\mu\text{-}\eta^2\text{-PPhCH}_2\text{PPhC}_6\text{H}_4)(CO)_9$ **(5)** while both **(4)** and **(5)** react with dihydrogen to yield $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$ **(6)** (see Scheme 3). In contrast, the hydrogenation of $Os_3(\mu\text{-dppm})(CO)_{10}$ or $Os_3(\mu\text{-dppm})\{\mu\text{-PPh}_2\text{CH}_2\text{PPh}(C_6H_4)\}(CO)_{10}$[21] afforded $Os_3(\mu\text{-H})_2(\mu\text{-dppm})(CO)_8$[69,78].



(Scheme 3)

Hydrogenation of $Ru_3(dppe)(CO)_{10}$ **(7)** afforded two complexes, $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ **(8)** and $Ru_4(\mu\text{-}H)_4(dppe)(CO)_{10}$ **(9)**, in 34 and 23% yields, respectively (Scheme 4)[69]. Hydrogenation of $\{Ru_3(CO)_{11}\}_2(\mu\text{-}dppe)$ **(10)** afforded $Ru_4(\mu\text{-}H)_4(CO)_{12}$ **(1)** (39%) and $Ru_4(\mu\text{-}H)_4(dppe)(CO)_{10}$ **(9)** (37%) as the major products, accompanied by smaller amounts of $\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-}dppe)$ and $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9$ **(8)** (Scheme 4)[69].

(Scheme 4) Reactions of $Ru_3(CO)_{12}$-dppe complexes with $H_2$



Simple heating of $Ru_4(\mu\text{-}H)_4(dppm)(CO)_{10}$ **(11)** (80°C, 1h) gave $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}CO)_2(CO)_8$ **(12)**$^{69}$ in 76% yield, suggesting that the presence of a cluster-bonded hydride is necessary for dephenylation to occur. The molecular structures of **(11)** and **(12)** are shown in Fig. 2 and 3 respectively. Similarly, cleavage of the S-C bond has also been reported in the thermolysis or photolysis of $Os_3(\mu\text{-}H)(\mu\text{-}SAr)(CO)_{10}$$^{79}$.

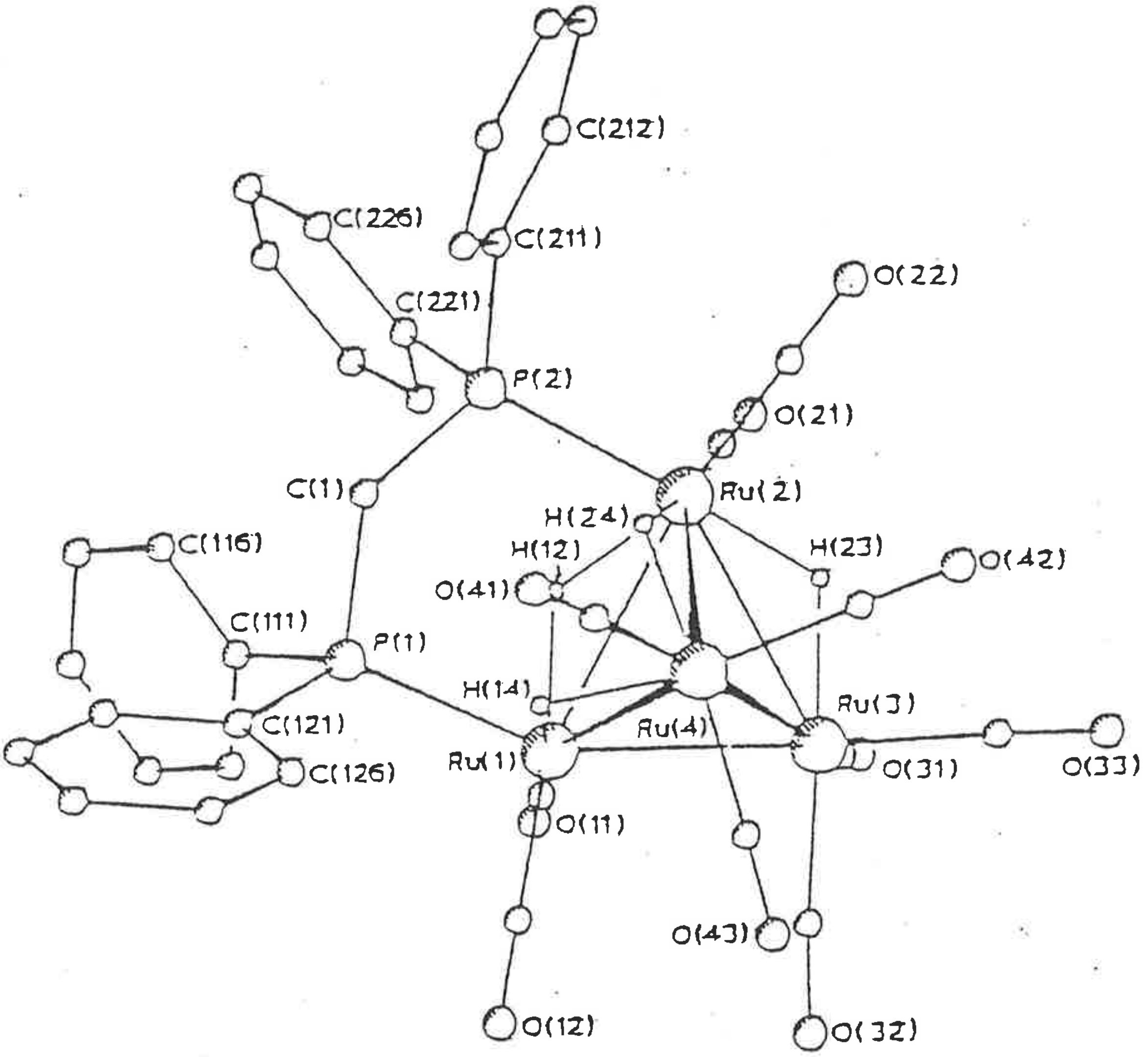


Figure 2 A molecule of $Ru_4(\mu\text{-}H)_4(\mu\text{-dppm})(CO)_{10}$ (11)

(by M.R. Snow and M.L. Williams)

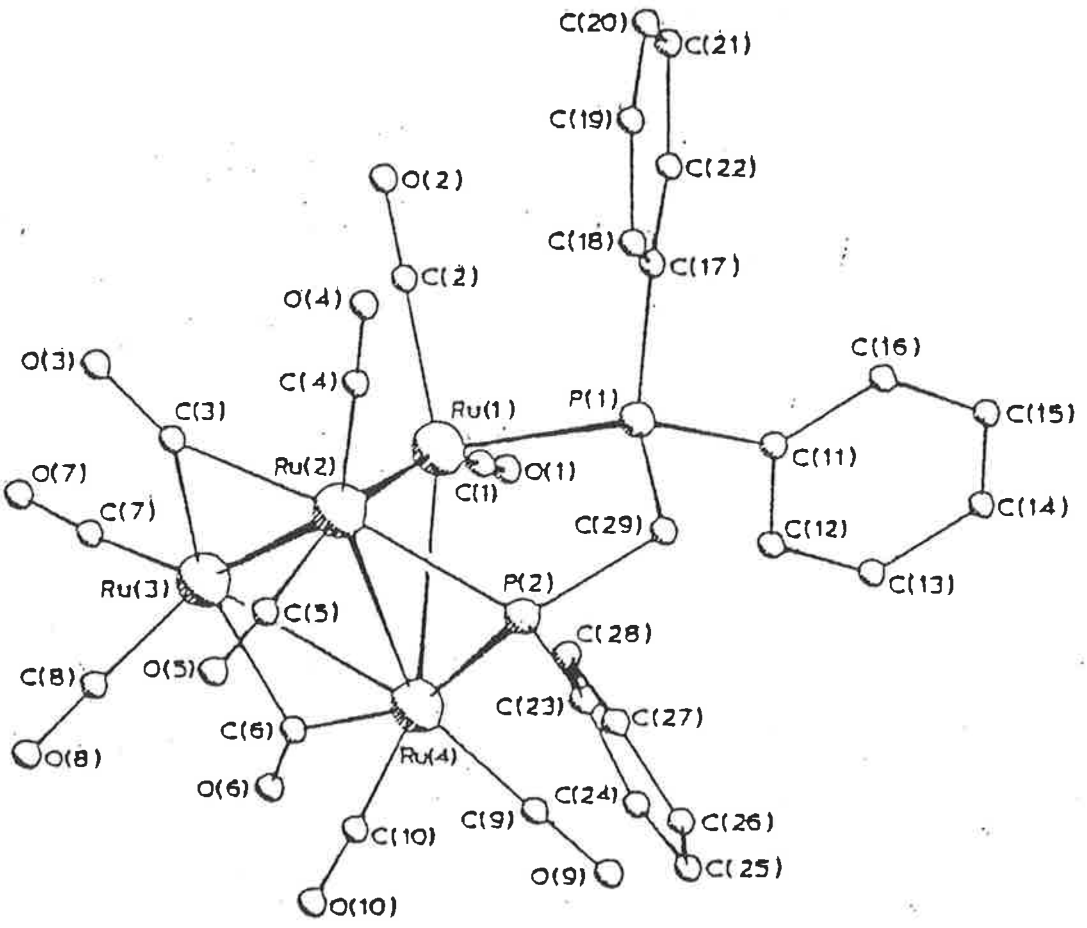


Figure 3  A Molecule of $Ru_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CO})_2(CO)_8$ (12)

(by M.R. Snow and E.R.T. Tiekink)

Interest in the use of sulphur, and of alkyl- and arylthiolate ligands, to cap cluster faces has arisen because of the expectation that such caps might hold the transition metal cluster together under the reaction conditions employed for catalytic hydrogenation or hydroformylation, for example[80]. Cluster carbonyls not containing capping ligands are often prone to degradation in these reactions[60].

The wide variety of bonding modes which sulphur can exhibit, and the reactivity of complexes of this type, can be said to culminate in the reactive sites of natural catalysts, such as those involved in nitrogen fixation or pyruvate metabolism[81]. Recent work, particularly by Adams and his group[82], has shown that the same propensity for linking transition metal atoms in cluster complexes is also found in sulphur-containing cluster complexes of osmium and, to a lesser extent, ruthenium.

The availability of a range of Group 15 ligand derivatives of $Ru_3(CO)_{12}$ from electron transfer-catalysed (ETC) substitution reactions of the parent carbonyls[25] prompted a study of their reactions with hydrogen. Representatives of complexes containing monodentate ligands were chosen and, after some preliminary studies, were hydrogenated under standard, mild conditions.

Hydrogenation of $Ru_3(LL)(CO)_{10}$ [(LL) = dppm or dpam] was also studied. We also chose to study the syntheses and some reactions of the complexes derived from $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(CO)_9$ **(14)** and $Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_9$ **(15)**.

The syntheses of $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(\mu\text{-dppm})(CO)_7$ **(16)** and $Ru_3(\mu\text{-H})(\mu_2\text{-SBu}^t)(\mu\text{-dppm})(CO)_8$ **(17)** were also studied and the results of hydrogenation of these complexes are compared with extensive investigation of similar complexes containing Group 15 donor ligands.

## 2. RESULTS AND DISCUSSION

### (a) Complexes containing monodentate ligands

Solutions of the complexes $Ru_3(CO)_{12-n}(L)_n$ [L = $PMe_3$, $PPh_3$, $PPh(OMe)_2$, $P(OMe)_3$; n = 1-3 in each case] in cyclohexane were hydrogenated (20 atm, 80°C, 2 h), and the products were separated by preparative thin layer chromatography (TLC). The yellow complexes so formed were readily identified as the tetranuclear derivatives $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(L)_n$[85-91,115], as detailed in Table 4 and in the Experimental section. Where these complexes were new, they were also made and characterised by appropriate reactions between $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and L.

In all cases, mixtures of complexes were obtained; the percentage yields quoted in Table 4 (following p. 41) relate to isolated, pure material. In four cases, small amounts of the trinuclear precursors were recovered. However, we had no evidence of the formation of any complexes containing modified ligands, for example, by P-C or P-O bond cleavage, except possibly in the case of the $P(OMe)_3$ complex, where the reaction mixture was found to contain other complexes in trace amounts only; these were not investigated further.

Interpretation of the results is complicated by the following features:

(i) disproportionation of mixtures of $Ru_3(CO)_{12}$[83] or $Ru_3(CO)_{11}\{P(OMe)_3\}$ with $Ru_3(CO)_9\{P(OMe)_3\}_3$ gives $Ru_3(CO)_{12-n}\{P(OMe)_3\}_n$ (n = 1-3) on heating;

(ii) under the same conditions, disproportionation of mixtures of $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(L)_n$ also occurs.

(iii) exchange of CO between $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ occurs, but not exchange of one metal for another[83], although both $Fe_2Ru(CO)_{11}\{P(OMe)_3\}$ and $FeRu_2(CO)_{10}\{P(OMe)_3\}_2$ are formed by heating a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_9\{P(OMe)_3\}_3$, suggesting that the tertiary phosphite does not migrate from ruthenium to iron[83];

(iv) disproportionation of mixtures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ to give $Ru_nOs_{3-n}(CO)_{12}$ occurs on heating[84];

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

(vi) direct, reversible substitution of 2H for CO is well-established for several metal cluster complexes, and although we have not observed the reaction

$$Ru_3(CO)_{12-n}(L)_n + H_2 \rightarrow Ru_3H_2(CO)_{11-n}(L)_n + CO$$

it is reasonable to consider that reactions of this type are among the first to occur under hydrogenation conditions. The extent to which similar substitution of L by $H_2$, and also by CO, might occur under these conditions could not be determined.

Our results, therefore, show that hydrogenation of $Ru_3(CO)_{12-n}(L)_n$ is not a viable synthetic route to complexes $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(L)_n$, since we find that mixtures of products are obtained. The route of choice remains the radical-ion initiated stoichiometric substitution of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ or its derivatives[25]. Nor do our results suggest any more than possible courses of the cluster formation, although we favour initial oxidative addition of $H_2$ to the substituted cluster followed by cleavage of one of the Ru-Ru bonds to give mono- or bi-nuclear intermediates which can then reaggregate to the tetranuclear complexes. However, the mononuclear fragments would also rapidly form stable mononuclear dihydrido complexes, which were not detected in the reaction mixtures.

### (b) Complexes containing bidentate ligands
### Derivatives of dppm and dpam

As mentioned above, reactions of complexes $Ru_3(CO)_{12-2n}(LL)_n$ (n = 1 or 2) with $H_2$ result in loss of arene and formation of derivatives containing $\mu_3$-$EPhCH_2EPh_2$ (E = P or As) ligands[44,69]. More recently, similar reactions of $Fe_2(CO)_9$ with $PR_2CH_2PHR$ (R = Me, $Pr^i$, $CH_2Ph$) to give $Fe_3$ clusters containing similar $\mu_3$-$PRCH_2PR_2$ ligands has been described[92]. Pyrolysis of cluster hydrides containing $\mu_3$-SR ligands also results in alkane or arene loss[93].

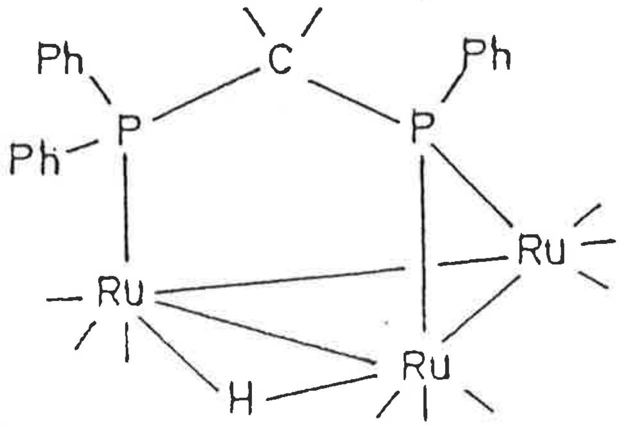
We have now found that prolonged treatment of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** or $Ru_3(\mu\text{-H})(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ **(6)** with dihydrogen results in the formation of $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_8(PMePh_2)$ **(13)**. The complex, which forms yellow crystals, exhibits a six-band ν(CO) pattern, while the

$^1$H NMR spectrum contains the expected doublet at δ 2.14 for the $PMePh_2$ ligand, higher field doublets at δ -18.7 and -18.9, and aromatic resonances between δ 7.3-8.2.

The highest mass ion in the mass spectrum (centred on m/z 839) corresponds to the parent ion $[C_{27}H_{20}P_2O_8Ru_3]^+$; other major ruthenium-containing ions are formed by stepwise loss of eight CO groups followed by stepwise loss of three Ph groups. At m/z 305, the ion cluster corresponds to $[Ru_3]^+$. Strong doubly-charged ions $[M-nCO]^{2+}$ (n = 8-0) are also found. The compound was fully characterised by an X-ray structure determination (see below).

Formation of **(13)** occurs by addition of 2H to the cluster and to the bridging methylene of the $\mu_3$-$PPhCH_2PPh_2$ ligand in the precursor **(6)** to give a $PMePh_2$ ligand; the resulting cleavage of the P-C bond generates a phenylphosphinidene ligand which caps the $Ru_3$ core. Similar complexes have been obtained from $Ru_3(CO)_{12}$ and primary phosphines[94,95] and by pyrolysis of $Fe_3(\mu\text{-}H)(\mu_3\text{-}PRCH_2PR_2)(CO)_9$ (R = Me, $Pr^i$, $CH_2Ph$)[92].

Prolonged treatment of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** or $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ **(6)** with dihydrogen yields $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}CO)_2(CO)_8$ **(12)**. Complex **(12)** was also formed by heating $Ru_4(\mu\text{-}H)_4(dppm)(CO)_{10}$ **(11)** (see Introduction) (Figs. 2 & 3). The unusual formation of (11) or (12) from hydrogenation of **(4)** or (6) further indicates that cluster integrity can still be lost even in the presence of a potential $\mu_3$-bridging ligand under the reaction conditions employed.



(6)

### Structure of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (13)

The molecular structure of complex (13) (see Fig. 4) is similar to previously studied examples (Table 1). The three ruthenium atoms, which define an isosceles triangle, are capped on one side by the $\mu_3$-phenylphosphinidene ligand to give a distorted tetrahedral core. There are four other complexes containing the $Ru_3P$ core which have been structurally characterised previously, namely $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PPh_3)$[96] and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PR)(CO)_9$ [R = Ph[95], $C_6H_4OMe\text{-}4$[94] and $C_6H_{11}$[97]]; this type of complex has been obtained from reactions between $Ru_3(CO)_{12}$ and the corresponding $PH_2R$ reagents. As found previously, there are two long Ru-Ru bonds [Ru(1)-Ru(2) 2.934(1), Ru(1)-Ru(3) 2.942(1) Å] and one short bond [Ru(2)-Ru(3) 2.841(1) Å]. The hydride ligands were not located directly but the two long

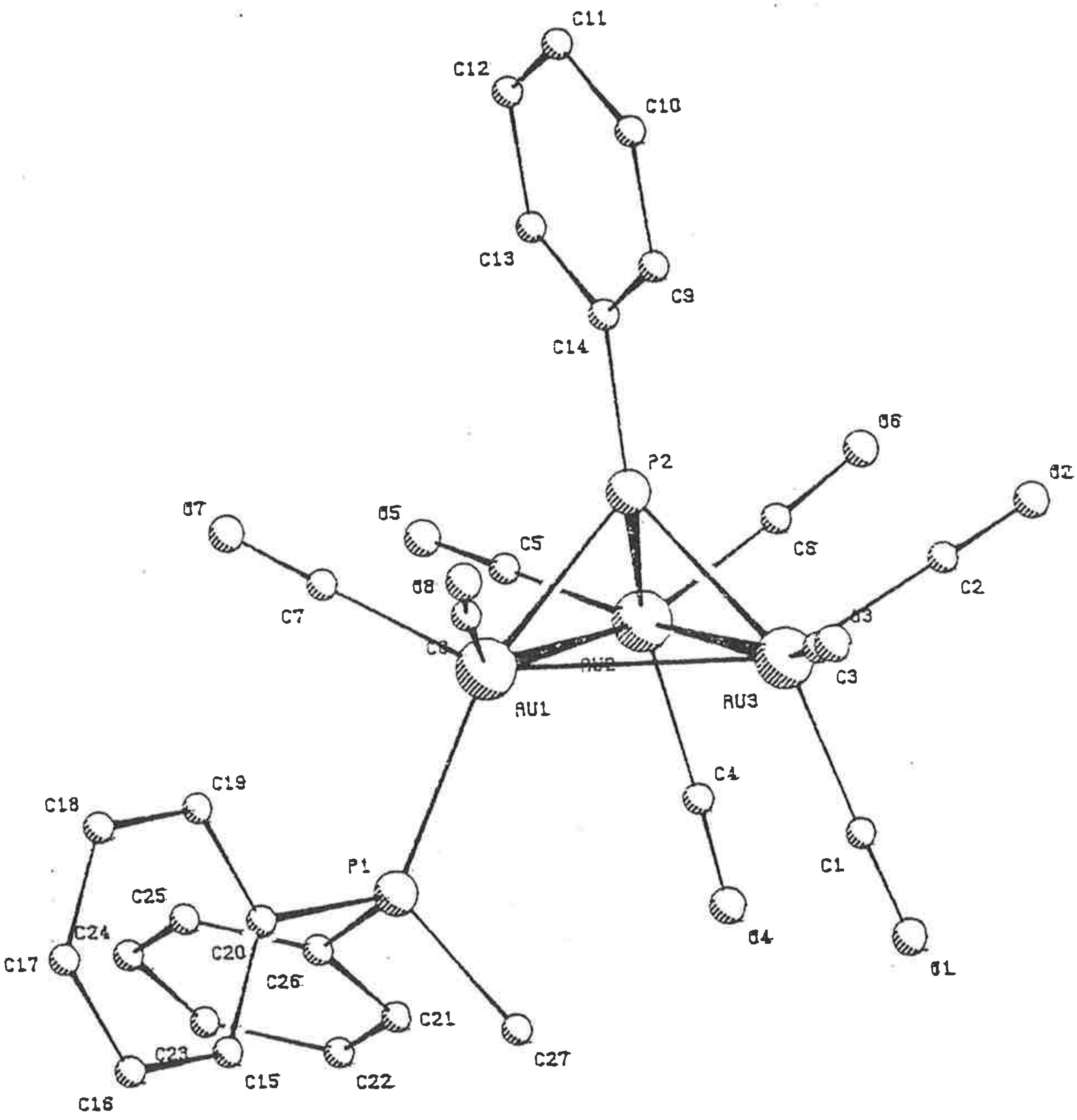
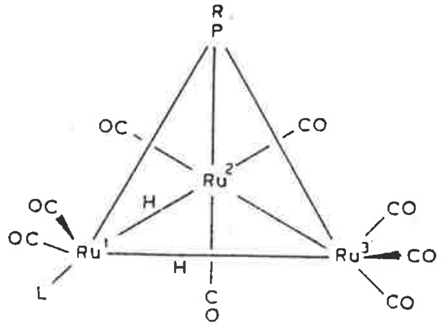


Figure 4 PLUTO plot of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PPh_2Me)$ (13) showing atom numbering scheme.

## TABLE 1 STRUCTURAL PARAMETERS FOR $Ru_3(\mu-H)_2(\mu_3-PPh)(CO)_9$ AND RELATED COMPLEXES

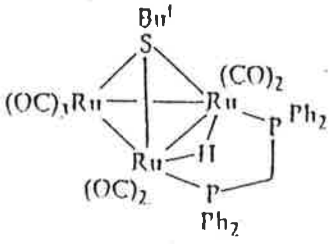


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| L = | $CO^{97}$ | $PMePh_2$ | $PPh_3{}^{96}$ | $CO^{94}$ | | $CO^{95}$ | |
| R = | $C_6H_{11}$ | Ph | Ph | $P(OC_6H_4Me-4)$ | | Ph | |
| <u>Bond lengths (Å)</u> | | | | | | | |
| Ru(1)-Ru(2) | 2.931(1) | 2.953(1) | 2.934(1) | 2.959(1) | 2.937(2) | 2.932(3) | 2.938(3) |
| Ru(1)-Ru(3) | 2.953(1) | 2.930(1) | 2.942(1) | 2.958(1) | 2.928(2) | 2.939(3) | 2.947(3) |
| Ru(2)-Ru(3) | 2.830(1) | 2.833(1) | 2.841(1) | 2.842(1) | 2.844(2) | 2.849(3) | 2.842(3) |
| Ru(1)-P(1) | - | - | 2.366(2) | 2.408(1) | - | - | - |
| Ru(1)-P(2) | 2.331(3) | 2.288(3) | 2.310(2) | 2.304(1) | 2.320(4) | 2.329(5) | 2.333(5) |
| Ru(2)-P(2) | 2.291(3) | 2.333(3) | 2.296(2) | 2.282(1) | 2.275(4) | 2.288(5) | 2.296(5) |
| Ru(3)-P(2) | 2.291(3) | 2.285(3) | 2.303(2) | 2.284(1) | 2.273(4) | 2.278(5) | 2.279(5) |
| Ru-CO(av) | 1.891 | 1.898 | 1.906 | 1.916 | 1.94 | 1.939 | 1.918 |
| range | 1.85 - 1.94 | 1.83 - 1.97 | 1.894 - 1.937 | 1.892 - 1.961 | 1.89 - 2.05 | 1.895 - 1.985 | 1.367 - 1.969 |
| <u>Bond angles (deg)</u> | | | | | | | |
| Ru(2)-Ru(1)-P(1) | | 112.2(1) | 117.1(1) | | | | |
| Ru(3)-Ru(1)-P(1) | | 114.7(1) | 119.5(1) | | | | |
| P(2)-Ru(1)-P(1) | | 160.0(1) | 164.8(1) | | | | |

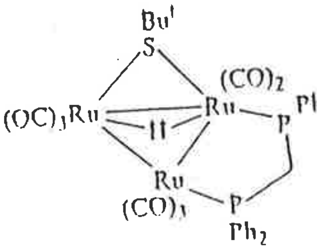
Ru-Ru distances and the positions of the equatorial CO groups on these two edges, suggest that they bridge Ru(1)-Ru(2) and Ru(1)-Ru(3) occupying the cavities formed by the splayed-out CO groups. The eight CO ligands are all in terminal positions and are distributed three each to Ru(2) and Ru(3), and two to Ru(1). The latter metal atom is also associated with the $PMePh_2$ ligand [Ru(1)-P(1) 2.366(2) Å], which occupies an axial site. This arrangement is similar to that found in $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PPh_3)$ [Ru-P 2.408(1) Å][96]. The $\mu_3$-<u>P</u>Ph-Ru bond distances [Ru(1)-P(2) 2.310(2); Ru(2)-P(2) 2.296(2), Ru(3)-P(2) 2.303(2) Å] show a similar pattern to those observed in the other $Ru_3(\mu\text{-}H)_2\text{-}(\mu_3\text{-}PR)(CO)_8(L)$ complexes [L = CO, R = Ph, $C_6H_4OMe\text{-}4$, $C_6H_{11}$; L = $PPh_3$, R = Ph][94-97] where the longer Ru-P distance is associated in all cases with the Ru atom bonded to both hydride ligands. The unusual formation of **(13)** is in effect a net conversion of the dppm ligand to benzene, coordinated phenylphosphinidine and $PMePh_2$ mediated by the cluster.

## (c) Complexes containing sulphur ligands

The complex $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(CO)_9$ **(14)** is a known compound, and was prepared in 69% yield from $Ru_3(CO)_{12}$ and $Bu^tSH$ in refluxing heptane[98]. Sodium diphenylketyl- or [ppn][OAc]-catalysed substitution of CO groups in $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(CO)_9$ **(14)** by dppm afforded two products, identified as the hepta- and octa-carbonyl complexes **(16)** and **(17)**. X-ray crystallographic studies of these two compounds showed that in **(16)** (Fig. 5), the $SBu^t$ ligand acts as a five-electron donor to the cluster, capping the $Ru_3$ face, while in **(17)** (Fig. 6), it acts as a three-electron donor, bridging one of the Ru-Ru edges[99]. In both cases the dppm ligand bridges two of the ruthenium atoms, the P atoms occupying equatorial positions; in **(16)** the dppm bridged Ru atoms are also attached to sulphur. The hydride ligand is thought to bridge the Ru-Ru bond bridged by the dppm ligand. In **(17)**, the dppm ligand also occupies equatorial positions on the two metal atoms; in this case, the hydride bridges the Ru-Ru bond bridged by the $SBu^t$ ligand.



**16**



**17**

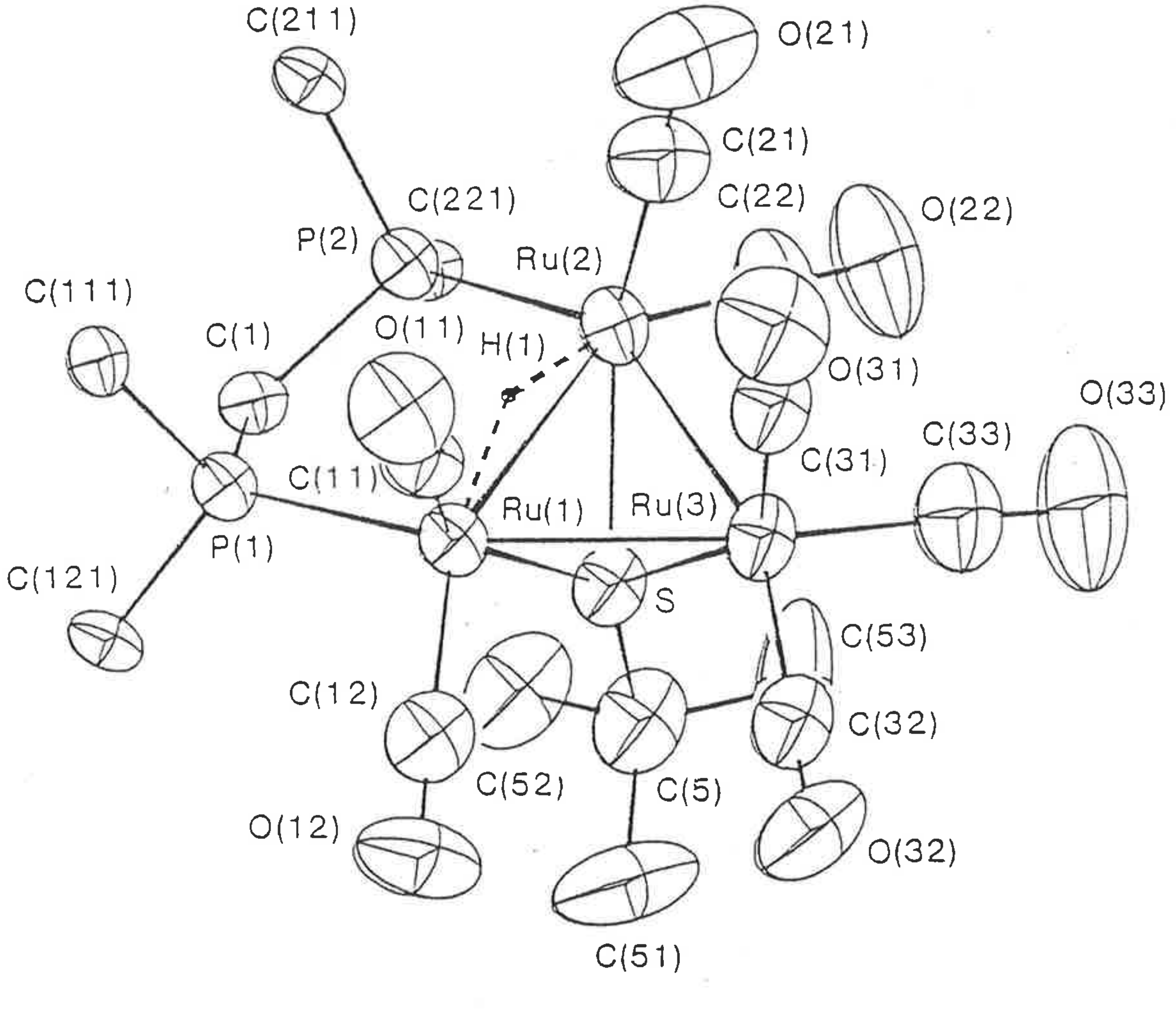


Figure 5 ORTEP plot of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(\mu\text{-}dppm)(CO)_7$ **(16)**. Only the ipso carbon atoms of the phenyl groups are shown here and in Fig 6 (by F.W.B. Einstein and A.C Willis)

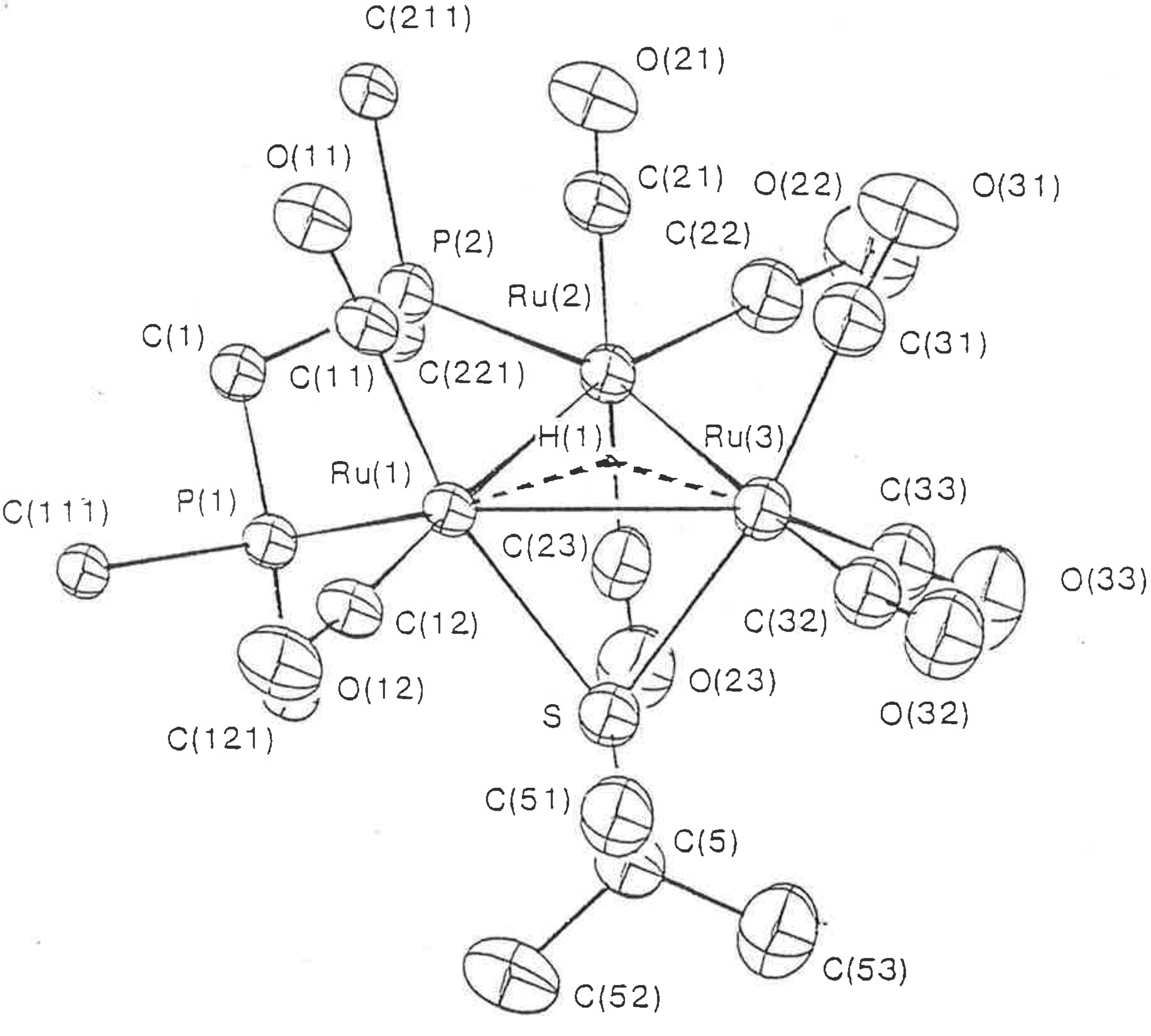
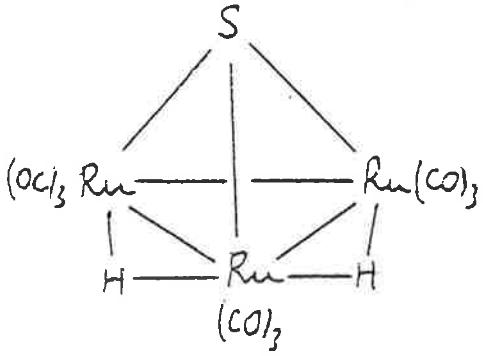


Figure 6 ORTEP plot of $Ru_3(\mu\text{-}H)(\mu\text{-}SBu^t)(\mu\text{-}dppm)(CO)_8$ (17)

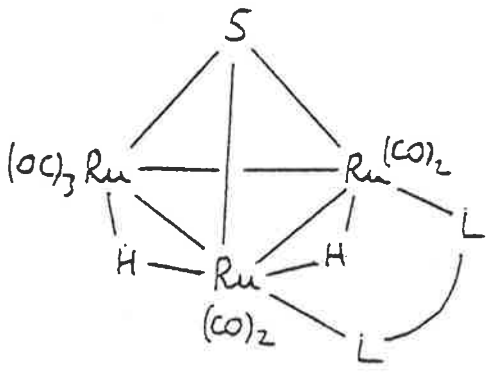
(by F.W.B. Einstein and A.C. Willis)

The physical properties of **(16)** and **(17)** are consistent with their solid-state structures. The complex ν(CO) spectra suggest the presence of isomers in solution, while the single metal-bonded proton resonates at δ -18.2 in **(16)** and -15.5 in **(17)**. Examination of spectra obtained at 400 MHz showed a small (< 3Hz) splitting for each component of the ca 33 Hz doublet for **(17)**. The solution of **(16)** initially exhibited a triplet resonance, but on standing a broad unresolved signal at δ -17.6 slowly grew in intensity, reaching an equilibrium intensity ratio of 1/3.5. This may result from a slow isomerisation by change in configuration of the Ph groups of the dppm ligand.

The formation of both **(16)** and **(17)** in the reaction of **(14)** with dppm is of interest. Evidently, substitution of CO and following displacement of one of the sulphur lone-pairs from the adjacent ruthenium atom by the second phosphorus atom is competitive with displacement of the second CO molecule from this metal atom. We find that interconversion of **(16)** and **(17)** can be achieved readily, either by heating **(17)** in octane for 1.5 hours, or by carbonylating **(16)** under mild conditions. In each case, conversion of one complex to the other is quantitative, and TLC shows no evidence for the formation of any other products. The interchange between $\mu_2$ and $\mu_3$ modes of bonding of sulphur-ligand coordination has also been observed for the cluster $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ **(14)**[98] and also the isopropyl analogue[103] of **(14)**. Even more interesting is the reaction of $Os_3(\mu\text{-}H)(\mu_3\text{-}SR)(CO)_9$ [R = Me or Et] with ethylene, where a change to μ-SR releases a coordination site for the olefin under mild conditions[100].



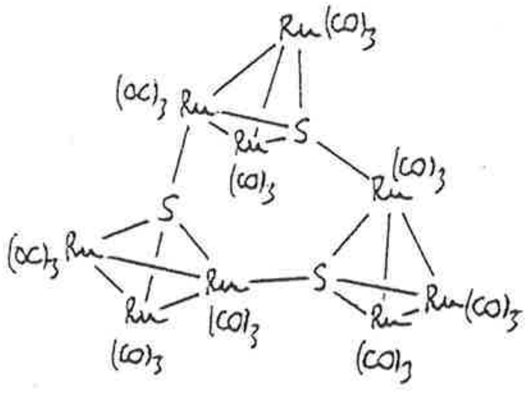
(15)



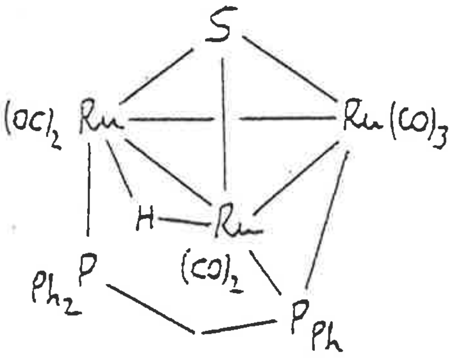
(18) L-L = $Ph_2PCH_2PPh_2$

(19) L-L = $Ph_2AsCH_2AsPh_2$

(20) L-L = $Ph_2PCH=CHPPh_2$



(21)



(22)

Some related cluster complexes derived from $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ **(15)** were also made. The parent complex can be obtained in high yield from $Ru_3(CO)_{12}$ and hydrogen sulphide in refluxing heptane[98]. ET-catalysed reactions[25] of **(15)** with dppm, dpam and ebdp [cis-1,2-ethenebis(diphenylphosphine), $CH(PPh_2)=CH(PPh_2)$] afforded the complexes $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dppm})(CO)_7$ **(18)**, $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dpam})(CO)_7$ **(19)** and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-ebdp})(CO)_7$ **(20)**, respectively. Complexes **(18)** and **(19)** were also obtained from reactions between $H_2S$ and $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** or $Ru_3(\mu\text{-dpam})(CO)_{10}$, respectively.

These complexes were characterised by microanalytical and spectroscopic methods, and in the case of **(20)**, by an X-ray structure determination (see below). Spectroscopic data are to be found in the Experimental section; the presence of the metal-bonded hydrogens, for example, was confirmed by the observation of high-field resonances at $\delta$ -18.0 **(18)**, -18.2 **(19)** and -17.9 **(20)**, all of which fall in the region normally associated with bridging hydrogens.

## Hydrogenation reactions

The reaction between **(14)** and dihydrogen (20 atm, 80°C, 20 h) resulted in almost quantitative conversion to the known $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ **(15)**. Cleavage of the S-Bu$^t$ bond to give $CHMe_3$ (undetected) and sulphur, which acts as a five-electron donor to the $Ru_3$ cluster, has occurred. This type of reaction has been reported previously, for example, in the thermolysis or photolysis of $Os_3(\mu\text{-}H)(\mu\text{-SAr})(CO)_{10}$ (Ar = Ph, $C_6F_5$)[79]; dissolution of $Ru_3(\mu\text{-}H)(\mu_3\text{-SEt})(CO)_9$ in concentrated $H_2SO_4$ resulted in protonation of the complex; subsequent heating and dilution with water resulted in isolation of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ **(15)**[101].

Hydrogenation of either of the complexes **(16)** or **(17)** afforded $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dppm})(CO)_7$ **(18)**, identified by comparison with the compound obtained from **(15)** and dppm. Similar reactions with **(20)** gave a multitude of products, as evidenced by a multi-hued TLC plate, and we have not pursued this reaction further. In contrast, we have found that the $\mu_3$-S complexes **(15)**, **(18)**, **(19)** and **(20)** do not react with $H_2$ under the conditions in which cleavage of the S-$Bu^t$ bond occurs. In none of our reactions did we obtain any evidence for the formation of $\{Ru_3(\mu\text{-}H)_2(\mu_4\text{-}S)(CO)_8\}_3$ **(21)** or related molecules; **(21)** was obtained on pyrolysis of **(15)** in 25% yield by Adams and co-workers[102].

## Structure of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-ebdp})(CO)_7$ **(20)**

The molecular structure of complex **(20)** (Fig. 7) is similar to that of the parent complex **(15)**[103] Tables 2 and 3 list significant bond lengths and angles. The three ruthenium atoms form an isosceles triangle, capped by the sulphur atom. Two of the Ru-Ru bonds are long [Ru(1)-Ru(2) 2.865(1), Ru(1)-Ru(3) 2.870(1) Å] and are only slightly shorter than the H-bridged Ru-Ru bonds in **(15)** [2.879(1), 2.882(1) Å]; the third, Ru(2)-Ru(3) [2.743(1) Å], is also commensurate with that in **(15)** [2.743(1), 2.760(1) Å, respectively]. Bonds from the metal atoms to sulphur [2.354(1), 2.357(1), 2.358(1) in **(20)**; 2.357(1), 2.360(1), 2.375(1) Å in **(15)**] also do not differ significantly in the two complexes. The ebdp ligand bridges Ru(1)-Ru(2) [Ru(1)-P(1) 2.332(1), Ru(2)-P(2) 2.319(1) Å], the P atoms coordinating in approximately equatorial positions; the Ru-P distances are similar to those in $Ru_3(\mu\text{-dppe})(CO)_{10}$ **(7)** [both are 2.330(2) Å][26], or $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** [2.322(2), 2.334(2) Å][107]. Interestingly, the Ru-Ru distance bridged by the bidentate phosphine in the former complex is 2.8956(1) Å, so that any lengthening as a result of the presence of the hydrogen atom in **(20)** cannot be detected. The hydrogen atoms were located in the X-ray refinement, and bridge the Ru(1)-Ru(2) and Ru(1)-Ru(3) edges.

The CH=CH double bond of the ebdp ligand does not interact with the cluster; the seven CO ligands are distributed three to Ru(3), and two each to Ru(1) and Ru(2). In contrast with **(15)** the 'equatorial' Ru-C and Ru-P vectors are not coplanar with the $Ru_3$ triangle: the 'axial'

Ru-C vectors also deviate considerably from perpendicularity with the $Ru_3$ triangle.

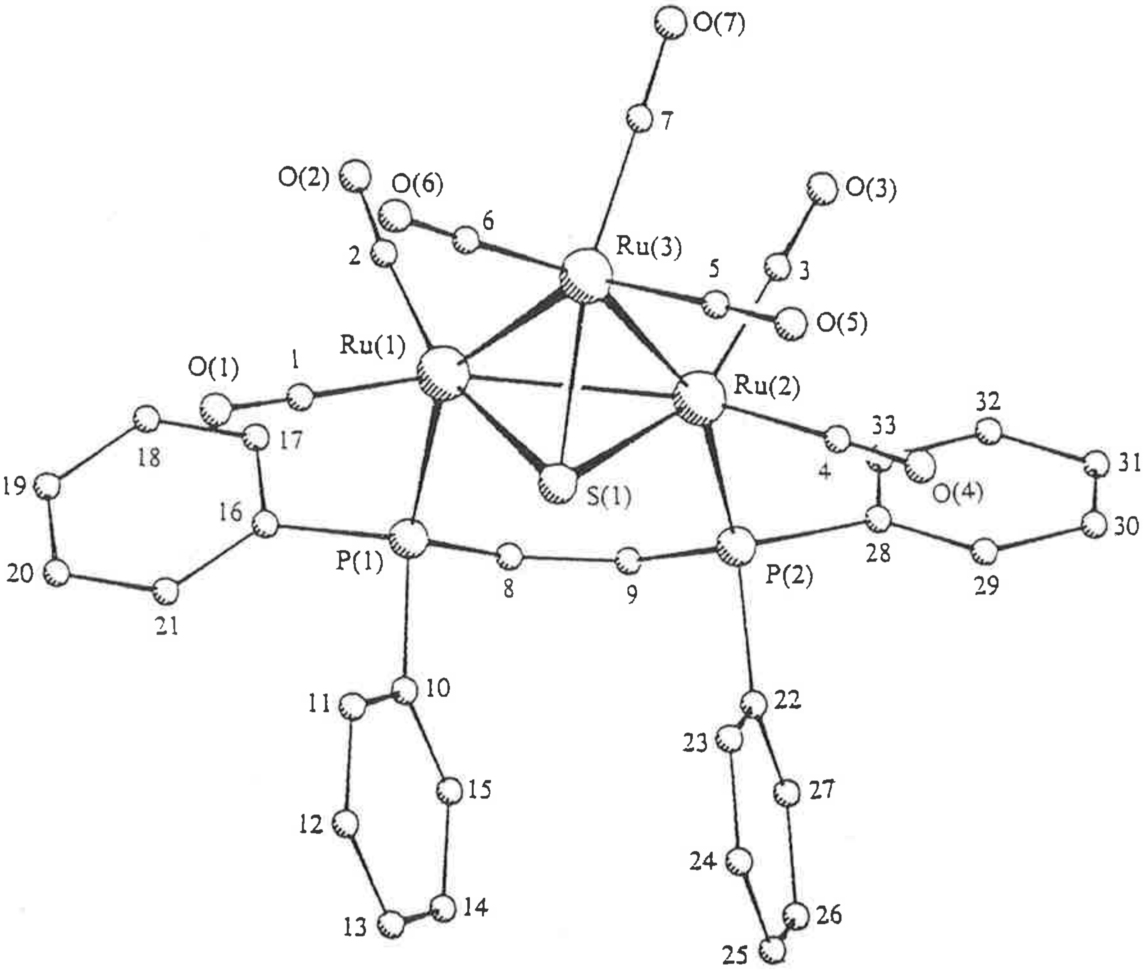


Figure 7 The molecular structure and numbering scheme for $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$ (20)

## Table 2 BOND DISTANCES (Å) FOR $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$ (20)

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| Ru(2) --- Ru(1) | 2.865(1) | Ru(3) --- Ru(1) | 2.870(1) |
| S(1) --- Ru(1) | 2.357(1) | Ru(1) --- Ru(1) | 2.882(1) |
| C(1) --- Ru(1) | 1.898(6) | C(2) --- Ru(1) | 1.898(6) |
| Ru(3) --- Ru(2) | 2.743(1) | S(1) --- Ru(2) | 2.358(1) |
| P(2) --- Ru(2) | 2.319(1) | C(3) --- Ru(2) | 1.889(6) |
| C(4) --- Ru(2) | 1.868(6) | S(1) --- Ru(3) | 2.354(1) |
| C(5) --- Ru(3) | 1.892(7) | C(6) --- Ru(3) | 1.930(6) |
| C(7) --- Ru(3) | 1.894(7) | C(8) --- P(1) | 1.798(5) |
| C(10) --- P(1) | 1.820(4) | C(16) --- P(1) | 1.816(4) |
| C(9) --- P(2) | 1.813(5) | C(22) --- P(2) | 1.828(3) |
| C(28) --- P(2) | 1.827(4) | O(1) --- C(1) | 1.135(7) |
| O(2) --- C(2) | 1.138(8) | O(3) --- C(3) | 1.131(8) |
| O(4) --- C(4) | 1.138(8) | O(5) --- C(5) | 1.134(8) |
| O(6) --- C(6) | 1.129(8) | O(7) --- C(7) | 1.137(9) |

Table 3 BOND ANGLES (DEG) for $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$ (20)

| Atoms | Angle |
|---|---|
| Ru(3) - Ru(1) - Ru(2) | 57.1(1) |
| S(1) - Ru(1) - Ru(3) | 52.4(1) |
| P(1) - Ru(1) - Ru(3) | 146.4(1) |
| C(1) - Ru(1) - Ru(2) | 144.1(2) |
| C(1) - Ru(1) - S(1) | 92.3(2) |
| C(2) - Ru(1) - Ru(2) | 115.3(2) |
| C(2) - Ru(1) - S(1) | 164.7(2) |
| C(2) - Ru(1) - C(1) | 97.7(2) |
| S(1) - Ru(2) - Ru(1) | 52.6(1) |
| P(2) - Ru(2) - Ru(1) | 102.5(1) |
| P(2) - Ru(2) - S(1) | 106.1(1) |
| C(3) - Ru(2) - Ru(3) | 102.0(2) |
| C(3) - Ru(2) - P(2) | 96.0(2) |
| C(4) - Ru(2) - Ru(3) | 95.8(2) |
| C(4) - Ru(2) - P(2) | 93.2(2) |
| Ru(2) - Ru(3) - Ru(1) | 61.3(1) |
| S(1) - Ru(3) - Ru(2) | 54.5(1) |
| C(5) - Ru(3) - Ru(2) | 92.9(2) |
| C(6) - Ru(3) - Ru(1) | 101.9(2) |
| C(6) - Ru(3) - S(1) | 105.7(2) |
| C(7) - Ru(3) - Ru(1) | 108.6(2) |
| C(7) - Ru(3) - S(1) | 149.3(2) |
| C(7) - Ru(3) - C(6) | 101.8(3) |
| S(1) - Ru(1) - Ru(2) | 52.6(1) |
| P(1) - Ru(1) - Ru(2) | 96.7(1) |
| P(1) - Ru(1) - S(1) | 95.8(1) |
| C(1) - Ru(1) - Ru(3) | 97.6(2) |
| C(1) - Ru(1) - P(1) | 93.8(2) |
| C(2) - Ru(1) - Ru(3) | 114.4(2) |
| C(2) - Ru(1) - P(1) | 95.0(2) |
| Ru(3) - Ru(2) - Ru(1) | 61.5(1) |
| S(1) - Ru(2) - Ru(3) | 54.3(1) |
| P(2) - Ru(2) - Ru(3) | 159.4(1) |
| C(3) - Ru(2) - Ru(1) | 111.3(2) |
| C(3) - Ru(2) - S(1) | 154.8(2) |
| C(4) - Ru(2) - Ru(1) | 148.7(2) |
| C(4) - Ru(2) - S(1) | 97.2(2) |
| C(4) - Ru(2) - C(3) | 93.5(3) |
| S(1) - Ru(3) - Ru(1) | 52.5(1) |
| C(5) - Ru(3) - Ru(1) | 146.5(2) |
| C(5) - Ru(3) - S(1) | 95.7(2) |
| C(6) - Ru(3) - Ru(2) | 158.9(2) |
| C(6) - Ru(3) - C(5) | 96.8(3) |
| C(7) - Ru(3) - Ru(2) | 96.1(2) |
| C(7) - Ru(3) - C(5) | 94.3(3) |
| Ru(2) - S(1) - Ru(1) | 74.8(1) |

**TABLE 3 (cont.)**

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| Ru(3) - S(1) - Ru(1) | 75.1(1) | Ru(3) - S(1) - Ru(2) | 71.2(1) |
| C(8) - P(1) - Ru(1) | 116.8(2) | C(10) - P(1) - Ru(1) | 118.1(1) |
| C(10) - P(1) - C(8) | 103.5(2) | C(16) - P(1) - Ru(1) | 111.5(1) |
| C(16) - P(1) - C(8) | 100.1(2) | C(16) - P(1) - C(10) | 104.6(2) |
| C(9) - P(2) - Ru(2) | 117.7(2) | C(22) - P(2) - Ru(2) | 118.7(1) |
| C(22) - P(2) - C(9) | 101.8(2) | C(28) - P(2) - C(22) | 112.5(1) |
| C(28) - P(2) - C(9) | 101.5(2) | C(28) - P(2) - Ru(1) | 102.2(2) |
| O(1) - C(1) - Ru(1) | 176.0(5) | O(2) - C(2) - Ru(1) | 175.1(5) |
| O(3) - C(3) - Ru(2) | 177.8(5) | O(4) - C(4) - Ru(2) | 178.2(5) |
| O(5) - C(5) - Ru(3) | 178.1(6) | O(6) - C(6) - Ru(3) | 178.2(6) |
| O(7) - C(7) - Ru(3) | 177.3(6) | O(9) - C(8) - P(1) | 130.6(4) |
| C(8) - C(9) - P(2) | 128.4(4) | Ru(2) - H(1') - Ru(1) | 101.3(1) |
| Ru(3) - H(2') - Ru(1) | 104.6(1) | C(23) - C(22) - P(2) | 120.5(2) |
| C(27) - C(22) - P(2) | 119.5(3) | C(29) - C(28) - P(2) | 118.2(3) |
| C(33) - C(28) - P(2) | 121.6(3) | C(11) - C(10) - P(1) | 119.2(3) |
| C(15) - C(10) - P(1) | 120.8(3) | C(17) - C(16) - P(1) | 118.2(3) |
| C(21) - C(16) - P(1) | 121.8(3) | | |

## 3. CONCLUSION

Hydrogenation of complexes $Ru_3(CO)_{12-n}(L)_n$ [L = $PMe_3$, $PPh_3$, $PPh(OMe)_2$; n = 1-3) under mild conditions (80°C, 20 atm, 2h) afforded a mixture of tetranuclear complexes $Ru_4(\mu\text{-}H)_4\text{-}(CO)_{12-m}(L)_m$, where m is not directly related to n. Clearly these reactions are complex and the present results do not allow any detailed speculation about mechanism. However, under the conditions used, little or no fragmentation of the coordinated Group 15 ligand occurs.

In contrast, cleavage of P-C or As-C bonds occurs in similar reactions of complexes $Ru_3(CO)_{10}(LL)$ (LL = dppm or dpam), with formation of $\mu_3$-phosphido-phosphine or $\mu_3$-arsenido-arsine ligands and the elimination of benzene. Further reaction of dihydrogen with a complex containing the $\mu_3$-$PPhCH_2PPh_2$ ligand resulted in fragmentation to give $\mu_3$-PPh and $PMePh_2$ ligands. In both cases, hydrogen also adds to the metal core.

How does P-C bond cleavage occur? After addition of hydrogen across a metal-metal bond to form a hydrido-cluster, intramolecular combination of a P-phenyl group and cluster-bonded H occurs to give arene and a P-metal bond. Our results do not require initial oxidative addition of the P-aryl group across a metal-metal bond, although the intermediacy of reactions of this type is suggested by the variety of products obtained by simply heating trinuclear tertiary phosphine-containing osmium clusters.

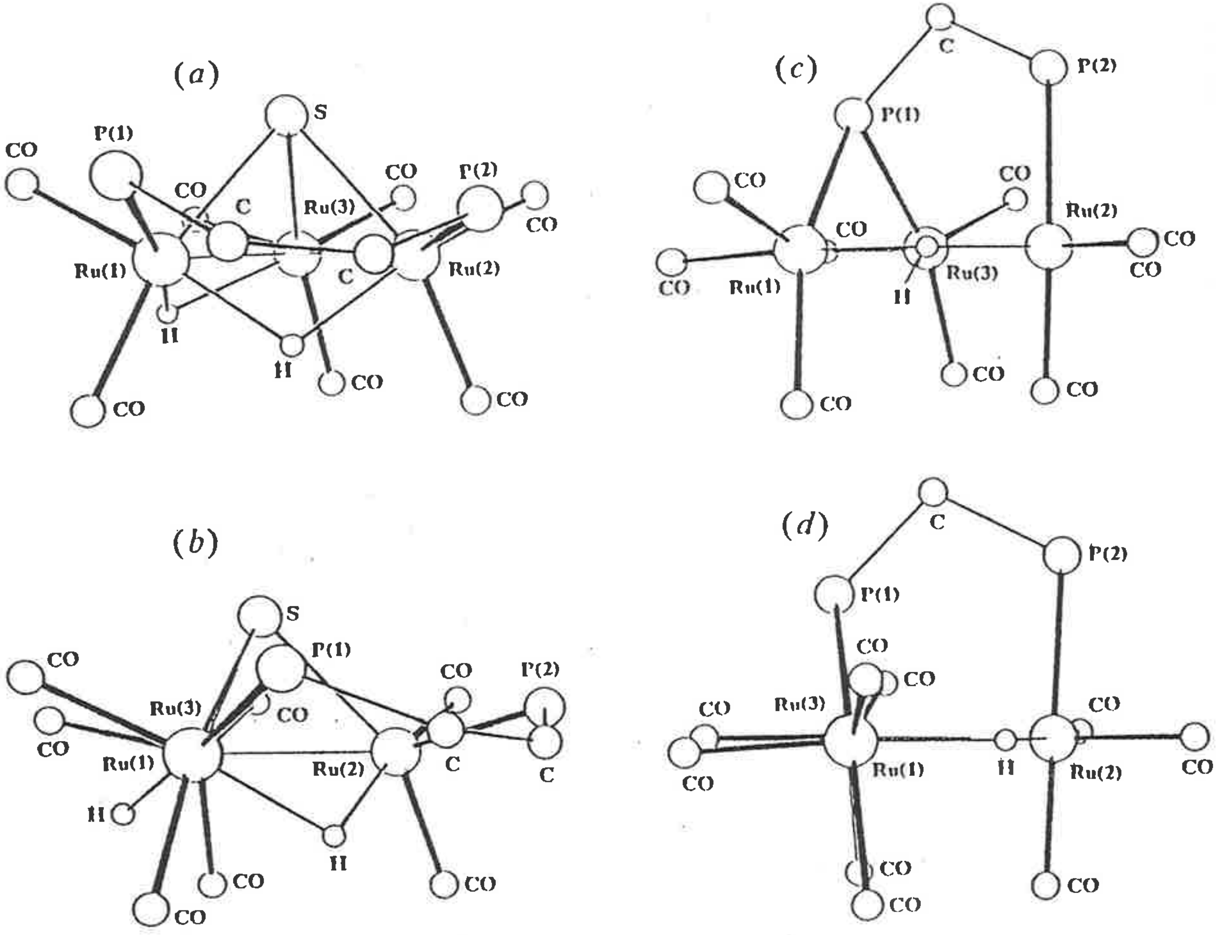
Comparisons of the cluster chemistry of ruthenium and osmium show that the latter are generally the more stable, and that their disproportionation does not occur so readily. The formation of $Os_3(\mu\text{-}H)_2(\mu\text{-dppm})(CO)_8$[69] by hydrogenation of $Os_3(dppm)(CO)_{10}$ is paralleled by the conversion of $Os_3(CO)_{12}$ to $Os_3(\mu\text{-}H)_2(CO)_{10}$; however, activation of the chelating bis-tertiary phosphine in $Ru_3(\mu\text{-dppm})(CO)_{10}$ appears to be greater than in $Os_3(dppm)(CO)_{10}$, since loss of arene and preservation of the $Ru_3$ cluster is found on hydrogenation, in contrast to the reaction of $Ru_3(CO)_{12}$ which affords the tetranuclear $Ru_4(\mu\text{-}H)_4(CO)_{12}$[66].

The above results do not suggest the absolute course of the formation of the tetranuclear clusters. However, we favour the initial oxidative addition of $H_2$ to the substituted cluster followed by cleavage of one of the Ru-Ru bonds to give mono or bi-nuclear fragments which can then reaggregate to the tetranuclear complexes.

These results bear out the conclusions of several other groups concerning the role of tertiary phosphines in modifying cluster complexes as potential cluster precursors. The Group 15 ligands are not inert under mild hydrogenation conditions, so that active species may contain μ-phosphido or $\mu_3$-phosphinidene ligands, which in turn may facilitate some or all of the steps in catalytic reactions by bridge-opening and creation of vacant coordination sites[73].

## Cleavage of S-C versus P-C bonds

An interesting feature of the chemistry reported above is the ready cleavage of the S-C bonds in the μ-thiolato clusters. Related dephenylation reactions, in which P-C or



<u>Figure 8</u> Views of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$ (20) and $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ (6); (a) and (c) along the $Ru_3$ plane, (b) and (d) down an Ru-Ru bond showing the disposition of the axial CO groups relative to the $Ru_3$ planes.

As-C bonds are cleaved, are characteristic of several cluster complexes containing dppm or dpam ligands. However, when both S-C and P-C bonds are present, as in $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(\mu\text{-}dppm)(CO)_7$ **(16)**, only dealkylation of the thiolato group occurs on pyrolysis or hydrogenation; no dephenylation of the cluster-bound dppm ligands occurs to give a complex such as **(22)**, even when reaction conditions considerably more vigorous than those required to dephenylate $Ru_3(\mu\text{-}dppm)(CO)_{10}$ **(4)** are used. We found that μ-thiolato or $\mu_3$-thio complexes could not be obtained from $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ **(6)** and $Bu^tSH$ or $H_2S$ under any conditions that we tried.

The major structural change which occurs upon dephenylation is a migration of the phosphorus ligand from two equatorial sites to three axial sites where it now functions as a face-capping group. We have considered further the structural and bonding requirements for this change. Figure 8 illustrates the cluster atom cores of (20) and of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$ **(6)**, from two viewpoints. It is apparent from these diagrams that the orbital requirements of the two face-capping groups differ, insofar as these can be assessed by probing the location of the bonding orbitals by looking at the alignment of the CO ligands on the side of the $Ru_3$ triangle opposite to that of the $\mu_3$-ligand. In the case of **(20)**, the three 'axial' CO groups are splayed outwards, and each is approximately <u>trans</u> to the $\mu_3$-S ligand. In contrast, the CO groups are almost normal to the $Ru_3$ plane in **(6)**. Thus it appears that for both types of $\mu_3$-ligand to be present on the same cluster, considerable reorganisation of the cluster orbitals must occur; our results suggest that this is an unfavourable process energetically, at least under our reaction conditions.

In this connection it is interesting to note that both faces of an $Ru_3$ cluster can be capped by two $\mu_3$-$EPhCH_2EPh_2$ ligands (E = P or As) as found in $Ru_3(\mu\text{-H})_2(\mu_3\text{-EPhCH}_2\text{EPh}_2)_2(CO)_6$[44]. In the formation of these complexes, dephenylation of the intermediate $Ru_3(\mu\text{-H})(\mu_3\text{-EPhCH}_2\text{EPh}_2)(\mu\text{-LL})(CO)_7$ (LL = dppm or dpam) results in formation of the second face-capping ligand which can readily interact with appropriate orbitals which are approximately normal to the $Ru_3$ plane, that is, similar to those involved in bonding the axial CO ligands in **(6)** [as shown in Fig. 8, (c) and (d)]. In general, the presence of a face-capping ligand attached by a single atom (S, O or C) serves to inhibit alteration of bridging dppm or dpam ligands by dephenylation. Examples of the 'stabilisation' of cluster-bonded dppm in this way now include the complexes $Ru_3(\mu_3\text{-O})(\mu_3\text{-CO})(\mu\text{-dppm})_2(CO)_5$[105] and $Co_3(\mu_3\text{-CMe})(\mu\text{-dppm})(CO)_7$[106] in addition to the complexes described above.

These observations may have some relevance to the problem of activation of clusters for use as potential catalyst precursors.

## 4. EXPERIMENTAL

### General Experimental Procedures

A dry nitrogen atmosphere was used routinely for (i) distilling solvents before use as described in Vogel[121] and (ii) carrying out all reactions (unless stated otherwise), but no special precautions were taken to exclude air during work-up procedures. Light petroleum refers to a fraction of b.p. 62-65°C.

$Ru_3(CO)_{12}$[7], $Ru_4(\mu\text{-}H)_4(CO)_{12}$[66] and Group 15 ligand-substituted derivatives[25] were prepared by the cited literature methods. Group 15 ligands were commercial products, and used as received from BDH, England ($PPh_3$) or Strem Chemicals, Newburyport, U.S.A. (others).

Chemical reagents were commercial products and were used as received. High purity nitrogen and hydrogen were obtained from Commonwealth Industrial Gases (CIG) Limited and carbon monoxide (high purity) from Matheson Gas Products; gases were used as received.

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

Column chromatography was carried out on columns of Florisil initially packed in light petroleum.

Thin layer chromatography was carried out on preparative plates (20 x 20 cm) coated with silica Kieselgel $60GF_{254}$ (0.5 mm thick).

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

Infrared Spectra were recorded (using sodium chloride solution cells) on a Perkin Elmer 683 double beam infrared spectrophotometer and were calibrated with polystyrene (1601 $cm^{-1}$).

N.M.R. Spectra were recorded on Bruker WP80DS ($^{1}H$, 80 MHz, $^{13}C$, 20.1 MHz) instruments. Deuterated solvents were required for the deuterium resonance lock and were used in 2.5, 5 or 10mm tubes. Shifts were reported relative to internal $SiMe_4$ ($^{1}H$, $^{13}C$).

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

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically $10^{-6}$ mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca 0.5 M solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip. Spectra are reported below in the form: $m/z$, assignment, relative intensity; multi-isotopic species are normalised on the most abundant metal isotopes, e.g. $^{56}Fe$, $^{58}Ni$ and $^{184}W$.

## Crystallography

The X-ray crystallographic work was performed on a Enraf-Nonius CAD4 four-circle diffractometer. The CAD4 is a fully automated machine and required no specific crystal alignment. All the crystallographic work was performed in an airconditioned environment at 21°C.

General techniques and details given below apply to the two crystal structure analyses performed by the author.

Suitable crystals were mounted on a glass fiber and coated with cyanoacrylate super glue. Lattice parameters were determined from a least-squares fit to the setting angles of 25 high angle reflections on an Enraf-Nonius CAD4 four-circle diffractometer with monochromated Mo-$\underline{K}\alpha$ radiation.

Intensity data were measured using a $\underline{\omega}$-(n/3)$\theta$ scan where $\underline{n}$ was optimised by a $\underline{\omega}/\theta$ profile and scan analysis. The $\underline{\omega}$ scan angles and horizontal counter apertures were varied according to ($\underline{A}$ + $\underline{\mathrm{Btan}\theta}$)° and ($\underline{C}$ + $\underline{\mathrm{Dtan}\theta}$)mm respectively, where $\underline{A}$, $\underline{B}$, $\underline{C}$ and $\underline{D}$ depend on the half-width of the individual reflection and the wavelength of radiation used. The intensities of three standard reflections were monitored every 60 mins to check for crystal and machine stability.

Data reduction and application of Lorentz and polarization corrections were performed by the programme SUSCAD[107]. Absorption corrections were applied using the programme ABSORB[108]; crystal dimensions were determined with a microscope equipped with calibration scales.

Computing for all solution and refinement work was performed using the SHELX[109] system of programmes. Reflections with intensities $\underline{I} < 2.5\sigma(\underline{I})$ and systematically absent reflections were rejected, and equivalent reflections were averaged. Structures were solved by direct methods to give the metal atom positions, with all other non-hydrogen atoms being revealed in the Fourier difference maps of successive blocked-matrix least-squares refinements. Phenyl rings were included as rigid groups (C-C 1.395Å) with individual isotropic thermal parameters. Hydrogen atoms were placed in calculated positions (phenyl C-H 1.08Å, methylene C-H 0.97Å) with common group thermal parameters. In the final refinement cycles (with all non-hydrogen atoms and non-phenyl carbons anisotropic) the following weighting scheme was employed

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

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

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

$$\underline{Rw} = \frac{\Sigma w^{1/2}(||F_o| - |Fc||)}{\Sigma w^{1/2}(|F_o|)}$$

Bond lengths, valence angles, non-bonded distances and their standard deviations were all calculated using SHELX[109].

Diagrams were plotted using the programme PLUTO[110]. All programmes were implemented on the CYBER 173 computing system at the University of Adelaide.

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

## Preparation of $Ru_3(CO)_8[P(OMe)_3]_4$

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $P(OMe)_3$ (233 mg, 1.88 mmol) was heated in refluxing octane (25 ml) for 30 min. After this time, a trace of $Ru_3(CO)_9\{P(OMe)_3\}_3$

was present (TLC) together with a major product. On cooling to room temperature and allowing to stand overnight, a red crystalline complex separated from the solution. Filtration, washing with hexane (3 x 5 ml) and drying (0.1 mm Hg) afforded $Ru_3(CO)_8\{P(OMe)_3\}_4$ (280 mg, 87%), m.p. 160°C. Found: C 23.48, H 3.67; $C_{20}H_{36}O_{20}P_4Ru_3$ requires: C 23.47, H 3.54%. IR ($CH_2Cl_2$): ν(CO) 1990s(sh), 1975vs $cm^{-1}$. $^1H$ NMR: δ ($CDCl_3$) 3.61, m, OMe.

Preparation of $Ru_3(CO)_8[P(OPh)_3]_4$

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $P(OPh)_3$ (583 mg, 1.88 mmol) was heated in refluxing cyclohexane (30 ml) for 3 min. The product (orange powder) precipated out of solution. On cooling to room temperature, filtration, washing with light petroleum (3 x 10 ml) and drying (0.1 mm) afforded $Ru_3(CO)_8[P(OPh)_3]_4$ (495 mg, 90.4%), m.p. 147°(dec). Found: C 54.00, H 3.41, P 5.31 $C_{80}H_{60}O_{20}P_4Ru_3$ requires: C 54.34, H 3.42, P 7.01%; Found: M(FAB MS) 1769, calc. 1769. IR($CH_2Cl_2$): ν(CO) 2054w, 2003(sh), 1990s, IR(Nujol): ν(CO) bands 2060w, 2005s, 1978(br),s, 1953m, 1943m $cm^{-1}$. $^1H$ NMR: δ($CDCl_3$) 7.1m, Ph.

Reactions of substituted ruthenium cluster carbonyls with hydrogen

(a) Complexes containing monodentate tertiary phosphines or phosphites

Standard reaction conditions were as follows. The cluster was dissolved in cyclohexane in a glass liner. The glass liner was placed in a small laboratory autoclave and the apparatus was pressurized with hydrogen to 20 atmospheres. The reaction was left stirring at 80°C for 2 hours. After cooling, solvent was removed (rotary evaporator), and the residue was dissolved in the minimum amount of $CH_2Cl_2$. Separation was achieved by preparative TLC [Kieselgel $GF_{254}$ (type 60)] on glass plates (20 cm x 20 cm), developing with 1/9 acetone/petroleum ether. The products were identified by comparison with authentic samples (IR ν(CO) and TLC behaviour) and are summarised in Table 4.

(b) Characterisation of tetranuclear complexes

(a) $Ru_4(\mu\text{-}H)_4(CO)_{11}\{PPh(OMe)_2\}$, m.pt. 140°C (dec.). Found: C 25.88, H 1.66, P 3.10, $C_{19}H_{15}O_{13}PRu_4$ requires: C 25.74, H 1.71, P 3.49%. Infrared (cyclohexane): ν(CO) 2097m, 2092w(sh), 2070vs, 2060vs, 2034vs, 2018s(sh), 2010s, 1998m, 1981m $cm^{-1}$. $^1H$ NMR: δ($CDCl_3$) 7.5, m, 5H, PPh; 3.6, m, 6H, OMe; -17.6, m, 4H, RuH. Mass spectrum: $M^+$ at m/z 888 with ions formed by competitive loss of 11 CO and 2 OMe groups.

(b) $Ru_4(\mu\text{-}H)_4(CO)_{10}\{PPh(OMe)_2\}_2$, m.pt. 113°C. Found C 30.30, H 2.56; $C_{26}H_{26}O_{14}P_2Ru_4$ requires: C 30.36, H 2.55%. Infrared (cyclohexane): ν(CO) 2080s, 2059vs, 2044ms, 2025vs, 2014(sh), 2001vs, 1997(sh), 1987(sh), 1976m, 1972m, $cm^{-1}$. $^1H$ NMR: δ($CDCl_3$) 7.5, m, 10H, PPh; 3.5, m, 12H, OMe; -17.4, m, 4H, RuH. Mass spectrum: $M^+$ at m/z 1032 with ions formed by competitive loss of 10 CO and 4 OMe groups.

(c) $Ru_4(\mu\text{-}H)_4(CO)_9\{PPh(OMe)_2\}_3$, m.pt. 115°C. Found: C 33.71, H 3.09; $C_{33}H_{37}O_{15}P_3Ru_4$ requires: C 33.85, H 3.19%. Infrared (cyclohexane): ν(CO) 2066vs, 2036vs,

**Table 4 Products from reactions of $Ru_3(CO)_{12-n}(L)_n$ with $H_2$**

| L | n | $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(L)_n$ | | | | |
|---|---|---|---|---|---|---|
| | | n=0 | 1 | 2 | 3 | 4 |
| $P(OMe)_3$ | 1 | 7.1 | 57.9 | 4.0 | n.d. | n.d. |
| | 2 | 0.5 | 14.9 | 50.5 | 2.7 | n.d. |
| | 3[a] | n.d. | n.d. | 12.3 | 11.5 | 2.7 |
| $PMe_3$ | 1[b] | 2.8 | 67.6 | 13.4 | n.d. | n.d. |
| | 2[c] | n.d. | n.d. | 55.8 | 1.7 | n.d. |
| | 3[d] | n.d. | n.d. | 49.3 | n.d. | n.d. |
| $PPh(OMe)_2$ | 1 | 4.4 | 69.9 | 5.2 | 1.2 | n.d. |
| | 2 | n.d. | 34.2 | 43.9 | 10.4 | n.d. |
| | 3 | n.d. | 2.2 | 28.1 | 21.5 | n.d. |
| $PPh_3$ | 1 | 4.9 | 67.0 | 7.8 | n.d. | n.d. |
| | 2 | 1.7 | 62.8 | 10.8 | n.d. | n.d. |
| | 3 | n.d. | n.d. | 64.3 | n.d. | n.d. |

[a] 17.9% $Ru_3(CO)_9[P(OMe)_3]_3$ recovered; [b] 5.6% $Ru_3(CO)_{11}(PMe_3)$ recovered; [c] 33.3% $Ru_3(CO)_{10}(PMe_3)_2$ recovered; [d] 43.5% $Ru_3(CO)_9(PMe_3)_3$ recovered.

2016s, 1999s, 1905m, 1978m cm$^{-1}$. $^1$H NMR: δ($CDCl_3$) 7.4, m, 15H, PPh; 3.5, m, 18H, OMe; -17.3, m, 4H, RuH. Mass spectrum: M$^+$ at m/z 1167 with ions formed by competitive loss of 9 CO and 6 OMe groups.

## Reaction between $Ru_3(CO)_{11}\{P(OMe)_3\}$ and $Ru_3(CO)_9\{P(OMe)_3\}_3$

An equimolar mixture of the two complexes (0.084 mmol) was heated in refluxing cyclohexane (25 ml) for 1.5 h, when IR spectra showed the presence of all three complexes $Ru_3(CO)_{12-n}\{P(OMe)_3\}_n$ (n = 1, 2 and 3). After a further 18 h heating, evaporation of solvent and preparative TLC (developer, 1/9 acetone/petroleum ether) enabled isolation of $Ru_3(CO)_{11}\{P(OMe)_3\}$ (12.5 mg, 20.2%), $Ru_3(CO)_{10}\{P(OMe)_3\}_2$ (43.7 mg, 31.3%) and $Ru_3(CO)_9\{P(OMe)_3\}_3$ (28 mg, 35.9%), all of which were identified from their ν(CO) spectra. Several other complexes were present in trace amounts and but were not further investigated.

## Hydrogenation of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)**

(a) Under mild conditions - The reaction between $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** (in cyclohexane) and $H_2$ (80°C, 20 atm, 2 h) was carried out as previously described[111] to give $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$ **(6)** in 67% yield, together with $Ru_4(\mu\text{-H})_4(\mu\text{-dppm})(CO)_{10}$ **(11)** (12.6%) and recovered $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** (10%).

(b) Under more vigorous conditions - $Ru_3(CO)_{10}(dppm)$ (300 mg, 0.31 mmol) was dissolved in cyclohexane (70 ml) and the solution placed in the glass liner of a small autoclave. Hydrogen (high purity) was charged into the autoclave (20 atm) and mixture was heated at 80°C for

40 h. After cooling, solvent was removed (rotary evaporator), and the solid residue was dissolved in the minimum amount of $CH_2Cl_2$. Preparative TLC (3/17) acetone/petroleum ether gave three bands: Band 1, ($R_f$ = 0.89) contained the major product, yellow $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_8(PMePh_2)$ **(13)** (102 mg, 45.4%), m.p. 124°C, which was recrystallised from $CH_2Cl_2$/MeOH. Found: C 38.65, H 2.44; $C_{27}H_{20}Ru_3O_8P_3$ requires C 38.72, H 2.41%. Infrared (cyclohexane): ν(CO) 2077s, 2044vs, 2008vs, 1999(sh), 1996vs, 1980m $cm^{-1}$; $^1H$ NMR: δ($CDCl_3$) 7.27-8.18, m, 15H, <u>Ph</u>; 2.14, d, <u>J</u>(PH) 7.7 Hz, 3H, <u>Me</u>; -18.71, d, <u>J</u>(HP) 12.9 Hz, 1H, Ru<u>H</u>; -18.91, d, <u>J</u>(HP) 12.0 Hz, 1H, Ru<u>H</u>. Mass spectrum: $M^+$ at <u>m/z</u> 839 with ions formed by competitive loss of 8 CO and 3 Ph groups. Band 2, ($R_f$ = 0.83) contained $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9$ **(6)** (40 mg, 13.3%). Band 3, ($R_f$ = 0.72) contained $Ru_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2PPh_2)(CO)_{10}$ **(12)** (30 mg, 12.9%).

## Hydrogenation of $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9$ (6)

Complex **(6)** was hydrogenated (20 atm, 70°C) as described for $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** for 90 h. Preparative TLC afforded $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_8(PMePh_2)$ **(13)** (56.2%), $Ru_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2PPh_2)(CO)_{10}$ **(12)** (25.2%) and recovered $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9$ **(6)** (20%) as the major products; six other unidentified complexes were present in trace amounts only.

## Hydrogenation of $Ru_3(\mu\text{-dpam})(CO)_{10}$

### (a) Under mild conditions -

The hydrogenation of $Ru_3(\mu\text{-dpam})(CO)_{10}$ (80°C, 20 atm, 2 h) afforded $Ru_3(\mu\text{-H})(\mu_3\text{-AsPhCH}_2AsPh_2)(CO)_9$ in 65% yield[111].

(b) Under more vigorous conditions -

The reaction between $Ru_3(\mu\text{-dpam})(CO)_{10}$ (200 mg, 0.19 mmol) (in cyclohexane) and $H_2$ (80°C, 20 atm, 65 h) was carried out as described above in to give orange-yellow crystals of $Ru_3(\mu\text{-H})(\mu_3\text{-AsPhCH}_2\text{AsPh}_2)(CO)_9$[114] (105 mg, 58%) identified by comparison of its IR ν(CO) spectrum with that of an authentic sample[111].

## Preparation of $Ru_3(\mu\text{-H})(\mu\text{-SBu}^t)(CO)_9$ **(14)** and Group 15 ligand derivatives

### (a) $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(CO)_9$ **(14)**

Complex **(14)** was prepared by a literature method from $Ru_3(CO)_{12}$ and $Bu^tSH$[98].

### (b) $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(\mu\text{-dppm})(CO)_8$ **(17)**

(i) Sodium diphenylketyl (10 drops of a 0.025M solution in thf) was added to a mixture of (14) (150 mg, 0.23 mmol) and dppm (92 mg, 0.23 mmol) in dry deoxygenated thf (15 ml). After 15 min, evaporation and preparative TLC (developed with 2/3 acetone/light petroleum) of a dichloromethane extract of the residue allowed separation of red $Ru_3(\mu\text{-H})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_8$ **(17)** (118 mg, 52%) (recrystallised from n-heptane), m.p. 162°C. (Found: C, 45.04; H, 3.25; $C_{37}H_{32}O_8P_2Ru_3S$ requires: C, 44.38, H, 3.22%). Infrared (cyclohexane): δ(CO) at 2069s, 2046w, 2025m, 2012vs, 1998s(sh), 1983m, 1971m, 1960w, 1949w, 1941w $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 7.5, m, 20H, Ph; 4.5, m, 2H, $CH_2$; 1.1, s, 9H, $CMe_3$; -15.5, d, J(HP) 32.7 Hz, 1H, Ru$\underline{H}$.

(ii) Addition of [ppn][OAc] (5 mg) to a solution of **(14)** (100 mg, 0.16 mmol) in thf (20 ml) resulted in darkening of the solution. After 10 min., work-up by preparative TLC (developed with 1/4 acetone/light petroleum) gave three major bands: Band 1, ($R_f$) 0.53), yellow, containing $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ **(14)** (10 mg, 10%) (IR identification); Band 2, ($R_f$ 0.45), red, containing $Ru_3(\mu\text{-}H)$-$(\mu\text{-}SBu^t)(\mu\text{-}dppm)(CO)_8$ **(17)** (15 mg, 10%) (IR identification); Band 3, ($R_f$ 0.38), orange, containing $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)$-$(\mu\text{-}dppm)(CO)_7$ **(16)** (85 mg, 56%), m.p. 160°C (dec.) (recrystallised from dichloromethane/methanol as the hemi-$CH_2Cl_2$ solvate). (Found: C, 42.32; H, 3.21; $C_{36}H_{32}O_7P_2Ru_3S.0.5CH_2Cl_2$ requires C, 41.40; H, 2.95%). Infrared (cyclohexane): δ(CO) 2062m, 2050vs, 2009vs, 2002s(sh), 1995s(sh), 1983vs, 1967m, 1954m, 1934w $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 7.4, m, 20H, Ph; 5.3, s, 1H, $CH_2Cl_2$; 3.8-2.4, m, 2H, $CH_2$; 1.3, s, 9H, $CMe_3$; -18.2, t, J(HP) 10 Hz, 1H, Ru$\underline{H}$.

Interconversion of complexes **(16)** and **(17)**

(i) A solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(\mu\text{-}dppm)(CO)_7$ **(16)** (20 mg, 0.02 mmol) in cyclohexane (15 ml) was placed in the glass liner of a small laboratory autoclave. Pressurisation with CO (10 atm) and heating (80°C, 1 h) gave a solution which IR and TLC examination showed to contain only $Ru_3(\mu\text{-}H)(\mu\text{-}SBu^t)(\mu\text{-}dppm)(CO)_8$ **(17)**.

(ii) A solution of $Ru_3(\mu\text{-}H)(\mu\text{-}SBu^t)(\mu\text{-}dppm)(CO)_8$ **(17)** (30 mg, 0.03 mmol) in n-octane (30 ml) was heated at 110°C for 90 min. IR and TLC examination of the resulting solution showed that complete conversion to the $\mu_3\text{-}SBu^t$ complex **(16)** had occurred.

Preparation of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7L_2$

(a) L = CO. Complex **(15)** was prepared by a literature method[101] from $Ru_3(CO)_{12}$ and $H_2S$.

(b) $L_2$ = dppm. (i) A mixture of **(15)** (100 mg, 0.17 mmol) and dppm (65.2 mg, 0.17 mmol) in dry, deoxygenated thf (15 ml) was treated dropwise with sodium diphenylketyl (10 drops of a 0.025 M solution in thf). The reaction mixture darkened immediately, and after 15 min., TLC showed that there was no **(15)** remaining. Evaporation, extraction with diethyl ether, and crystallisation (diethyl ether/n-heptane) afforded orange crystals of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)$-$(\mu\text{-dppm})(CO)_7$ **(18)** (126 mg, 76%), m.p. 220°C (dec.) (Found: C, 42.02; H, 2.46; $C_{32}H_{22}O_7P_2Ru_3S$ requires: C, 41.88; H, 2.64%). Infrared (cyclohexane): $\nu(CO)$ at 2068vs, 2045vs, 2010vs, 1999vs, 1996s(sh), 1986m, 1961m, 1955m $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 7.3, m, 20H, Ph; 3.5, m, 2H, $CH_2$; -18.0, m, 2H, RuH.

(ii) Passage of $H_2S$ (Matheson purified grade) through a refluxing solution of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(4)** (100 mg, 0.11 mmol) in cyclohexane (40 ml) resulted in a change of colour from red to yellow after 1 h; after 2 h, TLC showed there to be no starting material remaining. Evaporation and recrystallisation (n-heptane) gave pure yellow $Ru_3(\mu\text{-}H)_2$ $(\mu_3\text{-}S)(\mu\text{-dppm})(CO)_7$ **(18)** (77 mg, 79%), identified from its infrared $\nu(CO)$ spectrum.

(c) LL = dpam. In a reaction similar to (b) (ii) above, $H_2S$ was passed through a refluxing solution of $Ru_3(\mu\text{-dpam})(CO)_{10}$ (200 mg, 0.19 mmol) in cyclohexane (80 ml) for 1 h. Preparative TLC (1/9 acetone/light petroleum) separated two bands: band 1 ($R_f$ 0.5), yellow, containing $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dpam})(CO)_7$ **(19)** (107 mg, 56%), m.p. 180°C (dec.) (from n-hexane) (Found: C, 38.33, H, 2.30; $C_{32}H_{24}As_2O_7Ru_3S$ requires C, 38.22; H, 2.41%). Infrared (cyclohexane): ν(CO) 2071vs, 2046vs, 2008vs, 1999vs, 1988w(sh), 1965w, 1953ms(br) $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 7.40, m, 20H, Ph; 3.0, m, 2H, $CH_2$; -18.2, s, 2H, RuH. Band 2 ($R_f$ 0.42) gave $Ru_3(\mu\text{-dpam})(CO)_{10}$ (10 mg, 5%).

(d) LL = ebdp. [ppn][OAc] (5 mg) was added to a mixutre of **(15)** (50 mg, 0.085 mmol) and ebdp (34 mg, 0.085 mmol) in dry, deoxygenated thf (10 ml). After heating at reflux point for 30 min, preparative TLC (with 3/7 acetone/light petroleum) separated: band 1, ($R_f$ 0.89), containing **(15)** (5 mg, 10%); band 2, ($R_f$ 0.78), containing orange $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-ebdp})(CO)_7$ **(20)** (55 mg, 70%), m.p. 198°C (dec.) (from $CH_2Cl_2$/MeOH) (Found: C, 42.26; H, 2.62; $C_{33}H_{24}O_7P_2Ru_3S$ requires C, 42.63; H, 2.60%). Infrared (cyclohexane): ν(CO) 2069vs, 2047vs, 2012vs, 1999vs, 1985m, 1963m, 1954w $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 7.34, m, 20H, Ph + $C_2H_2$; -17.9, s, 2H, RuH.

## Hydrogenation experiments

### (a) $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ (14)

Complex **(14)** (200 mg, 0.31 mmol) in cyclohexane (60 ml) was placed in the glass liner of a small autoclave. The apparatus was pressurised (20 atm) with dihydrogen and heated with stirring (80°C, 20 h). After cooling and venting, solvent was removed (rotary evaporator) and the residue dissolved in the minimum amount of $CH_2Cl_2$ and applied to a preparative TLC plate. Development (1/9 acetone/light petroleum) gave two bands: Band 1, ($R_f$ 0.81), $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ **(15)** (150 mg, 82%), identified by IR; Band 2, ($R_f$ 0.72), yellow, trace only of unidentified complex with ν(CO) (cyclohexane) at 2109m, 2065s, 2050m, 2012m, 2002w(sh) $cm^{-1}$.

### (b) $Ru_3(\mu\text{-}H)(\mu\text{-}SBu^t)(\mu\text{-}dppm)(CO)_8$ **(17)**

Complex (17) (100 mg, 0.10 mmol) in cyclohexane (40 ml) was treated with dihydrogen in a small autoclave (25 atm, 100°C, 5 h). Isolation of the products by preparative TLC gave $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}dppm)(CO)_7$ **(15)** ($R_f$ 0.51; 72 mg, 76%), identified by comparison with an authentic sample, and an orange compound (2.1 mg) which was not identified, with ν(CO) (cyclohexane) at 2056m, 2043m, 2028m, 2002m(br) $cm^{-1}$. Trace amounts of three other substances were also separated on the plate.

### (c) $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(\mu\text{-}dppm)(CO)_7$ **(16)**

A similar reaction between (16) and dihydrogen (20 atm, 100°C, 4 h) resulted in total conversion to $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)$-($\mu$-dppm)($CO_7$) **(15)** (IR identification), which was isolated in 89% yield after evaporation of the reaction mixture and recrystallisation (diethyl ether/heptane).

## X-ray structure determinations of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$ **(20)** and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ **(13)**

The general procedure has been outlined above. Suitable crystals of both complexes were obtained from

$CH_2Cl_2$/MeOH by liquid/liquid diffusion. The density was determined by flotation using a mixture of petroleum spirit (b.p. 120-160°C) and 1,2-dibromoethane.

## $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-dbdp})(CO)_7$ **(20)**

Crystal Data:

$C_{33}H_{24}O_7P_2Ru_3S$, M 929.78, monoclinic, $P2_1/n$, ($C_{2h}^5$ No. 14), a 13.454(3), b 17.748(2), c 14.706(2) Å, β 94.50(1)°, U 3500.7 Å$^3$, $D_{meas}$ 1.74, Z 4, $D_{calc}$ 1.764 Mg m$^{-3}$, Mo$K_\alpha$- (graphite monochromator) radiation, λ 0.71073 Å, $1° < \theta < 25°$, μ 1.412 mm$^{-1}$, F(000) 1824 electrons.

Intensity data for 6898 reflections were measured with the use of Mo$K_\alpha$-radiation and the ω-2θ scan technique. No significant decomposition of the crystal occurred during the data collection.

The structure was solved by the direct methods routine EEES in SHELX[109] and refined by a blocked-matrix least-squares procedure. Phenyl ring carbons were refined as hexagonal rigid groups and organic hydrogen atoms were included in the model at their calculated positions. Anisotropic thermal parameters were introduced for the remaining atoms. A weighting scheme, $w = k/[\sigma^2(F) + g|F|^2]$, was included. The subsequent difference maps enabled the location of two electron density peaks consistent with the expected positions of the metal-bonded hydrogen atoms. The parameters associated with these atoms were not refined. At convergence R and $R_w$ were 0.036 and 0.038, respectively for k 2.23 and g 0.00025. The maximum residual electron density peak in the final difference map was 1.09 eÅ$^{-3}$ in the vicinity of a phenyl ring and the analysis of variance showed no special features.

### $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ **(13)**

Crystal Data:

$C_{27}H_{20}O_8P_2Ru_3$, M = 837.6, $P2_1$ ($C_2^2$ No. 4), $a$ 9.952(1), $b$ 14.337(2), $c$ 11.164(1) Å, β 104.44(1)°, μ 1542.6 Å$^3$, $D_{meas}$ 1.80, Z = 2, $D_{calc}$ 1.803 Mgm$^{-3}$, MoK$_\alpha$- (graphite monochromator) radiation, λ 0.71073 Å, $1.4 < \theta < 25°$, μ 1.57 mm$^{-1}$, F(000) 816 electrons.

Intensity data for 2387 reflections were measured with the use of MoK$_\alpha$- radiation using an $\omega{:}n/_3\theta$ scan technique, where n(=2) was optimized by profile analysis for a number of typical reflections. For the analytical absorption correction, the maximum and minimum transmission factors were estimated to be 0.64 and 0.37 respectively. Of the 2387 reflections collected, 2286 with $I > 2.5\sigma(I)$ were considered observed and used in the subsequent analysis.

The structure solution and refinement for **(13)** was as for $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}ebdp)(CO)_7$. The hydrogen atom thermal parameters were refined as a common group factor. In the final blocked-matrix least-square calculation all atoms were modelled anisotropically except the phenyl carbons and the hydrogen atoms. The refinement converged with $R$ = 0.032 and $Rw$ = 0.037. The weighting scheme employed converged at $w = 3.33/[\sigma^2(F) + 0.0004|F|^2]$. The largest peak remaining in the final difference map was less than 0.90 eÅ$^{-3}$ in height. The absolute configuration of the structure was determined on the basis of differences in Friedel pairs included in the data set.

In the course of the refinement of (13) it became evident that there was disorder associated with the $Ru_3$ triangle. In contrast to the previously reported disorder associated with the $Ru_3$ clusters, which has been described as a 'Star-of-David' arrangement of partially occupied metal atoms sites[7,112-113], the disorder in (13) is best described as two $Ru_3$ triangles translated one to each side of the parent $Ru_3$ triangle. In the final refinement cycle of (13) the site occupation factors of each of the two 'translated' $Ru_3$ triangles were set at 2% and that of the parent $Ru_3$ triangle at 96%.

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# CHAPTER 2

# PHOSPHORUS-CARBON BOND CLEAVAGE REACTIONS ON METAL CLUSTERS

# PHOSPHORUS-CARBON BOND CLEAVAGE REACTIONS ON METAL CLUSTERS

## 1. INTRODUCTION

Studies by Nyholm[1-3], and later by Deeming[4,5], and their co-workers on the reaction of $Os_3(CO)_{12}$ with $PPh_3$ provided the first evidence for activation of tertiary phosphines when coordinated to metal clusters. Reactions of $Os_3(CO)_{12}$ with $PPh_3$ in a 1:2 molar ratio in refluxing xylene gave nine products that were separated by fractional crystallisation and chromatography; six of these complexes were characterised by X-ray structural studies (Fig. 1).

$$Os_3(CO)_{12} + PPh_3 \rightarrow Os_3(CO)_{12-n}(PPh_3)_n (n = 1,2,3) + \text{six other complexes } (1) - (6) \qquad \ldots 1$$

Complexes (3), (4) and (5) were shown to be monohydrides by $^1H$ high-field NMR although the hydride atoms were not located crystallographically. Although initially obtained from mixtures of $Os_3(CO)_{12}$ and $PPh_3$, it was shown that complexes (1) - (6) resulted from the thermal decomposition of $Os_3(CO)_{10}(PPh_3)_2$. The pyrolysis of $Ru_3(CO)_9(PR_3)_3$ (R = Ph[6,7], p-$MeC_6H_4$[6], m-$MeC_6H_4$[6]) gave five complexes (see Fig. 2). In contrast with the osmium work one observes a preponderance of binuclear ruthenium complexes and no isolable ruthenium hydride species were found. However, the $\mu_3$-benzyne system, formed via P-Ph cleavage [(2) vs (11)] appears to be a stable structure in both systems. P-C bond cleavage reactions mediated by transition-metals have been recently reviewed by Garrou[8].

$$\underset{1}{Os_3(CO)_{12}} + \underset{2}{PPh_3} \xrightarrow[\Delta]{\text{xylene}} 9\ \text{Products}$$

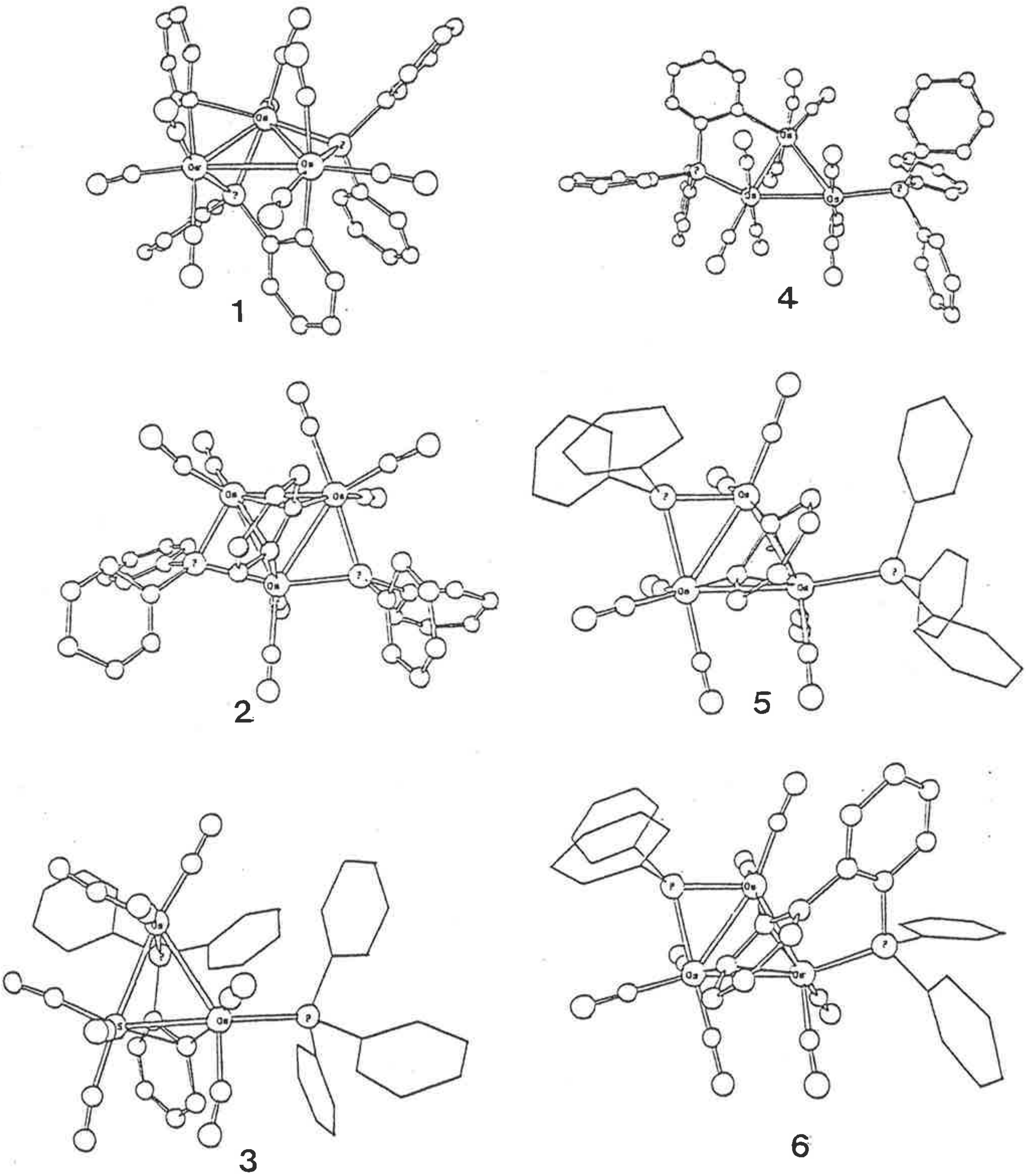
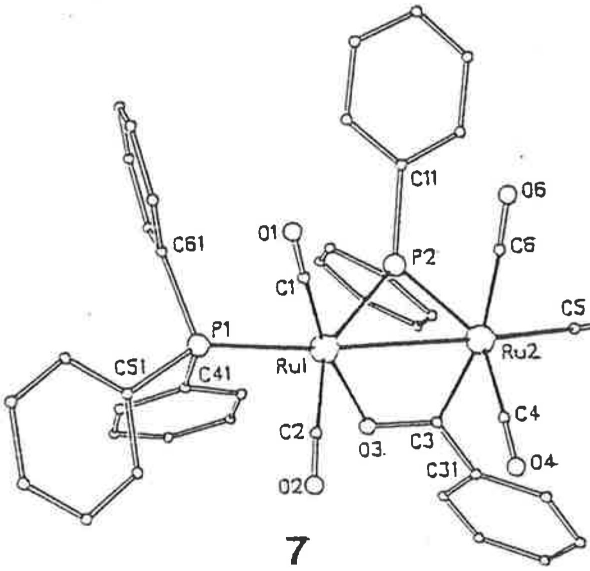


Figure 1



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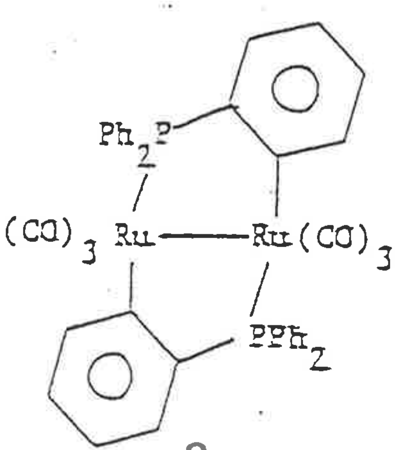

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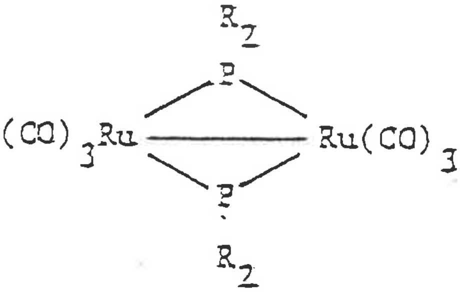

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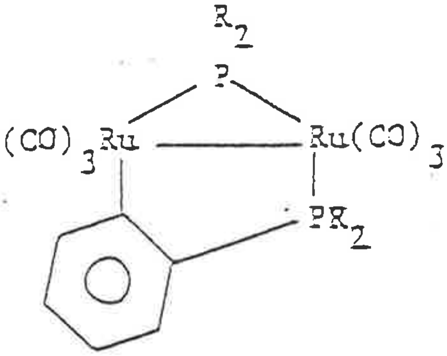

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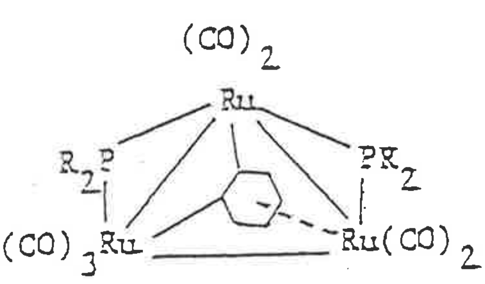


**11**

Figure 2

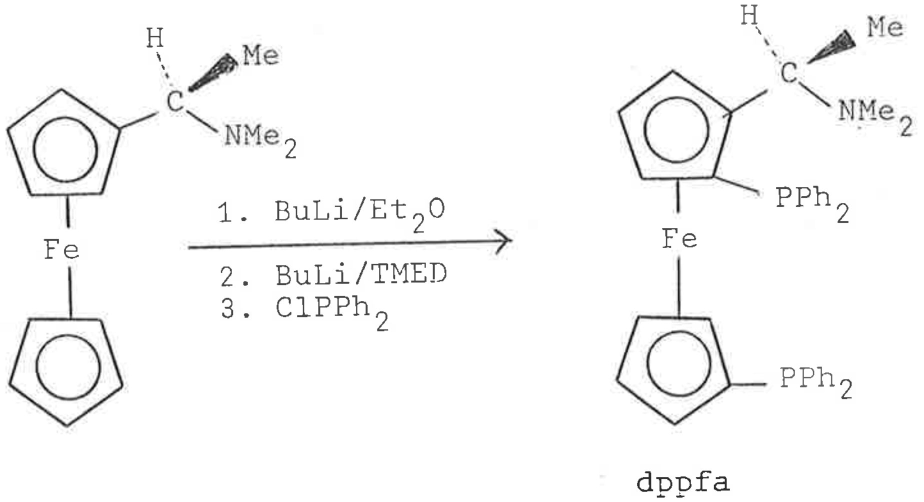
The pyrolysis of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(12)** gave $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(CO)_9$ **(13)**[9], while the hydrogenation of **(12)** gave a high a yield of $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$ **(14)**[10]. However, $Ru_3(\mu\text{-dppe})(CO)_{10}$ **(15)** is much less reactive and similar pyrolysis and hydrogenation reactions proceed to a much lesser extent[10,11]. The formation of the $\mu_3$-phosphidophosphine ligand is favoured sterically in the case of dppm; with a two-carbon backbone, these reactions are not as facile. We considered that it would be interesting to examine the pyrolysis of cluster complexes containing a ligand with a longer backbone, but one that is more rigid than a $(CH_2)_n$ chain would be. Such a ligand is available in the form of 1,1'-bis(diphenylphosphino)ferrocene (dppf), and accordingly we have commenced a study of the syntheses and reactions of ruthenium cluster complexes containing this ligand.

## Ferrocenylphosphines

The first ferrocenylphosphine to be described was triferrocenylphosphine, [$PFc_3$ Fc = ferrocenyl, $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)$][12], reported in 1962, while the first transition metal complex containing this tertiary phosphine was trans-{$RhCl(CO)(PFc_3)_2$}[13]. Ferrocene-containing metal complexes were reviewed several years ago by Cullen et al.[14]. Since that time much effort has been devoted to their use in transition metal catalysis for reactions affording optically active products. Chiral phosphines are useful in catalytic or stoichiometric asymmetric reactions. The planar chirality of asymmetric 1,2-disubstituted ferrocenes can be utilised to synthesise optically active ferrocene derivatives.

Extensive research in the area of asymmetric syntheses catalysed by chiral ferrocenylphosphino-transition metal complexes, carried out independently by Cullen[15] and Kumada[16] and their co-workers, was initiated by Ugi's paper published in 1970[17].

Ugi reported that optical resolution of (1-ferrocenylethyl)dimethylamine was particularly easy, both antipodes were obtained in high yield, and lithiation of the amine proceeded with high stereoselectivity (for example see Equation 2).

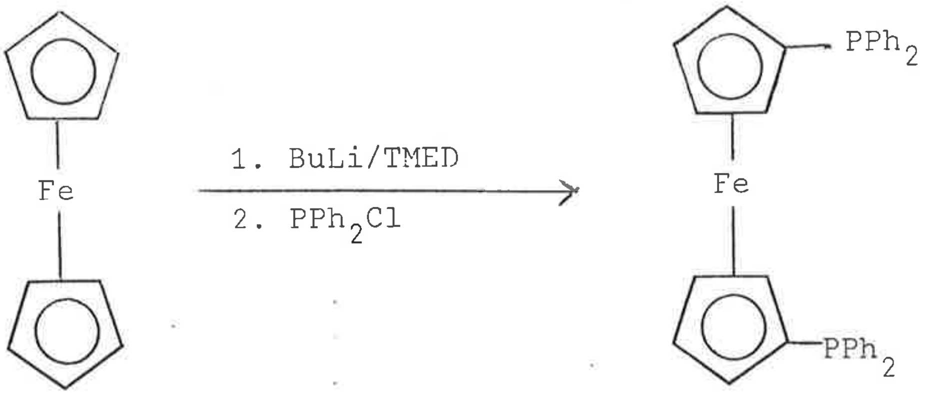


...2

The area of asymmetric syntheses catalysed by chiral ferrocenylphosphine-transition metal complexes has been reviewed by Kumada et al.[18]. An optically active bidentate phosphine such as dppfa is particularly useful as a ligand in transition metal complexes, which are very efficient catalysts in asymmetric syntheses[19].

Before this work, no metal cluster carbonyl complexes containing ferrocenylphosphines had been described. Since the synthesis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)**[20], other iron or ruthenium cluster carbonyl complexes containing ferrocenylphosphines such as $PPh_2Fc$, $PPhFc_2$, $PFc_3$ and Fc'PPh* have been synthesised[21]. These include $Fe_3(CO)_{11}(PPh_2Fc)$, $Fe_3(CO)_{10}$- $(PBuPhFc)_2$, $Ru_3(CO)_{11}L$ (L = $PPh_2Fc$, $PPhFc_2$ and $PFc_3$) and $Ru_3(CO)_{10}(PPh_2Fc)$[21].

1,1'-Bis(diphenylphosphino)ferrocene (dppf) is readily prepared in high yield[22]; mixtures of n-butyllithium and N,N,N',N'-tetramethylethylenediamine (TMED) readily dilithiate ferrocene, and dilithioferrocene readily reacts with organohalophosphines (Equation 3).



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* Fc' = 1,1'-ferrocenediyl

## 2. RESULTS AND DISCUSSION

### (a) Reaction of $Ru_3(CO)_{12}$ and dppf in 1:1 Molar Ratio

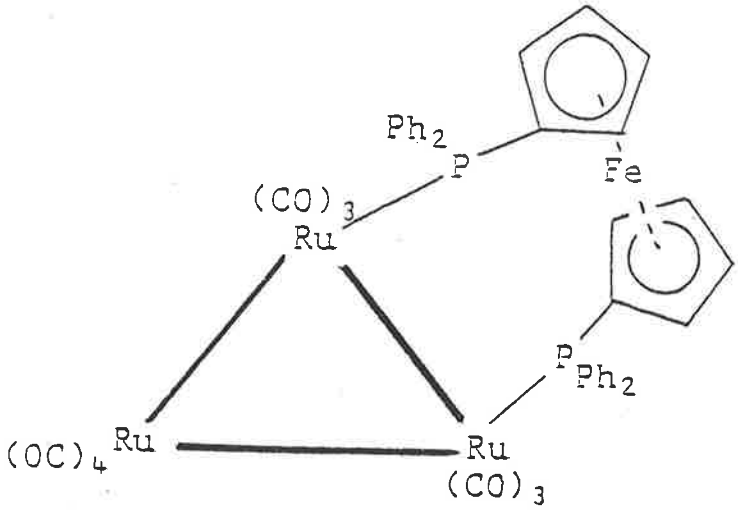
#### (i) [ppn][OAc]-catalysed reactions

The reaction of $Ru_3(CO)_{12}$ with dppf in deoxygenated tetrahydrofuran has afforded $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** in 76% yield after separation by preparative TLC. The complex was obtained in crystalline form as an unusual bis-cyclohexane solvate. Traces of the starting materials, $Ru_3(CO)_{12}$ and dppf, were also isolated and identified by IR ($Ru_3(CO)_{12}$) and by comparison with an authentic sample (dppf).

The $^1H$ NMR spectrum of **(16)** contains a complex set of resonances at δ ca. 7.4 for the Ph groups, and resonances at δ 4.36 and 4.47 are due to the $C_5H_4$ protons. A singlet at δ 1.43 with intensity of 24H was assigned to occluded cyclohexane, as indicated by the microanalysis. The infrared spectrum is similar to that of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(12)**[23]. The $C_5H_4$ region of the $^{13}C$ NMR spectrum contains three sets of resonances; a doublet at δ 73.7 and singlets at δ 76.8 and 77.4. All these results are consistent with the formulation $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** for this complex.

#### (ii) BPK-catalysed reaction

Attempted syntheses of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** from equimolar amounts of $Ru_3(CO)_{12}$ and dppf, using a $Na[Ph_2CO]$-catalysed reaction in tetrahydrofuran, gave a number of products. These could be separated, with difficulty, by preparative thin-layer or column chromatography, and were generally oxidatively unstable in solution. Such properties contrast with the high stability in solution or as solids found previously for tertiary phosphine derivatives of $Ru_3(CO)_{12}$, including those derived from basic phosphines such as $PMe_3$, and may result from the presence of an easily oxidised ferrocenyl centre. One product was isolated from the mixture in pure form as long, dark red-purple needles and characterised by X-ray chyrstallography as $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** (Figure 3). The X-ray crystal structure shows that the dppf ligand bridges one of the ruthenium-ruthenium bonds as previously found in $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(12)**[24] and $Ru_3(\mu\text{-dppe})(CO)_{10}$ **(15)**[25].



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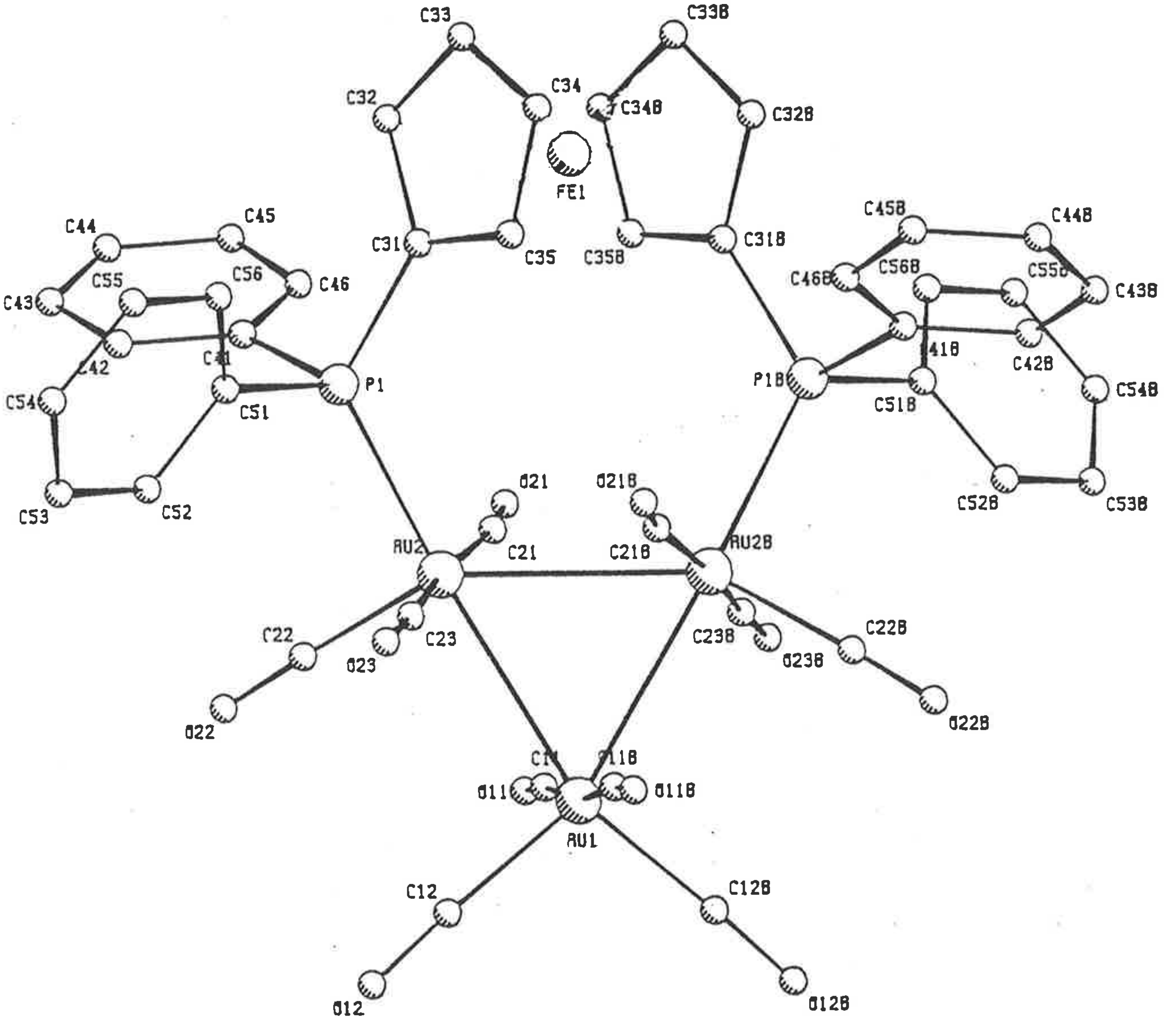


Figure 3  PLUTO plot of $Ru_3(\mu\text{-dppf})(CO)_{10}$ (15) showing atom numbering scheme (by F.W.B. Einstein and A.C. Willis).

### (iii) Reaction of $Ru_3(CO)_{12}$ and dppf in 1:2 Molar Ratio in Refluxing Cyclohexane

The thermal reaction of $Ru_3(CO)_{12}$ and dppf (1:2) in refluxing deoxygenated cyclohexane is complete after one hour (monitored by TLC). Separation by column chromatography afforded a trace amount of dppf and a purple powder. Analytical and mass spectral data for the latter suggest the formula $Ru_3(dppf)_2(CO)_8$ **(17)**. The infrared ν(CO) spectrum is similar to that of $Ru_3(\mu\text{-dppm})_2(CO)_8$ **(18)**[26]. The $^1H$ NMR spectrum contains multiplets at δ 7.37 for the Ph protons and between δ 4.21-3.90 for the $C_5H_4$ protons. Further characterisation was limited by its relative insolubility which precluded a $^{13}C$ NMR spectrum being obtained.

### (iv) Hydrogenation of $Ru_3(\mu\text{-dppf})(CO)_{10}$ (16)

The hydrogenation of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** [18 atm, 80°C, 18h] gave numerous compounds. Only the major red product (20% yield) could be identified. Analytical data suggested the formula $Ru_4(\mu\text{-H})_4(\mu\text{-dppf})(CO)_{10}$ **(19)**. The infrared ν(CO) spectrum is similar to that of $Ru_4(\mu\text{-H})_4(\mu\text{-dppm})(CO)_{10}$ **(20)**[23]. The highest ion in the FAB MS (centred on m/z 1244) corresponds to the parent ion $[C_{44}H_{32}FeO_{10}P_2Ru_4]^+$; other major ruthenium-containing ions are formed by stepwise loss of the ten CO groups. The complex probably has a structure with the dppf ligand bridging a metal-metal bond.

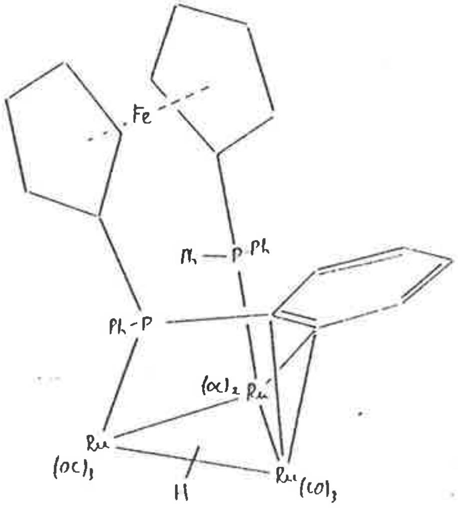
The hydrogenation is in a way similar to that of $Ru_3(\mu\text{-dppe})(CO)_{10}$ **(15)** which also gave numerous products.

However, it has been noted (see Chapter 1) that hydrogenation of $Ru_3(\mu\text{-dppm})(CO)_{10}$ **(12)**, which also gives $Ru_4(\mu\text{-H})_4(dppm)(CO)_{10}$ **(20)** is much cleaner. Presumably hydrogen displaces one $PR_2$ group to give a monodentate dppf and disproportionation and aggregation reactions then result in the formation of $Ru_4(\mu\text{-H})_4(\mu\text{-dppf})(CO)_{10}$ **(19)**.

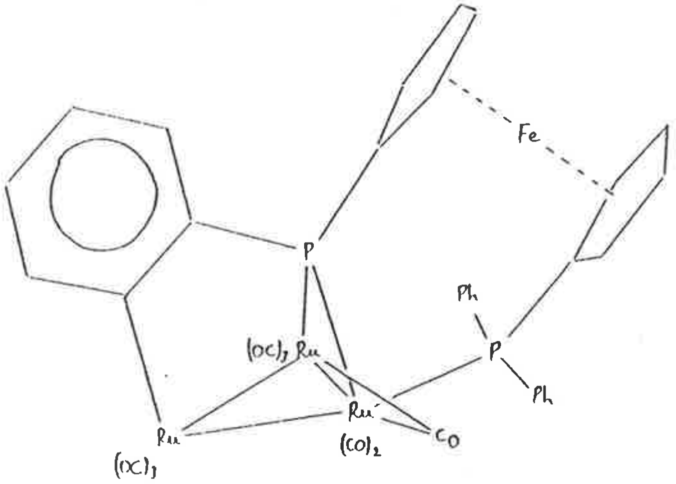
### (v) Pyrolysis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)**

The pyrolysis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** under mild conditions (80°C, 2h) yielded about 18 bands when the reaction mixture was worked up by preparative TLC. Twelve bands contained trace amounts of compounds only and we have not characterised any of these minor products. However, six products were present in reasonable quantities and four of these have been fully characterised. It should be noted that only the pyrolysis in refluxing cyclohexane for a short period has been examined in detail. Interestingly, pyrolysis over longer periods also gives many products; however, two are obtained in much higher yields. Other experiments (see below) suggest that a number of the minor products eventually form one or the other of these major products as the net result of a complex set of intramolecular rearrangements.

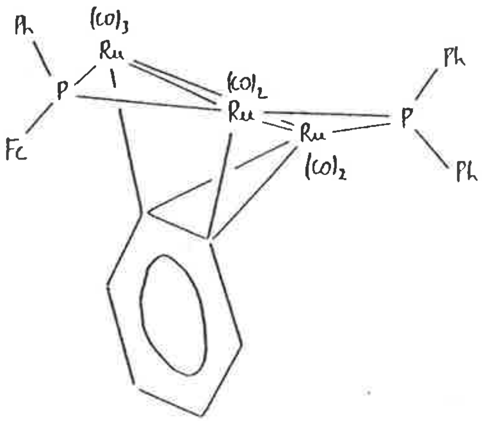
Figure 4 Molecular Structures of Complexes (A)-(D)

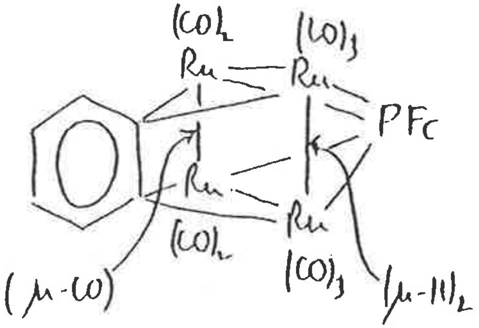


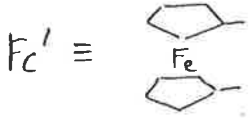
(A) $Ru_3(\mu\text{-}H)\{\mu_3\text{-}(\eta^1,\eta^2\text{-}C_6H_4)PPhFc'PPh_2\}(CO)_8$



(B) $Ru_3\{\mu_3\text{-}(C_6H_4)PFc'PPh_2\}(\mu\text{-}CO)(CO)_8$







(C) $Ru_3(\mu_3\text{-}C_6H_4)(\mu\text{-}PPh_2)(\mu\text{-}PPhFc)(CO)_7$

(D) $Ru_4(\mu\text{-}H)_2(\mu_4\text{-}PFc)(\mu_4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_{10}$

For the purpose of this discussion, the four products so far characterised will be described individually. Their structures are shown in Fig. 4; the labels **(A-D)** are for identification only and do not signify any order of formation.

## Complex **(A)**

The pyrolysis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(16)** yields complex **(A)** in much higher yield than any of the others over a short period of time (2h). The analytical data for complex **(A)** suggest the formula $Ru_3(dppf)(CO)_8$. The infrared ν(CO) spectrum consists of seven bands.

The highest ion in the FAB MS (centred on <u>m/z</u> 1083) corresponds to the parent ion $[C_{42}H_{28}FeO_8P_2Ru_3]^+$; other major ruthenium-containing ions are formed by stepwise loss of eight CO groups and three Ph groups. The ion $[Ru_3]^+$ was also detected.

The $^1H$ NMR spectrum contains a complex set of resonances between δ 7.1-7.7 for the phenyl protons, while the ferrocenyl protons lie between δ 3.2-4.7 ppm. There is also a high field resonance at δ -16.7 ppm due to the cluster-bound hydrogen.

Both the phenyl [δ 122.8-154.6 ppm] and the ferrocenyl regions [δ 70.6-77.5 ppm] of the $^{13}C$ NMR spectrum are complex, and do not give any useful structural information. The structure of complex **(A)** has been determined by X-ray crystallographic methods (see Figs. 5 and 6).

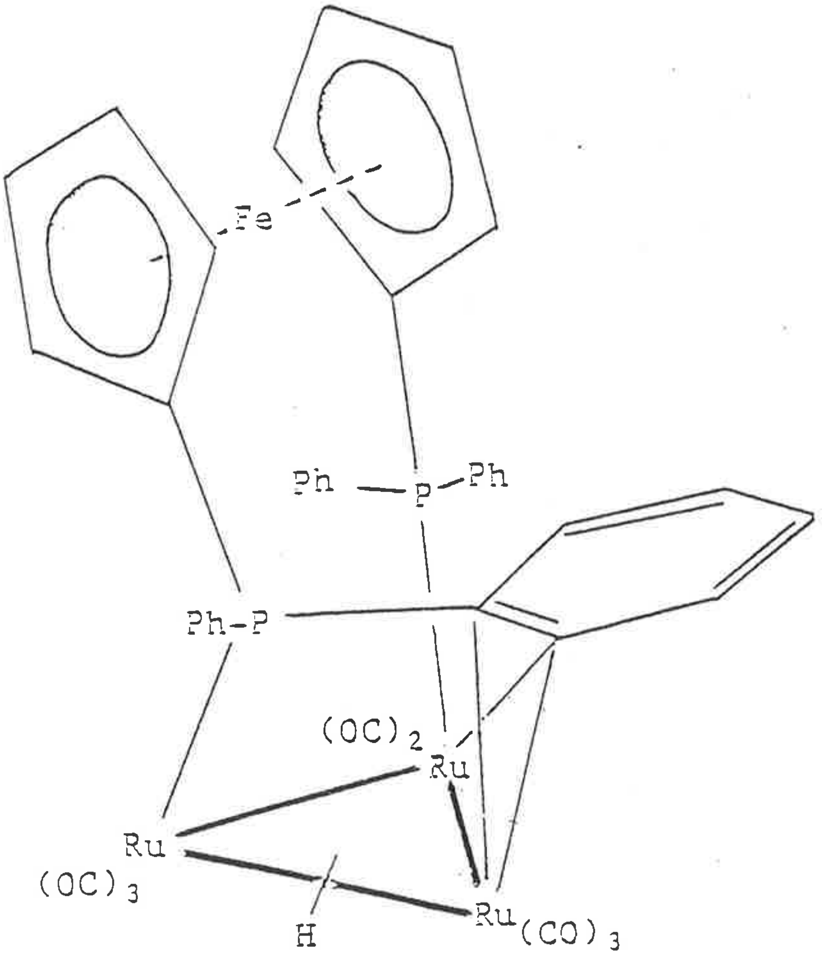


Figure 5 Molecular structure of complex **(A)** showing the mode of bonding of the $C_6H_4$ ring to the cluster.

The molecular structure of complex **(A)** consists of a triangle of ruthenium atoms. One edge of the triangle is bridged by the two P atoms of a modified dppf ligand [Ru(1)-P(1) 2.330(4), Ru(2)-P(2) 2.316(4) Å].

The eight terminal CO ligands are distributed three each to Ru(2) and Ru(3), and two to Ru(1). The hydride ligand was not located directly, but probably bridges the Ru(1)-Ru(2) vector. One of the phenyl groups of the dppf ligand has been metallated, the carbon ortho to P bridging

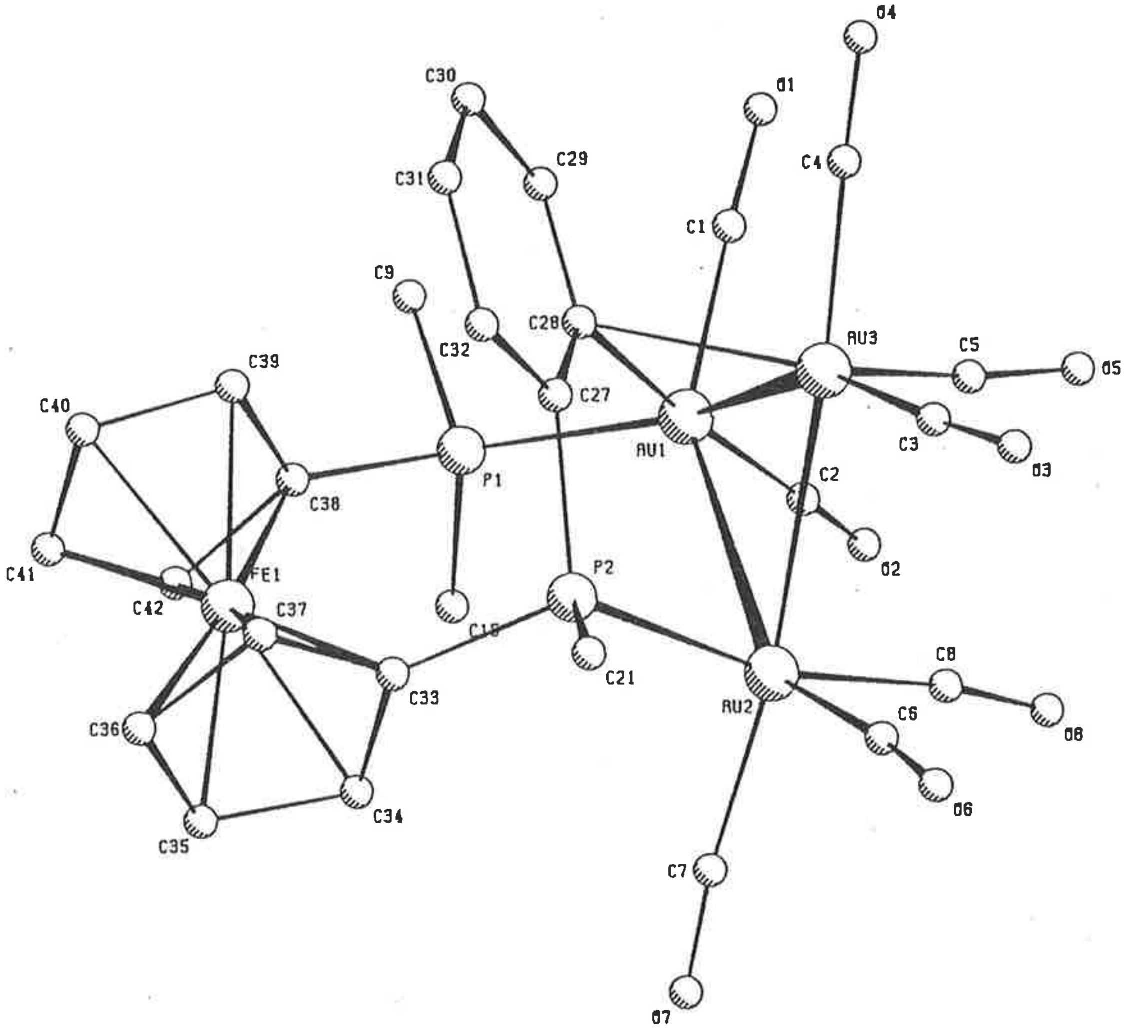


Figure 6 PLUTO plot of complex **(A)**

$Ru_3(\mu\text{-}H)\{\mu\text{-}(\eta^1,\eta^2\text{-}C_6H_4)(PPhFc'PPh_2)\}(CO)_8$.

(by M.R. Snow and E.R.T. Tiekink).

the Ru(1)-Ru(3) bond [Ru(1)-C(28) 2.125(17), Ru(3)-C(28) 2.341(13) Å]; the P-bonded carbon, C(27), is also within bonding distance of Ru(3) [Ru(3)-C(27) 2.494(18) Å].

Compound **(A)** is formed by (i) oxidative-addition of the aryl C-H bond across an Ru-Ru bond and (ii) coordination of one aryl C=C double bond of the resulting $\sigma$-$C_6H_4$ group to give effectively a $\sigma$, $\eta^2$-vinyl system. This mode of bonding of a $C_6H_4$ group is the first example observed on an $Ru_3$ cluster. However, a similar mode of bonding has been observed before in the complex $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2$-$[OP(OPh)_2]$ **(21)** obtained by the controlled pyrolysis of $Ru_3(CO)_9[P(OPh)_3]_3$[27]. In contrast, the bonding of the $\sigma,\eta^2$-$C_6H_4$ group in **(21)** differs by virtue of coordination of carbons 2 and 3 to the metal rather than 1 and 2 as found in complex **(A)**.

Complex **(B)**

The highest ion in the FAB MS of complex **(B)** is centred on m/z 1033 and corresponds to the ion $[C_{37}H_{22}FeO_9P_2Ru_3]^+$. This formulation indicates the loss of $C_6H_6$ from the precursor **(16)**. Other major ruthenium-containing ions are formed by the simultaneous loss of two carbonyl ligands followed by stepwise loss of five carbonyl ligands, and the two CO ligands together. This is followed by sequential loss of two Ph ligands. The ion $[Ru_3]^+$ was also detected.

Analytical data are also consistent with the formulation $Ru_3(dppf\text{-}Ph)(CO)_9$. The infrared ν(CO) spectrum consists of eight bands including one in the bridging carbonyl region at 1870 cm$^{-1}$. The $^1H$ NMR spectrum contains a complex set of resonances between δ 7.1-7.6 for the phenyl protons, while the ferrocenyl proton resonances lie between δ 3.4-4.7 ppm. There are no high field resonances. The structure of complex **(B)** has been determined by X-ray crystallographic methods (see Figs. 7 and 8).

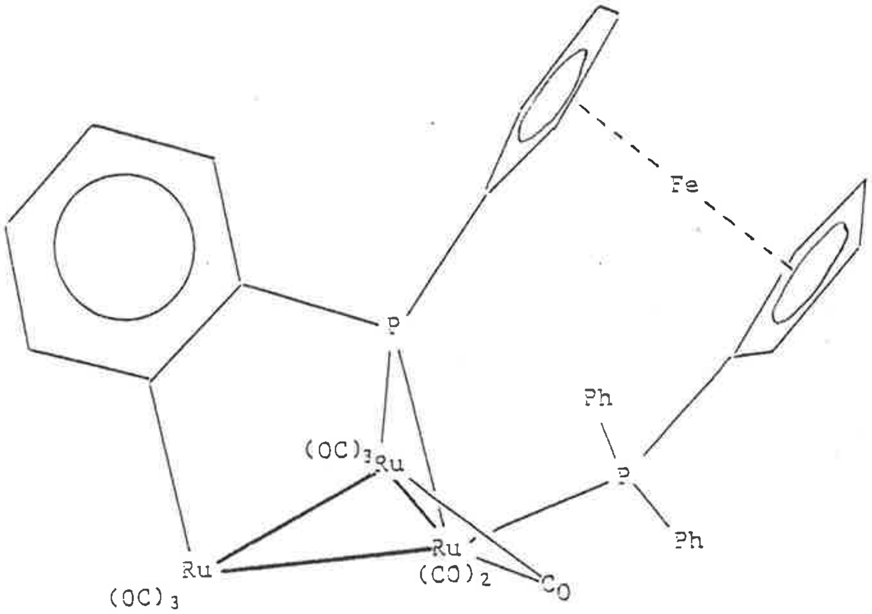


Figure 7 Complex **(B)**

The molecular structure of complex **(B)** consists of three ruthenium atoms, which define an isosceles triangle. There are two shorter Ru-Ru bonds [Ru(1)-Ru(2) 2.837(1), Ru(2)-Ru(3) 2.836(1)] and one longer bond [Ru(1)-Ru(3) 2.869(1)]. The Ru(1)-Ru(2) bond is bridged by both the phosphorus atom of a phosphido group [Ru(1)-P(1) 2.396(3), Ru(2)-P(1) 2.335(3)] and asymmetrically by a CO ligand

[Ru(1)-C(3) 1.988(13), Ru(2)-C(3) 2.415(12) Å]. There are eight terminal CO ligands, which are distributed three each

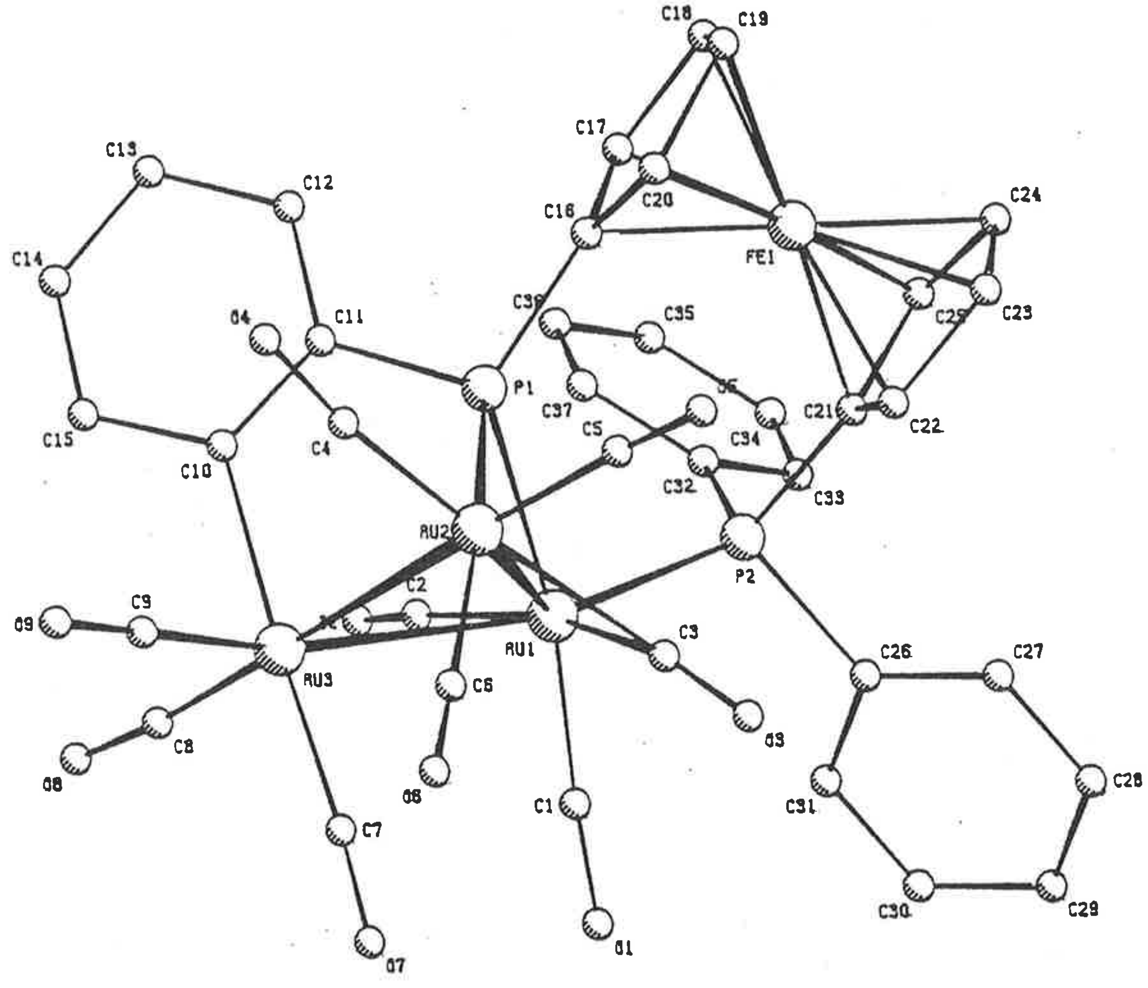


Figure 8 PLUTO plot of Complex (B) showing atom numbering scheme.

(by M.R. Snow and E.R.T. Tiekink).

to Ru(2) and Ru(3), two to Ru(1). The latter atom is also bonded to the other P atom [Ru(1)-P(2) 2.354(3) Å], which occupies an equatorial site. The phenyl group remaining attached to P(1) has been metallated so that the resulting $C_6H_4$ unit bridges Ru(3) [Ru(3)-C(10) 2.148(11) Å] and P(1).

The formation of complex **(B)** involves the loss of a phenyl group, presumably as benzene by combination with cluster-bound hydrogen. The formation of this dephenylated, cyclometallated complex may be compared with the formation of $Ru_3[\mu_3\text{-}PPhCH_2PPh(C_6H_4)](CO)_9$ **(13)** from the pyrolysis of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (80°C, 10h)[9] (see Fig. 9). The formation of the latter complex involves movement of the ligand from the equatorial sites to a capping position on the cluster, with bonding of the phosphido group atom to the third ruthenium atom, in other words all three ruthenium atoms become bonded to the two phosphorus atoms.

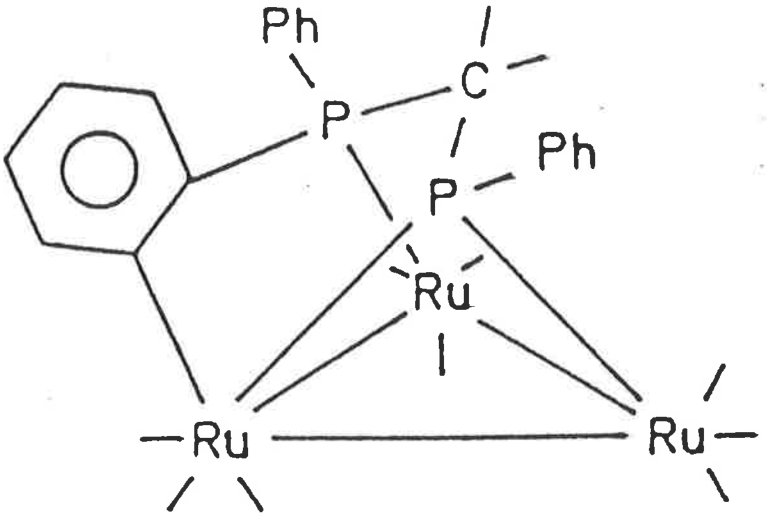


Figure 9 Molecular structure of $Ru_3[\mu_3\text{-}PPhCH_2PPh(C_6H_4)](CO)_9$ **(13)**

However, in the case of complex (B) the movement of the ligand over the cluster does not occur, probably because the presence of the ferrocenyl group which, as a backbone, would make the resulting ligand too large to span the cluster. In this case, the dephenylated phosphorus atom bonds to the Ru atom that is already bonded to the other phosphorus atom, i.e. it chelates rather than bridges.

Complex (C)

The structure of complex (C) has been determined by X-ray crystallographic methods (see Figs. 10 and 11). The molecule consists of a triangle of ruthenium atoms [Ru(1)-Ru(2) 2.794(1), Ru(2)-Ru(3) 2.779(1), Ru(1)-Ru(3) 2.938(1)Å], two edges of which are bridged by $\mu_2$-$PR_2$ units.

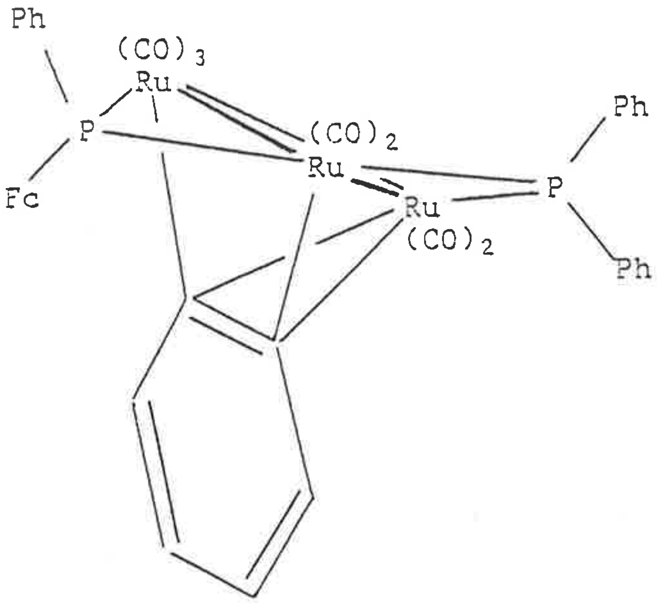


Figure 10 Complex (C)

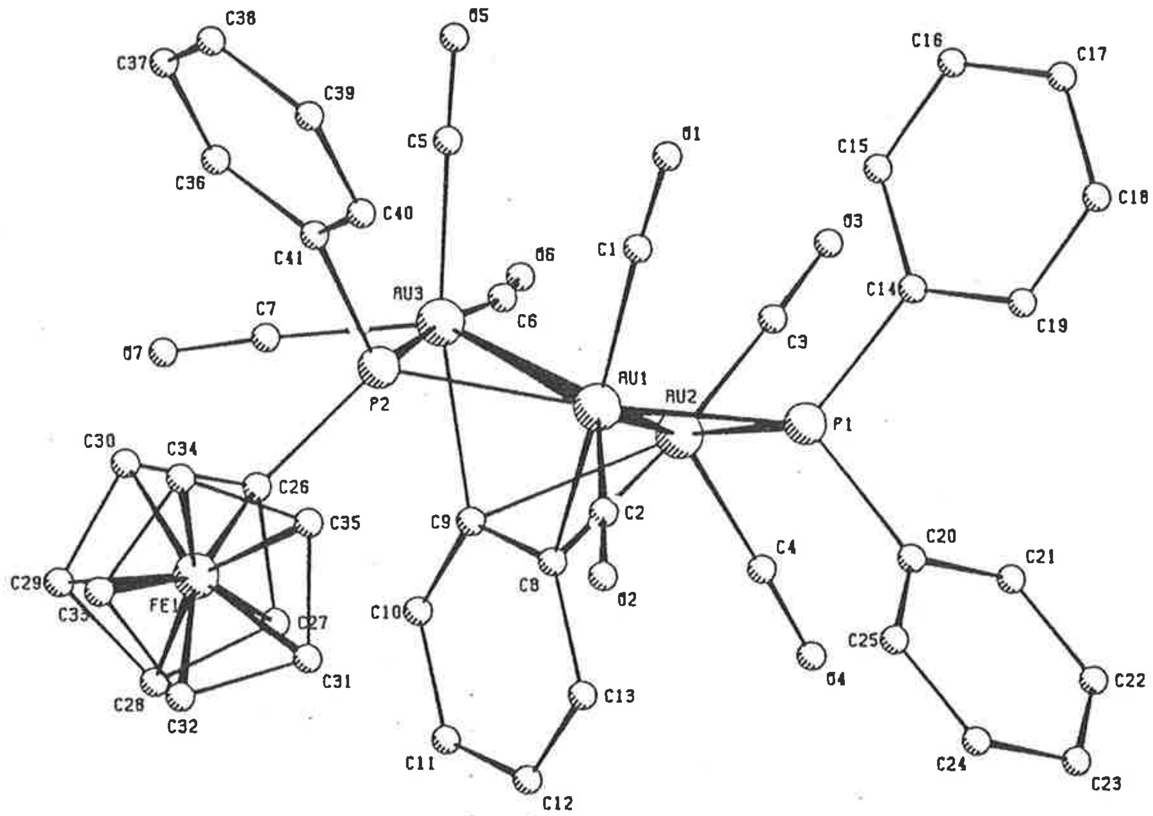


Figure 11 PLUTO plot of complex (C) showing atom numbering scheme.

(by M.R. Snow and E.R.T. Tiekink).

There are seven terminal CO ligands, which are distributed two each to Ru(1) and Ru(2), and three to Ru(3). The Ru-C-O angles for all CO ligands except CO(6) are in the range [176.2-179.0°] while Ru(3)-C(6)-O(6) [169.8(9)°] is slightly bent towards Ru(2). This has also been observed in $Ru_3(\mu_3-C_6H_4)(\mu_2-PPh_2)_2(CO)_7$ **(11)** [Ru-C-O 159.1(4)°]$^{28}$. One side of the $Ru_3$ triangle is capped by a $\mu_3-C_6H_4$ group [Ru(1)-C(8) 2.138(8), Ru(2)-C(8), 2.313(8), Ru(2)-C(9) 2.374(8), Ru(3)-C(9) 2.116(8)].

Analytical data for complex **(C)** are consistent with the formulation found above. The infrared ν(CO) spectrum consists of six bands and is similar to that of $Ru_3(\mu_3-C_6H_4)-(\mu_2-PPh_2)_2(CO)_7$ **(11)**$^6$. The highest ion in the FAB MS (centred on m/z 1055) corresponds to the parent ion $[C_{41}H_{28}FeO_7P_2Ru_3]^+$. Other major ruthenium-containing ions are formed by loss of two carbonyl ligands followed by the sequential loss of five carbonyl ligands and three phenyl ligands.

The $^1H$ NMR spectrum contains a complex set of resonances between δ 6.3-7.8 ppm for the phenyl protons, while the ferrocenyl proton resonances are between δ 3.8-4.6 ppm. There are no high field resonances. The $^{13}C$ NMR spectrum is complex in the phenyl (δ 125-133 ppm) and ferrocenyl regions (δ 70-73 ppm). The CO carbons were not detected.

The formation of complex **(C)** involves cleavage of two P-C bonds in the original dppf ligand, but no loss of phenyl occurs. The rearrangement also involves migration of a hydrogen atom to the ferrocenyl nucleus to give a mono-substituted ferrocenyl group. It should also be noted that two isomers of complex **(C)** are possible from the interchange of R and R' group positions in the bridging PRR' group (R = Ph, R' = Fc). However no evidence for the formation of a second isomer was obtained.

Complex **(D)**

The X-ray structure of complex **(D)** reveals a totally new type of benzyne complex. It contains a square $Ru_4$ cluster, capped on one side by a $\mu_4$-PR group and on the other side by a $\mu_4$-$C_6H_4$ group (see Figs. 12 and 13).

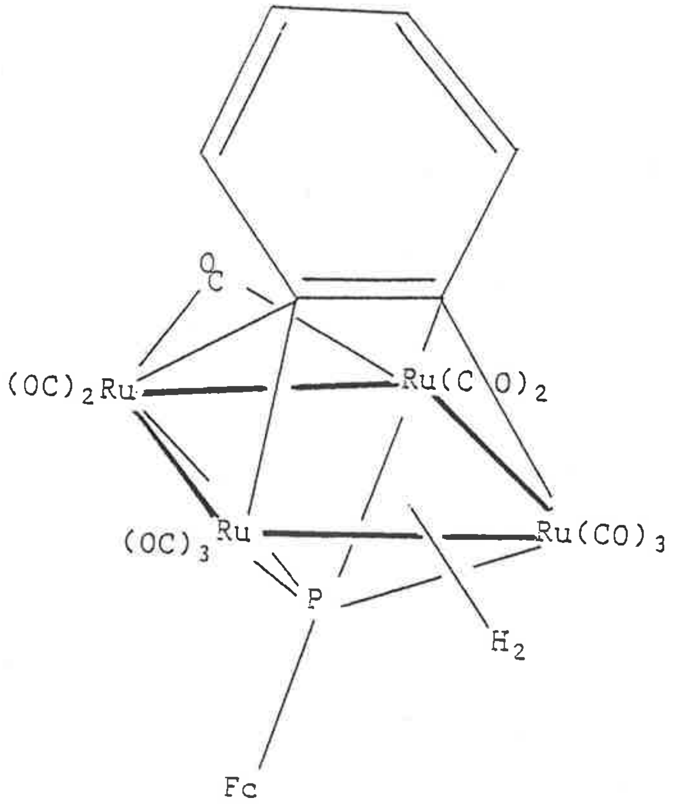


Figure 12 Complex **(D)**

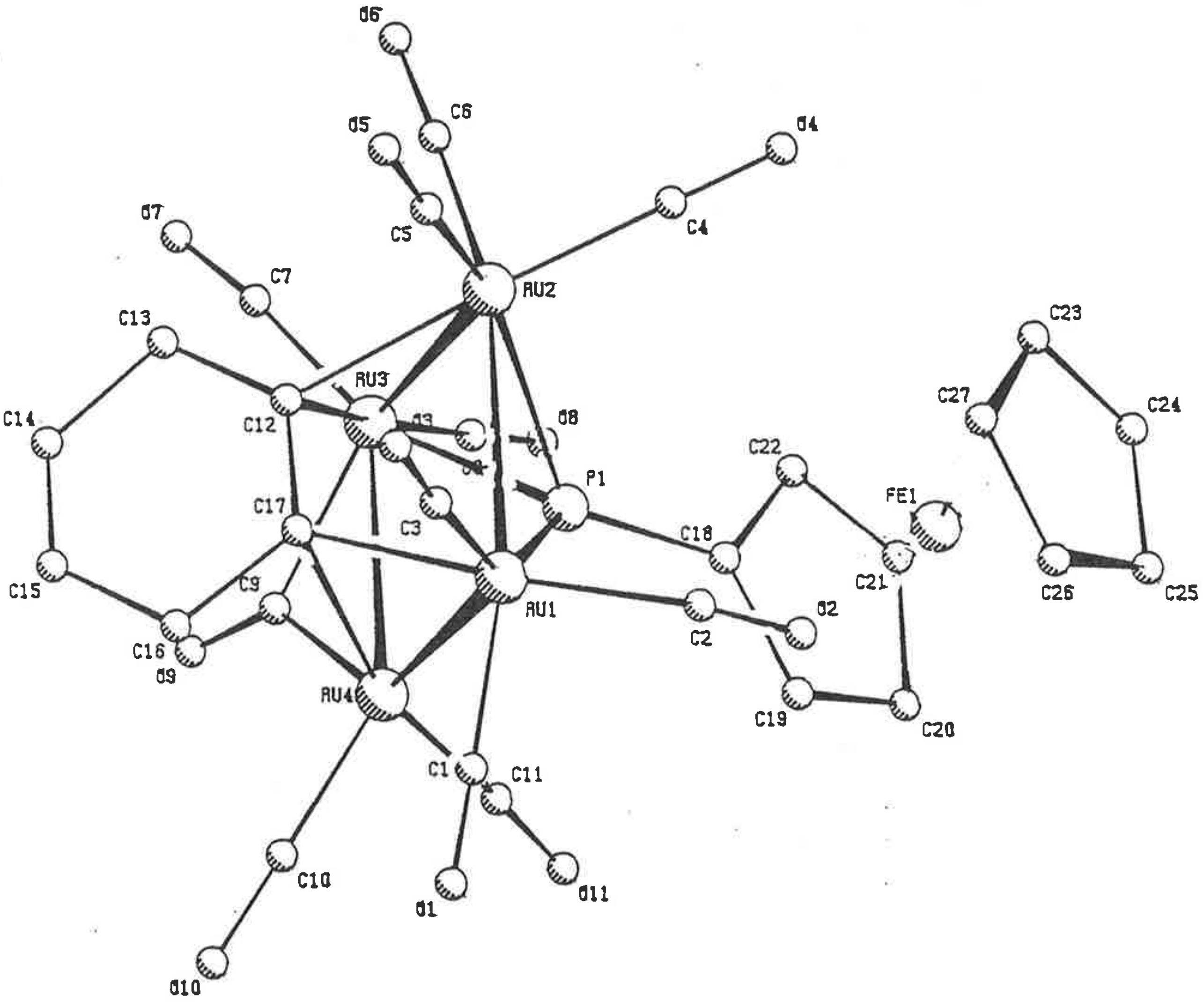
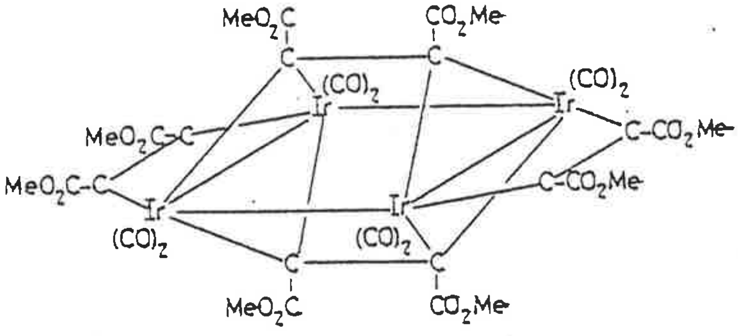


Figure 13 PLUTO plot of complex (D) showing atom numbering scheme.

(by M.R. Snow and E.R.T. Tiekink)

The infrared ν(CO) spectrum consists of seven bands including one in the bridging carbonyl region at 1826 $cm^{-1}$. The highest ion in the FAB MS (centred on m/z 1008) corresponds to the parent ion $[C_{27}H_{15}FeO_{11}PRu_4]^+$. Other ruthenium-containing ions are formed by loss of three carbonyl ligands followed by the loss of a $(C_6H_4 + H)$ group, presumably as $C_6H_5$ formed by combination of the $C_6H_4$ group with one of the cluster-bound hydrides. This is followed by the simultaneous loss of a further two CO ligands and sequential loss of three CO ligands and the ferrocenyl group. The ion $[Ru_4]^+$ was also detected. As only small amounts of this compound were isolated, analytical data and $^1H$ or $^{13}C$ NMR spectra have not yet been obtained. Complex **(D)** is assumed to have two bridging hydrogen atoms on the basis of electron-counting. The probable location is suggested by the longer Ru(2)-Ru(4) bond [2.996(3) Å] compared with the other three metal-metal bonds [Ru(1)-Ru(2) 2.878(2), Ru(1)-Ru(3) 2.842(3), Ru(3)-Ru(4) 2.897(2) Å], and the disposition of the CO ligands about this bond.

Complex **(D)** contains the first example of a benzyne ligand bonded to all four atoms of a square $M_4$ cluster. There have been few examples of an alkyne bonding in a $\mu_4$-fashion to a $M_4$ cluster. The first such example was reported in 1978 by Johnson, Lewis and co-workers[29] who described the reaction of $Ir_4(CO)_{12}$ with $C_2(CO_2Me)_2$; the product was $Ir_4\{\mu_4\text{-}C_2(CO_2Me)_2\}_2\{\mu\text{-}C_2(CO_2Me)_2\}_2(CO)_8$ **(22)**, in which the $\mu_4$-alkyne ligands capped both sides of planar $Ir_4$ cluster. As found in **(D)**, the mode of attachment can be described as 4σ, with the central C-C bond of the alkyne lying parallel to two of the M-M bonds; the alkyne acts as a 4e donor.



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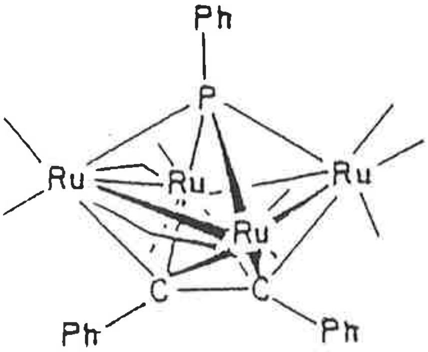

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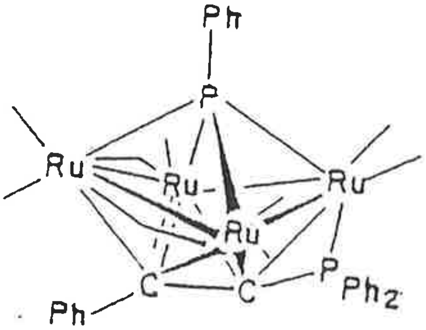


**25**

Other complexes containing $\mu_4$-alkynes are $Ru_4(\mu_4-C_2Ph_2)-(\mu_4-NH)(CO)_{11}$[32] **(23)** and the two related derivatives $Ru_4(\mu_4-C_2Ph_2)(\mu_4-PPh)(CO)_{11}$[30] and $Ru_4(\mu_4-PhC_2PPh_2)-(\mu_4-PPh)(CO)_{10}$[31], which have structures **(24)** and (25) respectively. In all three complexes, the $Ru_4$ cluster is non-planar, and the alkyne lies diagonally across one 'face', bonding in a 2σ, 2π mode. Although structurally different from the situation found in **(22)** and in (D), the alkyne contributes only 4e to the cluster.

Complex **(D)** thus combines the alkyne bonding mode found in **(22)** with the phosphinidine cap found in **(24)** and **(25)**; this suggests that these two modes of attachment of the alkyne differ little in energy, and that the observed structure may depend on the nature of the other ligands present on the $C_2Ru_4E$ core (E = N or P).

The formation of complex **(D)** must involve at least five P-C bond cleavages of the original dppf ligand and loss of three Ph groups. It also involves migration of cluster-bound hydrogen to the ferrocenyl group to give a *mono*-substituted ferrocenyl group.

### Complexes (E) and (F)

For complex **(E)**, only infrared and FAB MS data are presently available. The infrared ν(CO) spectrum contains seven bands, and except for the band at 2063 $cm^{-1}$ it is very similar to that of complex **(A)**. The highest ion in the FAB MS spectrum (centred on *m/z* 1162) corresponds to the ion $[Ru_4(CO)_8(dppf) - Ph]^+$. Other major ruthenium ions are formed by loss of the CO ligands, followed by two Ph groups. The ion $[Ru_3]^+$ was also detected. No reasonable structure can be proposed at the moment and the characterisation of this unusual cluster must rely on an X-ray crystallographic analysis.

Complex **(F)** is rather more interesting in that crystals separate during the prolonged pyrolysis (18h) of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)**. The analytical data suggest the formula $Ru_3(dppf)(CO)_8$; the ion at highest mass (*m/z* 1080) corresponds to the loss of 2H from this formulation. The fragmentation pattern is nearly identical with that of complex **(A)**.

The infrared ν(CO) spectrum contains only four bands including one broad band. However, the $^1H$ NMR spectrum differs from that of complex **(A)**; no $^{13}C$ NMR spectrum was obtained because of the low solubility of complex **(F)** in suitable solvents. The $^1H$ NMR spectrum contains a complex set of resonances between δ 7.2-7.6 ppm for the phenyl protons, while the ferrocenyl protons are between δ 4.5-5.4 ppm. There are at least three sets of high field resonances (δ -2.5, -4.7 and -12.0 ppm). Complex (F) is only sparingly soluble in cyclohexane. The precise molecular structure of complex (F) must await the result of an X-ray crystallographic analysis.

## PYROLYSIS OF INDIVIDUAL COMPONENTS

### (i) Complex **(A)**

The pyrolysis of complex **(A)** (80°C, 2h) gives nine other complexes including a reasonable amount of complex **(C)** and traces of **(D)**. The formation of **(C)** from **(A)** involves the cleavage of two P-C bonds and also migration of the cluster bound hydride of **(A)** to the ferrocenyl carbon. The formation of **(D)** probably involves both disproportionation and aggregation reactions. It should be noted that complexes **(B)** and **(E)** are not formed from the pyrolysis of complex **(A)**.

### (ii) Complex **(B)**

The pyrolysis of complex **(B)** gives ten other complexes including complex **(E)** and trace amounts of complexes **(C)** and **(D)**. The formation of complex **(C)** from complex **(B)** must involve P-C bond formation, presumably by an intermolecular reaction as complex **(B)** has two Ph groups and one $C_6H_4$ group while **(C)** has three Ph groups together with one $C_6H_4$ group. Complex **(D)** probably formed by disproportionation and aggregation. Complex **(A)** is not formed in the pyrolysis of **(B)**.

### (iii) Complex **(C)**

The pyrolysis of complex **(C)** only give trace amounts of three other complexes including complex **(D)**. This result suggests that complex **(C)** is rather stable. The formation of **(D)** from **(C)** presumably involves P-C bond cleavage of P-Ph and disproportionation of the $Ru_3$ cluster and aggregation to form an $Ru_4$ cluster. Complexes **(A)**, **(B)** and **(E)** are not formed from pyrolysis of **(C)**.

### (iv) Complex **(E)**

The pyrolysis of complex **(E)** produces three products in trace amount including **(A)** and **(C)**. However, complexes **(B)** and **(D)** are not formed.

### (v) Prolonged pyrolysis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)**

The pyrolysis of **(15)** over a longer period of time produces at least 18 complexes including **(A)**, **(B)**, **(C)**, **(D)**, **(E)** and **(F)**. However only **(D)** and **(F)** are formed in reasonable amounts. However, it should be noted that none of the complexes **(A)**, **(B)**, **(C)** or **(E)** form complex **(F)** upon pyrolysis.

## 3. CONCLUSION

The complex $Ru_3(\mu\text{-dppf})(CO)_{10}$ can be prepared in high yields from the reaction of $Ru_3(CO)_{12}$ and dppf in thf with a catalytic amount of [ppn][OAc]. Hydrogenation of this complex produces several complexes, including $Ru_4(\mu\text{-H})_4(\mu\text{-dppf})(CO)_{10}$, also made independently from $Ru_4(\mu\text{-H})_4(CO)_{12}$ and dppf. These results suggest that the presence of dppf confers no special stability to the cluster framework. Mild thermolysis results in a variety of interesting and unusual transformations of the cluster-bonded dppf; four complexes have been identified by X-ray methods. The chemistry is substantially different from that of $Ru_3(\mu\text{-dppf})(CO)_{10}$ (**12**), as a result of the presence of the ferrocene nucleus.

### Formation of **(A)-(D)**

The X-ray structures of **(A)-(D)** show several interesting features which indicate that the following types of reactions must have occured during their formation:-

(i) cyclometallation - this reaction occurs during the formation of complex **(B)**

(ii) interaction of $C_6$ ring with the cluster as in complex **(A)** which also involves transfer of H from the Ph group to the cluster. Both complexes **(C)** and **(D)** also involve interaction of a $C_6$ ring, which was formerly a phenyl group, with the cluster.

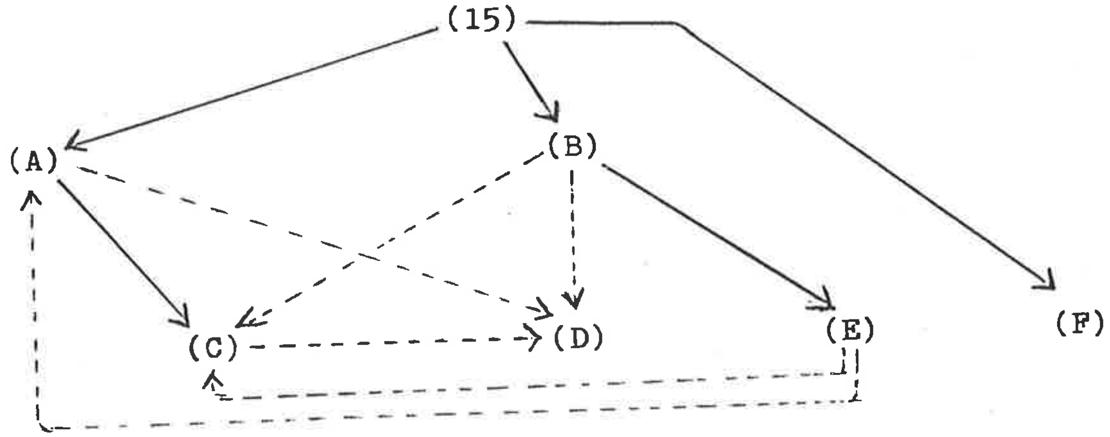
(iii) P-C bond cleavage reactions. Both Ph-C and Fc-C bond cleavage reactions have been observed in the formation of complexes **(B)**, **(C)** and **(D)**.

(iv) Hydrogen migration from cluster to the ferrocenyl group as in the formation of complexes **(C)** and **(D)**.

(v) Disproportionation of $Ru_3$ cluster to form $Ru_4$ cluster in the formation of complex **(D)**.

In the formation of **(C)** only one isomer (Fc on the same side as the $C_6H_4$ group) has been obtained suggesting some regiospecificity in the formation of this complex.

We cannot at this stage comment much on the sequence of formation and hence probable reaction course. However initial studies of the pyrolysis of **(A)**, **(B)**, **(C)** and **(E)** can be summarised as follows:-



These results indicate that there are at least three competitive reactions occurring; one has to conclude that the apparently simple complex $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)** is extremely reactive undergoing several complex intra- and inter-molecular rearrangements and reactions.

Two examples of complexes containing $C_6$ rings bonding in new ways to metal clusters have been obtained, namely $\sigma,\eta^2\text{-}C_6H_4$ in **(A)**, and the $\mu_4\text{-}C_6H_4$ in **(D)**. However, formation of benzyne is preferred over that of the elusive 'ferrocyne'.

## 4. EXPERIMENTAL

General experimental conditions were described in Chapter 1. The ligand, 1,1'-bis(diphenylphosphino)ferrocene (dppf) was a gift from Prof. W.R. Cullen (University of British Columbia).

### (a) Preparation of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)**

A mixture of $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) and dppf (88 mg, 0.158 mmol) was dissolved in dry deoxygenated THF (20 ml). [ppn][OAc] (15 mg) was added to the reaction mixture and the colour changed immediately to dark red. The reaction mixture was left stirring for 5 minutes, after which time solvent was removed in vacuo. The residue was redissolved in the minimum amount of dichloromethane and purified by preparative TLC (Kieselgel $GF_{254}$, developing with 3/1/1 light petroleum/diethyl ether/acetone). The following bands were obtained: Band 1 (orange, $R_f$ 0.92) identified (IR) as $Ru_3(CO)_{12}$; Band 2 (orange; $R_f$ 0.83) trace, identified as dppf by comparison with an authentic sample; Band 3 (dark red; $R_f$ 0.71) was recrystallised from $CH_2Cl_2$/ cyclohexane at -30°C to give dark red crystals of $Ru_3(\mu\text{-dppf})(CO)_{10}\cdot 2C_6H_{12}$ **(16)** (146 mg, 76.5%), m.p. 205°C (dec) (Found: C, 51.39; H, 4.00; $C_{56}H_{52}FeO_{10}P_2Ru_3$ requires C, 51.98, H, 4.05%). IR: $\nu$(CO) (cyclohexane) 2086s, 2020(sh), 2010vs, 1972(sh), 1967w $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 1.43, s, 24H, $C_6H_{12}$; 4.36, s, 4.47, br, 4H each, $C_5H_4$; 7.43, m, 20H, Ph. $^{13}C$ NMR: $\delta(CDCl_3)$ 28.7, s, $C_6H_{12}$; 73.7, d, *J*(CP) 7Hz, C(1); 76.8, 77.4, 2s, C(2,5), C(3,4); 129.8-134.3, m, Ph; 214.3, m, CO.

### (b) Preparation of $Ru_3(\mu\text{-dppf})_2(CO)_8$ **(17)**

A mixture of $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and dppf (88 mg, 0.158 mmol) was dissolved in dry deoxygenated THF (40 ml). The reaction was heated at reflux point for 1h, after which time the reaction was judged to be complete (monitoring by TLC). After cooling, the solvent was removed *in vacuo*, and the mixture was separated by column chromatography (silica). Light petroleum eluted a trace amount of dppf; acetone then gave $Ru_3(\mu\text{-dppf})_2(CO)_8$ **(17)** (recrystallised from $CH_2Cl_2$/heptane): 85 mg (67%) m.p. 160°C (dec) (Found: C, 54.78; H, 3.67, M(FAB MS) 1636; $C_{76}H_{56}O_8Fe_2P_4Ru_3$ requires C, 55.78; H, 3.45%, M 1637. IR: $\nu(CO)(CH_2Cl_2)$ 2052m, 1980vs(br), 1910w $cm^{-1}$. $^1H$ NMR: $\delta$ ($CDCl_3$) 7.73, m, 40H, Ph; 4.21-3.90, m, 16H, $C_5H_4$ ppm.

### (c) Hydrogenation of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)**

$Ru_3(\mu\text{-dppf})(CO)_{10}$ (100 mg, 0.09 mmol) was dissolved in cyclohexane (50 ml) and the solution placed in a glass liner of a small autoclave. Hydrogen (high purity) was charged into the autoclave (18 atm) and mixture was heated at 80°C for 18h. After cooling, solvent was removed (rotary evaporator), and the solid residue was dissolved in the minimum amount of $CH_2Cl_2$. Preparative TLC (3/1/1 light petroleum/acetone/diethyl ether) gave seven bands: Bands 1 ($R_f$ = 0.94), 2, ($R_f$ - 0.81), 3, ($R_f$ = 0.75), 4, ($R_f$ = 0.69), 5, (0.63) and 7 (0.19) contained only trace amounts of compounds, which were not identified. Band 6 ($R_f$ = 0.50), red, $Ru_4(\mu\text{-}H)_4(\mu\text{-dppf})(CO)_{10}$ (50 mg, 46%) (identified by comparison with an authentic sample of $Ru_4(\mu\text{-}H)_4(\mu\text{-dppf})$-$(CO)_{10}$, made from the reaction of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and dppf).

### (d) Reaction of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and dppf

A mixture of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (100 mg, 0.134 mmol) and dppf (78 mg, 0.14 mmol) was dissolved in dry deoxygenated THF (25 ml). A solution of $Na[Ph_2CO]$ in thf (*ca* 0.025 mol $l^{-1}$) was added dropwise from a syringe until the solution darkened and the 2084 $cm^{-1}$ band of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ was absent (0.2 ml), after which time solvent was removed *in vacuo*. The residue was redissolved in the minimum amount of dichloromethane and purified by preparative TLC (developing with 3/1/1 light petroleum/diethyl ether/acetone). The following bands were obtained: Band 1 (yellow; $R_f = 0.93$); Band 2 (yellow; $R_f = 0.87$); Band 3 (orange; $R_f = 0.77$); Band 4 (yellow, $R_f = 0.67$) and Band 6 (yellow, $R_f = 0.10$) were in trace amounts only and not characterised. Band 5 (red; $R_f = 0.50$) was recrystallised from dichloromethane/methanol at -30°C to give dark red crystals of $Ru_4(\mu\text{-}H)_4(\mu\text{-}dppf)(CO)_{10}$ (80 mg, 48%), m.pt 160°C (dec), (Found: C, 42.53; H, 2.60; $C_{44}H_{32}FeO_{10}P_2Ru_4$ calcd: C, 41.43; H, 2.54%) $\nu$(CO) cyclohexane 2088w(sh), 2076s, 2054s, 2036vs, 2016s, 1998m, 1985m, 1977s $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 4.4,m(br), 8H, $C_5H_4$; 7.4m, 20H, Ph; -16.9, s, 4H, RuH. FAB MS: $M^+$ at *m/z* 1244 with ions formed by loss of two CO groups followed by sequential loss of eight CO groups.

### (e) Pyrolysis of $Ru_3(\mu\text{-}dppf)(CO)_{10}$ **(15)**

#### (i) under mild conditions

Tables 1, 2 and 3 list the analytical and spectroscopic data for complexes **(A)-(F)**.

A sample of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)** (500 mg, 0.44 mmol) was heated in refluxing cyclohexane (200 ml) for 2h. IR and TLC showed that reaction had taken place. Evaporation and preparative TLC [silica gel; petroleum spirit/acetone/diethyl ether 60:20:20] gave 18 bands. Bands 1, 2, 5, 6, 7, 8, 11, 12, 14, 16, 17, 18 contained trace amounts of unidentified complexes. Band 3 ($R_f$ = 0.82) yellow, gave $Ru_4(\mu\text{-H})_2(\mu_4\text{-}C_6H_4)(\mu_4\text{-PFc})(\mu_2\text{-CO})(CO)_{10}$ **(D)** (10 mg, 2.3%), recrystallised from n-hexane. Crystals suitable for X-ray analysis were grown by slow evaporation of an n-hexane solution of **(D)**. Band 4 ($R_f$ = 0.76) purple, gave $Ru_3(\mu_3\text{-}C_6H_4)(\mu_2\text{-}PPh_2)(\mu_2\text{-PPhFc})(CO)_7$ **(C)** (45 mg, 9.7%) recrystallised from $CH_2Cl_2$/MeOH. Crystals suitable for X-ray analysis were grown by diffusion of MeOH into a $CH_2Cl_2$ solution. Band 9 ($R_f$ = 0.54) orange, contained complex **(E)** (10 mg, 2.0%) recrystallised from n-hexane. Band 10 ($R_f$ = 0.48) red, gave $Ru_3\{\mu_3\text{-}(C_6H_4)\text{-}PFc'PPh_2\}(\mu_2\text{-CO})(CO)_8$ **(B)** (20 mg, 4.4%) recrystallised from $CH_2Cl_2$/MeOH. Crystals suitable for X-ray analysis were grown by diffusion of MeOH into a $CH_2Cl_2$ solution. Band 13 ($R_f$ = 0.34) orange, was $Ru_3(\mu\text{-H})\{\mu_3\text{-}(\eta^1,\eta^2\text{-}C_6H_4)PPhFc'PPh_2\}\text{-}(CO)_8$ **(A)** (60 mg, 12.6%) recrystallised from $CH_2Cl_2$/MeOH. Crystals suitable for X-ray analysis were grown by diffusion of MeOH into a $CH_2Cl_2$ solution. Band 15 ($R_f$ = 0.27) yellowish green, complex **(F)** (20 mg, 4.1%) recrystallised from acetone/n-hexane. Crystals suitable for X-ray analysis separated from solution when complex **(15)** is pyrolysed in cyclohexane for 18h.

### (ii) Under vigorous conditions

When a solution of $Ru_3(\mu\text{-dppf})(CO)_{10}$ **(15)** (400 mg, 0.35 mmol) was pyrolysed in cyclohexane for 18h, preparative TLC still produced 18 bands. However the only products in significant amount were complexes **(C)** (50 mg, 13.6%) and **(F)** (150 mg, 39.8%).

### (f) Pyrolysis of Complex (A)

Complex **(A)** was heated in refluxing cyclohexane for 2h. Preparative TLC showed ten bands, of which some starting material, and complexes **(C)** and **(D)** were identified as being in major amount.

### (g) Pyrolysis of Complex (B)

Complex **(B)** was heated in refluxing cyclohexane for 2h. Complexes identified from this reaction included **(B)**, **(C)**, **(D)** and **(E)** out of the eleven bands separated by preparative TLC.

### (h) Pyrolysis of Complex (C)

Similarly pyrolysis of complex **(C)** in refluxing cyclohexane (2h) only gave four bands when the mixture was separated by preparative TLC; complexes **(C)** and **(D)** were identified amongst these.

### (i) Pyrolysis of Complex (E)

A solution of complex **(E)** in cyclohexane was heated at reflux point for 2h. Preparative TLC gave four bands of which complexes **(C)** and **(E)** were identified.

NOTE: In the pyrolysis of the individual components **(A)**, **(B)**, **(C)** and **(E)**, the mixture was separated by preparative TLC developing with petroleum spirit/acetone/diethyl ether 60/20/20.

**TABLE 1 ANALYTICAL DATA FOR COMPLEXES (A)-(F)**

| Complex | $R_f$ | m.p. | Analysis found % (calcd) | | Mol. wt |
|---|---|---|---|---|---|
| | | (°C) | C | H | found[a] |
| | | | | | (calcd) |
| **(A)** | 0.34 | 180° | 46.46 | 2.86 | 1083 |
| | | (dec) | (46.68) | (2.61) | (1083) |
| **(B)** | 0.48 | 111-113° | 43.08 | 2.30 | 1033 |
| | | (dec) | (43.08) | (2.15) | (1033) |
| **(C)** | 0.76 | 130° | 47.41 | 2.84 | 1055 |
| | | (dec) | (46.74) | (2.68) | (1055) |
| **(D)** | 0.82 | | | | 1008 |
| | | | | | (1008) |
| **(E)** | 0.54 | | | | 1160 |
| **(F)** | 0.27 | 210° | 45.92 | 2.71 | 1080 |

[a] Mass spectrometry

### TABLE 2 INFRARED ν(CO) AND $^1$H NMR SPECTRA OF COMPLEXES (A) - (F)

| Complex | ν(CO) (cm$^{-1}$) in cyclohexane [$CH_2Cl_2$] | $^1$H NMR in $CDCl_3$ δ(ppm) |
|---|---|---|
| **(A)** | 2071vs,2031vs,2019vs,2004m<br>1987s,1972m,1955m | 7.1-7.7 (m, 19H,Ph)<br>3.2-4.7 (m, 8H, Fc)<br>-16.7 (m, 1H, RuH) |
| **(B)** | 2080vs,2043vs,2029vs,2010s,<br>2002(sh),1989m(sh),1983s | 7.1-7.6 (m, 14H, Ph)<br>3.4-4.7 (m, 9H, Fc) |
| **(C)** | 2060s,2021(sh),2012vs,2003(sh)<br>1971s,1959m | 6.3-7.8 (m, 19H, Ph)<br>3.8-4.6 (M, 9H, Fc) |
| **(D)** | 2076vs,2043vs,2014vs,1997w<br>1985vs,1974vs | |
| **(E)** | 2063w,2033vs,2021vs,2007w,<br>1989m,1972w,1953w | |
| **(F)** | 2064s,2024vs,2006vs,1962s<br>[2060vs,2018vs,1999vs,1946m(br)] | 7.2-7.6 (m, Ph)<br>4.5-5.4 (m, Fc)<br>-2.5, -4.7 and -12.0 (RuH) |

**TABLE 3**

| | |
|---|---|
| Complex Ions in FAB Mass Spectra of Complexes **(A)** - **(F)**<br>$Ru_3$ = 305 | |
| **(A)** | 1083, 44, $[M]^+$; 1055, 31, $[M-CO]^+$; 1027, 46, $[M-2CO]^+$; 999, 47, $[M-3CO]^+$; 971, 63, $[M-4CO]^+$; 943, 100, $[M-5CO]^+$; 915, 89, $[M-6CO]^+$; 887, 53, $[M-7CO]^+$; 859, 88, $[M-8CO]^+$; 782, 89, $[M-8CO-Ph]^+$; 705, 97, $[M-8CO-2Ph]^+$; 628, 92 $[M-8CO-3Ph]^+$. |
| **(B)** | 1033, 22, $[M]^+$; 977, 36, $[M-2CO]^+$; 949, 29, $[M-3CO]^+$; 921, 18, $[M-4CO]^+$; 893, 65, $[M-5CO]^+$; 865, 100, $[M-6CO]^+$; 837, 39, $[M-7CO]^+$; 809, 26, $[M-8CO]^+$; 781, 68, $[M-8CO]^+$; 704, 43, $[M-8CO-Ph]^+$; 627, 42, $[M-8CO-2Ph]^+$. |
| **(C)** | 1055, 16 $[M]^+$; 999, 8, $[M-2CO]^+$; 971, 21, $[M-3CO]^+$; 943, 32, $[M-4CO]^+$; 915, 47, $[M-5CO]^+$; 887, 32, $[M-6CO]^+$; 859, 89, $[M-7CO]^+$; 782, 71, $[M-7CO-Ph]^+$; 705, 79, $[M-7CO-2Ph]^+$; 628, 100 $[M-7CO-3Ph]^+$. |
| **(D)** | 1008, 2, $[M]^+$; 924, 7, $[M-3CO]^+$; 847, 39, $[M-3CO-Ph]^+$; 791, 37, $[M-5CO-Ph]^+$; 763, 85 $[M-6CO-Ph]^+$; 735, 62, $[M-7CO-Ph]^+$; 707, 79, $[M-8CO-Ph]^+$; 679, 100, $[M-9CO-Ph]^+$. |
| **(E)** | 1160, 32, $[M]^+$; 1132, 6, $[M-CO]^+$; 1104, 6, $[M-2CO]^+$; 1076, 95, $[M-3CO]^+$; 1048, 45, $[M-4CO]^+$; 1020, 59, $[M-5CO]^+$; 992, 100, $[M-6CO]^+$; 964, 27, $[M-7CO]^+$; 936, 41, $[M-8CO]^+$; 908, 32, $[M-9CO]^+$; 880, 95, $[M-10CO]^+$; 803, 73, $[M-10CO-Ph]^+$; 7.26, 55, $[M-10CO-2Ph]^+$. |

**TABLE 3 (cont...)**

**(F)** 1080, 24, $[M]^+$; 1052, 29, $[M-CO]^+$; 1024, 25, $[M-2CO]^+$; 996, 32, $[M-3CO]^+$; 968, 60, $[M-4CO]^+$; 940, 59, $[M-5CO]^+$; 912, 100, $[M-6CO]^+$; 884, 42, $[M-7CO]^+$; 856, 49, $[M-8CO]^+$; 779, 59, $[M-8CO-Ph]^+$; 751, 71, $[M-8CO-2Ph]^+$; 674, 51, $[M-8CO-3Ph]^+$.

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# CHAPTER 3

## GOLD IN MIXED-METAL CLUSTERS

PAGE

# GOLD IN MIXED-METAL CLUSTERS

## 1. INTRODUCTION

The area of transition metal cluster compounds has attracted an increasing interest over the past 20 years. This is particularly notable in the field of mixed-metal cluster compounds, i.e. complexes containing at least three metal atoms linked by homo- and hetero- nuclear metal-metal bonds[1-6]. A particular class of mixed-metal cluster compounds, namely those containing gold-transition metal bonds, has enjoyed exponentially increasing interest over the last five years[7,8].

Most interest has been centred on gold-ruthenium[9-22] and gold-osmium[23-29] complexes, although species with bonds from gold to vanadium[30], manganese[31], rhenium[32,33], iron[34-39] iridium[40] and platinum[41] are also known, together with several examples which contain more than one type of transition metal[42-46]. An increasing number of clusters which contain ligands such as $\mu_3$-COMe[10], $\mu_3$-$C_2R$[12] or $\mu_3$-C=CHR[20], $\mu_3$-cyclododeca-trienyl[19], $\mu_3$-PR[9], $\mu_3$-S[16,21], $\mu_3$-$PhPCH_2$-$PPh_2$[79] and $\mu_3$-SR[21], in addition to CO, tertiary phosphine or $\eta$-$C_5H_5$, have been described.

Much interest in gold-containing heterometallic clusters has been aroused by the proposal that the $Au(PR_3)$ moiety is isolobal with H. This means that both H and $Au(PR_3)$ fragments have similar frontier orbitals containing a single electron[42,47]. It would seem that a gold phosphine group and a hydrogen would have little in common from either an electronic or steric viewpoint. Upon closer examination, however, they are not so different. Gold atoms are large, but there is no steric problem since with longer bonds they are further away from a transition metal. Hydrogen bonds to a metal by using its 1s orbital; gold uses primarly its 6s orbital.

As a consequence, structures of complexes containing $Au(PR_3)$ group might be useful indicators of the geometries of related hydrido compounds[47], for which the position of the hydride ligand is more difficult to ascertain by X-ray diffraction[48]. The isolobal analogy between $Au(PR_3)$ and H has been found to be very useful in predicting the synthesis and structures of many clusters containing one $Au(PR_3)$ fragment since it generally occupies the edge-bridging or face-capping position of the H in the corresponding hydrido cluster. This is nicely verified in the cases where the hydride ligand has been located in the molecular structure of the cluster, as in, for example, $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9$[49]. The corresponding $Ru_3Au$ cluster has been shown to have the $Au(PR_3)$ fragment occupying the position of the H atom which it replaces[12].

However, a feature of the gold derivatives which is not shown by the corresponding cluster hydrides is the tendency towards formation of gold-gold interactions in systems containing more than one gold atom. Some recent examples are $Ru_3Au_2(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2$[10], $Ru_4Au_3(\mu\text{-}H)(CO)_{12}(PPh_3)_3$[10,13], $Os_4Au_2(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2$ and $Ru_3CoAu_3(CO)_{12}(PPh_3)_3$[43,44].

While the majority of these can be obtained from the reactions between the appropriate cluster anion and $AuCl(PPh_3)$, or by methane elimination between the poly-hydrido clusters and $AuMe(PPh_3)$, Bruce and co-workers[44] have found that up to three $Au(PPh_3)$ units per cluster may be added in the reactions of the anions with trigold-oxonium ion, $[O\{Au(PPh_3)\}_3][BF_4]$.

## Methods of Synthesis

Various modes of synthesis have been utilised to introduce $Au(PPh_3)$ units into a cluster. Some of these synthetic methods are:-

### (i) Methane elimination from $AuMe(PR_3)$

$$AuMe(PR_3) + HM_xL_y \longrightarrow M_xAuL_yPR_3 + CH_4 \qquad ...1$$

The precusor complexes $AuMe(PR_3)$ have been used extensively by Stone and co-workers to prepare a series of mixed metal-gold clusters including $Ru_3Au(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)$,[10], $Ru_3Au(\mu\text{-}COMe)(CO)_{10}(PPh_3)$[10], $Ru_3Au_2(\mu_3\text{-}S)(CO)_8(PPh_3)_3$[16], $Ru_3Au_2(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2$[10], $Ru_3Au(\mu\text{-}COMe)(CO)_9(PPh_3)$[10] and $Ru_4Au_3(\mu\text{-}H)(CO)_{12}(PPh_3)$[10].

### (ii) From $AuCl(PR_3)$

Many clusters have been prepared by reaction of an anionic mononuclear or cluster complex with $AuCl(PR_3)$ eg.:

$$[ppn][Ru_3(\mu\text{-}NO)(CO)_{10}] + AuCl(PPh_3) \longrightarrow Ru_3Au(\mu\text{-}NO)(CO)_{10}(PPh_3) + [ppn]Cl \qquad ...2$$

Also $AuCl(PR_3)$ can oxidatively add to neutral clusters[18], eg.:

$$Ru_3(CO)_{12} + AuCl(PPh_3) \longrightarrow Ru_3Au(\mu\text{-}Cl)(CO)_{10}(PPh_3)$$

The highly reactive cationic fragment $[Au(PPh_3)]^+$ can be generated in situ using a chloride abstractor e.g. $TlPF_6$. This method was originally used by Lewis and co-workers[11] and a wide range of gold-mixed metal clusters have been prepared. Examples include $Os_4Au_2(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2$[24], $Os_5Au_2C(CO)_{14}(PPh_3)_2$[50] and $Os_8Au_2(CO)_{22}(PPh_3)_2$[27].

Recently the complex $Ru_4Au_2(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}$[22] has been made from the reaction of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ and $[Au_2(\mu\text{-}PPh_2CH_2PPh_2)Cl_2]$ in the presence of $TlPF_6$.

(iii) From $[(Ph_3PAu)_3O]^+$

The oxonium reagent, which was first described by Russian workers[56], was prepared from the reaction of $AuCl(PPh_3)$, freshly prepared silver oxide, and sodium tetrafluoroborate in acetone (Equation 3).

$$3AuCl(PPh_3) + Ag_2O + NaBF_4 \longrightarrow [O\{Au(PPh_3)\}_3][BF_4] + 2AgCl + NaCl \qquad ...3$$

The trigold-oxonium reagent was used to replace reactive hydrogen atoms in organic molecules, such as $CH_2(CN)_2$, $PhC_2H$, $C_5HPh_4$ and ferrocene, by $Au(PPh_3)$ groups. In the examples cited, the products were $Au[CH(CN)_2](PPh_3)$, $Au(C_2Ph)(PPh_3)$, $Au(C_5Ph_4)(PPh_3)$ and $[Au(PPh_3)]_3C_5Ph_4$, and $[Fe(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4Au_2(PPh_3)_2\}][BF_4]$, respectively[78].

This oxonium reagent has been successfully used for the introduction of one, two or three Au($PPh_3$) fragments into metal clusters. Bruce and co-workers have prepared a variety of clusters by this method, such as $Ru_4Au(\mu\text{-}H)_3(CO)_{12}(PPh_3)$[13], $Ru_4Au_2(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2$[13], $Ru_4Au_3(\mu\text{-}H)$- $(CO)_{12}(PPh_3)_3$[13] and $Ru_3CoAu_3(CO)_{12}(PPh_3)_3$[43,44].

The oxonium cation has the advantage of being able to replace one CO by two Au($PPh_3$) groups, in addition to being a source of $[Au(PPh_3)]^+$. This reagent thus has different synthetic potential than AuCl($PPh_3$) or AuMe($PPh_3$).

This Chapter deals with the reaction of some cluster anions with functional ligands such as $\mu_3\text{-}C_{12}H_{15}$, $\mu_3\text{-}C_2Bu^t$, $\mu_3$-S and $\mu_3$-SR with $[O\{AuPPh_3\}_3][BF_4]$. The reaction of the oxonium cation with $[Re(CO)_5]^-$ and also the reaction of some of the anions and AuCl($PPh_3$) has also been studied. The FAB spectra of three of the complexes obtained are discussed briefly.

## 2. RESULTS AND DISCUSSION

Several methods have been used to generate anionic species from cluster carbonyl hydrides. A favoured reagent used to deprotonate these complexes is an alkali-metal hydroxide, often KOH, in an appropriate solvent, usually MeOH or tetrahydrofuran[9]. More recently, the use of potassium hydride has been described[37]. The addition of the readily available solutions of the alkali metal alkyl-substituted borohydride reagent, K-Selectride ($K[HBBu^s_3]$) in tetrahydrofuran, to the cluster hydride results in rapid (minutes) formation of the cluster anion. In some cases, but not all, a colour change accompanies the reaction. This reagent as well as Superhydride ($Li[BHEt_3]$) have been used to generate anionic species from binuclear metal carbonyl derivatives[57], via cleavage of the S-S bond in $Fe_2(\mu\text{-}S_2)\text{- }(CO)_6$[58].

The complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9$[51] **(1)**, $Ru_3(\mu\text{-}H)(C_2Bu^t)(CO)_9$[52] **(3)**, $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$[53], and $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$[53] were chosen for the following reasons:-

(i) they are cluster hydrides that can be easily synthesized in high yields, and can be deprotonated readily

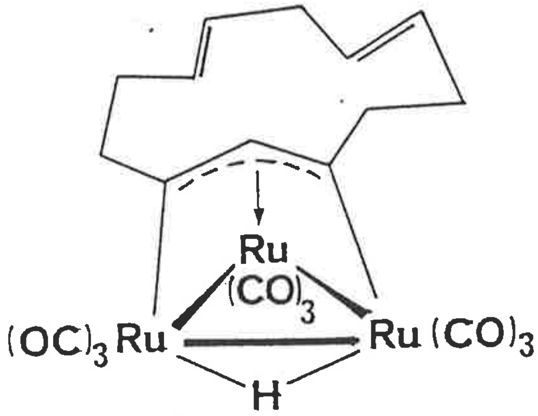
(ii) They all have functional groups such as allylic ($\mu_3\text{-}C_{12}H_{15}$), alkyne ($C_2Bu^t$), thiolate ($\mu_3$-SR) and sulphur ($\mu_3$-S) ligands. It was hoped that there might be some reactivity of these functional groups.

## I. Reaction between $[Ru_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_9]^-$ and $[O\{Au(PPh_3)\}_3][BF_4]$

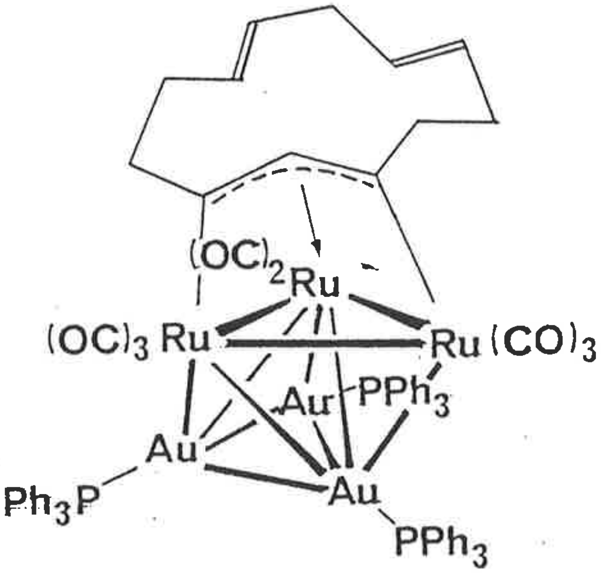
Addition of a solution of $K[HBBu^s_3]$ dropwise to $Ru(\mu\text{-}H)(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_9$ **(1)**, in tetrahydrofuran, results in immediate darkening of the solution; addition of $[O\{Au(PPh_3)\}_3][BF_4]$ then gave a purple compound as the major product, after preparative TLC. The purple compound was characterised as the novel hexanuclear cluster $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(2)**. The IR spectrum of **(2)** showed only four bands in the $\nu$(CO) region, and the $^1H$ NMR spectrum was similar to that of the parent hydride **(1)**, with the addition of resonances from the $PPh_3$ ligands. The allylic <u>CH</u> proton in **(2)** resonated as a singlet at $\delta$ 6.1, while in **(1)**, coupling between this proton and the cluster-bound $\mu$-H atom is found[51].

## II. Description of the structure of $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (2)

The metal framework in **(2)** has the capped trigonal bipyramidal geometry, formed conceptually by the addition of an Au atom to an $Ru_2Au$ face of an $Ru_3Au$ tetrahedron, followed by capping of an $Au_2Ru$ face of the resulting trigonal bipyramid. The $C_{12}H_{15}$ ligand remains attached to the $Ru_3$ face by the same $\mu_3\text{-}(2\eta^1,\eta^3)$ interaction found in the parent hydrido complex. Both Ru(1) and Ru(2) are bonded to three CO groups, but Ru(3) has only two; each gold atom carries one $PPh_3$ ligand (Figs. 1 and 2).



**(1)**



**(2)**

In **(2)** there are twelve metal-metal bonds: three Au-Au, 2.840-2.911(3) Å; six Au-Ru, 2.737-2.929(4) Å, and three Ru-Ru, 2.845-2.929(5) Å. The Au-Au separations in heterometallic clusters containing three interacting gold atoms range from 2.784(1) Å in $Ru_3CoAu_3(CO)_{12}(PPh_3)_3$[43,44] to 3.010(1) Å in

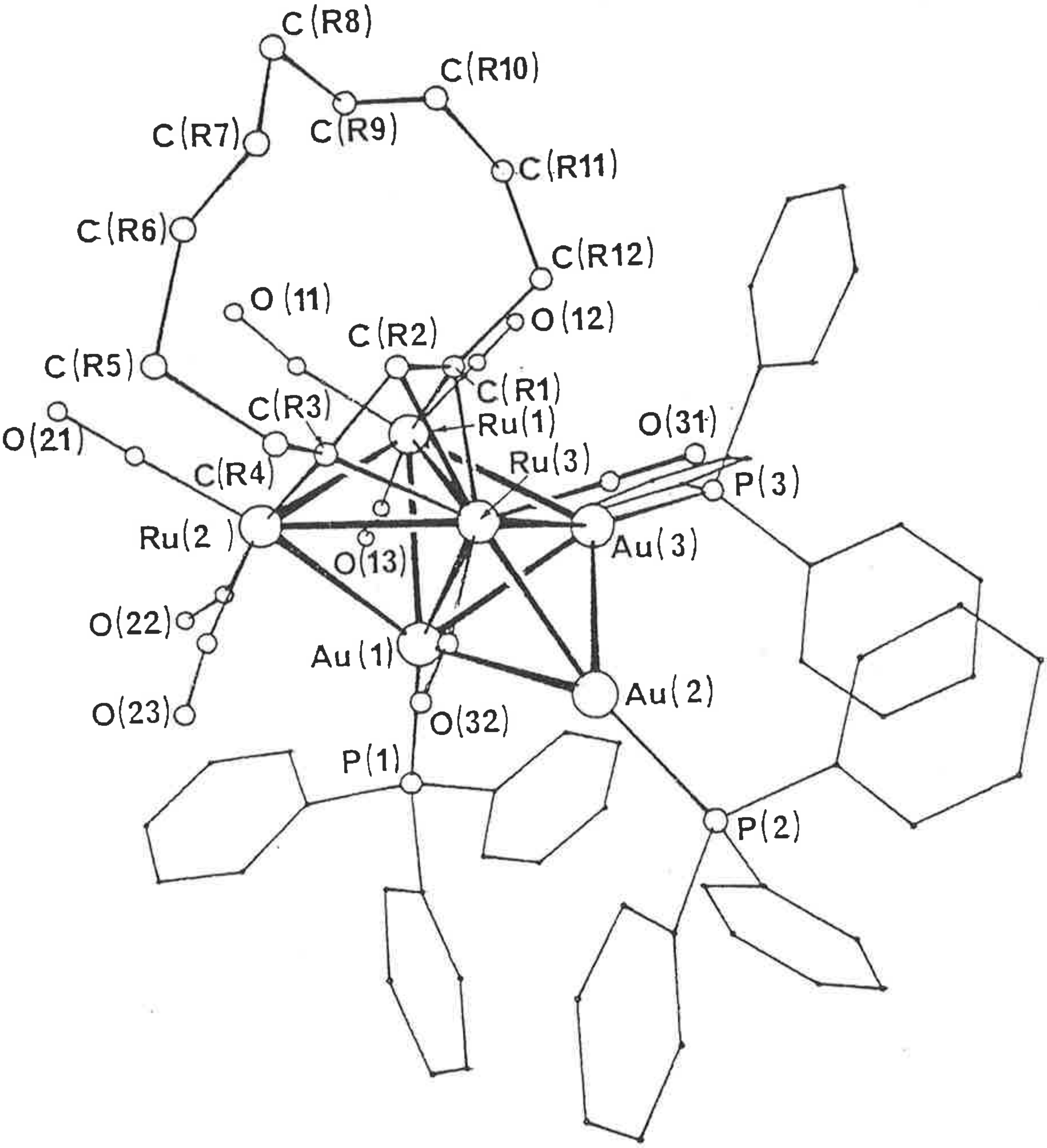


Figure 1 PLUTO plot of one molecule of $Ru_3Au_3(\mu_3-2\eta^1,\eta^3-C_{12}H_{15})(CO)_8(PPh_3)_3$ **(2)** showing atom numbering scheme.
(by B.K. Nicholson)

$Ru_3Au_3(\mu_3\text{-COMe})(CO)_9(PPh_3)_3$. In these complexes, the three $Au(PPh_3)$ moieties form an open, bent array, if considered in isolation from the remainder of the metal core (Fig. 2a). In contrast, **(2)** contains a triangular $Au_3(PPh_3)_3$ system (Fig. 2b), the three Au-Au distances being within the range mentioned above. The longer edge of the $Au_3$ face is common with the Ru(1)Au(1)Au(3) face. The Au-Ru distances separate into three short [between 2.737-2.775 Å, involving Ru(3)], two longer ones, which are the "opposite" edges of the $Au(1)Au(3)Ru_3$ trigonal bipyramid not involved with the capping Au(2) atom [2.882, 2.896(4) Å], and the equatorial edge of the same trigonal bypyramid [2.929(5) Å].

The Au-P distances are normal. One of the Au-P vectors [Au(2) $\leftarrow$ P(2)] intersects an $RuAu_2$ face, while the other two intersect the Ru(1)-Ru(3) and Ru(3)-Au(1) edges, respectively (Fig. 1).

In $Ru_3(\mu\text{-H})(\mu_3\text{-}C_{12}H_{15})(CO)_9$ **(1)**, the $Ru_3$ triangle has two short edges, (average 2.777 Å) and one long edge [2.929(4) Å]; the latter links the two metal atoms which are $\eta^1$-bonded to the $C_{12}$ ring, and is assumed to be bridged by the cluster-bound hydrogen atom[16]. The analogous separations in **(2)** are 2.922, 2.929, and 2.845 Å respectively: the short/long pattern of the parent hydride complex is reversed in the poly-gold derivative.

The $C_{12}$ ring does not differ significantly from that found in **(1)**, attachment being via $\eta^1$ interactions of Ru(1) and Ru(2) with C(R1) and C(R3), respectively; these two carbons are the terminal atoms of an allylic $C_3$ function which is $\eta^3$-bonded to Ru(3). As for **(1)**, atoms C(1)C(2)C(3)Ru(1)Ru(2) are essentially coplanar, and with Ru(3) form a considerably distorted pentagonal pyramid. Standard deviations in the individual C-C bond distances are too high for the latter to be used as unambiguous indicators of the locations of the two carbon-carbon double bonds. However, the coplanarity of C(R5)C(R6)C(R7)C(R8) and of C(R8)C(R9)C(R10)C(R11), taken with the short C(R6)-C(R7) and C(R9)-C(R10) distances strongly suggest that these latter are the uncoordinated double bonds. The ligand thus has the same conformation as found in the parent hydrido complex[60].

The $Ru_3Au_3$ core of **(2)** does not exhibit the common octahedral $M_6$ arrangement; rather a capped trigonal bipyramidal geometry is found. This geometry has been noted previously in $Ru_3Au_3(\mu_3\text{-COMe})(CO)_9(PPh_3)_3$[10], $Ru_4Au_2(\mu\text{-H})_2\text{-}(CO)_{12}(PPh_3)_2$, and $Ru_3CoAu_2(\mu\text{-H})(CO)_{12}(PPh_3)_2$[13,43,44] and in the homometallic $Os_6(CO)_{18}$[60]. In all cases this geometry is predicted by Wade's rules, and by other more sophisticated treatments of the electronic structures of metal clusters[61]. There is, however, one significant difference between the cores of **(2)** and those of all other clusters containing three $Au(PPh_3)$ groups. The formation of the $Ru_3Au_3$ skeleton may be considered formally to result from the addition of the first $Au(PPh_3)$ group to the opposite face of the $Ru_3$ triangle to that occupied by the $C_{12}$ hydrocarbon, followed by capping of an $Ru_2Au$ face by the second gold group. This generates a trigonal bipyramid, which is capped on a $RuAu_2$ face by the third $Au(PPh_3)$ group. This leads to a closo $Au_3(PPh_3)_3$ unit (Fig. 2b). For the other $Au_3M_3$ clusters mentioned above, a different sequence involves (formal) successive addition of the three $Au(PPh_3)$ groups to a $M_3$ triangle on the $Ru_3$, $Ru_2Au$ and $Ru_2Au$ faces to produce an

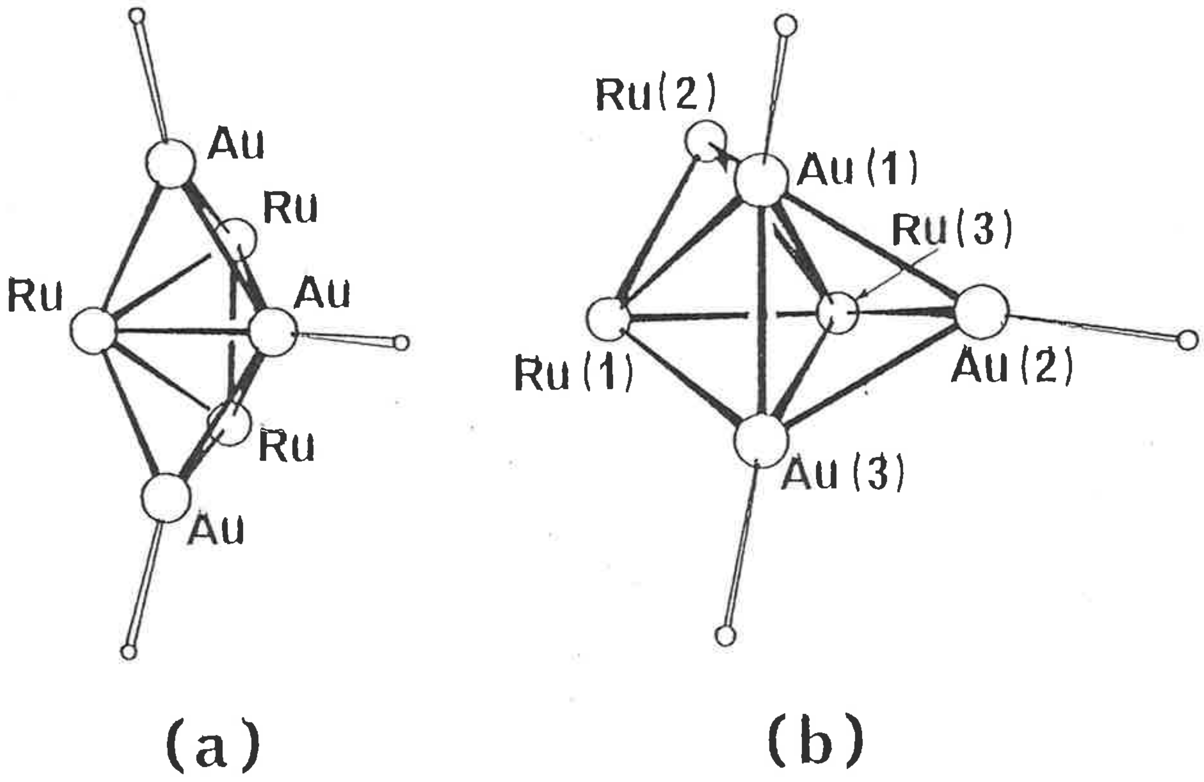


Figure 2 Projections of the $Au_3P_3$ sub-units onto the capped triangular $Ru_3$ faces. (a) The open arrangement found for $Au_3Ru_3(\mu_3\text{-COMe})(CO)_9(PPh_3)_3$[10], $HAu_3Ru_4(CO)_{12}(PPh_3)_3$[10,13] and for $Au_3CoRu_3(CO)_{11}(PPh_3)_3$[43,44]. (b) The closed triangular arrangement found for $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (2).

open $Au_3(PPh_3)_3$ sub-unit (Fig. 2a).

The reasons for the different geometries are not clear at present. A recent theoretical study[62] of poly-gold clusters indicated that closo-$Au_3$ units are particularly stable, suggesting that the less-common geometry found for **(2)** is in fact electronically favoured. Previously, this triangular sub-unit has been observed for the simple clusters $VAu_3(CO)_5(PPh_3)_3$[30], $MnAu_3(CO)_4(PPh_3)_3$[30] and $ReAu_3(CO)_4(PPh_3)_3$[32] and for homonuclear gold clusters. The different geometry in the other clusters may be determined by steric factors, and we note that in **(2)**, only eight CO ligands are associated with the $Ru_3$ face, which is thus less sterically constrained than those in $Ru_3Au_3(\mu_3\text{-COMe})(CO)_9\text{-}(PPh_3)_3$[10] and related species which have nine CO groups on the equivalent face. Furthermore, the "bond vector" used for the third, axial CO ligand of Ru(3) in the parent hydride **(1)** points to the centre of the triangular $Au_3$ unit (or alternatively, to the centre of the $Au_3Ru$ tetrahedron). Superficially the two $Au_3$ geometries are similar to the cyclopropenyl (closo-$C_3$) and allyl (open, bend $C_3$) shapes for three-carbon organic ligands, but the analogy does not appear to have any useful consequences. It is probable that the two arrangements differ little in energy since both lead to the same total number of metal-metal bonds.

There seems to be no pattern for the Au-Au bond lengths in **(2)** or in other cluster complexes containing $Au_3(PR_3)_3$ groups. The Au-Au separation in gold metal is 2.884Å, whereas the reported range of Au-Au distances is 2.60-3.10Å. This conformational softness is echoed in solution: $^{31}P$ NMR studies of the dynamic behaviour of $Ru_3Au_2(\mu_3\text{-}S)\text{-}(CO)_8(PPh_3)_3$ suggest that both Ru-Au and Au-Au interactions are sufficiently labile to allow facile rearrangements of the metal core[16].

If this is a general feature of heterometallic clusters containing gold, the solid state geometry of the metal core may be determined by a delicate balance of electronic, steric and crystal packing effects, with no one factor dominating.

## III. Reaction between $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ and $[O\{Au(PPh_3)\}_3][BF_4]$

The hydrido-alkynyl complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** reacts readily with K-Selectride ($K[HBBu^s_3]$) to generate the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$. This derivative has been obtained previously by reaction of the parent hydrido cluster with KOH/MeOH[63]; the present method was found to be experimentally more convenient, as the cluster-bound hydride can be titrated off with the complex hydride reagent. Addition of $[O\{Au(PPh_3)\}_3][BF_4]$ to a solution of the anion, followed by thin-layer chromatographic separation of the products, afforded two major products, the known complex, $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ **(4)**, which was identified by comparison of its IR and NMR spectra with those reported in the literature[12], and the digold adduct $Ru_3Au_2(\mu_3\text{-}C_2HBu^t)(CO)_9(PPh_3)_2$ **(5)**. The latter was formulated on the basis of analytical and NMR spectrometric measurements; the IR spectrum contains only terminal $\nu(CO)$ absorptions, while the $^1H$ NMR spectrum has resonances at $\delta$ 1.38 and 7.46, assigned to the $Bu^t$ and Ph protons, respectively, together with a singlet at $\delta$ 6.30, of relative intensity 1.

The major point of interest in this reaction is the transformation of the $\mu_3$-acetylide unit found in the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$, and the mono-gold complex **(3)**, to the $\mu_3$-vinylidene ligand concomitantly with the introduction of the second $Au(PPh_3)$ group. We have carried out separate experiments and find (i) stoichiometric generation of the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ followed by protonation ($H_3PO_4$) results in a 60% recovery of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$; (ii) addition of excess K-Selectride to a solution of an anion, followed by protonation ($HPF_6$) afforded a mixture of four neutral complexes, of which only $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)$- $(CO)_9$ (7% yield) was identified; (iii) addition of K-Selectride to a solution of **(1)**, followed by addition of $HPF_6$, gave a complex mixture of products, among which was identified $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ (15%). The low recovery of hydrido-cluster in experiment (i) was not unexpected: the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ is reported[63] to decompose slowly under CO, and we find it rapidly decomposes under $N_2$. While these experiments are generally inconclusive, it does not seem likely that any vinylidene complex is formed in significant amount in reactions that parallel the synthesis of **(5)**, nor is the hydrogen added to a mono-gold complex, followed by addition of a second $Au(PPh_3)$ moiety.

The isolobal replacement of H by $Au(PPh_3)$ in cluster carbonyl hydrides is now a well-established process;

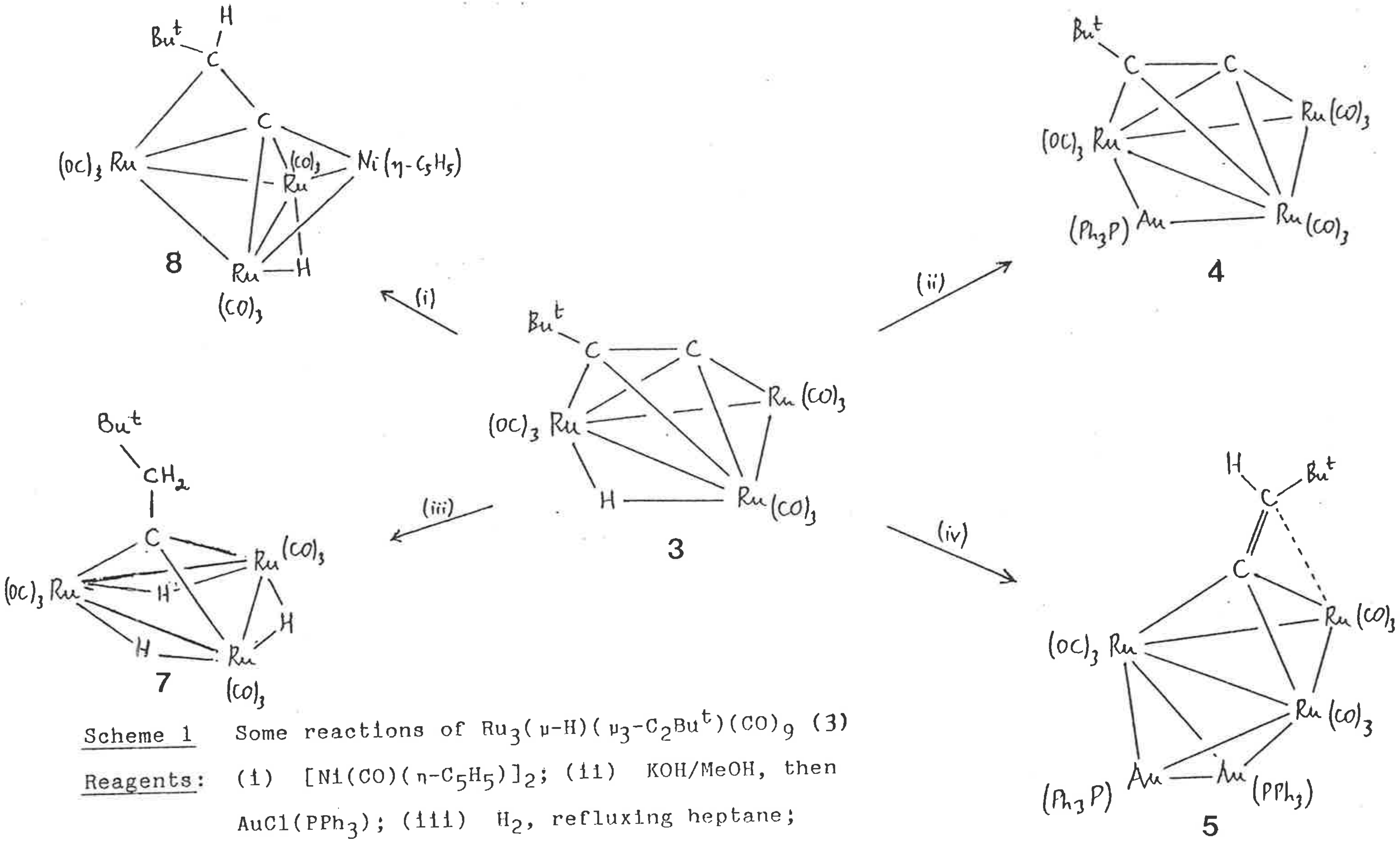
$$[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^- + H^+ \longrightarrow Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9 \qquad (1)$$

reaction (i), for example, has its isolobal equivalent in the formation of $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ from the anion and $AuCl(PPh_3)$[12]. We have shown that addition of three $Au(PPh_3)$ units to a mono-hydrido cluster can occur with loss of the hydrogen atom and a CO ligand, as found in the synthesis of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(2)** from $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9$ **(1)**. In the present example, however, addition of two $Au(PPh_3)$ units does not result in loss of CO. Instead a formal migration of H from the $Ru_3$ cluster to the $\mu_3$-acetylide (a 5e-donor) occurs to give a $\mu_3$-vinylidene ligand (a 4e-donor).

Of interest is the reaction between $H_2$, formally isolobal with $Au_2(PPh_3)_2$ and $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)**, which affords the alkylidene complex $Ru_3(\mu\text{-}H)_3$- $(\mu_3\text{-}CCH_2Bu^t)(CO)_9$ **(7)**. The auration and hydrogenation reactions are thus closely related, since the isolobal analogue of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$, namely $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9$, was considered to be a likely intermediate in the conversion of **(3)** to the alkylidene complex.

Conversion of $\mu_3$-alkyne to $\mu_3$-vinylidene has been observed on an $Os_3$ cluster[66], while formation of a vinylidene complex has also been found in the reaction between $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)$-$(CO)_9$ **(3)** and $[Ni(CO)(\eta\text{-}C_5H_5)]_2$, which affords $Ru_3Ni(\mu\text{-}H)$-$(\mu_4\text{-}C{=}CHBu^t)(\eta\text{-}C_5H_5)(CO)_9$[67] **(8)**.

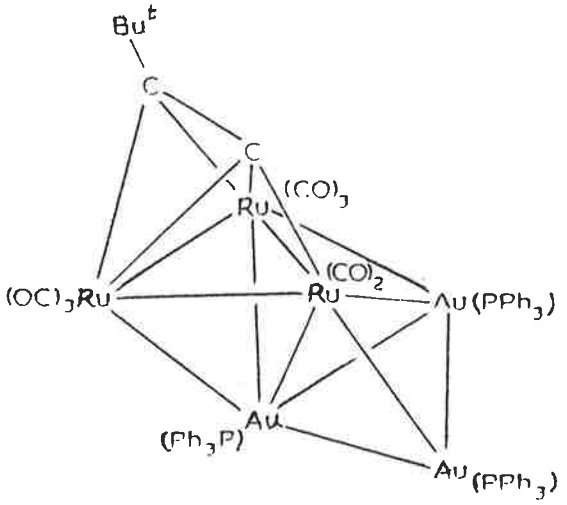
The isolobal replacement of H by $Au(PPh_3)$ in $Ru_3(\mu\text{-}H)$-$(\mu_3\text{-}C_2Bu^t)(CO)_9$ is consistent with the arguments advanced by Lauher and Wald[42] in their initial account which drew attention to this area. A formal extension of that work is the consideration of $Au_2(PR_3)_2$ as a 2e-donor ligand, and in the present instance such a ligand might be considered to bridge the Ru(1)-Ru(3) bond. If considered as a pseudo-olefin, one might anticipate bond-lengthening as a result of electronic interactions or Ru electron density with $\sigma^*$ orbitals of the Au-Au bond. In any case, the geometry of this interaction (including steric effects of associated ligands) also forces one gold to approach within bonding distance of Ru(2); it was noted above that the apparent preference of the orbital lying along the extension of the Au(2)P(1) vector for overlap in the Ru(2)-Ru(3) bond region.



<u>Scheme 1</u> Some reactions of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ (3)

<u>Reagents:</u> (i) $[Ni(CO)(\eta\text{-}C_5H_5)]_2$; (ii) KOH/MeOH, then $AuCl(PPh_3)$; (iii) $H_2$, refluxing heptane; (iv) $K[HBBu^s_3]$, then $[O\{Au(PPh_3)\}_3][BF_4]$.

A third product from this reaction is the hexanuclear product $Ru_3Au_3(C_2Bu^t)(CO)_8(PPh_3)_3$ **(6)**, which has been characterised from microanalytical and NMR data only, no crystals of X-ray quality having been obtained at this time. No hydrogens other than those of the $Bu^t$ and Ph groups were detected. Addition of the $Au_3(PPh_3)_3$ unit to the original hydrido cluster requires formal loss of (H+CO), and it is likely that this complex contains a cyclo-$Au_3(PPh_3)_3$ ligand attached to the $Ru_3$ cluster on the face opposite to that occupied by the $C_2Bu^t$ ligand. By similar arguments to those advanced in the case of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})\text{-}(CO)_8(PPh_3)_3$ **(2)**, it is suggested that an axial CO is lost from Ru(3), allowing the compact $Au_3(PPh_3)_3$ unit to become attached at this point, i.e. the original Ru-CO vector would point to the centre of the $Au_3$ triangle.



**6**

## IV Structure of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ **(5)**

A molecule of **(5)** is shown in Figure 3; sketches of the metal cores in **(4)** and **(5)** are given in Figure 4. The complex contains a trigonal bipyramidal $Ru_3Au_2$ core, with Ru(2) and Au(1) as apical atoms. The nine CO ligands are distributed, three to each ruthenium, while each gold atom carries one $PPh_3$ ligand. The hydrocarbon ligand no longer interacts with the $Ru_3$ core in the $\mu_3\text{-}\eta^1,2\eta^2$ mode found in $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)**; instead, C(10) interacts with all three rutheniums, but C(11) is attached only to Ru(2). The C(10)-C(11) separation [1.41(2)Å] is consistent with the presence of a C=C double bond, which is π-bonded to Ru(2). The C(12)-C(11) vector forms an angle of 130(1)° with the C=C bond, and the $^1H$ NMR spectrum confirms the presence of the hydrogen attached to C(11) suggested by the geometry around that atom. This hydrogen was not located in the difference map. In **(8)**, the vinylidene proton resonates at δ 4.80[67].

The metal-metal separations are of three types: three Ru-Ru [2.837(2)-2.918(2)Å], five Ru-Au [2.781(1)-2.916(1)Å], and one Au-Au [3.033(1)Å]. These values fall within the ranges already reported from complexes containing ruthenium-gold cores. However, there is an interesting asymmetry of the $Ru_3Au_2$ core, as indicated by individual atom separations, such as Ru(2)-Ru(1) [2.903(2)Å] and Ru(2)-Ru(3) [2.837(2)Å], Au(1)-Ru(1) [2.826(2)Å] and Au(1)-Ru(3) [2.781(1)Å], Au(2)-Ru(1) [2.829(2)Å] and Au(2)-Ru(3) [2.800(2)Å]. Although the vinylidene ligand lies across the $Ru_3$ face so that the C(10)-C(11) bond leans towards the Ru(2)-Ru(3) edge, we suggest that the main origin of these differences is to be found in the mode

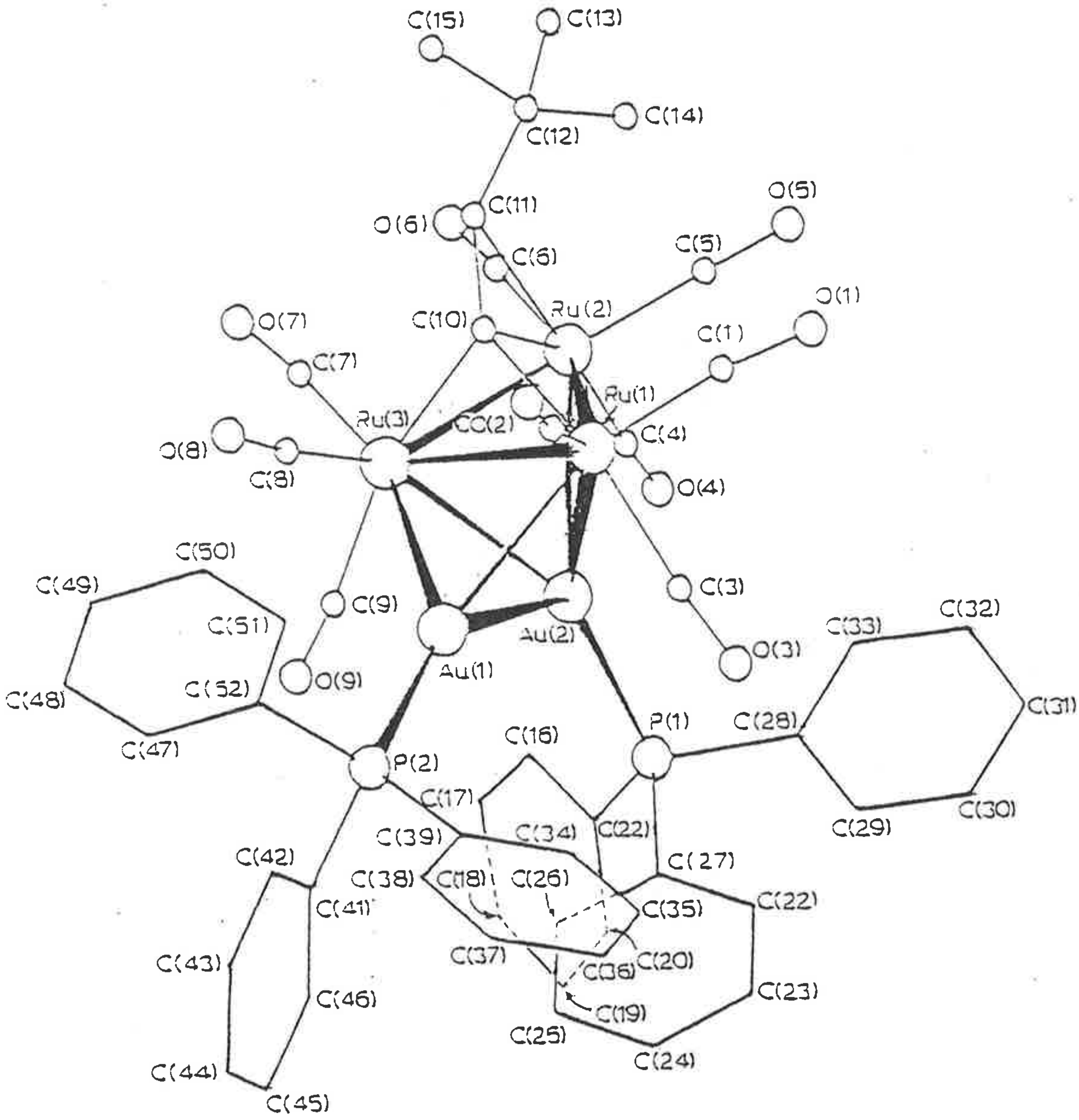
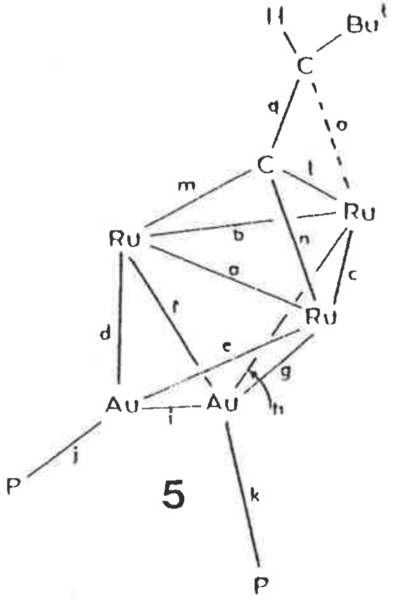
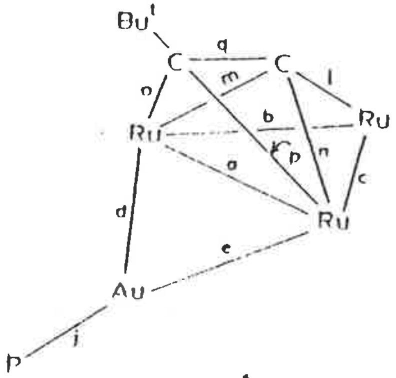


Figure 3 PLUTO plot of one molecule at $Ru_3Au_2(\mu_3$-$C{=}CHBu^t)(CO)_9(PPh_3)_2$ (5), showing atom numbering system. (by E. Horn and M.R. Snow) .



5

| | (5) | (4)[12] |
|---|---|---|
| a | 2.918(2) | 2.820(1) |
| b | 2.837(2) | 2.786(2) |
| c | 2.903(2) | 2.800(1) |
| d | 2.781(1) | 2.757(1) |
| e | 2.826(2) | 2.763(1) |
| f | 2.800(2) | - |
| g | 2.829(2) | - |
| h | 2.916(1) | - |
| i | 3.033(1) | - |
| j | 2.299(4) | 2.276(3) |
| k | 2.309(4) | - |
| l | 2.190(14) | 1.95(1) |
| m | 2.102(17) | 2.19(1) |
| n | 2.040(14) | 2.22(1) |
| o | 2.423(15) | 2.27(1) |
| p | - | 2.21(1) |
| q | 1.406(19) | 1.29(2) |



4

Figure 4 Heavy-atom cores of Ru$_3$Au($\mu_3$-C$_2$Bu$^t$)(CO)$_9$(PPh$_3$) **(4)** and Ru$_3$Au$_2$($\mu_3$-C=CHBu$^t$(CO)$_9$(PPh$_3$)$_2$ **(5)** showing modes of attachment of hydrocarbon ligands.

of attachment of the Au($PPh_3$) moieties to the $Ru_3$ cluster. Thus the P(1)-Au(2) vector points towards the Ru(2)-Ru(3) edge rather than to the centre of the $Ru_3$ face, while the P(2)-Au(1) vector intersects the Ru(1)Ru(3)Au(2) face near its centre. This feature is further emphasised by the torsion angle P(2)Au(1)Au(2)/Au(1)Au(2)P(1) (15.7°), which indicates the degree of skewing of the $Au_2(PPh_3)_2$ group about the Au-Au bond when bonded to this cluster.

Comparison of the cores of the $Ru_3Au$ **(4)** and $Ru_3Au_2$ **(5)** complexes shows that the addition of the second Au($PPh_3$) moiety results in considerable lengthening of the Au-Ru and Ru-Ru separations. In **(5)**, only Au(1)-Ru(3) approaches the values found for Au(1)-Ru(2) and Au(1)-Ru(3) in **(4)** [2.757, 2.763(1) Å, respectively], other separations all being >2.80 Å. In the two complexes, the Ru(2)-Ru(3) separations, bridged by the hydrocarbon as well as by Au($PPh_3$), differ little [2.820(1) Å in **(4)**, 2.837(2) Å in **(5)**], while the other two separations increase from 2.79 Å(av.) in **(4)** to 2.91 Å(av.) in **(5)**. In the hydrido analogue, $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)**, all Ru-Ru separations are equal at 2.80 Å[49]. These observations are in accord with previous observations of bond lengthening which occurs on addition of more than one Au($PPh_3$) moiety to cluster complexes[10,13,44].

Comparison of the modes of attachment of the hydrocarbon ligands in the two complex shows that the acetylide is bonded to the $Ru_3$ cluster in **(4)** by one short [1.95(1) Å] and four long [2.22 Å(av.)] Ru-C interactions, while the vinylidene ligand in **(5)** is attached via three short bonds [2.11 Å(av)] from C(10), one to each Ru, and the long and rather weak C(11)-Ru(2) interaction [2.42(1) Å].

### V. Preparations of $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)**, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)** and $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ **(11)**

The cluster $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ is rapidly and cleanly deprotonated by $K[HBBu^s_3]$ in tetrahydrofuran to give the anions $[Ru_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9]^-$ and $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$ (equation 4).

$$Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9 \xrightarrow[-H_2,\ BBu^s_3]{K[HBBu^s_3]} [Ru_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9]^- \xrightarrow[-H_2,\ BBu^s_3]{K[HBBu^s_3]} [Ru_3(\mu_3\text{-}S)(CO)_9]^{2-} \qquad ...4$$

This route to cluster anions is proving to have wide applicability[13,19-21] and is generally simpler and more specific than the deprotonation reactions with other bases, such as KOH. The degree of deprotonation can be largely controlled by stoichiometric addition of $K[HBBu^s_3]$. Addition of $[O\{Au(PPh_3)\}_3]^+$ to the anion results in formation of the mixed metal clusters **(9)** and **(10)** (equations 5 and 6),

$$[Ru_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9]^- \xrightarrow{[O\{Au(PPh_3)\}_3]^+} AuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)\ \mathbf{(9)} \qquad ...5$$

$$[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-} \xrightarrow{[O\{Au(PPh_3)_3\}]^+} Au_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2\ \mathbf{(10)} \qquad ...6$$

which were separated by chromatography. The overall yields were only moderate, with the $Au_2Ru_3$ cluster **(10)** being the dominant product. A better route to the mono-gold cluster **(9)** involves the reaction between the anions and $AuCl(PPh_3)$ in the presence of $Tl[PF_6]$ as a halide-abstractor[11,28]. Although we have found previously that the trigold-oxonium reagent commonly adds up to three Au($PPh_3$) moieties to mono-anionic clusters[13,19], we have found no evidence for the formation of such species in this reaction.

In an analogous sequence, $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ was deprotonated by K[$HBBu^s_3$], and the reaction with AuCl($PPh_3$)/Tl[$PF_6$] afforded $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ **(11)** in reasonable yields. In addition, significant quantities of the$\mu$ $_3$-S cluster **(9)** and **(10)** were isolated, which indicated that cleavage of the S-C bond of the $\mu_3$-$SBu^t$ group was occurring during the deprotonation step. This was confirmed in a separate experiment; a mixture of $Ru_3(\mu\text{-}H)$- $(\mu_3\text{-}SBu^t)(CO)_9$ and [$HBBu^s_3$]$^-$ was allowed to react to completion and the resulting cluster anions protonated by $H_3PO_4$. The products were $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ and $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ in a 5:1 ratio.

To confirm the spectroscopic and analytical characterisation and to determine precise geometries, crystal structure analyses of **(9)** - **(11)** were carried out.

## The Structure of $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$, (9)

The overall geometry is shown in Figure 5. There is a triangular array of ruthenium atoms capped on one face by the $\mu_3$-S ligand. The Au($PPh_3$) group bridges one Ru-Ru edge, generating a butterfly metal core, while the hydride ligand, located in the structure analysis, lies across an adjacent edge. The structure is therefore that expected on replacing one of the hydride ligands of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$[64] by an isolobal Au($PPh_3$) moiety[39].

The Au-Ru distances (average 2.748 Å) are towards the

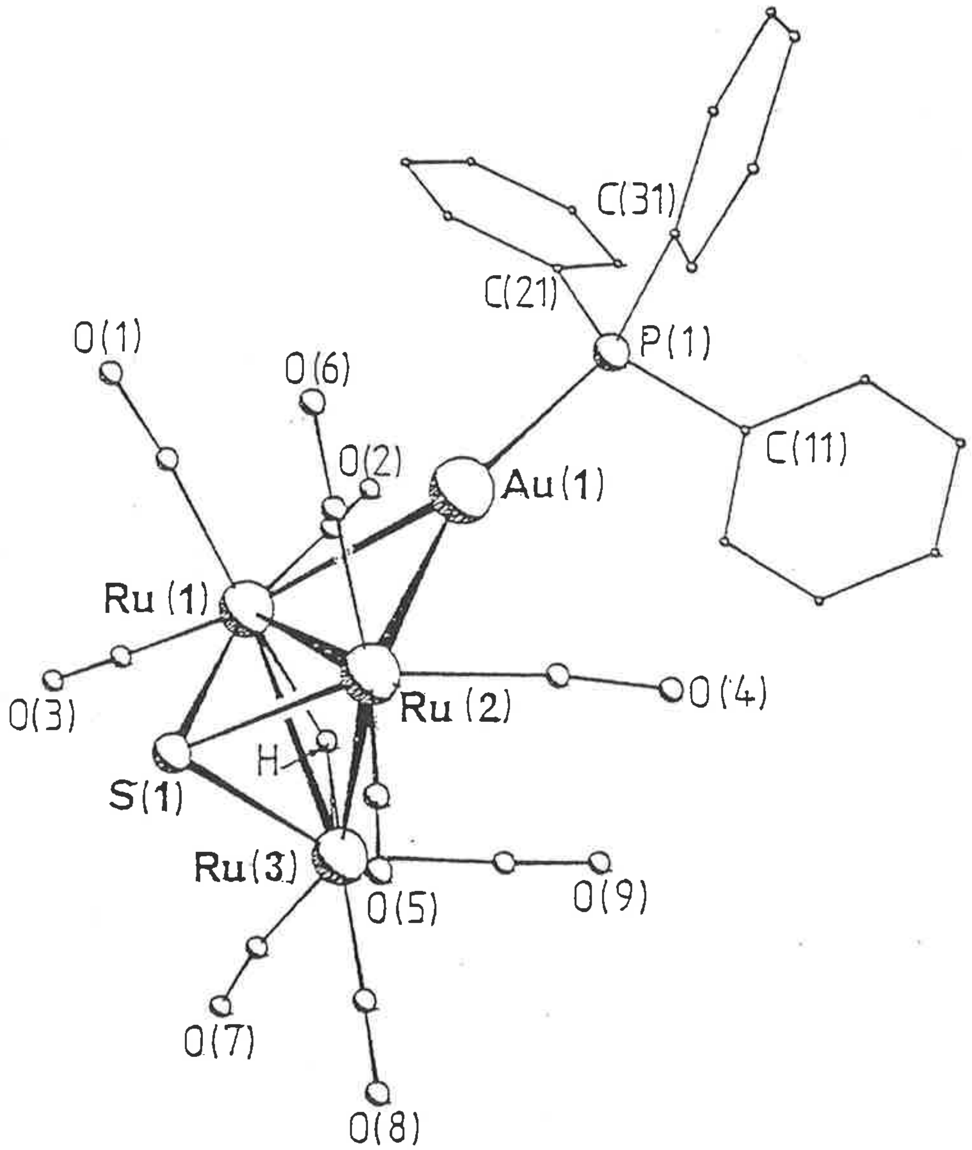


Figure 5 Molecular Structure of $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$ (9)
(by B.K. Nicholson)

shorter end of the range normally found for such bonds. The Ru-Ru bond lengths are all different which is expected since each Ru is chemically distinct. The shortest [Ru(2)-Ru(3), 2.737Å] is unbridged while the H-bridged [Ru(1)-Ru(3), 2.885Å] and the Au-bridged [Ru(1)-Ru(2), 2.933Å] examples are progressively longer, in accord with normal trends. Despite the inequivalence of the three ruthenium atoms the $\mu_3$-S ligand is only slightly displaced away from the most highly-substituted Ru(1); individual Ru-S distances are slightly but significantly shorter than in $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$[64].

## The Structure of $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$, **(10)**

This complex is illustrated in Figure 6. It consists of an $Au_2Ru_3$ trigonal-bipyramidal core with Au atoms in an apical and an equatorial site. This metallic unit is symmetrically capped on the $Ru_3$ face by a $\mu_3$-S atom. The cluster is formally derived from **(9)** by removing the H ligand and inserting the second $Au(PPh_3)$ group between the wing tips of the $AuRu_3$ butterfly. This change results in slightly increased Au-Ru, Ru-Ru and S-Ru bond lengths, although the effects are surprisingly small. The Au-Au bond length of 2.967Å is unexceptional as are all the Au-Ru bonds, which range from 2.783-2.866Å. Individual differences arise no doubt from the packing requirements of adjacent ligands. Not unexpectedly the overall geometry differs in only minor detail from that of $Ru_3Au_2(\mu_3\text{-}S)(CO)_8(PPh_3)_3$[16].

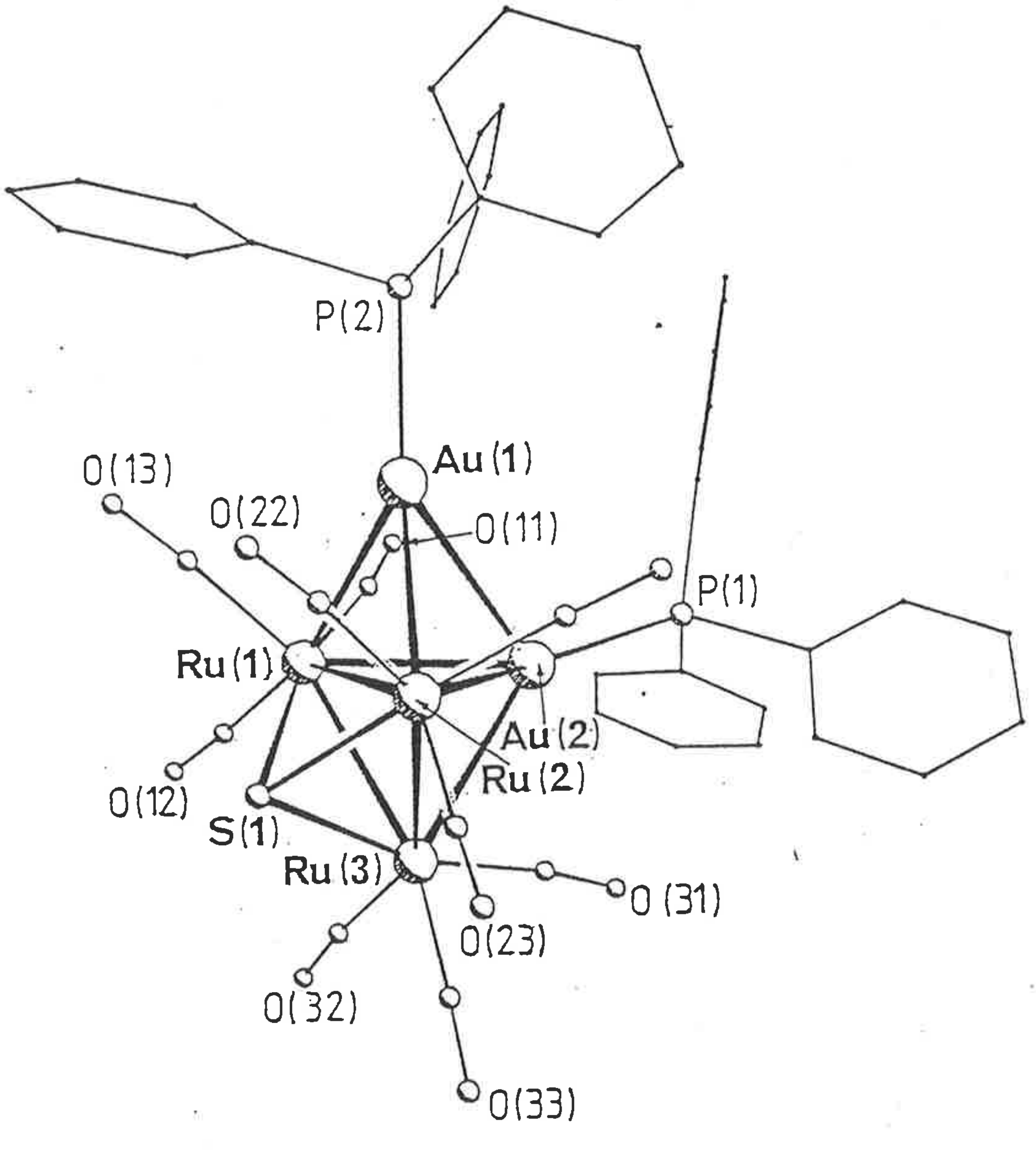


Figure 6 Molecular Structure of $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ (10) (by B.K. Nicholson).

## The Structure of $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$, **(11)**

The overall geometry of **(11)** is shown in Figure 7. Again the $Au(PPh_3)$ group bridges one edge of an isosceles triangle of ruthenium atoms, which is capped by the $\mu_3\text{-}SBu^t$ ligand. The butterfly angle for this cluster is unusually large (see below).

The $\mu_3\text{-}SBu^t$ group is symmetrically bonded to all three ruthenium atoms, with the $Bu^t\text{-}S$ vector making an angle of 87.2° with the $Ru_3$ plane. The Ru-S distances are 0.05 Å shorter than those found in **(9)** as a result of stronger bonding from the formally 5e donor ligand, compared with the 4e $\mu_3\text{-}S$ ligand in **(9)**. However, the Ru-S bonds in **(11)** are <u>ca</u> 0.03 Å longer than those in $Ru_3(\mu_3\text{-}SBu^t)\text{-}(\mu_3\text{-}C_7H_7)(CO)_6$, in which the electron - withdrawing $C_7H_7$ ligand encourages even stronger $S \longrightarrow Ru_3$ donation[53].

The $AuRu_2$ triangle of **(11)** is slightly larger than the equivalent part of **(9)** but it is unclear whether this arises because of the different hinge angle, or whether the electronic properties of the sulphur ligands are responsible. The Ru(1)-Ru(3) and Ru(2)-Ru(3) bond lengths of **(11)** lie between those of the H-bridged and non-bridged ones of **(9)**.

## The Butterfly Angle in **(9)** and **(11)**

The most striking difference between **(9)** and **(11)** is the $AuRu_2/Ru_3$ dihedral angles of 119.4° in the former and 147.5° in the latter. This means that in **(9)** the Au(1), Ru(1), Ru(2) and S atoms are nearly coplanar whereas the Au(1)Ru(1)Ru(2)/ Ru(1)Ru(2)S(1) dihedral angle in **(11)** is 146.5°. This marked change in butterfly angle has

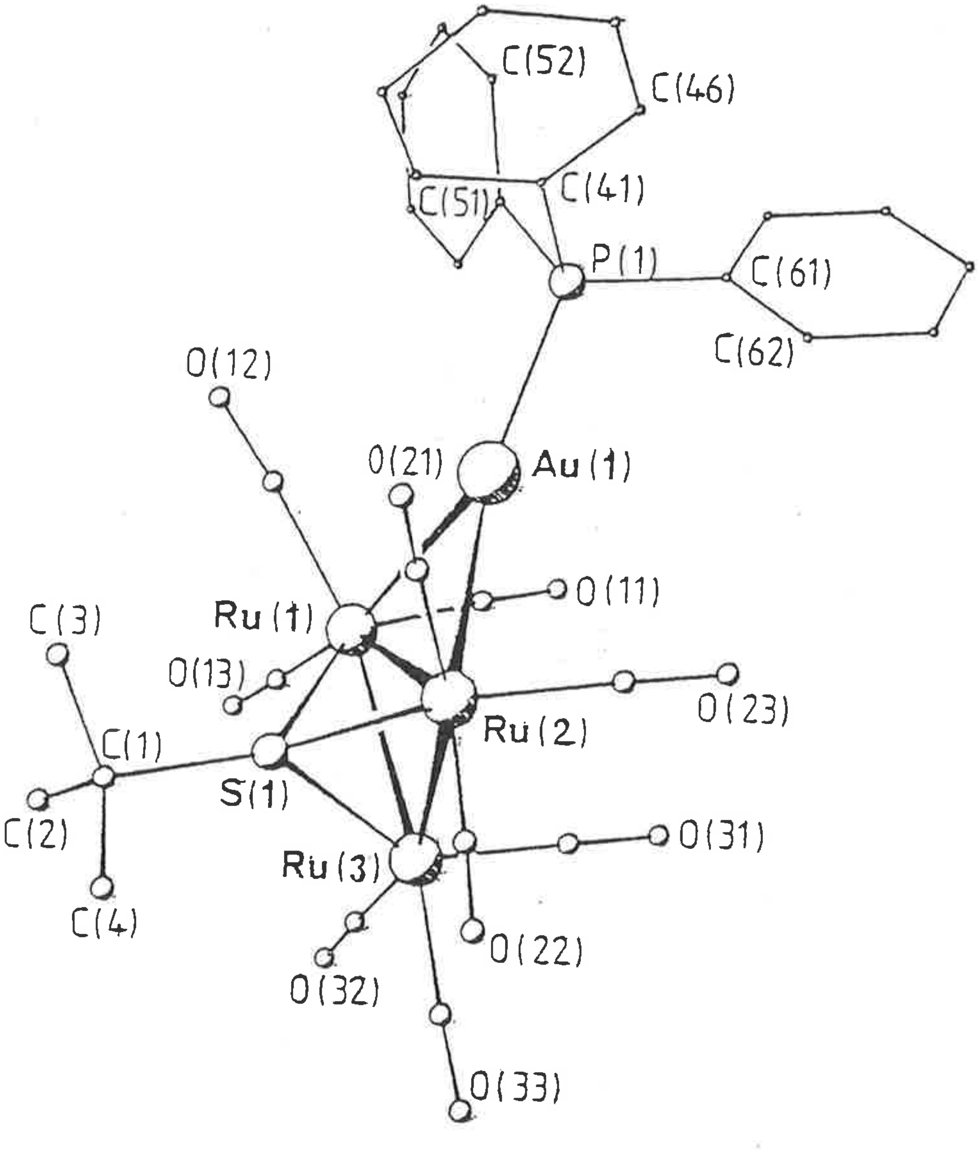
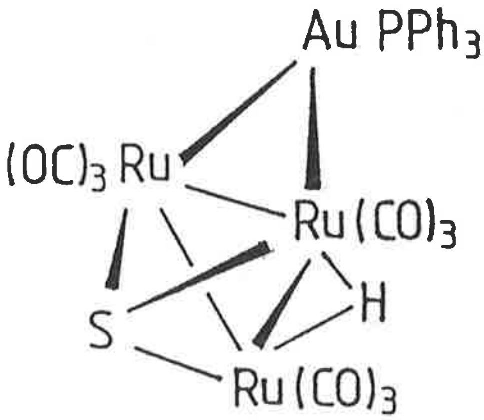


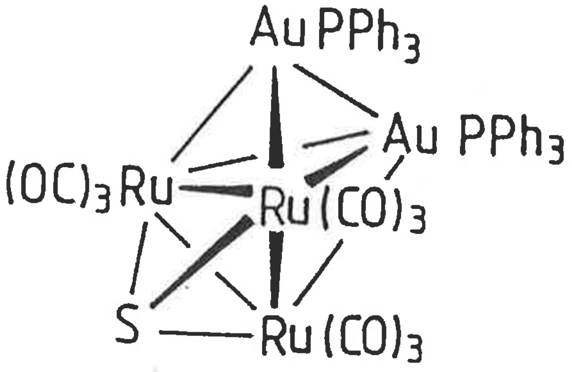
Figure 7 Molecular Structure of $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ **(11)** (by B.K. Nicholson).

remarkably little effect on the dispositions of the CO ligands [see Figs. 1 and 2]. The hinge angle of **(11)** is in fact very similar to the Au(1)Ru(1)Ru(2)/Ru(1)Ru(2)Ru(3) dihedral angle in **(10)** (146.5°) where the extra Au($PPh_3$) group holds the wing tips apart.

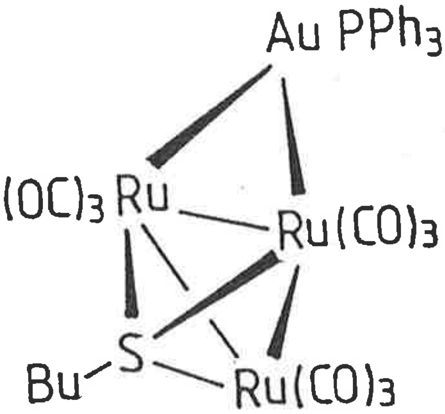
Although the butterfly angle in such tetranuclear clusters has been shown to be very flexible[38], the difference of 28° in this parameter for **(9)** and **(11)** is presumably caused by the electronic differences between $\mu_3$-S and $\mu_3$-$SBu^t$ ligands. Table 6 lists the butterfly angles found for a range of related clusters and it is clear that the normal range is 106° - 120°, so that the angle observed for **(9)** conforms to precedent whereas that of **(11)** is unusually large. Carty et al.[65] have shown a correlation between dihedral angles in tetranuclear butterfly clusters and the formal electron count; 62 electron clusters exhibiting 90° - 117° while 64 electron clusters give 140° - 180° angles. However, all the clusters in Table 2 give a formal 62-electron count. An extension of Carty et al.'s conclusions would suggest that the 5-electron $\mu_3$-$SBu^t$ group is more strongly electron-donating to the cluster core than the ligands associated with the other clusters in Table 2. Consistent with this, it was noted that the Ru-S bonds in **(11)** are relatively short. However caution must be exercised when comparing 'butterfly' angles from solid state measurements as these deviations may be an effect of crystal packing[38].


Au PPh$_3$
(OC)$_3$ Ru
Ru (CO)$_3$
H
S
Ru (CO)$_3$

**9**


Au PPh$_3$
Au PPh$_3$
(OC)$_3$Ru
Ru (CO)$_3$
S
Ru (CO)$_3$

**10**


Au PPh$_3$
(OC)$_3$ Ru
Ru(CO)$_3$
Bu
S
Ru(CO)$_3$

**11**

**Table 1 SELECTED BOND PARAMETERS FOR $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9PPh_3$, (9), $Ru_3Au(\mu_3\text{-}SBu^t)$ $(CO)_9PPh_3$, (11) AND $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$, (10)**

Bond Lengths (Å)

| | (9) | (11) | (10) |
|---|---|---|---|
| Au(1)-Ru(1) | 2.759 1) | 2.773(1) | 2.821(2) |
| Au(1)-Ru(2) | 2.736(1) | 2.766(1) | 2.783(2) |
| Ru(1)-Ru(2) | 2.933(1) | 2.950(1) | 2.996(2) |
| Ru(1)-Ru(3) | 2.885(1) | 2.782(1) | 2.869(2) |
| Ru(2)-Ru(3) | 2.737(1) | 2.780(1) | 2.878(2) |
| Ru(1)-S(1) | 2.363(4) | 2.298(2) | 2.351(5) |
| Ru(2)-S(1) | 2.336(4) | 2.302(2) | 2.355(5) |
| Ru(3)-S(1) | 2.344(4) | 2.300(2) | 2.352(6) |
| Ru(1)-H(1) | 1.84(2) | | |
| Ru(2)-H(1) | 1.79(2) | | |
| Au(2)-Au(1) | | | 2.967(2) |
| Au(2)-Ru(1) | | | 2.867(2) |
| Au(2)-Ru(2) | | | 2.859(2) |
| Au(2)-Ru(3) | | | 2.817(2) |
| C(1)-S(1) | | 1.861(7) | |

All other bonds were unexceptional: Ru-C (1.90 Å), C-O (1.14 Å), Au-P (2.29 Å), P-C (1.81 Å) and C-C (1.50 Å).

Bond Angles (degrees)

| | **(9)** | **(11)** | **(10)** |
|---|---|---|---|
| Ru(1)-Au(1)-Ru(2) | 64.5(1) | 64.4(1) | 64.6(1) |
| Au(1)-Ru(1)-Ru(2) | 57.3(1) | 57.7(1) | 57.1(1) |
| Au(1)-Ru(2)-Ru(1) | 58.1(1) | 57.9(1) | 58.3(1) |
| Ru(1)-Ru(2)-Ru(3) | 61.1(1) | 58.0(1) | 58.4(1) |
| Ru(2)-Ru(1)-Ru(3) | 56.1(1) | 57.9(1) | 58.7(1) |
| Ru(1)-Ru(3)-Ru(2) | 62.8(1) | 64.1(1) | 62.8(1) |
| Ru(1)-S(1)-Ru(2) | 77.2(1) | 79.8(1) | 79.1(1) |
| Ru(1)-S(1)-Ru(3) | 75.6(1) | 74.5(1) | 75.2(1) |
| Ru(2)-S(1)-Ru(3) | 71.6(1) | 74.3(1) | 75.4(2) |
| Ru(1)-S(1)-C(1) | | | 133.1(2) |
| Ru(2)-S(1)-C(1) | | | 133.4(2) |
| Ru(3)-S(1)-C(1) | | | 137.3(2) |

Dihedral Angles (degrees)

| | | | |
|---|---|---|---|
| Au(1)-Ru(1)-Ru(2)<br>Ru(1)-Ru(2)-Ru(3) | 119.4 | 147.5 | 146.5 |

**Table 2 DIHEDRAL ANGLES IN $AuRu_3$ BUTTERFLY CLUSTERS**

| | |
|---|---|
| $AuRu_3(\mu\text{-H})(\mu_3\text{-S})(CO)_9(PPh_3)$ **(9)** | 119.4° |
| $AuRu_3(\mu_3\text{-SBu}^t)(CO)_9(PPh_3)$ **(11)** | 147.5° |
| $AuRu_3(\mu\text{-H})(\mu_3\text{-PPh})(CO)_9(PMe_2Ph)$[9] | 106.2° |
| $AuRu_3(\mu_3\text{-COMe})(CO)_{10}(PPh_3)$[10] | 117° |
| $AuRu_3(\mu\text{-H})_2(\mu_3\text{-COMe})(CO)_9(PPh_3)$[10] | 111.8° |
| $AuRu_3(\mu\text{-Cl})(CO)_{10}(PPh_3)$ | 117.2° |
| $AuRu_3(\mu_3\text{-C}_2\text{Bu}^t)(CO)_9(PPh_3)$[12] | 129.3° |
| $AuRu_3(\mu_3PhPCH_2PPh_2)(CO)_9(PPh_3)$[79] | 144.2° |

## VI. Fast Atom Bombardment Mass Spectrometry (FAB MS) of Metal Clusters

Fast atom bombardment mass spectrometry (FAB MS) is a relatively new technique which uses a stream of neutral atoms (argon or xenon) to sputter ions from solids or liquids[68]. 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 particularly in the present context, of high molecular weight organometallic molecules, all of which are essentially involatile or thermally labile under 'normal' electron impact source conditions.

Perhaps the most complex organometallic compounds to be studied, which understandably were hailed as an indicator of the use of this new technique, were vitamin $B_{12}$ and its coenzyme[68-71]. Recent applications of FAB mass spectrometry to organometallics have been reviewed briefly[72]. The use of FAB MS in the characterisation of high molecular weight metal clusters is increasing in popularity[73-76].

Molecular and fragment ions were measured for each of the three complexes $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)** (m/z 1049), $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)** (m/z 1507) and $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(3)** (m/z 2065). We were not able to observe any ions other than those derived from $PPh_3$ in a conventional EI mass spectrum. To avoid tedious repetition, Table 3 lists only the nominal masses and compositions of ions observed in the FAB mass spectrum, between m/z 700-1050 for **(9)**, between m/z 1100-1500 for **(10)** and between m/z 1550-2100 for **(3)**. The

## Table 3 IONS IN FAB MASS SPECTRA OF THREE RUTNENIUM-GOLD CLUSTER COMPLEXES

(a) $Ru_3(\mu\text{-}H)Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)**
1048, 21, $[M-H]^+$; 1020, 5, $[M'-CO]^+$; 992, 8, $[M'-2CO]^+$;
946, 5, $[M'-3CO]^+$; 936, 13, $[M'-4CO]^+$;
908, 11, $[M'-5CO]^+$; 880, 5, $[m'-6CO]^+$;
852, 12, $[M'-7CO]^+$; 824, 100, $[M'-8CO]^+$;
796, 23, $[M'9CO]^+$; 770, 16, $[M'-SPh-6CO]^+$;
742, 85 $[M'-S-Ph-7CO]$; 714, 38, $[M-S-Ph-8CO]^+$.

(b) $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)**
1504, 100m, $M^+$; 1476, 36, $[M-CO]^+$; 1448, 60, $[M-2CO]^+$;
1420, 55, $[M-3CO]^+$; 1392, 63, $[M-4CO]^+$;
1364, 96, $[M-5CO]^+$; 1336, 44, $[M-6CO]^+$;
1308, 98, $[M-7CO]^+$; 1280, 98, $[M-8CO]^+$;
1252, 95, $[M-9CO]^+$; 1176, 67, $[M-9CO-Ph]^+$.

(c) $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(3)**
2067, 88, $[M+2H]^+$ (= M'); 2040, 38, $[M'-CO]^+$;
2012, 58, $[M'-2CO]^+$; 1980, 27, $[M'-3CO]^+$;
1960, 14, $[M'-CO-Ph]^+$; 1952, 51, $[M'-4CO]^+$;
1924, 54, $[M'-5CO]^+$; 1896, 28, $[M'-6CO]^+$;
1880, 12, $[M'-PPh]^+$; 1868, 39, $[M'-7CO]^+$;
1840, 11, $[M'-8CO]^+$; 1791, 16, $[M-7CO-Ph]^+$;
1760, 17, $[M-7CO-PPh]^+$; 1732, 10, $[M-8CO-PPh]^+$;
1686, 33, $[M-AuPPh_2]^+$; 1658, 27, $[M-CO-AuPPh_2]^+$;
1630, 60 $[M-2CO-AuPPh_2]^+$, 1602, 100, $[M'-AuPPh_3]^+$;
1574, 74, $[M-CO-AuPPh_3]^+$.

highest mass ions appear to be the commonly observed $[M+H]^+$ ions; the fragmentations are those which would be expected on the basis of conventional electron-impact induced fragmentations of similar complexes. In all cases, normalized values are given, corresponding to the most intense component of the isotopic cluster.

Figure 8 illustrates a portion of the FAB mass spectrum of **(3)** above $\underline{m/z}$ 2000, containing the ion clusters $[\underline{M}-nCO]^+$ (n = 0, 1 and 2). From Table 4, which lists the corresponding exact masses of the observed ions compared with the calculated values, together with relative intensities, it can be seen that the highest ion appears to be $[M+2H]^+$ (= $\underline{M}'$). Quasi-molecular ions $[M+H]^+$ have been found previously, for example, in the spectra of co-enzyme $B_{12}$ (at $\underline{m/z}$ 1579)[70,71], several rhodium complexes, and the trinuclear complex $Co_3(\mu\text{-}PPh_2)_3(CO)_6$[73,74]. Reactions of the polynuclear carbonyl clusters with both $H_2$ and $H^+$ are well documented[1], the former occurring with either loss of CO or opening of a metal-metal bond, and we suggest that similar processes may be occurring with complex **(3)**.

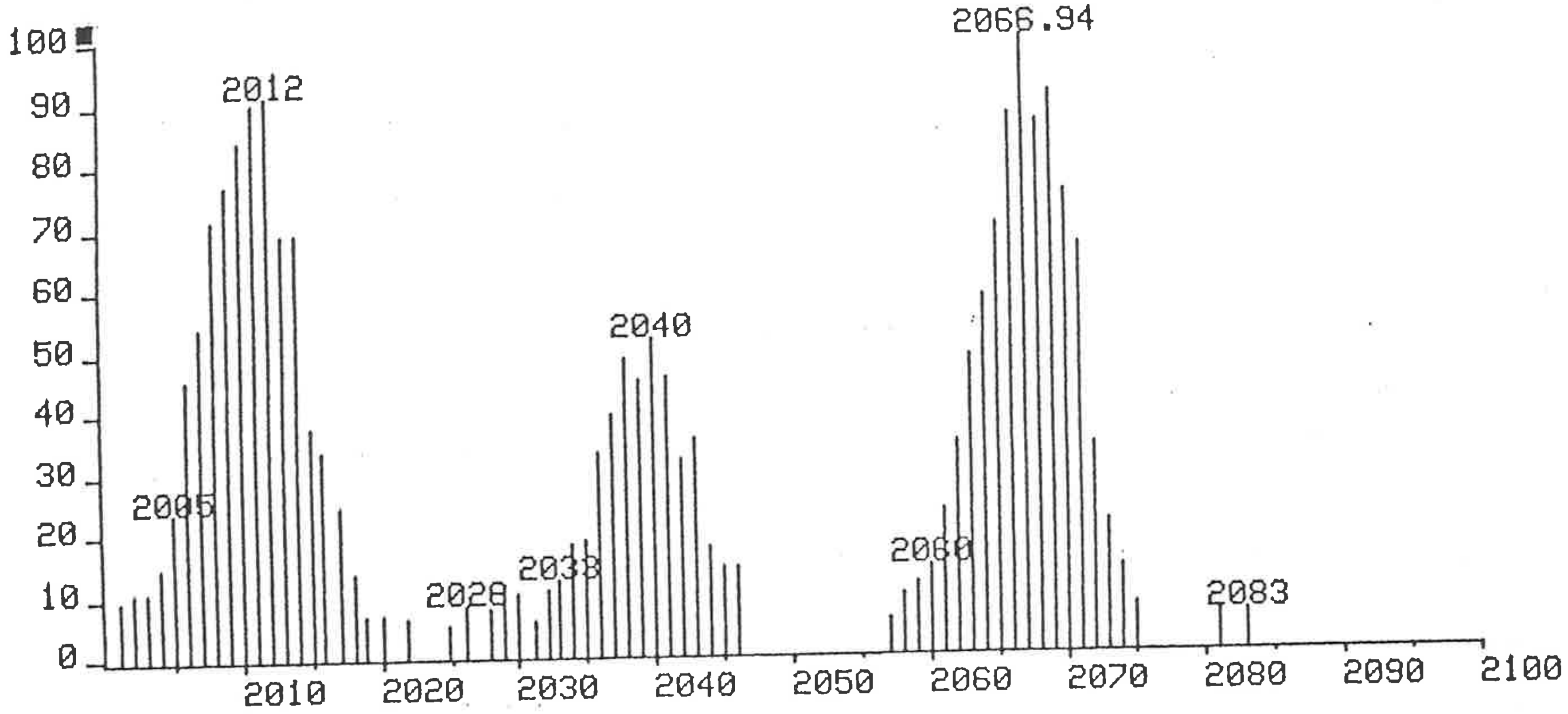


Figure 8 Portion of FAB mass spectrum of $Ru_3Au_3(\mu_3-C_{12}H_{15})(CO)_8(PPh_3)_3$ (3) above m/z 2000, showing $[M+2H]^+$, $[M+2H-CO]^+$ and $[M+2H-2CO]^+$ ion.

**Table 4 EXACT MASSES AND RELATIVE INTENSITIES OF IONS ($\underline{m/z}$ > 2000) IN FAB MASS SPECTRUM OF $Ru_3Au_3(\mu\text{-}C_{12}H_{15}(CO)_8(PPh_3)_3$ (3)**

| Nominal | Exact mass[a] | | Relative intensity[a] | |
|---|---|---|---|---|
| mass | Calculated | Observed | Calculated | Observed |
| 2000 | 1999.996 | 1999.887 | 3.1 | 5.5 |
| 2001 | 2000.996 | 2000.902 | 4.5 | 9.3 |
| 2002 | 2001.995 | 2001.931 | 7.8 | 10.0 |
| 2003 | 2002.994 | 2002.905 | 13.7 | 10.5 |
| 2004 | 2003.994 | 2003.890 | 19.2 | 14.4 |
| 2005 | 2004.993 | 2004.905 | 28.3 | 23.7 |
| 2006 | 2005.993 | 2005.906 | 40.6 | 45.4 |
| 2007 | 2006.992 | 2006.902 | 49.6 | 53.7 |
| 2008 | 2007.992 | 2007.896 | 66.0 | 70.6 |
| 2009 | 2008.991 | 2008.903 | 77.9 | 76.2 |
| 2010 | 2009.991 | 2009.903 | 84.7 | 83.1 |
| 2011 | 2010.991 | 2010.920 | 91.0 | 89.7 |
| 2012 | 2011.991 | 2011.908 | 85.5 | 91.0 |
| 2013 | 2012.992 | 2012.919 | 72.1 | 69.0 |
| 2014 | 2013.992 | 2013.917 | 61.8 | 68.2 |
| 2015 | 2014.994 | 2014.926 | 39.1 | 37.4 |
| 2016 | 2015.994 | 2015.915 | 28.3 | 33.0 |
| 2017 | 2016.996 | 2016.917 | 14.6 | 24.4 |
| 2018 | 2017.997 | 2017.949 | 7.5 | 13.3 |
| 2019 | 2018.998 | 2018.921 | 3.2 | 6.5 |
| 2020 | 2020.000 | 2019.955 | 1.1 | 6.0 |
| 2021 | 2021.003 | | 0.3 | |

Table 4 (cont'd)

| | | | | |
|---|---|---|---|---|
| 2022 | 2021.882 | | | 5.5 |
| 2025 | 2024.992 | 2024.911 | 0.3 | 4.5 |
| 2026 | 2025.992 | 2025.959 | 0.5 | 8.0 |
| 2027 | 2026.992 | | 0.7 | |
| 2028 | 2027.991 | 2027.899 | 1.7 | 7.5 |
| 2029 | 2028.990 | 2028.945 | 2.5 | 11.0 |
| 2030 | 2029.990 | 2029.928 | 4.4 | 9.5 |
| 2031 | 2030.989 | 2031.078 | 7.7 | 5.0 |
| 2032 | 2031.988 | 2031.963 | 10.8 | 10.5 |
| 2033 | 2032.988 | 2032.941 | 15.9 | 12.0 |
| 2034 | 2033.988 | 2033.924 | 22.8 | 17.5 |
| 2035 | 2034.987 | 2034.933 | 28.0 | 18.0 |
| 2036 | 2035.987 | 2035.924 | 37.2 | 32.7 |
| 2037 | 2036.986 | 2036 931 | 43.9 | 38.7 |
| 2038 | 2037.986 | 2037.927 | 47.9 | 48.2 |
| 2039 | 2038.986 | 2038.934 | 51.4 | 44.6 |
| 2040 | 2039.986 | 2039.931 | 48.4 | 51.2 |
| 2041 | 2040.987 | 2040.930 | 40.9 | 45.4 |
| 2042 | 2041.987 | 2041.940 | 35.0 | 31.9 |
| 2043 | 2042.989 | 2042.907 | 22.4 | 34.5 |
| 2044 | 2043.989 | 2043.986 | 16.1 | 17.4 |
| 2045 | 2044.991 | 2044.931 | 8.4 | 13.5 |
| 2046 | 2045.991 | 2045.958 | 4.3 | 13.5 |
| 2047 | 2046.993 | | 1.9 | |
| 2048 | 2047.995 | | 0.6 | |
| 2049 | 2048.998 | | 0.2 | |
| 2053 | 2052.987 | | 0.5 | |

Table 4 (cont'd)

| | | | | |
|---|---|---|---|---|
| 2054 | 2053.987 | | 0.8 | |
| 2055 | 2054.986 | | 1.4 | |
| 2056 | 2055.986 | | 3.3 | |
| 2057 | 2056.985 | 2056.984 | 4.8 | 5.0 |
| 2058 | 2057.985 | 2057.992 | 8.5 | 9.0 |
| 2059 | 2058.984 | 2058.930 | 15.0 | 11.2 |
| 2060 | 2059.983 | 2059.946 | 21.0 | 13.5 |
| 2061 | 2060.983 | 2060.939 | 30.9 | 22.5 |
| 2062 | 2061.983 | 2061.937 | 44.3 | 33.9 |
| 2063 | 2062.982 | 2062.934 | 54.3 | 47.7 |
| 2064 | 2063.981 | 2063.932 | 72.2 | 57.7 |
| 2065 | 2064.981 | 2054.938 | 85.4 | 69.1 |
| 2066 | 2065.981 | 2065.940 | 93.1 | 86.6 |
| 2067 | 2066.981 | 2066.943 | 100 | 100 |
| 2068 | 2067.981 | 2067.932 | 94.4 | 86.0 |
| 2069 | 2068.982 | 2068.939 | 79.9 | 90.5 |
| 2070 | 2069.982 | 2069.939 | 68.4 | 74.2 |
| 2071 | 2070.984 | 2070.946 | 43.9 | 65.6 |
| 2072 | 2071.984 | 2071.938 | 31.6 | 33.3 |
| 2073 | 2072.986 | 2072.967 | 16.6 | 20.5 |
| 2074 | 2073.986 | 2073.957 | 8.5 | 13.0 |
| 2075 | 2074.988 | 2074.867 | 3.7 | 7.0 |
| 2076 | 2075.990 | | 1.3 | |
| 2077 | 2076.993 | | 0.3 | |

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[a] Exact masses and relative intensities calculated for the ions $[C_{72}H_{62}Au_3O_6P_3Ru_3]^+$ ($[M+2H-2CO]^+$), $[C_{73}H_{62}Au_3O_7P_3Ru_3]^+$ ([M+2H-CO]+), and [C74H62Au3O8P3Ru3]+ ([M+2H]+).

## 3. CONCLUSION

It has been shown that the generation of cluster anions can be achieved by the addition of K-Selectride. The reactivity of these cluster anions with the $Au(PR_3)$ fragment is varied. The addition of one $Au(PR_3)$ fragment is the straightforward replacement of the H in the cluster hydride. The $Au(PR_3)$ fragments in $Ru_3Au(\mu\text{-}H)\text{-}(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)** and $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ **(11)** occupy the same edge-bridging positions as do the H in the corresponding hydrido clusters[64].

However, when there is more than one $Au(PR_3)$ fragment, as in $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(2)**, the resulting complexes do not model the cluster hydride. A feature of these gold derivatives which is not shown by the corresponding hydride is the tendency towards the formation of gold-gold bond when two or more $Au(PR_3)$ fragments are present.

The coordination of two $Au(PR_3)$ fragments on the cluster is similar to dihydrogen ($H_2$) as in $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)** and hence may model initial attack of $H_2$ on a cluster. While no cluster complexes containing molecular $H_2$ are known at present, mononuclear complexes, such as $W(H_2)(CO)_3(PPr^i_3)_2$ have been recently prepared[81].

We have also shown that a further type of reactivity associated with the generation of the cluster anions, $[Ru(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ and its poly-auration is the addition of H to the cluster-bound ligand, $C{\equiv}CBu^t$ and conversion to a vinylidene, $C{=}CHBu^t$. Thus auration and hydrogenation of $Ru_3(\mu\text{-}H)(C_2Bu^t)(CO)_9$ **(3)** are closely related since the isolobal analogue of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$, namely $Ru_3(\mu\text{-}H)_2\text{-}(\mu_3\text{-}C{=}CHBu^t)(CO)_9$, can be considered to be a likely intermediate in the conversion of **(3)** to the alkylidene complex, $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_2Bu^t)(CO)_9$ **(7)**.

When three $AuPR_3$ fragments are added to the cluster as in $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ **(2)**, this may model coordination of $H_3^+$ on the cluster (as $H_3^+$ is isolobal with $[Au_3(PPh_3)_3]^+$). The molecular structure of $H_3^+$ determined by foil-induced dissociation of a fast molecular ion beam is an equilateral triangle[82].

Thus in this cluster, the isolobal analogue of $H_3^+$ is present; no cluster complexes containing $H_3$ have been prepared so far.

## 4. EXPERIMENTAL

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. Subsequent work-up was carried out with no special precautions to exclude air. Reagent-grade solvents were dried and distilled under nitrogen before use. IR spectra were obtained with a Perkin-Elmer 683 double-grating spectrometer; $^1H$ NMR spectra were recorded on a Bruker WP80 instrument. Microanalyses were by the Canadian Microanalytical Service, Vancouver. FAB mass spectra of some of the complexes were recorded after FAB ionisation with Xe as the collision gas (ion gun conditions; 8 kV and 1 mA), using a VG ZAB2F(HF) mass spectrometer combined with a VG 11-250 data system, from solutions of the complexes in thioglycerol. Exact mass determinations were made after calibration of the instrument with suitable reference compounds.

The complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9$[51], $Ru_3(\mu\text{-}H)(C_2Bu^t)(CO)_9$[52], $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$[53], $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$[53], and $[PPN][Ru_3(\mu\text{-}NO)(CO)_{10}]$[54] were prepared by literature methods. <u>K</u>-Selectride ($K[HBBu^s_3]$), 0.5<u>M</u> in tetrahydrofuran was supplied by Aldrich, and used as received. The syntheses of $AuCl(PPh_3)$[55] and $[O\{Au(PPh_3)_3\}_3]\text{-}[BF_4]$[56] were minor modifications of those reported in the literature.

### A. Chloro(triphenylphosphine)gold, $AuCl(PPh_3)$

$$H[AuCl_4] + 2PPh_3 + H_2O \longrightarrow AuCl(PPh_3) + Ph_3PO + 3HCl$$

Triphenylphosphine (3.08 g, 11.74 mmole) was dissolved in 50 ml absolute (i.e. 100%) ethanol contained in a 100 ml conical flask, warming if necessary to complete dissolution. A solution of 2.0 g (5.87 mmole) hydrogen tetrachloroaurate(1-),

$H[AuCl_4].nH_2O$, in 10 ml ethanol was filtered, to remove any insoluble gold-containing material, into the stirred solution of triphenylphosphine. This gave a white precipitate. After stirring for 15 minutes, the white microcrystalline solid was collected on a fritted glass filter (Corning porosity 4), washed with ethanol (2 x 5 ml), and dried in vacuum (0.1 torr) to give pure $AuCl(PPh_3)$. Yield: 1.94-2.32 g, (67-80%), m.p. 242-243°C.

Anal. Calcd. for $C_{18}H_{15}AuClP$: C, 43.6, H, 3.1. Found: C, 43.5; H, 3.2.

### B. $\mu_3$-oxo-[tris(triphenylphosphine gold)] (1+) tetrafluoroborate, $[O\{Au(PPh_3)\}_3][BF_4]$

$$3AuCl(PPh_3) + Ag_2O + NaBF_4 \longrightarrow [O\{Au(PPh_3)\}_3][BF_4] + 2AgCl + NaCl$$

Silver oxide was prepared by adding a solution of 0.45 g (11.2 mmole) sodium hydroxide in 10 ml water to a solution of 1.88 g (11.0 mmole) silver nitrate in 10 ml water. The brown precipitate was removed by filtration on a glass frit, washed with water (2 x 5 ml), ethanol (2 x 5 ml), and acetone (2 x 5 ml), and air-dried. The freshly prepared solid silver oxide was added to a round-bottomed, 250 ml flask containing a solution of 1.5 g (3.0 mmole) $AuCl(PPh_3)$ in 100 ml acetone, together with a magnetic stirring bar. This was followed by addition of 1.88 g (17.1 mmole) sodium tetrafluoroborate. The mixture was stirred rapidly for 1 hour. After this time, the acetone was removed (rotary evaporator), and the solid residue was extracted with chloroform (3 x 15 ml). The combined extracts were filtered into 150 ml of freshly distilled dry diethyl ether to precipitate the $\mu_3$-oxo-trigold (1+) compound which was removed by filtration of a glass frit and air-dried. Yield: 1.14-1.20 g (76-80%), m.p. 207-208°C (dec). The product was sufficiently pure to be used in further reactions, but sometimes had a slight purple tinge. If necessary, the compound was recrystallised by dissolving in the minimum amount of chloroform and adding ca 1.5-fold volume of acetone. Anal. Calcd. for $C_{54}H_{45}Au_3BF_4OP_3$: C, 43.8; H, 3.1; Found: C, 43.7; H, 2.9. IR (nujol) 1040-1070(br) $cm^{-1}$ ($BF_4$).

### Reaction between $[Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_9]^-$ and $[O\{Au(PPh_3)\}_3][BF_4]$

K-Selectride (0.28 mmol) was added dropwise to a solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9$ **(1)** (200 mg, 0.28 mmol) in dry, deoxygenated tetrahydrofuran (15 ml), and the solution was stirred for 10 minutes. Solid $[O\{Au(PPh_3)\}_3][BF_4]$ (1328 mg, 0.093 mmol) was then added, and the mixture was stirred for 18 hr at room temperature. After removal of solvent in vacuo, excess K-Selectride was destroyed by addition of ethanol; after evaporation, the solid remaining was dissolved in acetone. Preparative TLC (2:3 acetone: cyclohexane) of the filtered solution gave four bands: Band 1 ($R_f$ 0.83) contained $Ru_3(\mu\text{-}H)$-$(\mu_3\text{-}C_{12}H_{15})(CO)_9$ (47 mg, 24%) (IR identification); Band 2 ($R_f$ 0.71) contained a trace of orange material, with ν(CO) (cyclohexane) at 2064w, 2044vs, 2032m, 2002s, 1994s, 1976(sh), 1956(sh), 1907(sh) $cm^{-1}$; Band 3 ($R_f$ 0.65) afforded only a trace of red solid with ν(CO) (cyclohexane) 2072w, 2044w, 2020m, 1998vs, 1966m, 1928m $cm^{-1}$; Band 3 ($R_f$ 0.60) contained the major product, purple $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})$- $(CO)_8(PPh_3)_3$ **(2)** (56 mg, 29%), m.p. 223°C (dec.), which was recrystallised from 1:4 benzene:cyclohexane (Found : C, 43.85; H, 2.64;

$C_{74}H_{60}Au_3O_8P_3Ru_3$ requires C, 43.03; H, 2.93%) IR ν(CO) (cyclohexane): 2040m, 1974vs, 1957(sh), 1918m cm$^{-1}$; $^1$H NMR : δ($CDCl_3$) 0.88-5.95, m, 14H, $C_{12}$ ring protons; 6.10, s, 1H, allylic CH; 7.2, m, 45H, PPh.

Reaction between $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ and $[O\{Au(PPh_3)\}_3][BF_4]$

A solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** (100 mg, 0.157 mmol) in dry deoxygenated tetrahydrofuran (THF) (15 ml) was treated with K-Selectride (0.31 ml of a 0.5 M solution in THF) for 15 minutes. Solid $[O\{Au(PPh_3)\}_3]$- $[BF_4]$ (232 mg, 0.157 mmol) was added and the mixture stirred for 3 hr. After removal of the solvent, the residue was separated by preparative TLC [silica gel, acetone/ cyclohexane (35/65)]. Four bands developed: Band 1: orange, $R_f$ 0.57, was recrystallised from n-hexane to give orange crystals, identified as $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ **(4)** (15 mg, 9%) m.p. 140°C (dec). Found: C, 35.92; H, 2.15. $C_{33}H_{24}AuO_9PRu_3$ calcd: C, 36.16; H, 2.19%. IR: ν(CO) (cyclohexane 2076s, 2054vs, 2036vs, 1999vs, 1990(sh), 1970m, cm$^{-1}$ [lit[5]: ν(CO) (hexane) 2074m, 2051s, 2036vs, 1996vs, 1968m, cm$^{-1}$]; $^1$H NMR: δ($CDCl_3$) 7.46, m, 15H, Ph; 1.38, s, 9H, $Bu^t$; Band 2: red, $R_f$ 0.51, was recrystallized from dichloromethane (petroleum spirit (1/2) to give deep red crystals, identified (X-ray crystallography) as $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ **(5)** (40 mg, 16%) m.p. 150°C (dec). Found: C, 40.03; H, 2.77. $C_{51}H_{40}Au_2O_9P_2Ru_3$ calcd: C, 39.36; H, 2.51%. IR: ν(CO) (cyclohexane) 2048m, 2039w, 2018vs, 1978m, 1962s cm$^{-1}$; $^1$H NMR: δ($CDCl_3$) 7.27, m, 30H, Ph; 6.30, s, 1H, =CH; 1.42, s, 9H, $Bu^t$; Band 3: red, $R_f$ 0.46, traces only, IR: ν(CO) (cyclohexane) 2047m, 2037s, 2008s(br), 1972s, 1958(sh), 1930w, 1910w cm$^{-1}$, not further investigated; Band 4: orange, $R_f$ 0.42, was recrystallised from $CH_2Cl_2$/n-heptane (1/2) to give orange crystals, identified as $Ru_3Au_3(C_2Bu^t)(CO)_8(PPh_3)_3$ **(6)** (10 mg, 3%) m.p. 150°C (changes colour). Found: C, 41.55; H, 2.54. $C_{68}H_{54}Au_3O_8P_3Ru_3$ calcd: C, 41.12; H, 2.74%. IR: ν(CO) (cyclohexane) 2048vs, 2018vs, 1982s, 1971m, 1964s, 1956w, 1912m cm$^{-1}$; $^1H$ NMR: δ($CDCl_3$) 7.44, m, 45H, Ph; 1.50, s, 9H, $Bu^t$.

Sequential reactions of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ with $H^-$ and $H^+$

(i) K-Selectride (0.16 mmol, 0.32 ml of 0.5 M solution in tetrahydrofuran) was added to a solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** (100 mg) in the same solvent (10 ml). The colour darkened immediately, and $H_3PO_4$ (5 drops) was added after one minute. After stirring (1 h), the solution was evaporated, the residue dissolved in $CH_2Cl_2$ (10 ml), and washed with water (3 x 10 ml). Evaporation and purification by preparative TLC (acetone/light petroleum 10/90) afforded $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** (60 mg, 60%); a considerable amount of material was left as a dark-coloured base-line.

(ii) Excess K-Selectride (0.48 mmol) was added to $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** (150 mg, 0.24 mmol) in tetrahydrofuran (20 ml). After 5 minutes, solvent was removed and the residue taken up in $CH_2Cl_2$ (10 ml). Addition of $HPF_6.OEt_2$ (5 drops) and separation (preparative TLC, acetone/light petroleum 10/90) afforded four fractions: (a) yellow unknown) (9 mg), $R_f$ 0.84, ν(CO) (cyclohexane) 2107w, 2100(sh), 2079s, 2074s, 2057vs, 2042s, 2024vs, 1996m cm$^{-1}$; (b) $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ **(3)** (11 mg, 7%); (c) orange unknown (trace), $R_f$ 0.46, ν(CO) (cyclohexane) 2070m, 2053m, 2040w, 2025m, 2009w cm$^{-1}$; (d) orange-brown unknown (trace), $R_f$ 0.24.

## Sequential reactions of $Ru_3Au(\mu_3-C_2Bu^t)(CO)_9(PPh_3)$ with $H^-$ and $H^+$

Addition of K-Selectride (0.064 mmol) to the $Ru_3Au$ complex **(4)** (70 mg, 0.064 mmol) in tetrahydrofuran (10 ml), was followed by solvent removal (after 2 minutes), and protonation ($HPF_6.OEt_2$) of a solution of the residue in $CH_2Cl_2$. After 2 h, evaporation and preparative TLC (acetone/light petroleum 30/70) afforded ten multi-colour bands, of which only two were obtained in more than trace amounts: (a) $Ru_3(\mu-H)(\mu_3-C_2Bu^t)-(CO)_9$ **(3)** (6 mg, 15%), and (b) bright yellow unknown (8 mg), $R_f$ 0.61, υ(CO) (cyclohexane) 2075s, 2038vs, 1991vs, 1982(sh), 1970s cm$^{-1}$.

## Reaction of $[Ru_3(\mu-H)(\mu_3-S)(CO)_9]^-$ with $[O\{Au(PPh_3)\}_3]^+$

A solution of $Ru_3(\mu-H)_2(\mu_3-S)(CO)_9$ (220 mg, 0.34 mmol in thf (15 ml) was treated with $K[HBBu^s_3]$ (0.34 mmol). After 2 minutes the orange solution was treated with solid $[O\{Au(PPh_3)\}_3[BF_4]$ (167 mg, 0.113 mmol). After *ca.* 20 hours, solvent was evaporated. A benzene extract of the residue was filtered and chromatographed, eluting with benzene-cyclohexane (1:1). Band 1, ($R_f$=0.83), orange-yellow, (20 mg). ν(CO) (cyclohexane) 2088, 2066vs, 2040vs, 2024w, 2004sh, 1998s, 1985w, 1983m cm$^{-1}$, not identified; Band 2, ($R_f$=0.72, orange $Ru_3Au(\mu-H)(\mu_3-S)(CO)(PPh_3)$ **(9)**, (10 mg, 3%), m.p. 159°C (dec), recrystallised from heptane. (Found: C, 31.21; H, 1.22;

$C_{27}H_{16}AuO_9PRu_3S$ requires C, 30.95; H, 1.54%). ν(CO) (cylohexane) 2084s, 2063vs, 2050m, 2038vs, 2010m, 1996vs, 1991m, 1958m cm$^{-1}$; $^1$H NMR: δ($CDCl_3$) 7.5 m, 15 H, Ph: -19.85 s, 1 H, Ru-H; Band 3, red, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)**, (70 mg, 14%) m.p. 186°C (dec), recrystallised from diethyl ether. (Found: C, 35.70; H, 1.80; $C_{45}H_{30}Au_2O_9P_2Ru_3S$ requires C, 35.87; H, 2.07%). ν(CO) 2060s, 2035vs, 2025vs, 1986w, 1973s, 1964s cm$^{-1}$; $^1$H NMR: δ($CDCl_3$) 7.1 m, Ph.

### Reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9]^-$ with $AuCl(PPh_3)/TlPF_6$

A solution of $[HRu_3(\mu_3\text{-}S)(CO)_9]^-$ (0.51 mmol) in thf (20 ml), prepared as above, was treated sequentially with $AuCl(PPh_3)$ (252 mg, 0.51 mmol) and $TlPF_6$ (178 mg, 0.51 mmol). After stirring overnight TlCl was filtered and the filtrate evaporated *in vacuo*. The residue was extracted with acetone and chromatographed, eluting with acetone-light petroleum (3:7): Band 1, yellow, $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$; Band 2, $R_f$=0.82), orange $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)** (150 mg, 28%); Band 3, red, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)** (99 mg, 13%).

### Reaction of $[Ru_3(\mu_3\text{-}SBu^t)(CO)_9]^-$ with $AuCl(PPh_3)/TlPF_6$

$Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ (150 mg, 0.23 mmol) was dissolved in thf (15 ml) and $K[HBBu^s_3]$ 0.23 mmol) was added. After 5 minutes conversion to $[Ru_3(\mu_3\text{-}SBu^t)(CO)_9]^-$ was complete (TLC); $AuCl(PPh_3)$ (115 mg, 0.23 mmol) and $TlPF_6$ (81 mg, 0.23 mmol) were added and the mixture stirred for 2 hours. After filtration and evaporation, the residue was extracted with $CH_2Cl_2$. Chromatography, eluting with acetone-light petroleum (3:7) gave 7 bands: Bands 1, ($R_f$=0.96), 3 ($R_f$=0.69) and 7 ($R_f$=0.31) were present in trace amounts only, and were not identified; Band 2 ($R_f$=0.89), traces, $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$; Band 4, ($R_f$=0.64), yellow/orange, $Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9(PPh_3)$ **(9)**, (10 mg, 4%); Band 5, ($R_f$=0.58), orange, $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$ **(11)**, (72 mg, 28%), m.p. 154°C (dec), recrystallised from heptane. (Found C, 33.82; H, 1.86; $C_{31}H_{24}AuO_9PRu_3S$ requires C, 33.73; H, 2.19%) $\nu$(CO) (cyclohexane) 2066s, 2030vs, 2024sh, 1998vs, 1983sh, 1975s, 1964s, $cm^{-1}$; $^1H$ NMR: $\delta(CDCl_3)$ 7.51-7.24 m, 15H, Ph; 1.48s, 9H, $Bu^t$; Band 6, ($R_f$=0.39), red, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ **(10)**, (11 mg, 3%).

### Reaction of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ with $K[HBBu^s_3]$ and subsequent protonation with $H_3PO_4$

A solution of $[Ru_3(\mu_3\text{-}SBu^t)(CO)_9]^-$ was generated from $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ (100 mg, 0.155 mmol) and $K[HBBu^s_3]$ (0.155 mmol) in thf (10 ml) for 5 minutes. Complete conversion was confirmed by TLC. $H_3PO_4$ (5 drops) was added and the mixture stirred for an hour. After evaporation, a $CH_2Cl_2$ (10 ml) extract of the residue was washed with water (5 x 10 ml) and dried by azeotropic distillation with benzene and ethanol. Subsequent chromatography [acetone-light petroleum, (1:9)] gave 3 bands: Band 1, ($R_f$=0.92) yellow, trace. $\nu$(CO) 2068vs, 2044m, 2028s, 2010m, 1979m $cm^{-1}$ (not identified); Band 2, ($R_f$=0.83) $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)\text{-}(CO)_9$ (9 mg, 10%); Band 3, ($R_f$=0.69) $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ (50 mg, 50%).

### Reaction of $[Re(CO)_5]^-$ and $[O\{Au(PPh_3)\}_3][BF_4]$

A filtered solution of $[Re(CO)_5]^-$ (0.067 mmol) was generated from the reaction of $Re_2(CO)_{10}$ (44 mg, 0.067 mmol) with Na amalgam (0.135 mmol) in thf (20 ml) in the usual manner[82]. After 90 min, the $[Re(CO)_5]^-$ solution was treated with $[O\{Au(PPh_3)_3\}_3][BF_4]$ (100 mg, 0.067 mmol). After *ca.* 4 hours, solvent was removed *in vacuo*. A dichloromethane extract of the residue was filtered and a four-fold excess of diethyl ether was added slowly and left at -30°C for *ca.* 18 hours. The golden orange microcrystalline needles that separated out were collected on a glass sinter to yield $[Re(CO)_4Au_3(PPh_3)_3]$ (45 mg, 37%), m.p. 140°C(dec) (Found: C, 41.38; H, 2.53; $C_{58}H_{45}Au_3O_4P_3Re$ requires C, 41.53; H, 2.71%) ν(CO) (THF) 2023m, 1940s(br) cm$^{-1}$; $^1$H NMR: ν($CDCl_3$) 7.1, m, Ph.

### Reaction of $[PPN][Ru_3(NO)(CO)_{10}]$ with $AuClPPh_3$

$[PPN][Ru_3(NO)(CO)_{10}]$ (200 mg, 0.174 mmol) was dissolved in freshly distilled $CH_2Cl_2$ (25 ml) and $AuCl(PPh_3)$ (86 mg, 0.174 mmol) was added and the mixture stirred for 2 hours. Solvent was removed *in vacuo* and a dichloromethane extract of the residue was filtered and chromatographed, eluting with diethyl ether: Band 1, (Rf=0.89), orange, $Ru_3Au(NO)(CO)_{10}$-$(PPh_3)$ (135 mg, 72.3%) m.p. 180°C (dec), recrystallised from diethyl ether/n-hexane. (Found: C, 31.20; H, 1.11, N, 1.25; $C_{28}H_{15}AuO_{10}PRu_3N$ requires C, 31.36; H, 1.41; N, 1.31%) ν(CO) 2092m, 2045vs, 2021m,sh, 2013vs, 2002w, 1995m, 1987w cm$^{-1}$; $^1$H NMR : δ($CDCl_3$) 7.2, m, Ph; Band 2, ($R_f$=0.17), pink (trace) not identified.

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# CHAPTER 4

# TRAPPING OF ARYLNITRENES ON TRINUCLEAR CLUSTERS

## 1. INTRODUCTION

One of the most fascinating fields of organometallic chemistry is concerned with the stabilization of labile organic species by coordination to a transition metal.

More generally, some classes of transition metal complexes are able to generate these species under relatively mild conditions *in situ* from a suitable precursor. Once formed, they may either be trapped on the metal, or they may give rise to reactions with another ligand bound to the metal, or they may be involved in reactions with an organic substrate, sometimes in a catalytic sequence.

Among these species, though not well studied, are the labile nitrogen-containing intermediates nitrenes, R-N: (R = alkyl, aryl, etc). Involvement of nitrene intermediates has been proposed in catalytic reactions where nitrobenzene is deoxygenated by carbon monoxide and water[1].

$$ArNO_2 + 3CO + H_2O \xrightarrow[\text{solvent}]{\text{catalyst}} ArNH_2 + 3CO_2 \qquad ...1$$

Recently, polynuclear metal carbonyls have been used as catalysts in the conversion of nitrobenzene into aniline[2]. Isolation of polynuclear complexes with RN groups interacting with more than one metal atom could be taken as indirect evidence for the involvement of such species in the catalytic reaction. The best-known nitrene complexes involve a metal in a high oxidation state. The first report on this reaction, employing a primary amine as a nitrene source, appeared more than 25 years ago[3].

$$OsO_4 + Bu^tNH_2 \xrightarrow{\quad\quad} (Bu^tN)OsO_3 + H_2O \qquad ...2$$

The reactions of organic azides, nitro compounds and isocyanates with transition metal complexes to give nitrene complexes have been reviewed briefly[4,5].

In 1967, Knox and co-workers[6] reacted nitromethane and $Fe_2(CO)_9$ to give the first $\mu_3$-NR complex, $Fe_3(\mu_3\text{-}NMe)_2(CO)_9$ **(1)**, which was assigned structure **(1)** by analogy to the known compound $Fe_3(\mu_3\text{-}S)_2(CO)_9$[7] and confirmed in 1969 by an X-ray crystal structure[8] [Figure 1]. The first nitrene $Ru_3$ cluster was reported in 1970 from the reaction of $Ru_3(CO)_{12}$ and $CF_3CHFCF_2N_3$[9] which gave $Ru_3(\mu_3\text{-}NCF_2CHFCF_3)_2(CO)_9$ **(2)**, assumed to have a structure analogous to that of complex (1).

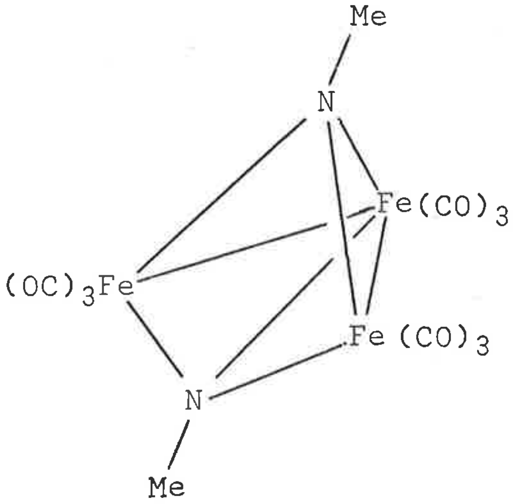


Figure 1 Molecular Structure of (1)

In 1978, Alper and Paik[18] described the reaction of nitrobenzenes with $Fe_3(CO)_{12}$ and CO under phase-transfer-catalysed (PTC) conditions to give anilines as the major products, and $Fe_3(\mu_3\text{-}NC_6H_4R)_2(CO)_9$ **(3)** and $Fe_2(\mu_2\text{-}NHC_6H_4R)_2\text{-}(CO)_6$ **(4)** (R = p-Me, p-OMe, p-Cl, m-$CH_2Cl$).

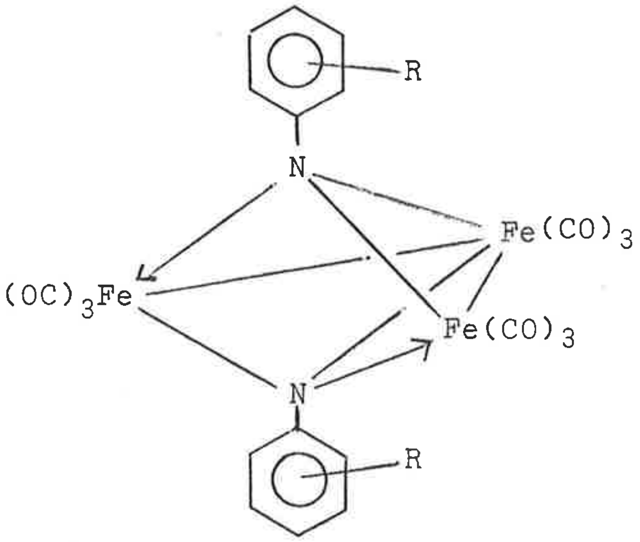


Figure 2  Proposed structure for (3)

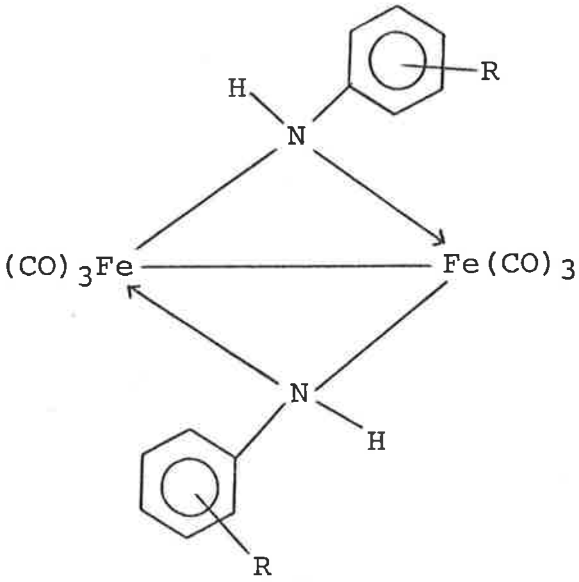


Figure 3  Proposed structure for (4).

The first successful cluster-catalysed reduction of nitrobenezene to aniline was reported by Calderazzo et al.[10] who used hydrogen at high pressures in the presence of $Ru_3(CO)_{12}$ or other ruthenium compounds such as $Ru(CO)_5$ or $Ru(acac)_3$. They postulated the formation of nitrenes stabilized by complexation on the metal, and of hydridocarbonyls in the hydrogen transfer step. This led to the investigation of reactions of $Ru_3(CO)_{12}$ with nitrobenzene and aniline by Sappa and co-workers[11]. Reactions of $Ru_3(CO)_{12}$ with $PhNO_2$ afforded $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(CO)_9$ (5) and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (6a) while with $PhNH_2$, $Ru_3(\mu\text{-H})(\mu\text{-NHPh})(CO)_{10}$ (7) was formed.

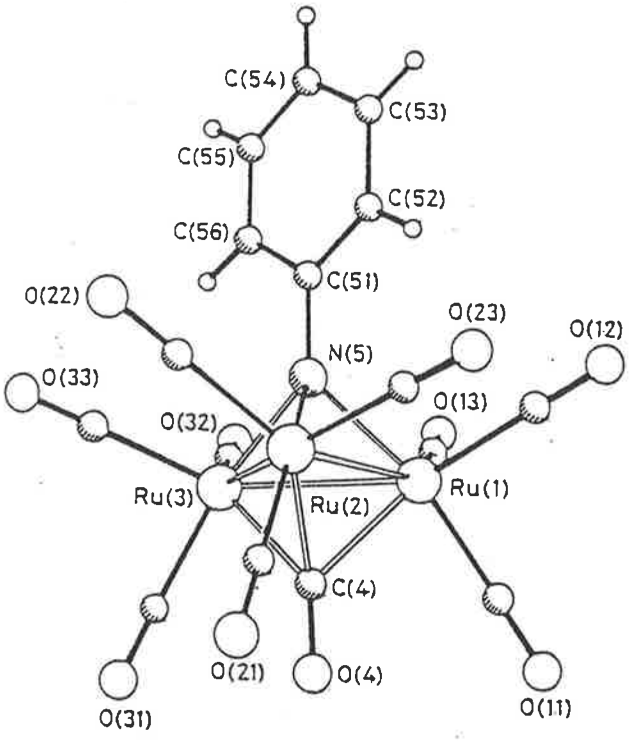
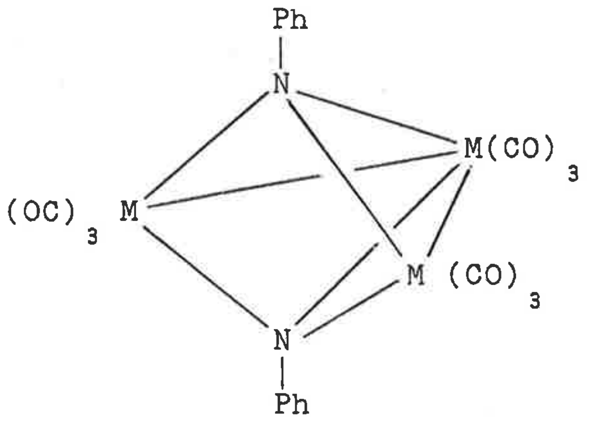


Figure 4 Molecular structure of (5)



(a) M = Ru

(b) M = Fe

Figure 5 Molecular structure of (6)

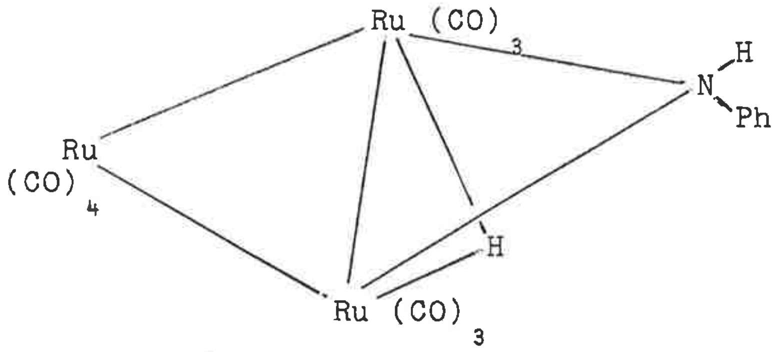
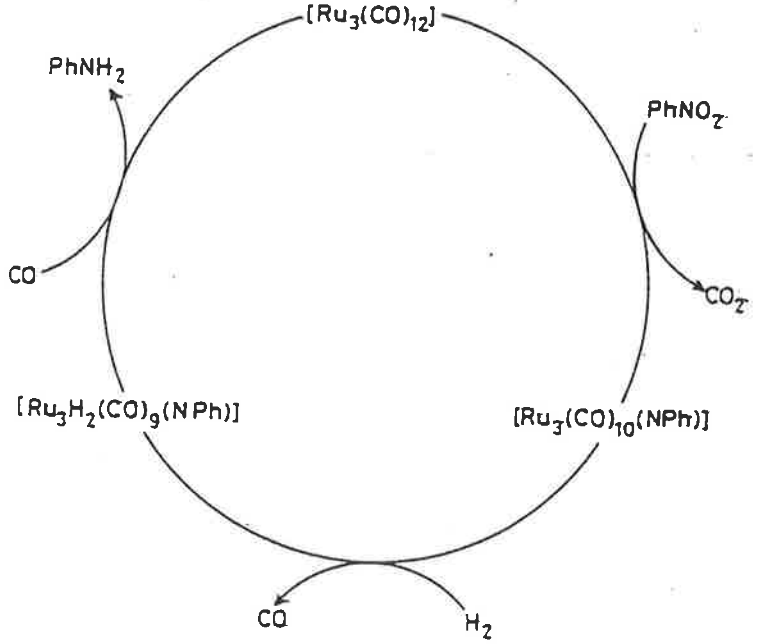


Figure 6 Proposed structure for (7)

The reaction of $Ru_3(CO)_{12}$ and PhNCO gave complex **(5)** and trace amounts of complex (6a), while PhNCS gave two unidentified products. The reaction of **(5)** with excess $PhNO_2$ gave (6a) in 30% yield. The complex $Ru_3(\mu_3\text{-NPh})$-$(\mu_3\text{-CO})(CO)_9$ also reacts with hydrogen (20 atm, 85°C, 2 h) to give $Ru_3(\mu\text{-H})_2(\mu_3\text{-NPh})(CO)_9$ **(8)** in 80% yield, together with $Ru_4(\mu\text{-H})_4(CO)_{12}$.[12]

Replacement of CO in **(5)** (a 2e donor) by NPh in (6a) (a 4e donor) results in an open $Ru_3$ cluster; formal electron counting requires three Ru-Ru bonds in **(5)** but only two in (6a). The observed Ru-Ru separations are in accord with this, those in **(5)** being 2.741(1), 2.750(1) and 2.735(1) Å; 2.754(1), 2.760(1) and 2.734(1) Å, (for 2 independent molecules)[12] while there are two short separations [2.710(1), 2.626(1) Å, consistent with bonding interactions] and one too long [3.290(1) Å] for there to be any significant bonding overlap[13].

Similar results were later reported by Bhaduri and co-workers[12]. The X-ray structures of $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(CO)_9$ **(5)**[12], $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ **(6a)**[13] and $Ru_3(\mu\text{-H})_2(\mu_3\text{-NPh})(CO)_9$ **(8)**[14], have been determined. Bhaduri et al.[14] also showed that $CO_2$ is produced in the reaction between $Ru_3(CO)_{12}$ and $PhNO_2$ while carbonylation of complex **(8)** produced $Ru_3(CO)_{12}$ and $PhNH_2$. They proposed the following catalytic scheme:- (Scheme 1).



(Scheme 1)

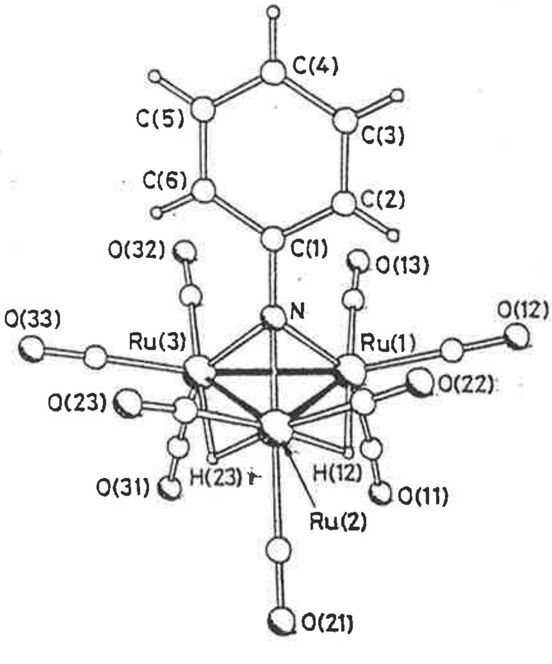


Figure 7 Molecular structure of (8)

Recently, Basu and co-workers isolated $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\eta^6\text{-}C_6H_6)(CO)_6$ and $Fe_2Co(\mu_3\text{-NPh})(CO)_9$ from the reaction of $PhNO_2$ and $M_3(CO)_{12}$ (M = Ru or Fe) when $Co_2(CO)_8$ is present [$M_3(CO)_{12}$:$PhNO_2$:$Co_2(CO)_8$ = 1:1.5:1] in refluxing benzene (5 h) under an atmosphere of CO.[40]

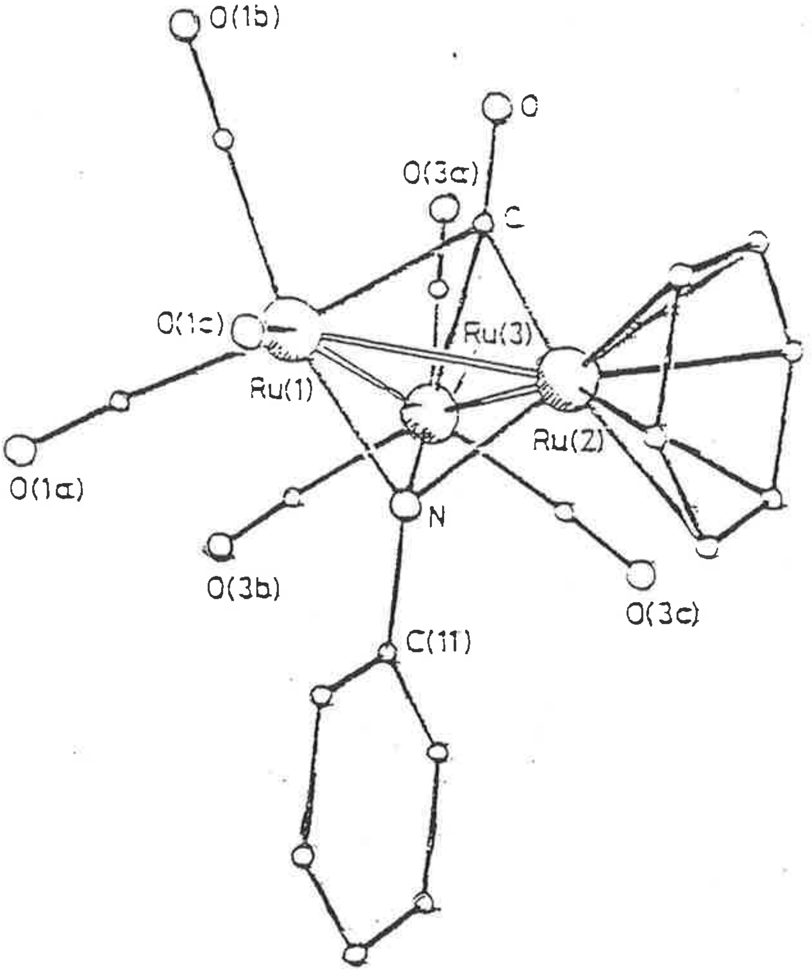
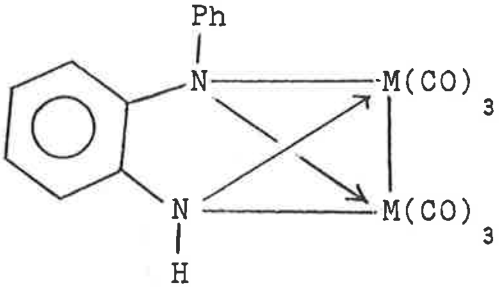


Figure 8 Molecular Structure of $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\eta^6\text{-}C_6H_6)(CO)_6$



**(a)** M = Ru

**(b)** M = Fe

Figure 9  Proposed structure for (9)

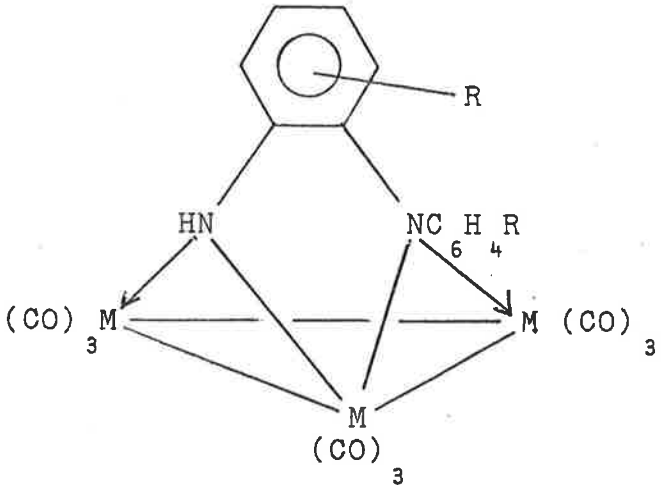


Figure 10

**(10a)** M = Ru, R = H

**(10b)** M = Fe, R = Me-4 or OMe-4

Reactions between $Ru_3(10)_{12}$ and azobenzene were described by Stone *et al.*[19] in 1971. They reported that the reaction between $Ru_3(CO)_{12}$ and a four-fold excess of azobenzene (petroleum ether, *ca* 100°C, 3.5 h) afforded three complexes which could be separated by chromatography on Florisil. The major product (about 42% yield) was a dark brown solid thought to have the formula $(C_{12}H_9N_2)Ru_2(CO)_6$ **(11)**; its reaction with lithium aluminium hydride gave azobenzene and its $^1H$ NMR spectrum confirmed the presence of chelating *ortho*-metallated (phenylazo)phenyl ligands. Bromination of **(11)** gave $\{Ru(C_6H_4N = NC_6H_5)(CO)_2Br\}_2$ suggesting that the azoaryl ligands chelate each metal atom. The following structure was proposed for **(11)**.

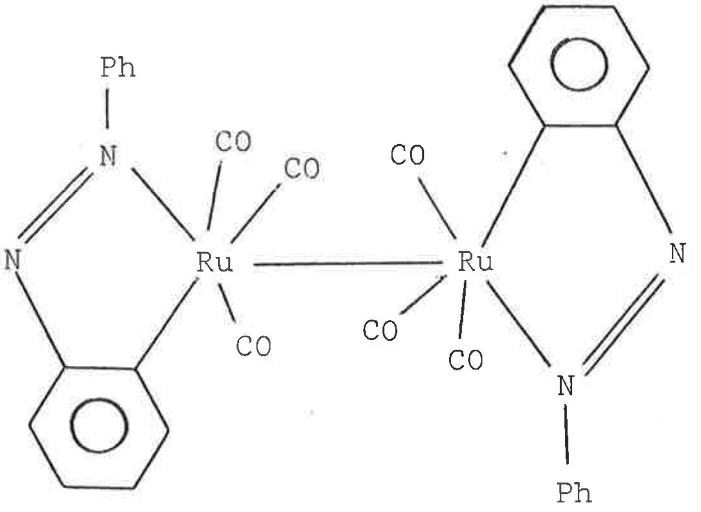


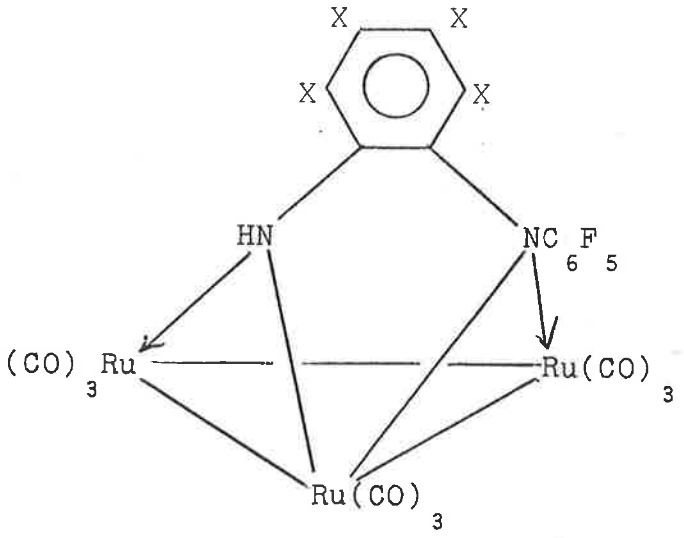
Figure 11 Proposed structure of **(11)**

The second complex isolated in ca 20% yield, forms deep red crystals. Analytical data suggested the formula $(C_{12}H_{10}N_2)Ru_3(CO)_9$ and structure **(10a)** with a semidine-derived ligand was proposed on the basis of comparisons of the IR spectrum with those of the iron complexes.

The third complex, obtained in approximately 8% yield, was an unstable rust-coloured solid, and analytical data gave the formula as $(C_{12}H_{10}N_2)Ru_2(CO)_6$ **(9a)**.

The infrared ν(CO) spectrum shows a band pattern consistent with the presence of an $Ru_2(CO)_6$ group and the following structure (see Figure 9) was proposed for **(9a)** and **(9b)**.

Reactions between $Ru_3(CO)_{12}$ and 2,3,4,5,6-pentafluoroazobenzenes and 2-H-nona-fluoroazobenzenes yielded trinuclear compounds assumed to have structures **(12a)** and **(12b)** respectively on the basis of comparison of their IR spectra with **(10a)**[20].



(a) X = H

(b) X = F

Figure 12 Proposed structure for **(12a)** and **(12b)**

The reactions between $M_3(CO)_{12}$ [M = Fe, Ru, Os] and $4\text{-}XC_6H_4NO$ (X = H, Cl, $CH_3$, OMe) to give both $M_3(\mu_3\text{-}NC_6H_4X\text{-}4)(\mu_3\text{-}CO)(CO)_9$ and $M_3(\mu_3\text{-}NC_6H_4X\text{-}4)_2(CO)_9$ were recently described by Gladfelter et al.[33]. However the yields of $Ru_3(\mu_3\text{-}NR)_2(CO)_9$ were only in the range of 20-30%; the reactions took nearly 6 days and required 50 psi of CO. By this route they managed to synthesise $Os_3(\mu_3\text{-}NPh)_2(CO)_9$ for the first time, in about 34% yield.

While this thesis was in preparation, a subsequent paper by Smieja et al.[39] described the synthesis of the bis(imido) cluster, $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}NAr')(CO)_9$ from the reaction of $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}CO)(CO)_9$ and azoarenes.

$$Ru_3(NAr)(CO)_{10} + Ar'NNAr' \longrightarrow$$

$$Ru_3(NAr)(NAr')(CO)_9 + Ar'NCO \qquad ...3$$

These bis(imido) clusters react with dihydrogen to give $Ru_3(\mu\text{-}H)_2(NAr)(NAr')(CO)_8$, (26), which can be used to catalyse the hydrogenation of olefins.

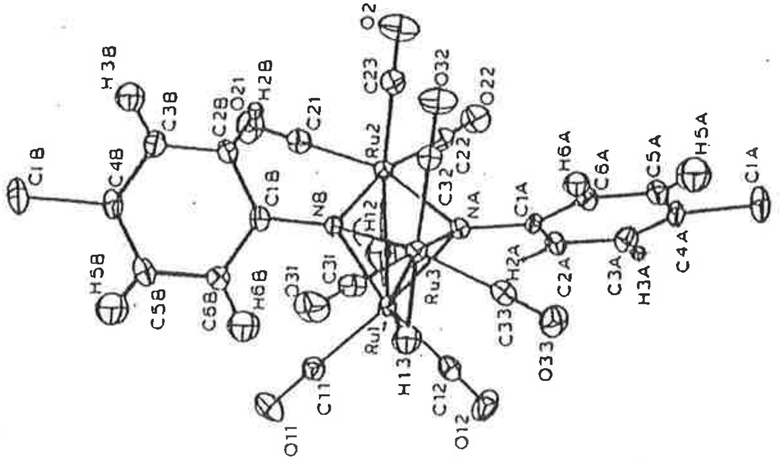


Figure 13 Molecular Structure of $Ru_3(\mu\text{-}H)_2(NC_6H_4Cl)_2(CO)_8$ [39]

We decided to reinvestigate the reactions between $Ru_3(CO)_{12}$ and azobenzenes for the following reasons:-

(i) to confirm the structure of the products from the reactions

(ii) a recent paper on alkyne ($C\equiv C$ bond) scission[21] on a trimetallic framework led to an interest in the possiblity of similar cleavage of N=N bonds.

## 2. RESULTS AND DISCUSSION

### (1) Reaction of $Ru_3(CO)_{12}$ and azobenzene

#### (a) .Under Nitrogen

In refluxing n-octane at ca 127°C, the reaction between $Ru_3(CO)_{12}$ and azobenzene afforded three complexes, which can be conveniently separated by column chromatography on Florisil. The most tractable compound **(6a)**, obtained in yields approaching 20%, is eluted first and forms deep red crystals. Analytical data (Tables 4, 5 and Experimental section) suggest the formula $Ru_3(Ph_2N_2)(CO)_9$.

The $^1H$ NMR spectrum contains a complex set of resonances between $\delta$ 7.29-6.71. No high field resonances were observed, nor was there any signal due to NH protons. The carbonyl region of the infrared spectrum (see Fig. 14b) consists of eight bands and is similar to $Ru_3(\mu\text{-}H)(\mu\text{-}C_{12}H_{15})(CO)_9$[32] suggesting that it may have a similar arrangement of the nine carbonyl ligands.

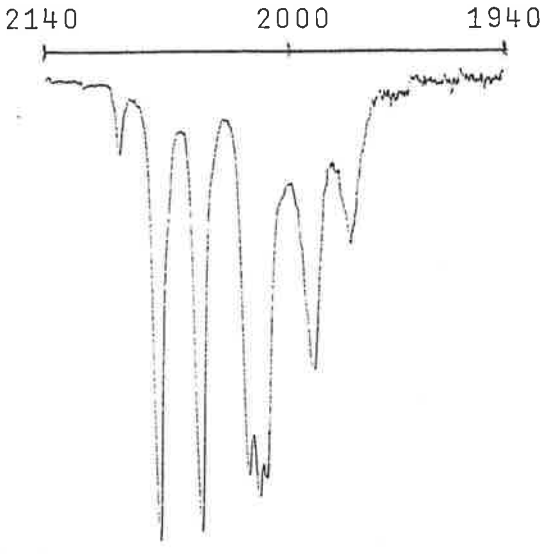


Figure 14a Infrared spectrum of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6a)**

The highest ion in the mass spectrum (centred on m/z 740) corresponds to the parent ion $[C_{21}H_{10}N_2O_9Ru_3]^+$; other major ruthenium-containing ions are formed by stepwise loss of the nine CO groups. Strong doubly-charged ions $[M-nCO]^{2+}$ (n = 4-0), and at m/z 460 ($[M-9CO-2H]^{2+}$), are also found but the ion $Ru_3^+$ was not detected. Neither bi- nor mono-nuclear fragments were observed.

The phenyl region of the $^{13}C$ NMR spectrum [$\delta(CDCl_3)$ 128.4, 124.2, 123.2 ppm] is simpler than expected for an o-semidine-derived structure and supports a bis(arylimido) structure of type **(6a)**, which has been confirmed by X-ray methods.

Comparison of the unit cell (orthorhombic, a = 19.72, b = 9.65, c = 13.03 Å, V = 2478 Å$^3$) with that found for $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6a)** (lit[13] orthorhombic, a = 19.73, b = 9.67, c = 13.04 Å, V = 2488 Å$^3$) shows that the two complexes are identical.

A second complex, obtained in only 4% yield, forms orange crystals and analytical data gave the formula $C_{26}H_{18}N_4O_2Ru$ **(13)**. The infrared ν(CO) spectrum shows only two bands consistent with the presence of a cis-$Ru(CO)_2$ group. The $^1H$ NMR spectrum is complex. The highest ion in the mass spectrum (centred on m/z 521) is the parent ion $[C_{26}H_{18}N_4O_2Ru]^+$, the isotope pattern corresponding to a monoruthenium compound; major ruthenium-containing ions are formed by stepwise loss of the two CO groups. The ion $[Ph_2N_2]^+$ is also found; presumably this is formed by protonation of a $[C_6H_4N = NC_6H_5]$ fragment in the mass spectrometer. All these results suggest that this complex might be $\overline{Ru(C_6H_4N = N}C_6H_5)_2\ (CO)_2$ **(13)**. This was confirmed by an X-ray structure determination (see below).

The third complex, formed in much higher yield, forms a black powder. The analytical data are not consistent.

The infrared spectrum has two broad $\nu(CO)$ bands at 2034 and 1984 $cm^{-1}$. However preparative TLC (developing with acetone/light petroleum (30/70)) resolves the substance into numerous bands; streaking occurs on the plate which suggests that the compound is either a complex mixture or decomposes during chromatography. The black powder does not contain any free azobenzene; however, some $\overline{Ru(C_6H_4N = N}C_6H_5)_2(CO)_2$ **(13)** can be extracted from it with hot light petroleum, probably as a result of decomposition; after extensive extraction the black residue affords more complex **(13)** on chromatography on silica TLC plates.

(b) Under Carbon Monoxide

The reaction between $Ru_3(CO)_{12}$ and azobenzene under the same conditions as above but with CO gas bubbling through the solution gave a somewhat higher yield of $Ru_3(\mu_3\text{-}NPh)_2\text{-}(CO)_9$ (*ca* 25%). However, some $Ru_3(CO)_{12}$ remained even after refluxing overnight (*ca* 18 h). The time-consuming extensive multiple chromatography required to separate $Ru_3(CO)_{12}$ from $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ does not warrant describing this route as an 'improved synthesis'.

### (II) Reactions of $Ru_3(CO)_{12}$ with other azoarenes

Having established the reaction conditions for the reaction of $Ru_3(CO)_{12}$ and azobenzene, reactions between several azoarenes and $Ru_3(CO)_{12}$ were carried out in similar fashion; the details being summarised in Table 3 (following p. 170)

The reaction between $Ru_3(CO)_{12}$ and azoarenes is complex (TLC examination of the reaction mixture indicating the presence of between nine and nineteen coloured components). All the azoarenes studied yielded the corresponding trinuclear complexes (between 9.6 and 19.7%). In one case ($N_2(C_6H_4Me\text{-}\underline{m})_2$) the mononuclear orthometallated complex $\overline{Ru(C_6H_3Me\text{-}\underline{m}N = N}C_6H_4Me\text{-}\underline{m})_2(CO)_2$ **(17)** was also isolated in between 2.2 and 7.7% yield. The spectroscopic properties of all the trinuclear complexes isolated are similar to those of the azobenzene analogues. In the $^1H$ NMR spectra of **(17)** the methyl signal is a multiplet which supports the above formulation because the two methyl groups are not in the same environment.

### (III) Reaction of $Fe_3(CO)_{12}$ and Azobenzene

In refluxing benzene at ca 80°C, the reaction between $Fe_3(CO)_{12}$ and azobenzene afforded four complexes, separation being achieved by column chromatography on Florisil followed by preparative TLC on silica (eluting with light petroleum). Trace amounts of $Fe_3(CO)_{12}$, the o-semidine derived binuclear complex **(9b)** and some excess azobenzene were found, together with a trinuclear complex, which was obtained in about 2.5% yield as deep purple crystals. Analytical data suggest the formula $Fe_3(Ph_2N_2)(CO)_9$.

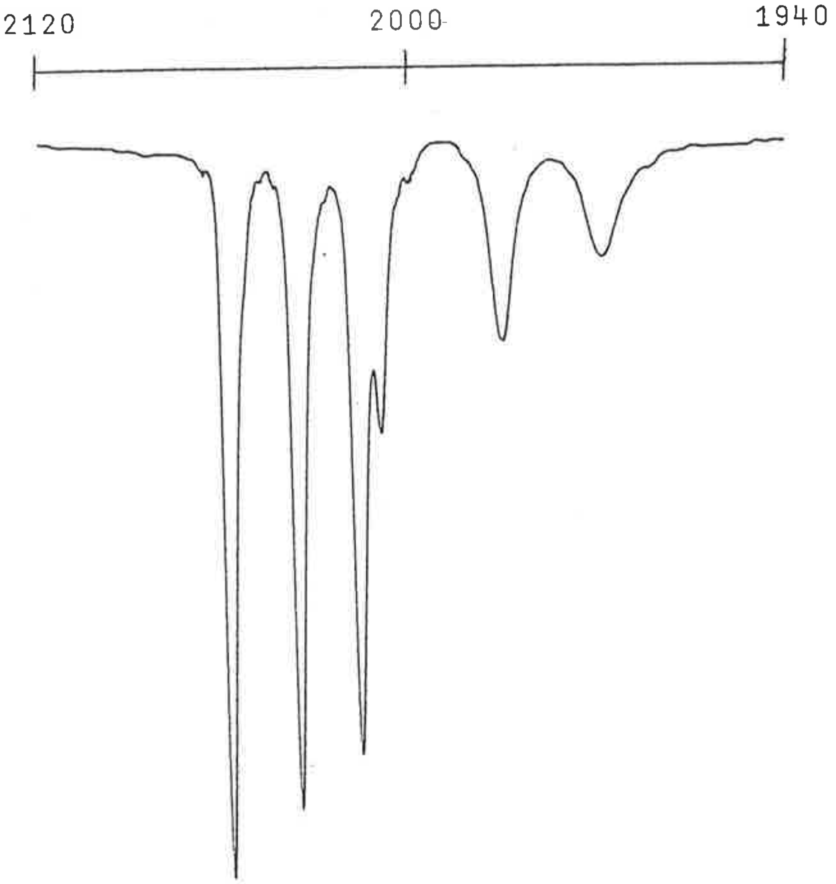


Figure 14b Infrared spectrum of $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6b)**

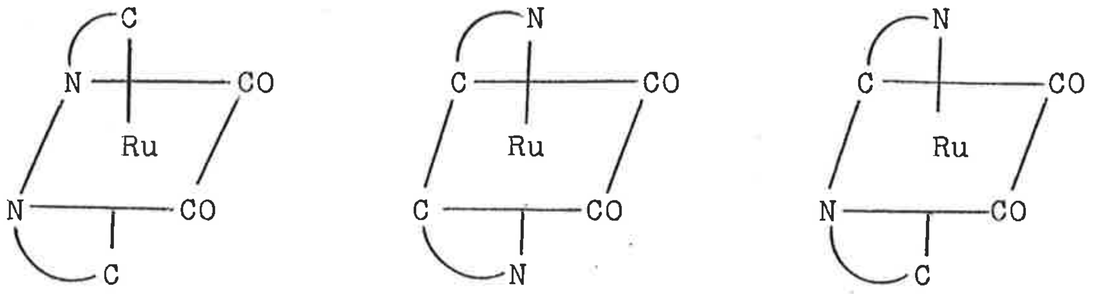
The $^1H$ NMR spectrum contains a complex set of resonances between δ 7.26-6.99. No high-field resonances were observed, nor was there any signal due to NH protons. The carbonyl region of the infrared spectrum resembles that of the Ru analogue **(6a)** in overall shape, however it has two peaks fewer (see Figure 14b).

The highest ion in the mass spectrum (centred on m/z 602) corresponds to the formula $[C_{21}H_{10}N_2O_9Fe_3]^+$; other major iron-containing ions are formed by loss of CO groups.

The phenyl region of the $^{13}C$ NMR spectrum [δ 128.4, 125.5, 123.1 ppm] is very similar to that of the Ru analogue **(6a)** and simpler than that expected for an o-semidine derived structure, supporting a bis(arylimido) structure of type **(6b)**. The molecular structure of $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6b)**, obtained from a reaction of $PhNO_2$ with $Fe_3(CO)_{12}$ in the presence of $Co_2(CO)_8$ has been established previously by X-ray methods[26]. That complex **(6b)** was the same compound was confirmed by comparison of its unit cell (monoclinic, $a$ = 11.34, $b$ = 13.66, $c$ = 15.42 Å, $\beta$ = 100.0°, V = 2352 $Å^3$) with that reported for **(6b)** (monoclinic, $a$ = 11.28, $b$ = 13.66, $c$ = 15.38 Å, $\beta$ = 99.8°, V = 2335 $Å^3$).

## IV Description of the structure of $\overline{Ru(C_6H_4N = N}C_6H_5)_2(CO)_2$ (13)

The cyclometallated mononuclear complex **(13)**, has the formula $\overline{Ru(C_6H_4N = N}C_6H_5)_2(CO)_2$. However, determination of the stereochemical arrangement from the possibilities (a)-(c) by spectroscopic methods was not possible.



(a) (b) (c)

Figure 15

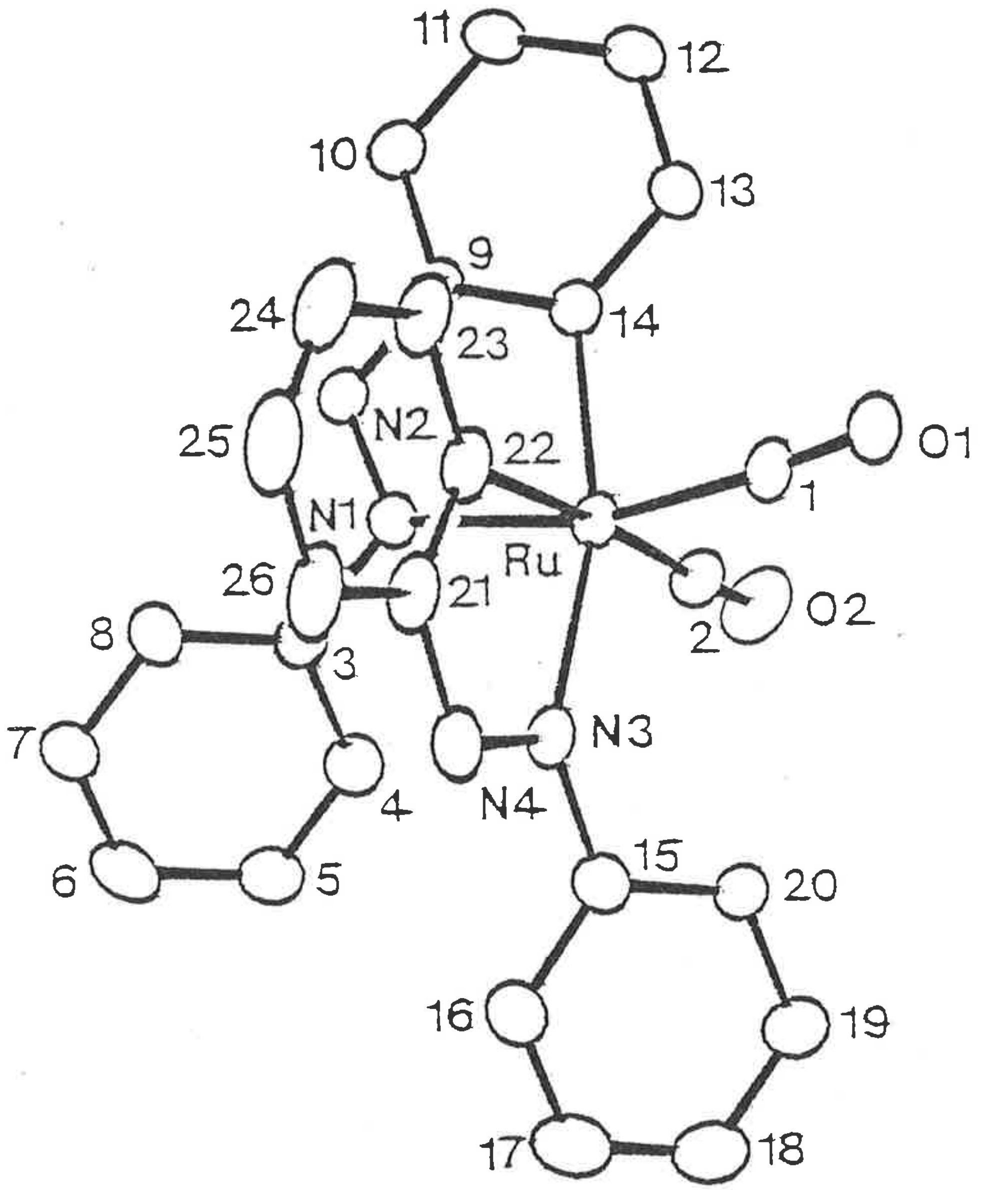


Figure 16 ORTEP plot of $\overline{Ru[C_6H_4N=N}C_6H_5]_2(CO)_2$ (13), showing the atom numbering scheme. Atoms not otherwise indicated are carbons.

(by M.R. Snow and E.R.T. Tiekink).

## TABLE 1 FOR SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

## FOR $\overline{\mathrm{Ru[C_6H_4N{=}N}}\mathrm{C_6H_5]_2(CO)_2}$ (13)

| | | | |
|---|---|---|---|
| Ru-C(1) | 1.879(9) | Ru-C(2) | 1.930(8) |
| Ru-N(1) | 2.103(6) | Ru-N(3) | 2.155(7) |
| Ru-C(14) | 2.052(7) | Ru-C(22) | 2.103(8) |
| C(1)-O(1) | 1.15(1) | C(2)-O(2) | 1.14(1) |
| N(1)-C(3) | 1.424(8) | N(3)-C(15) | 1.50(1) |
| N(1)-N(2) | 1.289(7) | N(3)-N(4) | 1.240(8) |
| N(2)-C(9) | 1.368(8) | N(4)-C(21) | 1.45(1) |
| C(9)-C(14) | 1.40(1) | C(21)-C(22) | 1.39(1) |

| | | | |
|---|---|---|---|
| C(1)-Ru-C(2) | 93.0(4) | C(1)-Ru-N(1) | 165.8(3) |
| C(1)-Ru-N(3) | 97.5(3) | C(1)-Ru-C(14) | 91.5(3) |
| C(1)-Ru-C(22) | 88.0(3) | C(2)-Ru-N(1) | 95.2(3) |
| C(2)-Ru-N(3) | 103.0(3) | C(2)-Ru-C(14) | 91.6(3) |
| C(2)-Ru-C(22) | 177.9(3) | N(1)-Ru-N(3) | 91.9(2) |
| N(1)-Ru-C(14) | 76.7(3) | N(1)-Ru-C(22) | 84.2(3) |
| N(3)-Ru-C(14) | 162.4(3) | N(3)-Ru-C(22) | 75.1(3) |
| C(14)-Ru-C(22) | 90.2(3) | | |

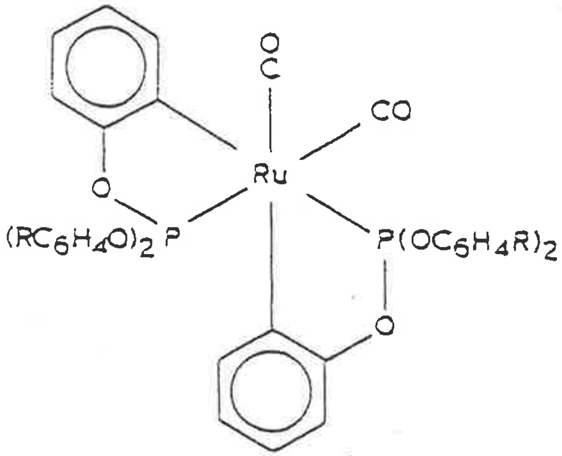
| | | | |
|---|---|---|---|
| Ru-C(1)-O(1) | 173.9(7) | Ru-C(2)-O(2) | 178.6(7) |
| Ru-N(1)-N(2) | 117.6(4) | Ru-N(3)-N(4) | 120.8(6) |
| Ru-N(1)-C(3) | 127.1(4) | Ru-N(3)-C(15) | 126.6(5) |
| C(3)-N(1)-N(2) | 114.9(5) | C(15)-N(3)-N(4) | 112.4(7) |
| N(1)-N(2)-C(9) | 113.2(5) | N(3)-N(4)-C(21) | 110.9(7) |
| N(2)-C(9)-C(14) | 120.1(6) | N(4)-C(21)-C(22) | 120.6(7) |
| N(2)-C(9)-C(10) | 118.5(6) | N(4)-C(21)-C(26) | 115.8(9) |

The X-ray structure determination has now shown unambigously that structure (c) is correct. The osmium analogue of **(13)** has been structurally characterised as one of several complexes obtained from $Os_3(CO)_{12}$ and azobenzene in refluxing octane[25].

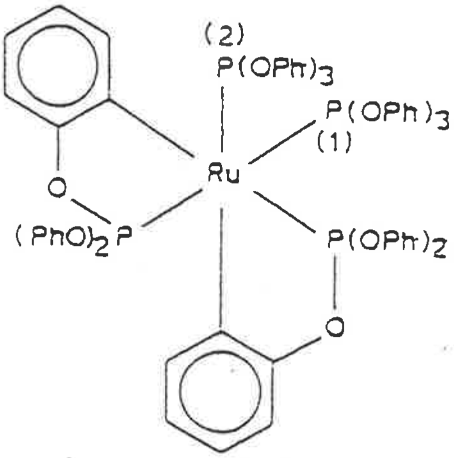
In complex **(13)**, the Ru atom displays a slightly distorted octahedral geometry, the two Ru-N bonds [Ru-N 2.103(6), 2.155(7) Å] are mutually *cis* as are the two Ru-C bonds to the $C_6H_4$ groups [Ru-C, 2.103(8), 2.052(7) Å]. The two carbonyl ligands [Ru-CO, 1.879(9), 1.930(8) Å] are also mutually *cis* as indicated by the IR spectrum, and are essentially linear [Ru-C-O 173.9(7), 178.6(7)°].

Angles C(22)-Ru-N(1) 84.2(3)°, C(14)-Ru-N(1) 76.7(3)° and C(22)-Ru-N(3) 75.1(3)° are less than 90° as a result of the restricted bite of the (phenylazo)phenyl ligand.

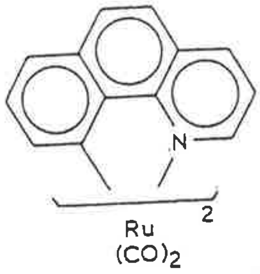
The Ru-N(3) [2.155(7) Å] and Ru-C(22) [2.103(8) Å] bonds *trans* to CO are longer than those *trans* to N or C(aryl) [Ru-N(1) 2.103(6) Å, Ru-C(14) 2.052(7) Å] as expected from the greater *trans* effect of the CO ligands. Similarly, the Ru-CO(2) [1.930(8) Å] bond is longer than Ru-CO(1) [1.879(9) Å] as a result of the greater trans effect of the C(aryl) *vs* N. The five-membered Ru-C-C-N-N rings are essentially planar; the dihedral angle between the planes is *ca* 109°.


O
C
CO
Ru
O
(RC6H4O)2 P
P(OC6H4R)2
O

(14)


(2)
P(OPh)3
P(OPh)3
(1)
Ru
O
(PhO)2 P
P(OPh)2
O

(15)


N
2
Ru
(CO)2

(16)

Complex (13) and the Os analogue adopt a conformation similar to that found for $\overline{Ru[(C_6H_4O)P}(OC_6H_5)_2]_2(L)_2$ with L = CO **(14)**[27] or L = $P(OC_6H_5)_3$ **(15)**[28]. An alternative conformation, with the N-atoms trans, and the metallated C-atoms cis to each other [isomer (a)], has been reported for $\overline{Rh[C_6H_4N=N}Ph]_2(O_2CMe)$[30]. The third possible isomer [isomer (b)] has been found in $Ru(bq)_2(CO)_2$ **(16)** (bq = benzo[h]quinolin-10-yl), in which both of the N atoms are trans to carbonyl groups[29].

## (V) Description of the structure of $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (21)

The molecular structure of complex **(21)** is shown in Figure 17. The molecule consists of an isosceles triangle of three ruthenium atoms, two edges of which are short enough for a bonding interaction [Ru(1)-Ru(2) 2.702(1), Ru(2)-Ru(3) 2.615(1) Å]; the third non-bonding edge is 3.291(1) Å. One side of the triangle is capped by an NPh group, the other by the $N(C_6H_4F\text{-}3)$ group; the Ru-N distances are not significantly different to each group, but bonds to the central ruthenium are longer [2.127(4), 2.131(4) Å] than those to the outer metal atoms [2.051(4), 2.098(4) Å]; there is a slight asymmetry in the bonding, distances to Ru(1) being shorter than those to Ru(3), and this is attributed to the relative disposition of the carbonyl groups as well as the orientation of the NAr ligands. Each ruthenium is bonded to three CO groups; neglecting the metal-metal vectors, coordination about each metal atom is approximately trigonal bipyramidal, the Ru(1) and Ru(3) atoms occupying the apical positions. Neglecting the fluorine substituent, an approximate mirror plane passes through the $Ru_3$ core. Overall, the molecular structure is similar to that reported for the unsubstituted complex (6a).

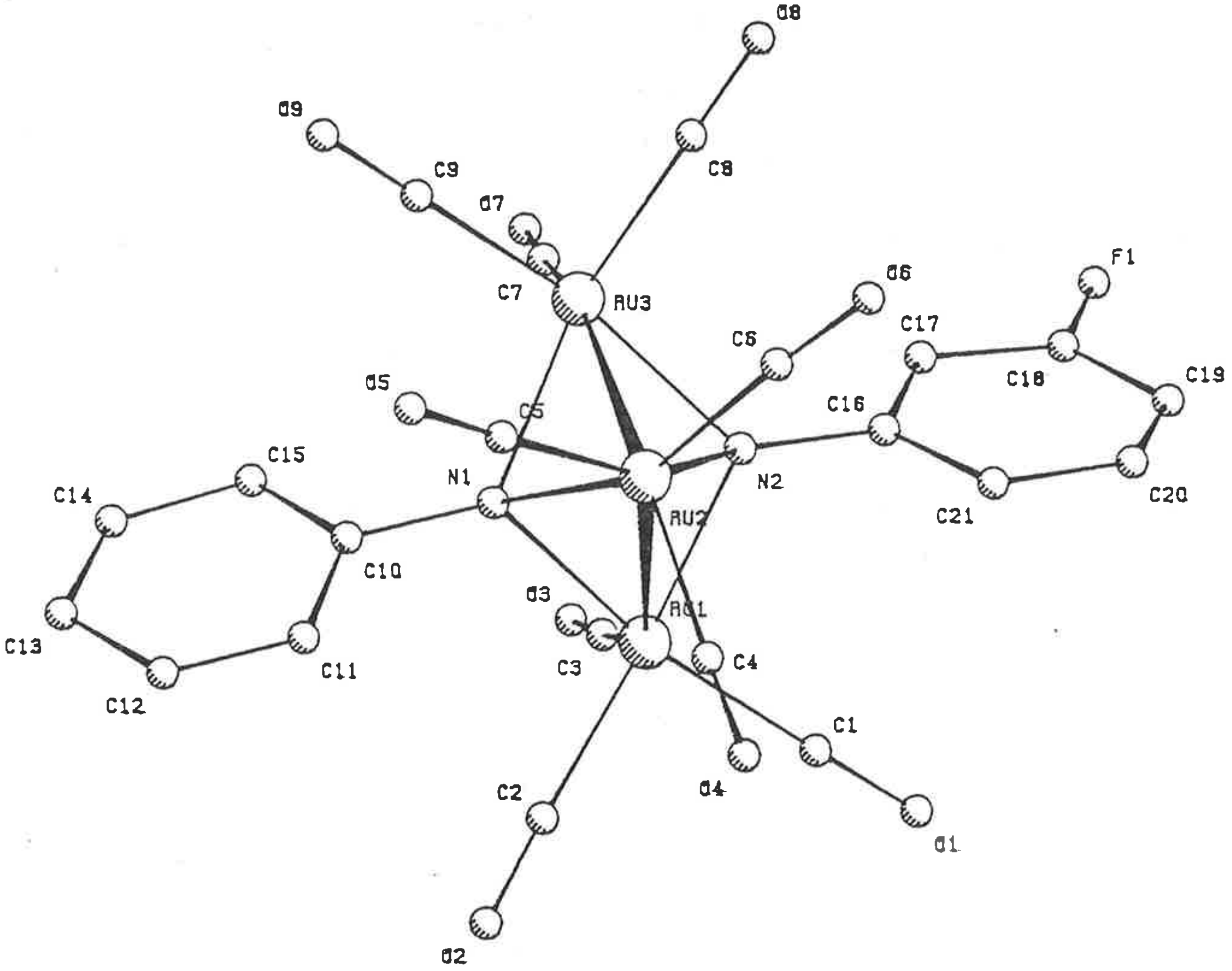
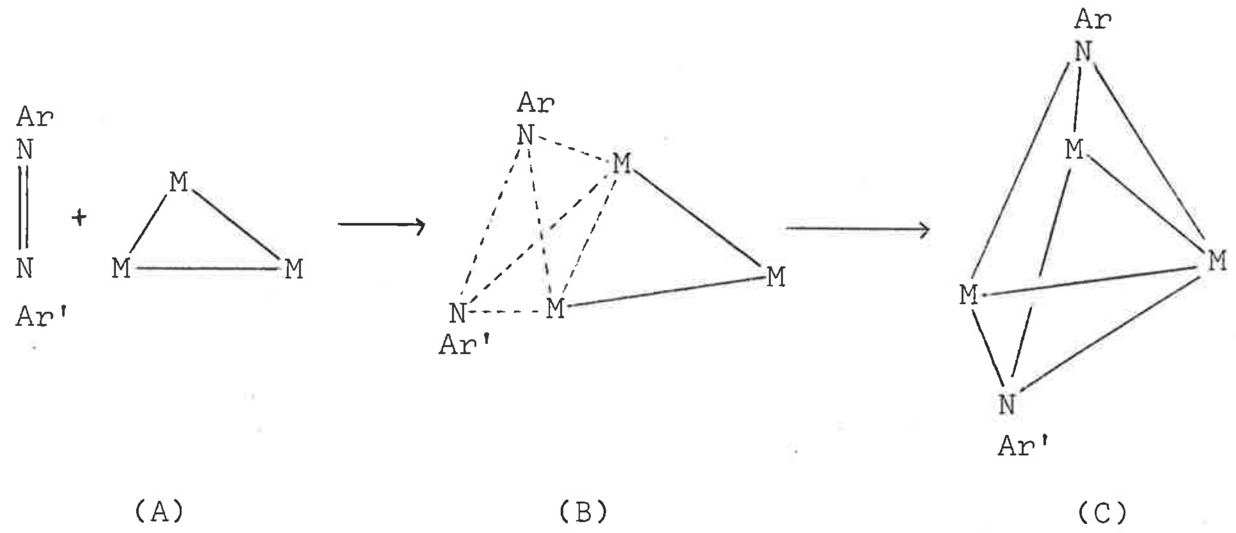


Figure 17 Structure of $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (21)
(M.R. Snow and E.R.T. Tiekink)

## (VI) Discussion of reactions

### (i) Cleavage of azoarenes with $M_3(CO)_{12}$ (M = Fe or Ru)

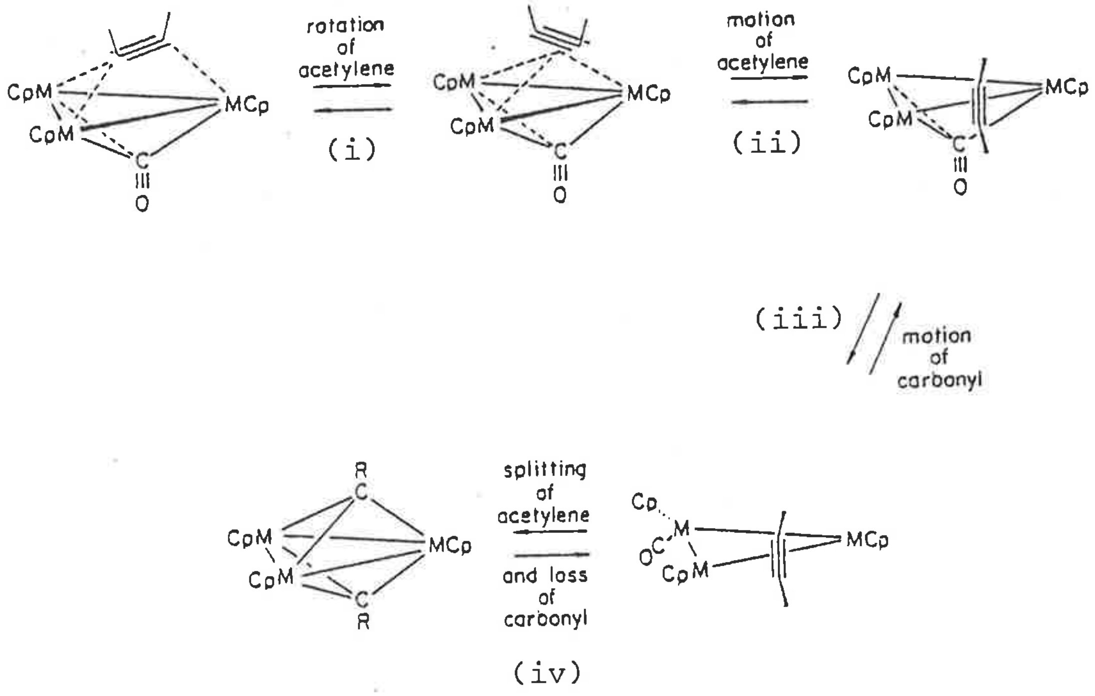


(Scheme 2)

A possible reaction course for the reaction of $M_3(CO)_{12}$ and azoarenes is shown in Scheme 2. The initial attachment of the azoarene may involve either the lone pairs on the nitrogen atoms or coordination via the nitrogen-nitrogen double bond (N=N). If N=N bond cleavage occurred before attachment to the cluster, we would expect the reaction to yield a mixture of $M_3(\mu_3\text{-NAr})_2(CO)_9$, $M_3(\mu_3\text{-NAr}')_2(CO)_9$ and $M_3(\mu_3\text{-NAr})(\mu_3\text{-NAr}')$-$(CO)_9$. However, the can be seen from the experimental reaction that the reaction between $Ru_3(CO)_{12}$ and ArN=NAr' only yields $Ru_3(\mu_3\text{-NAr})(\mu_3\text{-NAr}')(CO)_9$. The symmetric cleavage of azoarenes is uncommon.[36-38]

## TABLE 2 SELECTED BOND LENGTHS (A) FOR $Ru_3(\mu\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (21)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru(2) | - | Ru(1) | 2.702(1) | Ru(3) | - | Ru(1) | 3.291(1) |
| Ru(3) | - | Ru(2) | 2.615(1) | N(1) | - | Ru(1) | 2.051(4) |
| Ru(1) | - | N(2) | 2.057(4) | N(1) | - | Ru(2) | 2.127(4) |
| Ru(2) | - | N(2) | 2.131(4) | N(2) | - | Ru(3) | 2.082(4) |
| Ru(3) | - | N(1) | 2.098(4) | C(10) | - | N(1) | 1.428(6) |
| F(1') | - | C(14) | 1.265(13) | C(16) | - | N(2) | 1.403(6) |
| F(1) | - | C(18) | 1.370(13) | N(1) | - | N(2) | 2.424(6) |



(Scheme 3)

The mechanism of the splitting of acetylene on an $M_3$ framework has been analysed theoretically (see Scheme 3) by Clauss *et al.*[21] and supported by experimental evidence.

The rotation of the alkyne [step (i)] and motion over the edge [step (ii)] are 'allowed' processes and have barriers of ~ 0.5eV. The motion of the CO [step (iii)] to the third metal has a barrier of ~ 1.5eV. Step (iv) is 'allowed', with a very small barrier of < 0.2eV. If the motion of the carbonyl [step (iii)] and the acetylene splitting are combined, the net barrier will be much lower than 1.5eV. We suggest the same process is happening in azoarene in the last step (step iv) i.e. the N=N bond/vector is aligned along the edge of one of the metal-metal bond and it is this metal-metal bond that will be broken when the N=N bond is cleaved.

This cleavage of azoarenes provides a simple source of coordinated arylnitrenes (in fairly reasonable yield) because azoarenes are readily obtainable. Further reactions of the arylimido clusters may provide evidence for the release of NAr fragments and/or subsequent reaction with other functional groups.

The reactions of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6a)** with simple 2e-donor ligands have been explored in some detail[22]. It is found that **(6a)** reacts in the same way as $Ru_3(CO)_{12}$ under radical ion initiated conditions as shown in Scheme 4:-

$$\begin{tikzcd}
Ru_3(\mu_3\text{-}NPh)_2(CO)_9 + L \arrow[r] \arrow[d, "\begin{array}{c}(dppa)\\ Ph_2PC\equiv CPPh_2\end{array}"'] & Ru_3(\mu_3\text{-}NPh)_2(CO)_{9-n}(L) \\
{[Ru_3(\mu_3\text{-}NPh)_2(CO)_8]_2(\mu\text{-}dppa)} &
\end{tikzcd}$$

$n=1$, $L=PPh_3$, $P(OMe)_3$, m-xylyl-isocyanide

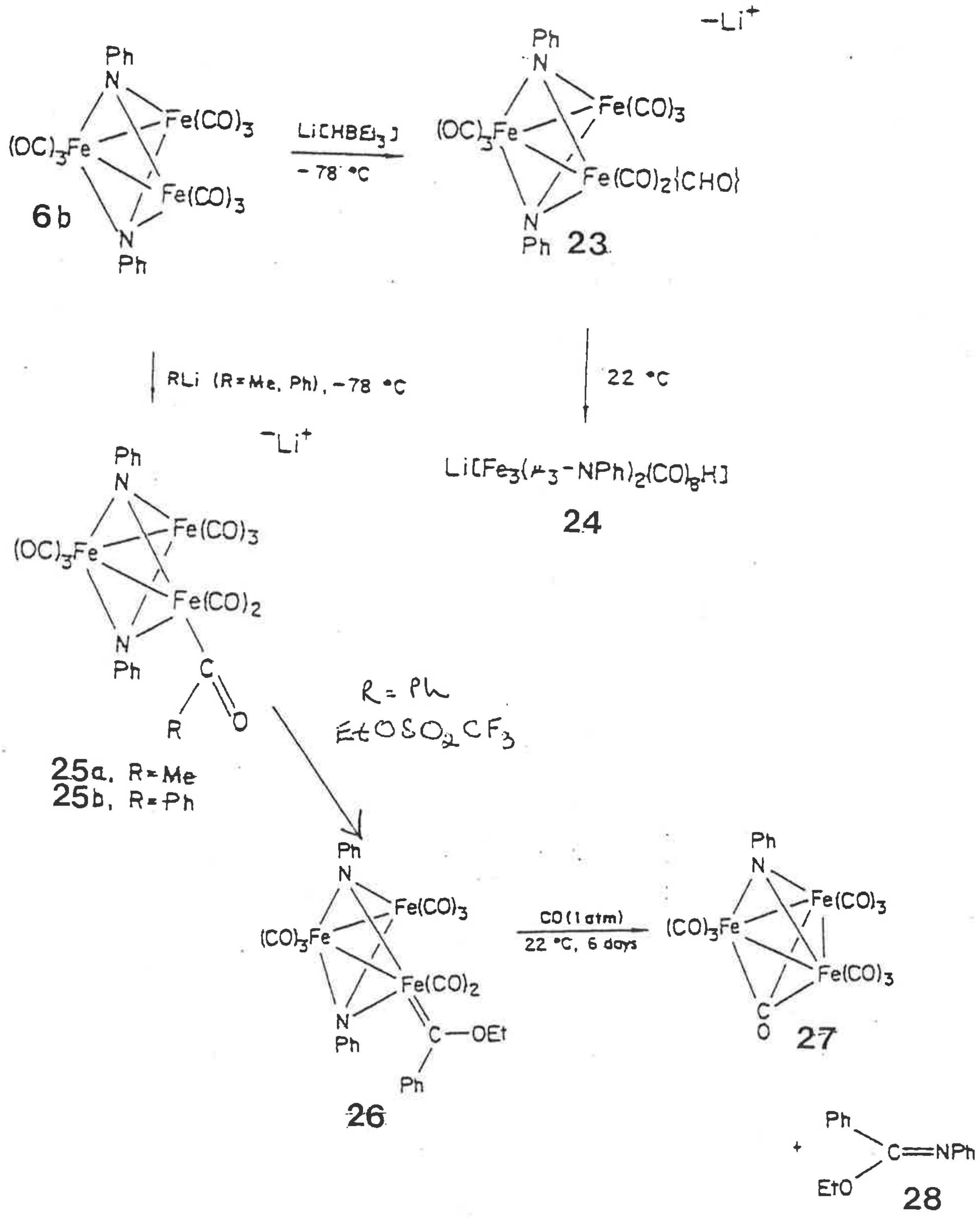
$n=2$, $L=Ph_2PCH_2PPh_2$
$Ph_2PCH_2CH_2PPh_2$

(Scheme 4)

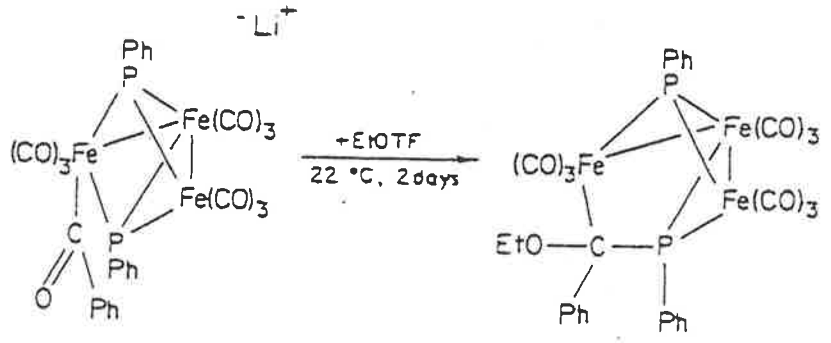
X-ray crystallographic studies of ligand-substituted products have revealed that phosphines and phosphites occupy equatorial positions while isocyanides occupy axial positions. The bidentate phosphine (dppm) bridges the non-bonded Ru atoms.

Of interest are the reactions of the related iron complexes, $Fe_3(\mu_3\text{-}ER)_2(CO)_9$ (ER = NPh and PPh) (Schemes 5 and 6)[34]. Complex **(6b)** reacts with $Li[BHEt_3]$ to give the relatively stable formyl derivative **(23)**, which at 22°C slowly deinserts with $t_{1/2}$ 1.5h to give **(24)**. Cluster **(6b)** also yields stable acetyl **(25a)** and benzoyl **(25b)** derivatives when treated with the appropriate LiR reagent. Alkylation of **(25b)** with $EtOSO_2CF_3$ yields the novel carbene-nitrene complex **(26)**. Although the carbene and nitrene ligands in **(26)** do not interact and are well separated with the carbene having formally replaced one of the original cluster carbonyls, they couple and are elimated as PhN=C(OEt)Ph **(28)** when complex **(26)** is exposed to CO. This reaction also gives the known cluster **(27)**[35] .

The reaction between $Fe_3(\mu_3\text{-}PPh)_2(CO)_9$ and PhLi generates the benzoyl complex **(29)**, which reacts with $CF_3SO_3Et$ at 22°C to give a mixture of products. The major product in 37% yield is the novel complex **(30)** (Scheme 6), which results from coupling of phosphinidene and carbene ligands. The X-ray structures of complex **(25)** and **(30)** have been determined.


6b
LiCHBEt3
−78 °C
−Li+
23
Fe(CO)2{CHO}
22 °C
Li[Fe3(μ3-NPh)2(CO)8H]
24
RLi (R=Me, Ph), −78 °C
−Li+
25a, R=Me
25b, R=Ph
R = Ph
EtOSO2CF3
26
CO (1 atm)
22 °C, 6 days
27
28
C=NPh
EtO
Ph

(Scheme 5)



**29** **30**

(Scheme 6)

### (ii) Cyclometallation

A reaction competing with the N=N bond cleavage in the reaction between $Ru_3(CO)_{12}$ and azobenzene is cyclometallation, which occurs to a somewhat lesser extent. The cyclometallation reaction occurs with a concomitant breakup of the cluster. This contrasts with the cyclometallation of aryldiazo compounds on an $Ru_3$ cluster in which a $\mu_3$-$PPhCH_2PPh_2$ ligand caps one $Ru_3$ face[31]. Thus, gentle heating of the $\mu$-$\eta'$-$N_2Ar$ complex, $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}\eta'\text{-}N_2Ar)(CO)_9$ **(26)** results in cyclometallation of the aryl group, the ortho-hydrogen being transferred to the cluster in a reaction which is essentially the oxidative addition of an aryl C-H bond to an Ru-Ru bond.

TABLE 3 : REACTIONS OF $Ru_3(CO)_{12}$ AND AZOARENES (UNDER NITROGEN)

| $Ru_3(CO)_{12}$ | $C_6H_4R$ N = $NC_6H_4R'$ | | | Solvent | Condition | Separation | Products | Yield |
|---|---|---|---|---|---|---|---|---|
| Amount (mmol) | R | R' | Amount(mmol) | ml | (°C, h) | technique | | % |
| 500 mg | H | H | 285 mg | n-octane | (127°, 4h) | Column | $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (6a) | 20 |
| (0.78) | | | (1.56) | (80) | | | $\overline{Ru(C_6H_4N=N}C_6H_5)_2(CO)_2$ (13) | 3.8 |
| 500 mg | H | H | 143 mg | n-octane | (127°, 4h) | Column | $Ru_3(\mu_3(NPh)_2(CO)_9$ (6a) | 16.1 |
| (0.78) | | | (0.78) | (70) | | | $\overline{Ru(C_6H_4N=N}C_6H_5)_2(CO)_2$ (13) | 3.2 |
| 300 mg | H | H | 171 mg | toulene | (110°, 6h) | Column | $Ru_3(\mu_3NPh)_2(CO)_9$ (6a) | 15.8 |
| (0.47) | | | (0.94) | (50) | | | $\overline{Ru(C_6H_4N=N}C_6H_5)_2(CO)_2$ (13) | 2.0 |
| 300 mg | $\underline{m}\text{-}CH_3$ | $\underline{m}\text{-}CH_3$ | 198 mg | n-octane | (127°, 4h) | TLC | $Ru_3(\mu_3\text{-}NC_6H_4Me\text{-}\underline{m})_2(CO)_9$ (18) | 19.7 |
| (0.47) | | | (0.94) | (50) | | | $\overline{Ru(C_6H_3Me\text{-}\underline{m}N=N}C_6H_4Me\text{-}\underline{m})_2(CO)_2$ (17) | 7.7 |
| 300 mg | $\underline{m}\text{-}CH_3$ | $\underline{m}\text{-}CH_3$ | 198 mg | n-octane | (127°, 18h) | TLC | $Ru_3(\mu_3\text{-}NC_6H_4Me\text{-}\underline{m})_2(CO)_9$ (18) | 10.0 |
| (0.47) | | | (0.94) | (50) | | | $Ru(C_6H_3Me\text{-}\underline{m}N=NC_6H_4Me\text{-}\underline{m})_2(CO)_2$ (17) | 2.2 |
| 500 mg | H | $\underline{m}\text{-}CH_3$ | 155 mg | n-octane | 127°, 2.3h) | TLC | $Ru_3(\mu_3NPh)(\mu_3\text{-}NC_5H_4Me\text{-}\underline{m})(CO)_9$ (19) | 12.8 |
| (0.78) | | | (0.79) | (70) | | | | |
| 500 mg | H | $\underline{m}\text{-}CF_3$ | 391 mg | n-octane | (127°, 18h) | TLC | $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4CF_3\text{-}\underline{m})(CO)_9$ (20) | 9.6 |
| (0.78) | | | (1.56) | (80) | | | | |
| 300 mg | H | $\underline{m}\text{-}F$ | 190 mg | n-octane | (127°, 18h) | TLC | $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}\underline{m})(CO)_9$ (21) | 11.3 |
| (0.471) | | | (0.94) | (60) | | | | |
| 500 mg | H | $\underline{p}\text{-}F$ | 313 mg | n-octane | (127°, 2.5h) | TLC | $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}\underline{p})(CO)_9$ (22) | 11.0 |
| (0.78) | | | (1.56) | (70) | | | | |

TABLE 4 ANALYTICAL DATA FOR $Ru_3(\mu_3\text{-}NC_6H_4R)(\mu_3\text{-}NC_6H_4R^1)(CO)_9$

| Complex | m.p. (°C) | Analyses found % (calcd) C | H | N | Mol. wt. found[a] (calcd) |
|---|---|---|---|---|---|
| R=R'=H | 156-157° | 34.18 | 1.43 | 3.79 | 740 |
| | | (34.20) | (1.37) | (3.80) | (739) |
| R=R'=*m*-$CH_3$ | 159-161° | 35.97 | 1.84 | 3.64 | 767 |
| | (dec) | (36.08) | (1.84) | (3.66) | (767) |
| R=H,R'=*m*-$CH_3$ | 143-144° | 35.19 | 1.66 | 3.75 | 753 |
| | | (35.16) | (1.61) | (3.73) | (753) |
| R=H,R'=*m*-$CF_3$ | 88-89° | 32.92 | 1.17 | 3.46 | 807 |
| | | (32.80) | (1.13) | (3.48) | (807) |
| R=H,R'=*m*-F | 148-151° | 33.29 | 1.20 | 3.70 | 757 |
| | (dec) | (33.39) | (1.20) | (3.71) | (757) |
| R=H,R'=*p*-F | 91-92° | 33.12 | 1.28 | 3.65 | 757 |
| | | (33.39) | (1.20) | (3.71) | (757) |

[a] mass spectrometry

## TABLE 5 INFRARED ν(CO) AND $^1$H NMR SPECTRA OF $Ru_3(\mu_3\text{-}NC_6H_4R)(\mu_3\text{-}NC_6H_4R')(CO)_9$

| Complex | ν(CO) (cm$^{-1}$) in cyclohexane | $^1$H NMR in $CDCl_3$ δ(ppm) |
|---|---|---|
| R=R'=H | 2098w, 2077vs, 2053vs, 2027vs, 2020vs, 2016vs, 1995s, 1984m | 7.29-6.71 (m, 10H, Ph) |
| R=R'=m-$CH_3$ | 2098w, 2076vs, 2052vs, 2024vs, 2018vs, 2014vs, 1994s, 1983m | 7.25-6.59 (m, 8H, Ph)<br>2.26 (s, 6H, $CH_3$) |
| R=H,R'=*m*-$CH_3$ | 2098w, 2077vs, 2053vs, 2027vs 2020vs, 2016vs, 1995s, 1984m | 7.25-6.60 (m, 9H, Ph)<br>2.27 (s, 3H, $CH_3$) |
| R=H,R'=*m*-$CF_3$ | 2099w, 2078vs, 2054vs, 2028vs, 2020vs, 2018vs, 1997s, 1986m | 7.34-6.75 (m, 9H, Ph) |
| R=H,R'=*m*-F | 2100w, 2080vs, 2056vs, 2028vs, 2021vs, 2018vs, 1997s, 1987m | 7.41-6.63 (m, 9H, Ph) |
| R=H,R'=*p*-F | 2100w, 2079vs, 2055vs, 2028vs, 2022vs, 2017vs, 1996s, 1986m | 7.42-6.64 (m, 9H, Ph) |

## 3. EXPERIMENTAL

### General Experimental Procedures

General Experimental conditions are as outlined in Chapter 1.

### Reaction of $Ru_3(CO)_{12}$ and azobenezene

(a) Under nitrogen

A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and azobenzene (285 mg, 1.56 mmol) was heated in degassed refluxing n-octane (80 ml) until the reaction was judged to be complete (monitoring the disappearance of the 2061 $cm^{-1}$ band of $Ru_3(CO)_{12}$; ca 4h). Solvent was removed under reduced pressure and the residue was chromatographed (Florisil). Light petroleum eluted an orange band, recrystallised (n-pentane) to give $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6a)** (115 mg, 20%). (See Table 4 for physical and analytical data; Table 5 for IR ν(CO) and $^1H$ NMR data). $^{13}C$ NMR: δ($CDCl_3$). 128.4, 124.2, 123.2 ($\underline{C}_6H_5$); 191.7 ppm (m, $\underline{C}O$). Light petroleum/ $CH_2Cl_2$ (9:1) eluted an orange band, recrystallised (n-hexane) to give $\overline{Ru(C_6H_4N=N}C_6H_5)_2(CO)_2$ **(13)** (20 mg, 3.8%) m.p. 130°C (dec) [Found: C, 60.18; H, 3.64; N, 10.73; $C_{26}H_{18}N_4O_2Ru$ requires C, 60.11; H, 3.49; N, 10.78%] IR (cyclohexane): ν(CO) 2036vs, 1986vs $cm^{-1}$. $^1H$ NMR: δ($CDCl_3$) 8.7-6.5 (m, 18H). Dichloromethane eluted a brown band; recrystallised from $CHCl_2$/hexane to give a brownish black powder (490 mg) (unidentified) IR (dichloromethane): ν(CO) 2034s(br), 1984s(br) $cm^{-1}$.

(b) Under CO

A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and azobenzene (145 mg, 0.79 mmol) was heated in refluxing n-octane (70 ml) with CO gas (high purity) bubbling through for 7 hours. The mixture was cooled, solvent removed under reduced pressure and the residue chromatographed (Florisil). Multiple chromatography was necessary to separate $Ru_3(CO)_{12}$ and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ and gave $Ru_3(CO)_{12}$ (50 mg, 10%) (IR identification) and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ **(6a)** (130 mg, 25%) (IR identification). The complex $Ru_3(\mu_3\text{-NPh})$-$(\mu_3\text{-CO})(CO)_9$ **(5)** was not detected.

## Reactions of $Ru_3(CO)_{12}$ with other azoarenes

Reactions between several azoarenes and $Ru_3(CO)_{12}$ were carried out under the conditions stated in Table 3. All the reactions gave trinuclear products. In the case of m-azotoluene (m-$CH_3C_6H_4N{=}NC_6H_4CH_3$-m), the mononuclear cyclometalled complex $\overline{Ru(C_6H_3Me\text{-}3N{=}N}C_6H_4Me\text{-}3)_2(CO)_2$ (2.2 - 7.7%) m.p. 163°C (dec). IR (cyclohexane): ν(CO) 2033vs, 1983vs $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$ 8.1-6.3 (m, 14H, Ph), 2.5-2.1, (m, 12H, $CH_3$) was also obtained.

## Reaction of $Fe_3(CO)_{12}$ and Azobenzene

$Fe_3(CO)_{12}$ (1.000g, 1.99 mmol) was dried in vacuo[23] (30 min) to remove the stablizer (acetone). Azobenzene (1.000 g, 5.48 mmol) and benzene (90 ml) were added and the mixture was heated at reflux point for 4.5 h. After cooling, solvent was removed in vacuo, and the residue chromatographed (Florisil). Light petroleum eluted a purple band [mixture of $Fe_3(CO)_{12}$, $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6b)** and azobenzene - see below] and diethyl ether/light petroleum (1/3) eluted an orange band (azobenzene, identified by comparison with an authentic sample). Preparative TLC of the purple band on silica, eluting with light petroleum, gave four bands. Band 1 ($R_f$ = 0.90), green, $Fe_3(CO)_{12}$ (trace) (IR identification). Band 2, ($R_f$ = 0.78) purple, $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ **(6b)** (30 mg, 2.5%), recrystallised (n-hexane) m.p. 138°C(dec), [Found: C, 41.74, H, 1.80; N, 4.63; $C_{21}H_{10}N_2O_9Fe_3$ requires C, 41.91; H, 1.67; N, 4.65%] IR (cyclohexane): $\nu$(CO) 2059vs, 2037vs, 2017vs, 2011s, 1986s, 1972s (lit.[18] 2050vs, 2028s, 2008s, 1987m, 1970w). $^1H$ NMR: $\delta(CDCl_3)$ 7.28-6.99 ppm (m, 10H Ph). $^{13}C$ NMR: $\delta(CDCl_3)$ 209.6-191.6 (m, $\underline{C}O$); 128.4, 125.5, 123.1 ($\underline{C}_6H_5$) ppm. Band 3, ($R_f$ = 0.60) orange, azobenzene (TLC identification). Band 4, ($R_f$ = 0.42) red, (trace), $Fe_2(\mu_2\text{-}C_6H_4NHNC_6H_5)(CO)_6$ **(9b)** (IR identification).

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