

## STRUCTURE AND CHEMISTRY OF SOME CARBONYL CLUSTER COMPOUNDS OF OSMIUM AND RUTHENIUM

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**Abstract** - A general review of the cluster compounds of ruthenium and osmium with particular reference to the alternative ways of bond breaking process. A survey of the chemistry of carbido-derivatives and some gold-osmium complexes is also undertaken

### INTRODUCTION

Extensive studies have been carried out on the structure and reactivity of the trimetallic cluster compounds,  $M_3(CO)_9$ ,  $M = Fe, Ru, Os$ , but little has been reported on the higher cluster compounds. This lecture is directed to a consideration of the chemistry and structural aspects of some of the higher cluster units of osmium and ruthenium. The presence of a large number of metal-metal bonds within the metal framework of the higher clusters, allows for a more extensive chemistry of these complexes involving fission of a number of metal-metal bonds and still maintaining the nuclearity of the cluster unit. Thus a large variety of cluster geometries may be expected, and the facility for the making of metal-metal bonds as well as their breaking will be examined.

As was discussed previously the bonding in the higher metal clusters often involves significant polar character in the metal-metal bonds (Ref. 1). This provides a potential kinetic lability that does not occur with the small cluster units. The sensitivity of the reactivity of many of the higher clusters to solvent also reflects this polarity in the metal-metal bonds.

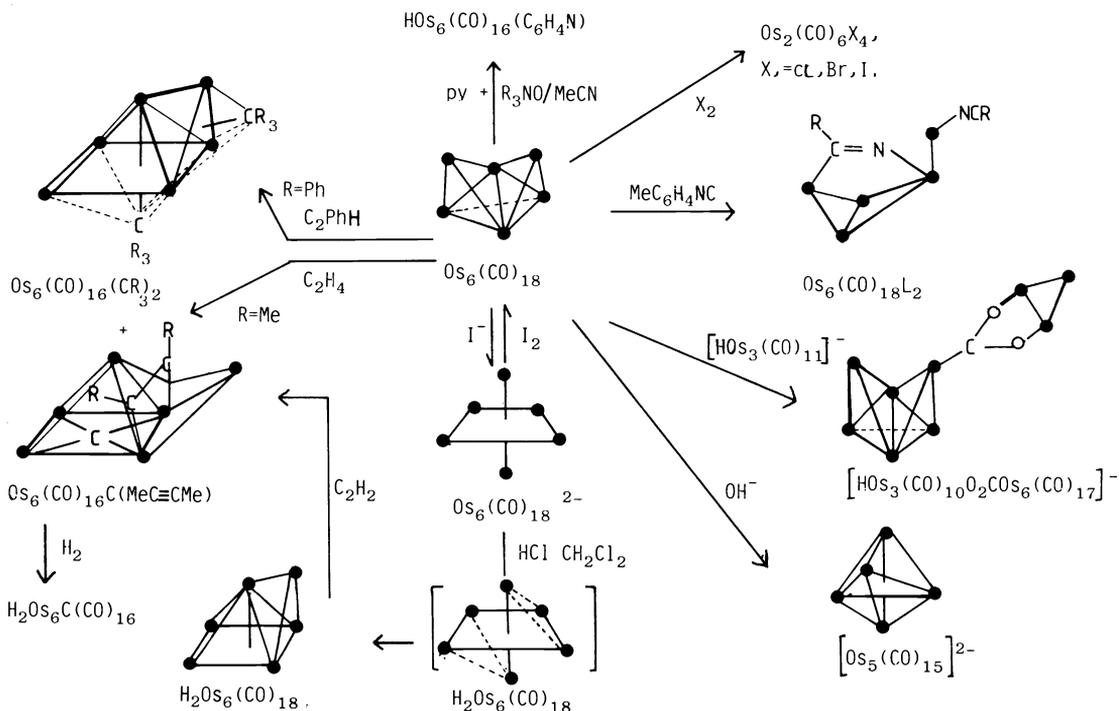
Four aspects of cluster chemistry will be considered:  
Hexanuclear Carbonyl of Osmium  
Pentanuclear Carbonyl of Osmium  
Carbonyl-Carbido derivative of Ruthenium and Osmium  
Mixed metal clusters of Gold with Osmium and Ruthenium

#### Hexanuclear carbonyls

The most extensively studied higher cluster compound of osmium is the hexanuclear carbonyl,  $Os_6(CO)_{18}$ , as this has produced in high yields (80%) by pyrolysis of  $Os_3(CO)_{12}$ . Scheme I summarises some of the chemistry observed for this compound. The majority of reactions with nucleophiles proceed via the fission of metal-metal bonds and the formation of a new cluster unit. This implies that the LUMO contains a large degree of M-M bonding character. In certain instances the reactions are reversible involving the reformation of the starting compound  $[Os_6(CO)_{18}/I_2]$  (Ref. 2). The structural variation within the series of cluster compounds  $[Os_6(CO)_{18}]^{2-}$ ,  $[HOs_6(CO)_{18}]^-$  and  $H_2Os_6(CO)_{18}$  is of interest (Ref. 3). As predicted by Wade's Rules the two ions are octahedral, based on an octahedron of  $O_h$  symmetry in contrast to the compound  $Os_6(CO)_{18}$  which is also octahedral but based on a  $C_{2v}$  symmetry. Acidification to  $H_2Os_6(CO)_{18}$  leads to a new cluster geometry based on the capping of a triangular face of a square based pyramid, although the total number of electrons within the cluster bonding remains constant. This illustrates the potential for more than one metal stereochemical arrangement within a given electron distribution. We have recently been able to obtain an unstable isomer of  $H_2Os_6(CO)_{18}$  (Ref. 4), by reaction of the anion with hydrogen chloride gas in methylene chloride, to give a red solid  $H_2Os_6(CO)_{18}$ . This isomer has an infra-red spectrum which is similar to that of  $H_2Ru_6(CO)_{18}$  (Ref. 5), the structure of which is based on the  $O_h$  octahedral system. The red solid is converted in all solvents to the stable isomer formed by acidification of the anions with sulphuric acid.

The structure of the stable modification of  $H_2Os_6(CO)_{18}$  provides the basic unit for the products of reaction of both phenylacetylene and ethylene with these hexanuclear osmium carbonyl species (Ref. 6). The products of the reaction, as indicated in Scheme (I), may involve fission of carbon-carbon bonds leading to  $\eta^4$  and  $\eta^3$  benzylidyne structures (Ref. 7), or proton rearrangements to yield  $\eta^4$  and  $\eta^3$  ethylidyne complexes. With ethylene, carbido species are also formed, as well as the production of butene complexes. The metal polyhedron is modified to include coordination of the butene group to a "butterfly" arrangement of metal atoms, a common form of bonding of organic groups to tetranuclear fragments. The same products may be obtained by reacting  $H_2Os_6(CO)_{18}$  with acetylene. Reaction of the carbido complex with hydrogen gives the hydrido-carbonyl  $H_2Os_6C(CO)_{16}$  although this is produced in low yield.

## SCHEME I

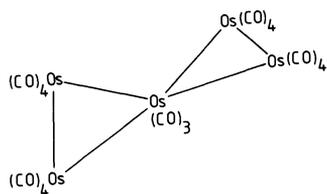
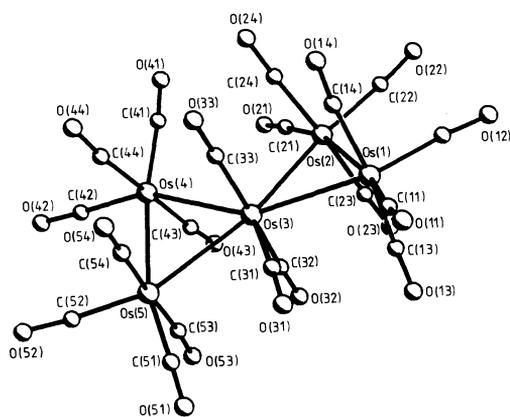


The isonitrile,  $\text{MeC}_6\text{H}_4\text{NC}$ , reacts with  $\text{Os}_6(\text{CO})_{18}$  to give the complex  $\text{Os}_6(\text{CO})_{18}(\text{CNC}_6\text{H}_4\text{Me})_2$  (Ref. 8). The two isonitrile molecules bond differently, one acting as a two electron donor to one metal centre whilst the other acts as a four electron donor and bridges between three metal centres. The metal framework modifies in response to this six electron addition by the fission of three metal-metal bonds of the  $\text{Os}_6(\text{CO})_{18}$  structure. Reaction with pyridine in the presence of amine oxide-acetonitrile yields an orthometallated hydrido derivative which has the same electron stoichiometry as the parent cluster.

An important reaction from the preparative view point is that with base to give in high yields, the pentanuclear osmium cluster (Ref. 1). This decapping of the osmium is reminiscent of the behaviour of borohydride clusters and provides a convenient way into the pentanuclear osmium series, as the yield of the parent carbonyl,  $\text{Os}_5(\text{CO})_{16}$ , in the pyrolysis of  $\text{Os}_3(\text{CO})_{12}$  is variable but low. The potential mechanism of this decapping reaction has been considered by us previously (Ref. 1) and reflects the variation in the polarity of the metal-metal bonds in the cluster unit, and in particular the presence of a metal donor bond to the capping metal atom. The reaction therefore opens the possibility of study of the penta-nuclear osmium derivatives from  $\text{Os}_6(\text{CO})_{18}$ .

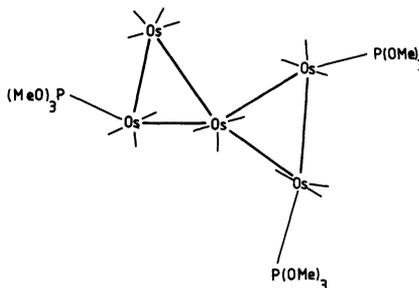
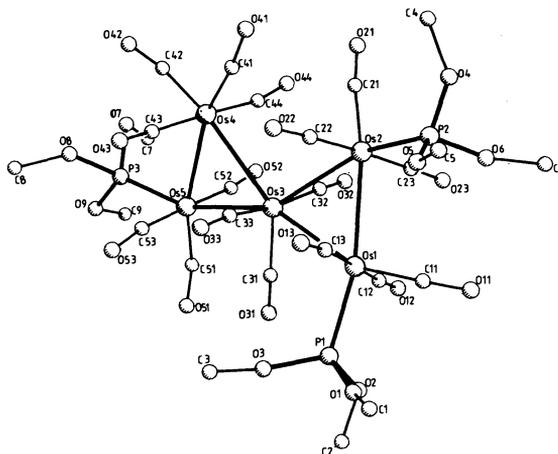
#### Pentanuclear carbonyl of osmium

The chemistry of the pentanuclear derivatives is summarised in Scheme (II). In addition to the preparation of the dianion  $[\text{Os}_5(\text{CO})_{15}]^{2-}$  from  $\text{Os}_6(\text{CO})_{18}$ , it is possible to prepare the anion directly from  $\text{Os}_5(\text{CO})_{16}$  with base (Ref. 9). The reactions may be considered in two groups those involving no breaking of metal bonds and those involving nucleophilic addition with metal-metal bond rupture. The iodination of the anion with iodine falls into the first of these two categories (Ref. 10). The product  $[\text{Os}_5(\text{CO})_{15}\text{I}]^-$  has a structure related to the parent carbonyl  $\text{Os}_5(\text{CO})_{16}$ , (Ref. 11) with iodine replacing a carbonyl in the equatorial plane. This may be viewed as an electrophilic attacked by an  $\text{I}^+$  ion, with no electron addition to the metal cluster, as with  $\text{H}^+$ . Further reaction with iodine gives the diiodide complex  $[\text{Os}_5(\text{CO})_{15}\text{I}_2]$  whose structure has not been determined. This complex behaves differently from the monoiodide reaction with iodide to regenerate the monoiodide,



$Os_5(CO)_{19}$

Fig. 1a Structure of  $Os_5(CO)_{19}$



$Os_5(CO)_{16}[P(O)Me]_3$

Fig. 1b Structure of  $Os_5(CO)_{16}[P(O)Me]_3$

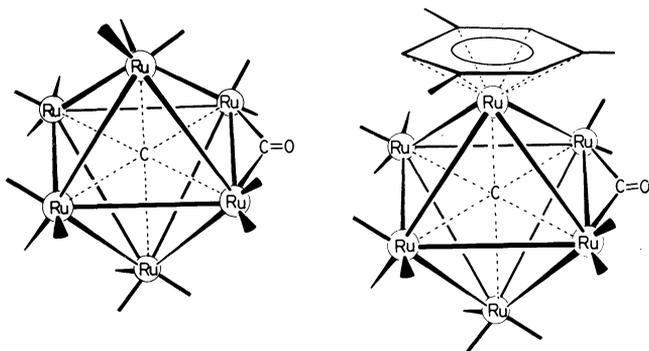


Fig. 2 Structures of  $Ru_6(CO)_{17}C$  and  $Ru_6(CO)_{14}(C_6H_5Me_3)C$

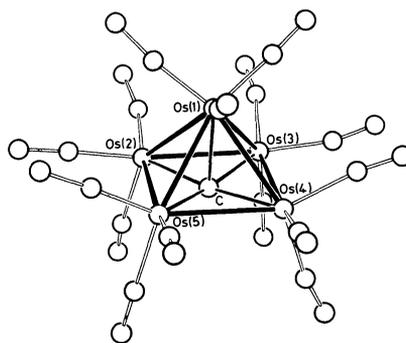
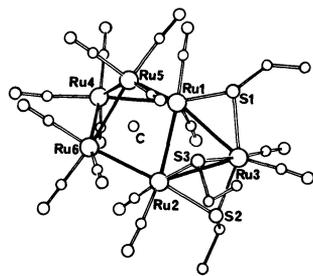


Fig. 3 Structure of  $Os_5(CO)_{15}C$

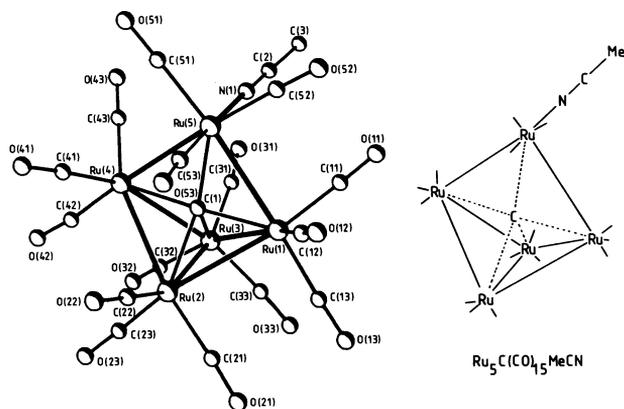
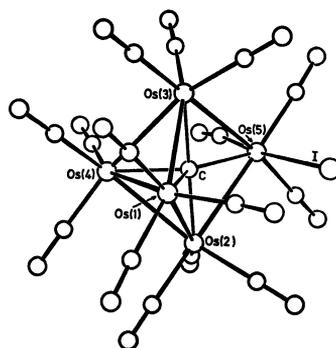
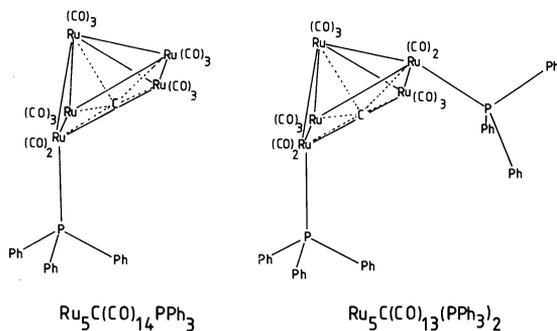
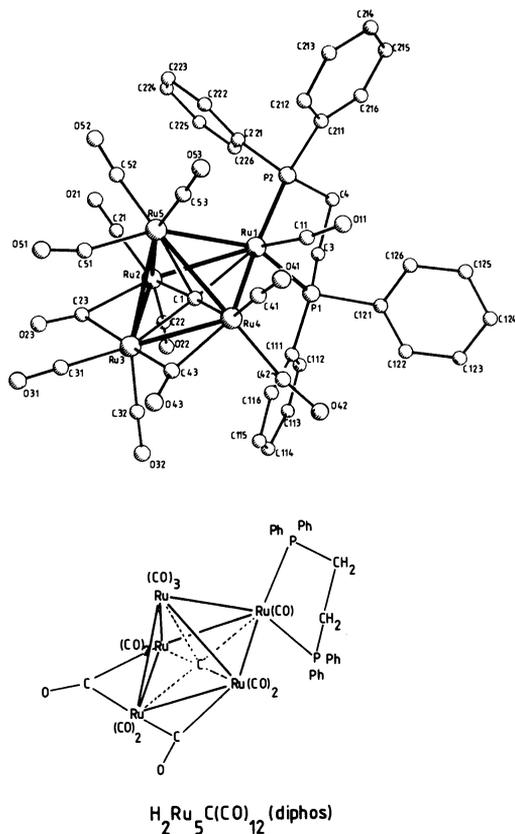
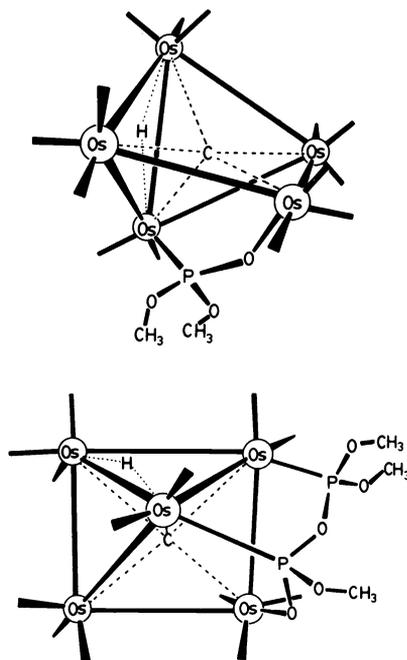


The structure of  $HRu_6(CO)_{15}(SC_2H_5)_3C$ , principal bond lengths (Å) are:

Ru(1)—Ru(2)	3.049	Ru(1)—Ru(3)	3.052	Ru(1)—Ru(4)	2.840	Ru(1)—Ru(5)	2.903
Ru(2)—Ru(3)	3.012	Ru(2)—Ru(6)	2.908	Ru(4)—Ru(5)	2.855	Ru(4)—Ru(6)	2.875
Ru(5)—Ru(6)	2.816	Ru(1)—S(1)	2.401	Ru(3)—S(1)	2.331	Ru(2)—S(2)	2.417
Ru(2)—S(3)	2.414	Ru(3)—S(2)	2.356	Ru(3)—S(3)	2.422	Ru(1)—C	1.966
Ru(2)—C	2.130	Ru(4)—C	2.150	Ru(5)—C	2.132	Ru(6)—C	2.001

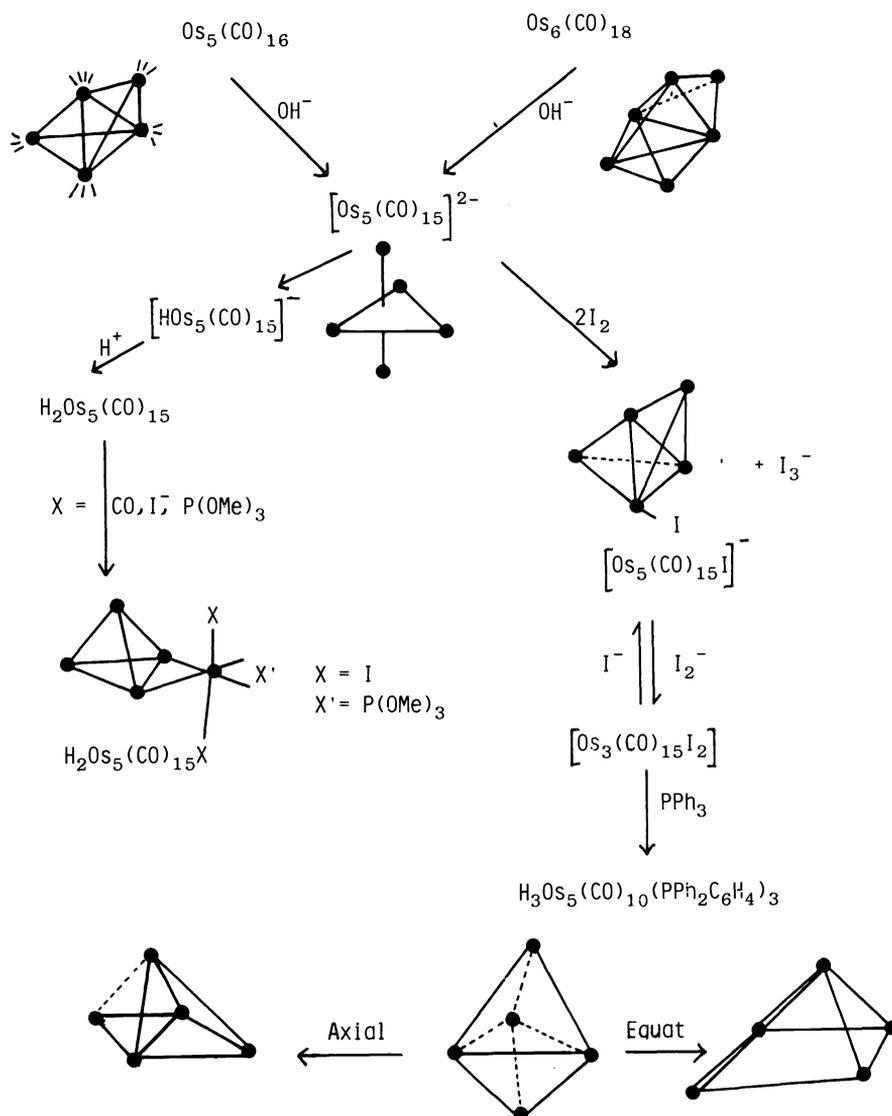
The e.s.d.'s average Ru—Ru 0.001, Ru—S 0.002, and Ru—C 0.004 Å. Relevant non-bonded contacts are Ru(2)—Ru(5) 4.011 and Ru(2)—Ru(4) 3.961 Å.

Fig. 4 Structure of  $Ru_6(CO)_{15}(HSEt)_3C$

Fig. 5 Structure of  $\text{Ru}_5\text{C}(\text{CO})_{15}\text{MeCN}$ Fig. 6 Structure of  $[\text{Os}_5\text{C}(\text{CO})_{15}]^-$ Fig. 7 Structures of  $\text{Ru}_5\text{C}(\text{CO})_{14}\text{PPh}_3$  and  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{PPh}_3)_2$ Fig. 8 Structures of  $\text{H}_2\text{Ru}_5\text{C}(\text{CO})_{12}(\text{diphos})$ Fig. 9 Structures of  $\text{HOs}_5\text{C}(\text{CO})_{14}[\text{PO}(\text{OMe})_2]$  and  $\text{HOs}_5\text{C}(\text{CO})_{13}[\text{PO}(\text{OMe})\text{P}(\text{OMe})_2]$

$[\text{Os}_5(\text{CO})_{15}\text{I}]^-$ . Reaction of the diiodide with triphenyl phosphine yields the hydrido orthometallated phosphine complex.

## SCHEME II



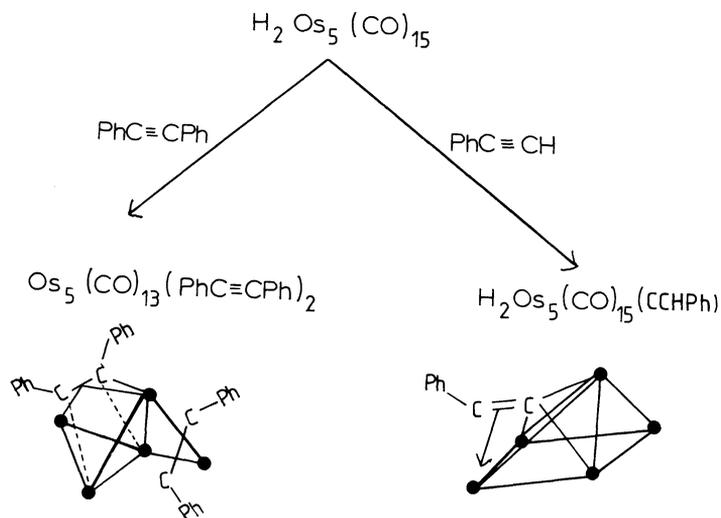
The parent hydrocarbonyl,  $\text{H}_2\text{Os}_5(\text{CO})_{15}$ , readily reacts with a range of nucleophiles leading to addition products and hence the breaking of a metal-metal bond within the trigonal bipyramidal structure. Two possible stereochemical arrangements are possible for the products depending upon the fission of an equatorial or an axial metal-metal bond. The most common stereochemical arrangement for an eight metal bonded system is the square based pyramid corresponding to the breaking of an equatorial edge (e.g.  $\text{Os}_5\text{C}(\text{CO})_{15}$ ). The addition of CO, phosphite or iodide leads to the alternative stereochemistry with the formation of an edge bridged tetrahedral arrangement corresponding to the breaking of an axial edge. (Ref. 12).

The use of alkyne or alkene molecules as donors normally leads to a more extensive modification of the metal framework, as the molecules normally donate four electrons (alkyne) or six electrons (alkene) to the cluster. This emphasises the difference in behaviour of these

ligands in polynuclear and mononuclear chemistry. In the case of mononuclear complexes both classes of compounds normally behave as two electron donors via the  $\pi$ -electrons.

Scheme III illustrates the behaviour of two alkyne molecules with  $\text{H}_2\text{Os}_5(\text{CO})_{15}$ . In both cases the compounds formed are the major products (> 60%), with phenyl acetylene addition of the anion  $(\text{C}_2\text{Ph})^-$  has occurred, with addition of four extra electrons to the  $\text{H}_2\text{Os}_5(\text{CO})_{15}$  cluster. The  $\pi$ -electrons of the unsaturated group donates two electrons to one metal

## SCHEME III

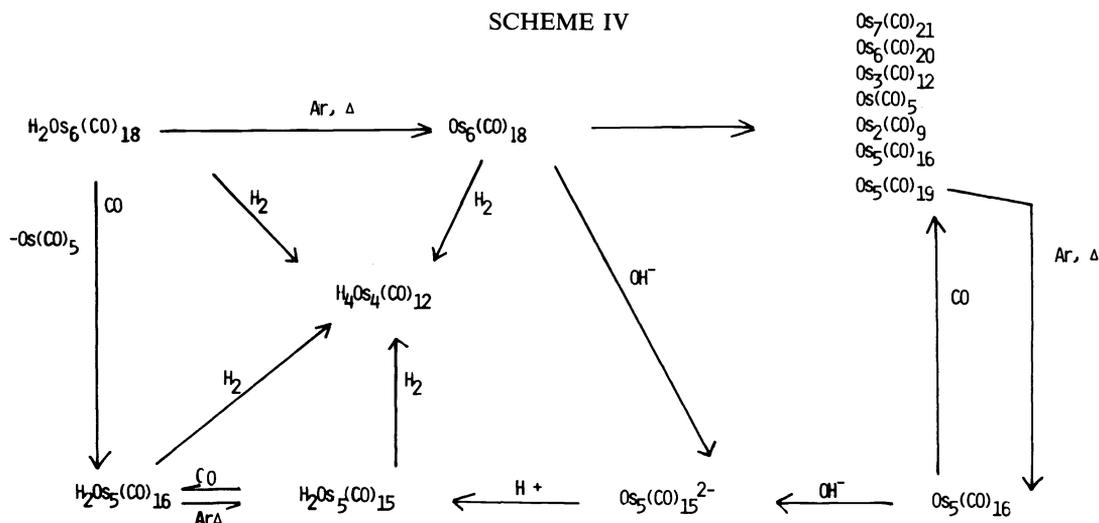


centre, whilst the carbon acts as a two electron donor to three metal centres. The four electrons lead to the breaking of two metal bonds, one axial and one equatorial.

With diphenyl acetylene, dehydrogenation of the cluster has occurred and two carbonyl groups have been displaced, involving a total of six electron loss by the cluster. The two diphenylacetylene groups bond in different modes. One acting as the bridge between four metal atoms, as in a tetrahedral butterfly arrangement whilst the remaining alkene bonds to a triangular face of cluster in a manner observed for the trinuclear complexes  $\text{M}_3(\text{CO})_{12}$ . Interestingly the two C-C bonds of the unsaturated centres differ significantly being 1.46 Å for the butterfly bonded group and 1.39 for the triangular alkene. In this instance the metal polyhedron has involved the breaking of two edges, as with in the molecule  $\text{H}_2\text{Os}_5(\text{CO})_{15}(\text{C}_2\text{Ph})$  but in this instance a new metal stereochemistry is produced by breaking two axial edges.

The ready attack on both the hexa and pentanuclear carbonyls by nucleophiles suggests that it should be possible to use CO as a nucleophile to produce some new carbonyl derivatives

## SCHEME IV



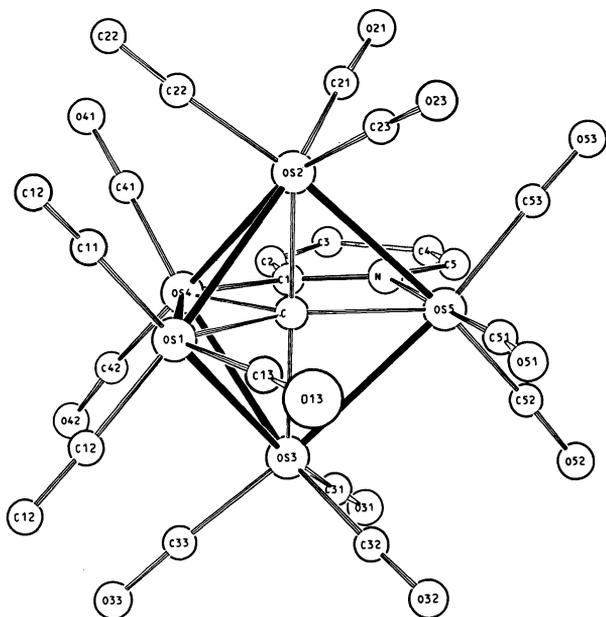
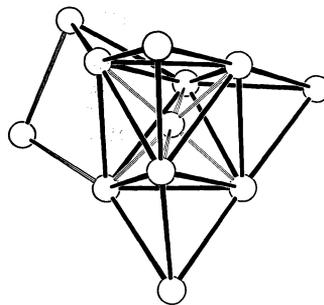


Fig. 10 Structure of  $\text{HO}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_4\text{N})$



$[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{-}$

Fig. 13a Structure of  $[\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}]^{-}$

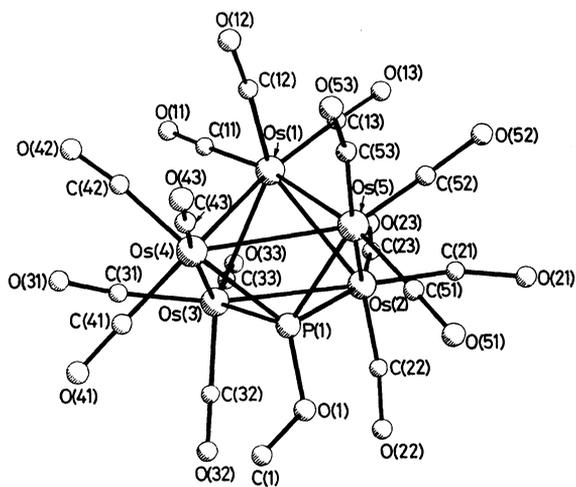
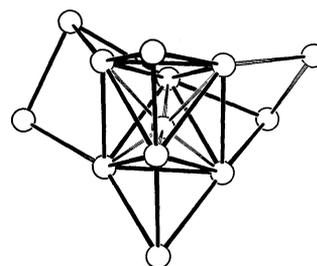


Fig. 11 Structure of  $\text{Os}_5(\text{CO})_{15}\text{POMe}$



$\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2$

Fig. 13b Structure of  $[\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2]^{2-}$

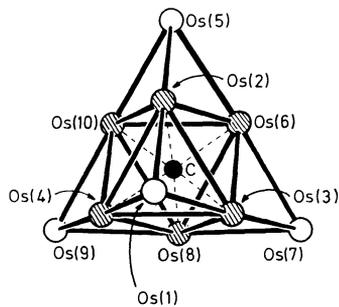


Fig. 12 Structure of  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$

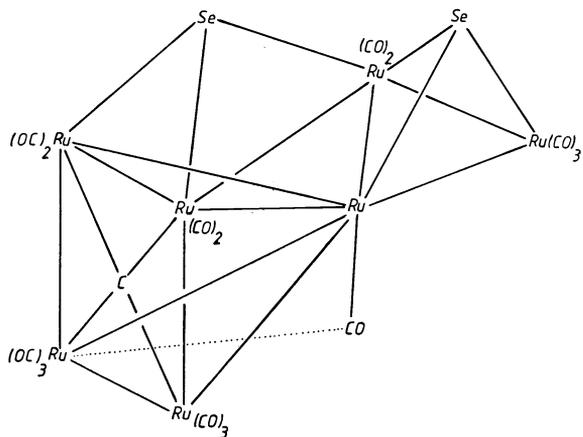


Fig. 14 Structure of  $H_4Ru_7C(CO)_{16}(Se)_2$

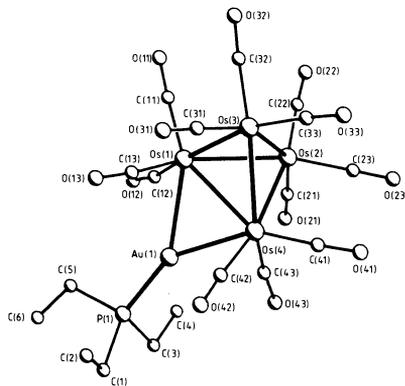


Fig. 15 Structures of  $H_3Os_4(CO)_{12}AuPEt_3$  and  $HOs_4(CO)_{13}AuPEt_3$

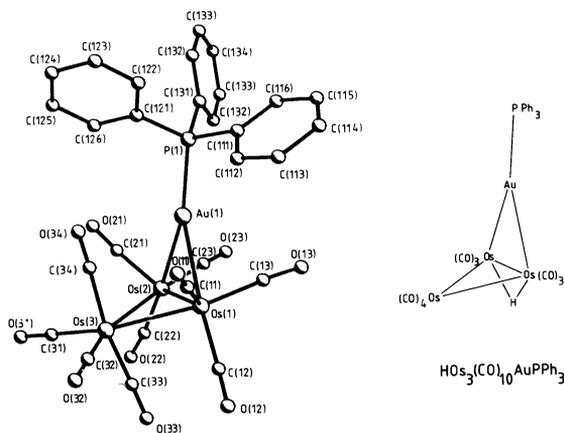
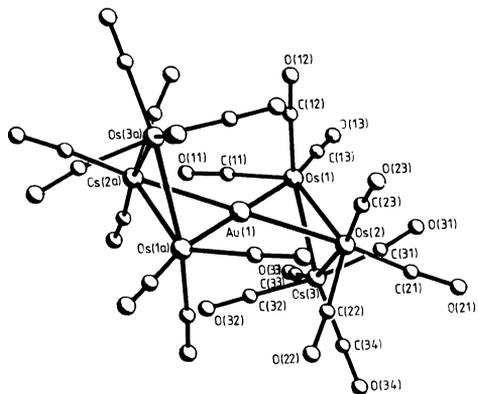


Fig. 16a Structures of  $HOs_3(CO)_{10}(AuPPh_3)$



$[HOs_3(CO)_{10}]_2Au$

Fig. 16b Structure of  $[HOs_3(CO)_{10}]_2Au$

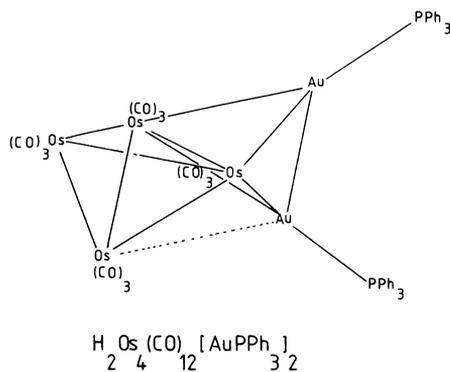
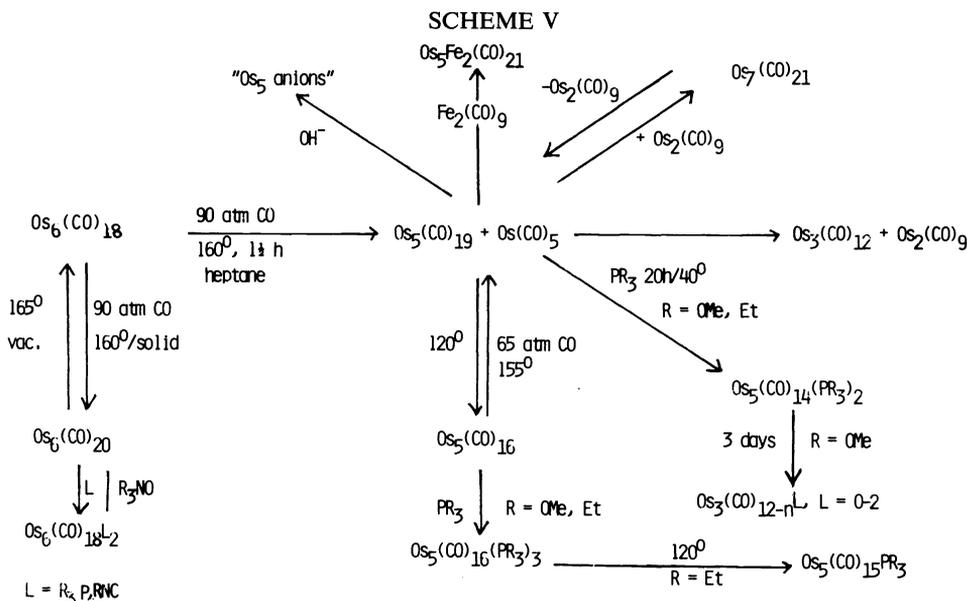


Fig. 17 Structure of  $H_2Os_4(CO)_{12}(AuPPh_3)_2$

of higher stoichiometry in carbonyl groups by the fission of metal-metal bonds. Studies with carbon monoxide under relatively mild conditions of pressure and temperature initially yielded the trinuclear carbonyl  $\text{Os}_3(\text{CO})_{12}$ , or with hydrogen the tetranuclear carbonyl hydride  $\text{H}_4\text{Os}_4(\text{CO})_{12}$  (see Scheme (IV)). A study of the infra-red spectra of these carbonyls under a variety of pressure of carbon monoxide at various temperatures indicated that there were a variety of intermediate products formed before the production of the trinuclear carbonyl,  $\text{Os}_3(\text{CO})_{12}$ .

Starting with the hexanuclear carbonyl  $\text{Os}_6(\text{CO})_{18}$ , in a variety of solvents, it was possible to isolate one of these intermediate compounds  $\text{Os}_5(\text{CO})_{19}$ , a new pentanuclear carbonyl as well as forming osmium pentacarbonyl. This mixture reacted with excess carbon monoxide (See Scheme V) to give the trinuclear carbonyl  $\text{Os}_3(\text{CO})_{12}$  and osmium monocarbonyl,  $\text{Os}_2(\text{CO})_9$ . The pentaosmium carbonyl,  $\text{Os}_5(\text{CO})_{19}$ , was readily decarbonylated to the previously known carbonyl  $\text{Os}_5(\text{CO})_{16}$  (Ref. 13).



The production of  $\text{Os}(\text{CO})_5$  and  $\text{Os}_2(\text{CO})_9$  was deduced from the infra-red spectra. Although  $\text{Os}_2(\text{CO})_9$  has been prepared previously it is known to be unstable and under the conditions employed we were not able to isolate the compound. However, further support for the presence of  $\text{Os}_2(\text{CO})_9$  comes from observation made on the carbonylation of  $\text{Os}_5(\text{CO})_{19}$  for a more limited time (160° for 1.5 h), when small amounts of the cluster  $\text{Os}_7(\text{CO})_{21}$  was detected presumably via the route



A pressure of CO would be expected to inhibit the formation of the hepta-nuclear carbonyl, consistent with the low yield observed in the carbonylation experiment. However, direct reaction of  $\text{Os}_5(\text{CO})_{19}$  with  $\text{Os}_2(\text{CO})_9$  (prepared in situ) at -40°C gave good yields of  $\text{Os}_7(\text{CO})_{21}$ . Reaction with  $\text{Fe}_2(\text{CO})_9$  yield the related mixed metal cluster,  $\text{Fe}_2\text{Os}_5(\text{CO})_{21}$  the complex being identified by mass spectroscopy and i.r.

The reaction of the two pentanuclear carbonyls with phosphine and phosphite is of interest. The  $\text{Os}_5(\text{CO})_{19}$  leads to bisubstituted derivative of the  $\text{Os}_5(\text{CO})_{16}$  series whilst the  $\text{Os}_5(\text{CO})_{16}$  leads to tris-substituted complexes of the  $\text{Os}_5(\text{CO})_{16}$  series indicating a general sensitivity of the metal-framework to the degree of carbonyl-phosphine substitution. The tris-complexes of the  $\text{Os}_5(\text{CO})_{19}$  are readily converted to  $\text{Os}_5(\text{CO})_{15}\text{PEt}_3$ , for triethylphosphine via extrusion of both carbonyl and phosphine, over a period of days the pentanuclear complexes fragment to the trinuclear species.

In contrast to the behaviour of CO on the hexacarbonyl  $\text{Os}_6(\text{CO})_{18}$  in solvents, the solid reacts with carbon monoxide at 90 atms. to produce a new hexanuclear carbonyl  $\text{Os}_6(\text{CO})_{20}$ ; the formulation is based on mass spectra and volume loss of carbon monoxide on heating to reform the hexacarbonyl  $\text{Os}_6(\text{CO})_{18}$ . This adduct relates to the intermediate postulated for  $\text{Os}_6(\text{CO})_{18}$  in many polar solvents. (See Ref. 1). Adducts  $\text{Os}_6(\text{CO})_{18}\text{L}_2$ , can be formed via reaction of  $\text{Os}_6(\text{CO})_{20}$  with phosphines, or isonitriles in the presence of an amine oxide (Ref. 14).

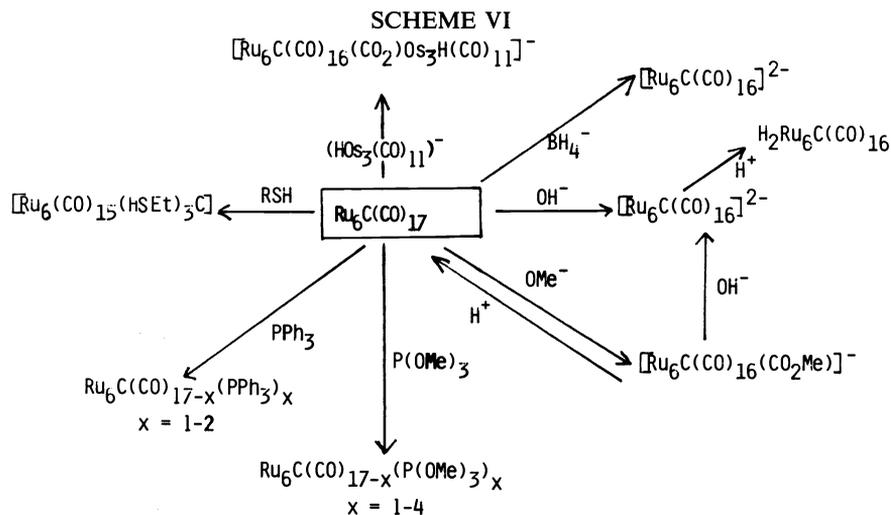
The X-ray structure of the  $\text{Os}_5(\text{CO})_{19}$  and  $\text{Os}_5(\text{CO})_{16}(\text{P}(\text{OMe})_3)_3$  are shown in Fig. 1 (Ref. 15). The addition of the six electrons from three two electron donors leads to the breaking of three metal bonds of the trigonal bipyramidal structure of  $\text{Os}_5(\text{CO})_{16}$ . The ready fragmentation of  $\text{Os}_5(\text{CO})_{19}$  to  $\text{Os}_2(\text{CO})_9$  and  $\text{Os}_3(\text{CO})_{12}$  may be viewed as the breaking of two of the metal bonds in one of the triangulated metal system. The phosphite derivative is simply related to the parent carbonyl  $\text{Os}_5(\text{CO})_{19}$ , involving replacement of three of the peripheral carbonyl groups.

#### Carbido-derivatives of osmium and ruthenium

The stability of higher nuclearity carbonyl clusters in general appears to increase on descending the triad Fe, Ru, Os, and reflects the increase in the strength of the metal-metal bonds down the series. The highest carbonyl cluster observed for ruthenium is  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ . The nuclearity of the metal clusters can be enhanced by the inclusion of interstitial non-metallic atoms. The most extensive series of compounds studied involve the use of carbon-carbido species as the interstitial atom. As will be obvious from the table, extensive cluster formation has been observed with carbido-complexes, involving the formation of hexanuclear clusters for ruthenium and deca-nuclear clusters for osmium.

Ruthenium carbonyl is readily transformed to  $\text{Ru}_6\text{C}(\text{CO})_{17}$ , by refluxing in an inert high boiling point organic solvent (Ref. 16); the yield may be considerably enhanced by reaction under a moderate pressure of ethylene. More reactive solvents may lead to direct substitution of part of the carbonyl umbrella i.e. with mesitylene the complex isolated is  $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{14}$  in which the arene bonds as a  $\eta^6$  group to one ruthenium atoms replacing three carbonyls within the initial  $\text{Ru}_6\text{C}(\text{CO})_{17}$  structure. The structure of the two complexes are shown in Fig. 2. The position of the carbon of the carbido group in the structure of these compounds may be contrasted with that in  $\text{M}_5\text{C}(\text{CO})_{15}$ ,  $\text{M} = \text{Fe, Ru, Os}$  (Ref. 17). All three of the pentanuclear compounds having the same overall structure, Fig. 3, which is based on a tetragonal pyramidal arrangement of metal atoms and involves the carbon atom being placed in a square face of the metal polyhedron. The contrasting situations of the carbon in the two classes of compounds, "encapsulated" as in  $\text{Ru}_6\text{C}(\text{CO})_{17}$ , and "exposed" as in  $\text{Ru}_5\text{C}(\text{CO})_{15}$ , suggests a potential difference in the reactivity of the bound carbon atoms. This variation in reactivity is one that is being explored by a number of workers, with particular emphasis of the potential equivalence between the "exposed" carbido species and carbide reactivity on metal surfaces (Ref. 18).

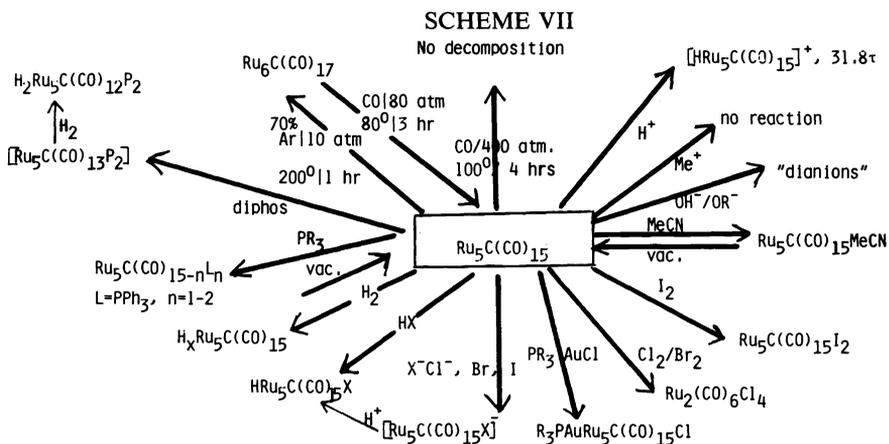
We intend, however, in this lecture to summarise the structural forms and chemistry observed to date for these ruthenium and osmium species. Scheme VI gives some of the more



salient aspects of the chemistry of the  $\text{Ru}_6\text{C}(\text{CO})_{17}$  species (Ref. 19). Direct substitution of carbonyl groups can occur with both phosphine and phosphite, reaction with the anion  $[\text{HOS}_3(\text{CO})_{11}]^-$  leads to an adduct similar to that observed with  $\text{Os}_6(\text{CO})_{18}$  (Scheme I). Treatment with borohydride or base leads to the formation of anions via attack on the coordinated carbonyl groups. The anion  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  appears to have a different structure depending on the cation used. The metal atoms form an octahedral array around the carbon in both structures but in the  $[\text{Ph}_4\text{As}]^+$  salt there are four asymmetrically edged bridging carbonyls and twelve terminal carbonyl groups whilst the  $[\text{Me}_4\text{N}]^+$  salt appears to be structurally similar to the  $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$  structure previously reported with the three edge-bridging carbonyls and the thirteen terminal groups (Ref. 20).

Reaction of the parent carbido-carbonyl with ethanthiol yields a variety of products. The X-ray of one of these compounds,  $\text{Ru}_6(\text{CO})_{15}(\text{HSET})_3\text{C}$ , is shown in Fig. 4 (Ref. 19). The encapsulating octahedral metal cage around the carbido group has been broken, exposing the carbon; the carbon has a distorted trigonal bi-pyramidal coordination to five of the ruthenium atoms, similar to that observed for some of the structure discussed below for the "exposed" carbido species. This illustrates the sensitivity of the metal cage to the nature of the ligands in the coordination sphere and the potential transposition from an encapsulated to an exposed carbido-situation.

The "exposed" carbido species are best illustrated by the chemistry of  $\text{Ru}_5\text{C}(\text{CO})_{15}$ . This compound has been obtained in good yield via carbonylation of the hexacarbido species  $\text{Ru}_6\text{C}(\text{CO})_{17}$ . The conditions for this reaction are however rather critical, (as appears to be the case for all the carbonyl carbides of both ruthenium and osmium). Scheme VII illustrates the chemistry of this complex. The enhanced stability of the metal cluster via the presence of the carbon within the metal framework is emphasised by the stability



of the compound to CO up to 400 atms. at  $100^\circ$  for appreciable periods of time. Electrophilic attack appears to occur only with protonation of the metal cluster, and the principal reaction involves nucleophilic attack at the metal centres. As with the  $\text{Os}_6$  and  $\text{Os}_5$  carbonyl cluster systems, the stereochemistry of the complex appears to be sensitive to solvent addition. Thus with acetonitrile, it is possible to detect an adduct  $\text{Ru}_5\text{C}(\text{CO})_{15}\text{MeCN}$ , the structure of which is shown in Fig. 5. The addition of the two electrons from the solvent molecule leads to the breaking of one of the metal-metal bonds and the transposition from tetragonal pyramidal array of metal atoms to a trigonal bipyramidal stereochemistry. Under vacuum the adduct reverts to the back to  $\text{Ru}_5\text{C}(\text{CO})_{15}$ . This once again emphasises the stereochemical mobility of the metal framework within these systems and the danger of using solid state structures as indicative of stereochemistry of these molecules in donor solvents.

Halogenation of the cluster unit occurs with iodine to give an addition complex whilst with chlorine and bromine cluster breakdown occurs. The phosphine gold halides, which may be viewed as a "pseudo-halogen", also gives an adduct similar to the iodine. Anionic formation via direct reaction with halides ions occurs readily and these complexes protonate to yield the hydrido species,  $\text{HRu}_5\text{C}(\text{CO})_5\text{X}$ . This series of complexes is related to the acetonitrile adduct above; the iodide is equivalent to the corresponding osmium complex  $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$  whose structure has been determined Fig. 6 (Ref. 17).

These complexes are based on bridged "butterfly" arrangement of the metal units with a metal atom spanning the two tips of the butterfly. The infra-red spectra in the  $700\text{--}800\text{ cm}^{-1}$  region have been useful differentiating between this form of bonding and the square based pyramid arrangement of the  $\text{Ru}_5\text{C}(\text{CO})_{15}$  group. For the latter stereochemistry three bands are observed in the region  $750\text{--}720\text{ cm}^{-1}$  whilst for the former stereochemistry two bands (occasionally with a shoulder on one of the bands) occur in the widely separated regions of  $820$  and  $670\text{ cm}^{-1}$ . These bands are attributed to the metal-carbon vibrations of the carbido-metal units, and reflect the difference in symmetry of the carbon-metal environment.

Reaction of the parent carbide with phosphine leads to mono and bis substituted adducts with displacement of carbonyl groups, without change in the metal cluster framework. The structure of the two adducts have been determined and are shown in Fig. 7. Reaction also occurs with dppe,  $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ , to yield an adduct with displacement of both

carbonyl groups at one metal centre. The phosphine derivatives react with molecular hydrogen to yield a hydrogen adduct. For the parent carbonyl an intermediate product is obtained from which hydrogen may be removed reversibly by applying vacuum. On reacting under more stringent conditions, a product is obtained which no longer evolves hydrogen. Both sets of products contain metal-hydrogen formation as indicated by both the i.r. and n.m.r. spectra. The X-ray of the final adduct in the reaction with the diphos complex is shown in Fig. 8, and involves hydrogen replacement of one carbonyl group, to give the compound  $\text{H}_2\text{Ru}_5\text{C}(\text{CO})_{12}$  (dppe).

These compounds illustrate the enhanced stability of the carbido-cluster complexes and illustrate the facility for both substitution and addition reactions to the cluster unit. The chemistry of the related osmium compound has not been investigated to the same detail as the yield in the preparation of the initial carbido-species,  $\text{Os}_5\text{C}(\text{CO})_{15}$ , is not as high. However, the structures of the parent carbido-carbonyl,  $\text{Os}_5\text{C}(\text{CO})_{15}$  and the iodide addition product  $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$  have been obtained (Ref. 17).

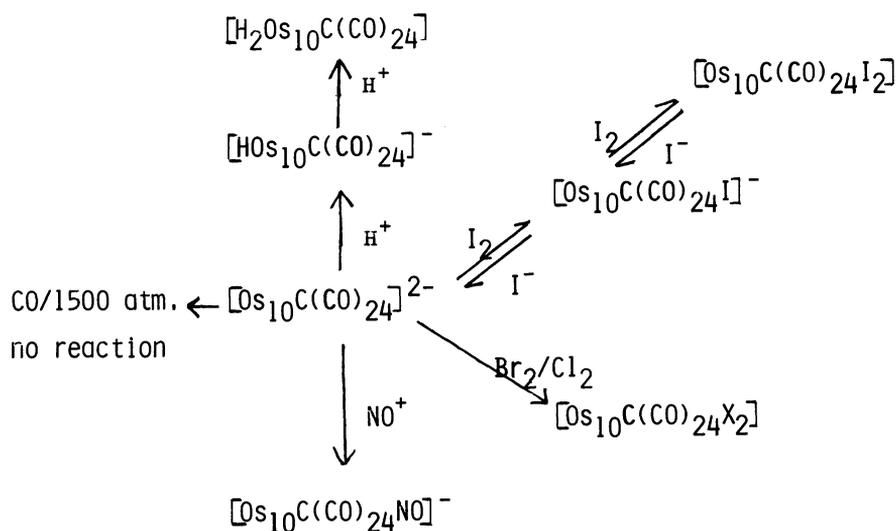
The thermolysis of the substituted trinuclear osmium carbonyl derivatives  $\text{Os}_3(\text{CO})_{11}\text{L}$ ,  $\text{L} = \text{P}(\text{OMe})_3$ ,  $\text{C}_6\text{H}_5\text{N}$ , lead to penta-nuclear carbido-clusters. For the trimethyl phosphite compound, two carbido clusters have been isolated in low yields, and involve fragmentation of the trimethyl phosphite ligand, i.e.  $\text{HOs}_5\text{C}(\text{CO})_{14}[\text{PO}(\text{OMe})_2]$ , and  $\text{HOs}_5\text{C}(\text{CO})_{13}[\text{PO}(\text{OMe})\text{P}(\text{OMe})_2]$  (Ref. 22). In both cases the ligands donate an extra two electrons to the basic  $\text{Os}_5\text{C}(\text{CO})_{15}$  unit and consistent with this the structure involves the breaking of one edge of the  $\text{Os}_5\text{C}(\text{CO})_{15}$  square based pyramidal structure; in the cases of the second complex a polymerization of the ligand group has also occurred. (See Fig. 9). The pyridine complex provides a useful entry to the higher cluster complexes (Ref. 23)  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  but in the preparation it was possible to isolate the complex  $\text{H Os}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_4\text{N})$  in which the pyridine is bonded as an orthometallated group, once again the ligand donating an extra two electrons to the  $\text{Os}_5\text{C}(\text{CO})_{15}$  structure, giving the same basic metal framework as for the phosphite substituted derivatives and the related ruthenium derivatives discussed above. Figure 10 (Ref. 24). It is interesting to note that in these complexes the formation of a metal-hydrogen linkage is consistent with the great facility of the osmium cluster to form metal-hydrogen bonds.

Another cluster obtained in the pyrolysis of the complex  $\text{Os}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)$ , is  $\text{Os}_5(\text{CO})_{15}(\text{POMe})$ . The structure of this complex is shown in Fig. 11 (Ref. 22). It is of interest to contrast the structure of this complex with that of  $\text{Os}_5(\text{CO})_{15}\text{C}$ . In both cases we have a square based pyramidal array of metal atoms. In the phosphorus complex, the phosphorus atom is coordinated as a four electron donor to the four metals of the basal plane, giving a square based pyramidal geometry around the phosphorus atom rather than the normal trigonal bipyramidal arrangement. The phosphorus is 1.185 Å below the  $\text{Os}_4$  square plane with Os-P distances of  $\sim 2.4$  Å to the atoms in this plane and  $\sim 3.0$  Å from the osmium in the apical position. This contrasts with the carbon position in the carbido-species when the carbon is  $\sim 0.1$  Å below the  $\text{Os}_4$  plane and  $\sim 2.1$  Å from all the osmium atoms. This is indicative of bonding of the carbon to the whole metal framework whilst for the phosphorus complex the bonding appears to be restricted to the atoms in the  $\text{Os}_4$  plane.

The two hexanuclear cluster reported in the table and shown in Scheme I are formed from reactions involving acetylene and  $\text{H}_2\text{Os}_6(\text{CO})_{18}$ , the higher hepta and octa nuclear complexes have been identified in a variety of thermolysis reactions involving osmium clusters but have not been studied in detail. The decanuclear anionic clusters  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ , has however been produced in good yields in a variety of reactions involving  $\text{Os}_3(\text{CO})_{12}$ , and appears to be an extremely stable cluster unit (Ref. 23). The chemistry studied to date is summarised in Scheme VIII, and the structure is shown in Fig. 12. The structure involves the first example of an octahedral encapsulated carbido-cluster for osmium, although this presumably occurs in the complex  $\text{H}_2\text{Os}_6\text{C}(\text{CO})_{16}$ . The chemistry, observed to date, is dominated by the facility for the breaking and reforming of the peripheral metal bonds, and involves attack by the electrophilic reagents,  $\text{NO}^+$ ,  $\text{I}^+$ ,  $\text{H}^+$ . With the nitrosyl and iodine, the ligand adds to the cluster, as a three electron donor, with concomitant breaking of a metal-metal bond. The structure of the two iodide derivatives are shown in Fig. 13. In particular it is of interest to note the extreme stability of the cluster to high pressure of carbon monoxide.

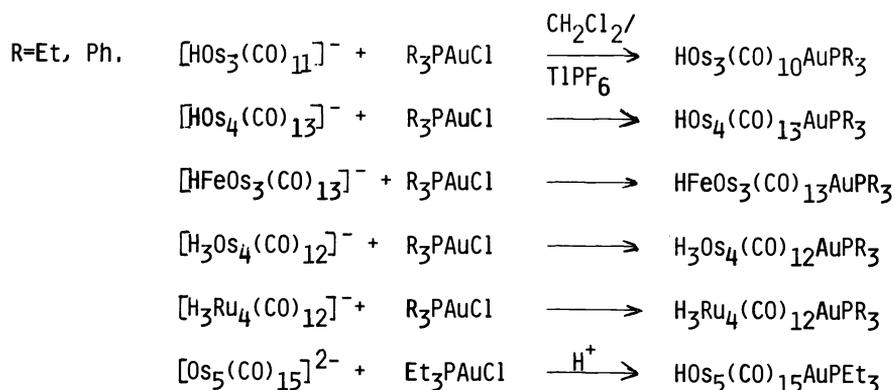
A final example which illustrates the use of more than one capping atom is provided by the reaction of  $\text{Ru}_6\text{C}(\text{CO})_{17}$  with sulphur and selenium, a variety of products may be obtained, but one of the complexes  $\text{H}_4\text{Ru}_7\text{C}(\text{CO})_{16}(\text{Se})_2$  provides an example of a heptanuclear cluster for ruthenium. The X-ray structure of the compound is shown in Fig. 14.

## SCHEME VIII

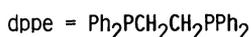
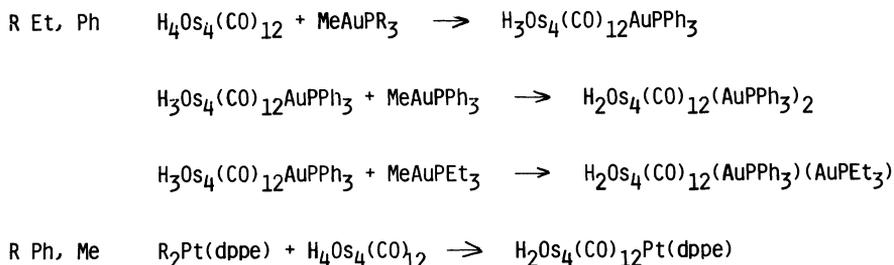
Reactions of  $[\text{Os}_{10}\text{C}(\text{CO})_4]^{2-}$ Gold-metal cluster compounds

The first systematic study of mixed metal bonded complexes was the gold complexes of the transition metal carbonyl complexes (Ref. 26). The gold-metal bonds proved to be stable, consistent with the high value of the electronegativity of gold. The study of complexes containing mixed metal bonds, of this type, provides a further example of systems in which the metal bonds have considerable polarity; a factor which was of importance in the homonuclear systems considered above. In addition to imposed polarity of the metal-metal bond, the use of gold as a metal atom extends the system to those in which the metal centres are not electronically saturated. For the complexes of ruthenium and osmium considered the electron configuration at each metal centre corresponds to that of the inert gas configuration with occupation of all the s, p and d orbitals in the valency shell. For the gold complexes, two of the p orbitals in the valency still remain unoccupied, the gold utilising an sp hybrid bonding mode. These empty p orbitals provides an alternative point of attack for nucleophiles, in reaction with these complexes.

The standard method employed in the preparation of the gold-metal complexes was the reaction of the carbonyl anion with the phosphine substituted gold-halide. We have utilised this reaction with a variety of the polynuclear anions and this leads to a wide range of gold substituted cluster complexes, which for osmium have high stability. The yield is increased by the addition of  $\text{TlPF}_6$ , which removes chloride as the thallos salt.



An alternative method of preparation is the use of alkyl gold phosphine complexes with the hydrido-carbonyls. In the case of dinuclear complexes Norton (Ref. 27) termed this reaction as "dinuclear elimination"  $M-H + M-R \rightarrow M-M' + RH$ , and the reaction has been used by Stone (Ref. 28) and coworkers to prepare binuclear gold-metal complexes. The yield in producing the monosubstituted gold complex is generally lower than with the chloride reaction, but this method has utility in providing disubstituted products with the tetranuclear osmium clusters and allows the preparation of mixed gold phosphine derivatives.



The disubstituted complex  $\text{H}_2\text{Os}_4(\text{CO})_{12}(\text{AuPPh}_3)_2$  exists in two isomeric forms, reminiscent of the behaviour of the anion  $[\text{H}_3\text{M}_4(\text{CO})_{12}]^-$ ,  $M = \text{Ru, Os}$  (Ref. 29). (See below). The alkyl reaction can be extended to other metals, thus with  $\text{R}_2\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ ,  $R = \text{Me, Ph}$ , and  $\text{H}_4\text{Os}_4(\text{CO})_{12}$ , the complex  $\text{H}_2\text{Os}_4(\text{CO})_{12}\text{Pt}(\text{dppe})$  is readily obtained.

The X-ray structures of the two complexes  $\text{H}_2\text{Os}_4(\text{CO})_{13}\text{AuPEt}_3$  and  $\text{H}_3\text{Os}_4(\text{CO})_{12}\text{AuPEt}_3$  are given in Fig. 15 (Ref. 30). A point of interest is the comparison of these complexes with the parent hydrido carbonyls. The general structural parameters of the metal framework are very similar for the hydrogen and gold complexes. The gold appears to be behaving as hydrogen, as a one electron donor group, and bridges two metal centres with a lengthening of the metal-metal bond of a similar order to that observed with hydrogen bridging. Thus stereochemically and electronically the  $\text{R}_3\text{PAu}$  appears to behave as a hydrogen atom.

Consistent with this, the structure of the trinuclear adduct  $\text{HOS}_3(\text{CO})_{10}(\text{AuPPh}_3)$ , shows a close similarity to  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ , with a short Os-Os distance for the bridged metal bond, being 2.69 Å in the gold complex and 2.68 Å in the dihydride (Ref. 31). The gold complex however undergoes further reaction with chloride in to give the phosphine free adduct  $(\text{HOS}_3(\text{CO})_{10})_2\text{Au}$ , the structure of which is given in Fig. 16. This may be viewed as the combination of two fragments,  $(\text{HOS}_3(\text{CO})_{10})$ , via a gold atom. Interestingly the complex does not react with phosphine at room temperature to return to the starting material.

These molecules provide a new aspect of reactivity in cluster chemistry with potential interaction at both the osmium and gold centres. The reactions of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with a wide range of nucleophiles has been of considerable preparative utility in osmium cluster chemistry and may be related to the formal "unsaturation" of the bridged osmium-osmium bond (Ref. 30). As discussed above in the substituted gold complex the gold atom provides an additional centre for nucleophilic attack.

Phosphines react with the gold complexes leading to cluster break down via initial attack at the gold centre (no reaction is noted for the reaction of triphenyl phosphine with the triphenyl phosphine substituted gold complex, presumably due to steric inhibition). With the dihydride,  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ , phosphines react via addition to an osmium centre, followed by carbon monoxide elimination to give the substituted derivatives,  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PR}_3)$ .

The potential sensitivity of the gold adducts to steric factors is illustrated in the reaction of the triethyl phosphine and triphenyl phosphine derivatives to carbon monoxide, for the triethyl phosphine cluster break down occurs on reaction with carbon monoxide in ethylene chloride whereas for the triphenyl adduct addition of carbon monoxide occurs to yield  $\text{H}(\text{AuPPh}_3)\text{Os}_3(\text{CO})_{11}$ , in a manner similar to that observed with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  which yields  $\text{H}_2\text{Os}_3(\text{CO})_{11}$ . As with the dihydride the complex loses carbon monoxide on standing to regenerate the parent molecule  $\text{H}(\text{AuPPh}_3)\text{Os}_3(\text{CO})_{10}$ . Similarly  $t\text{BuNC}$  adds to the triethyl phosphine gold complex to yield the adduct  $\text{HOS}_3(\text{CO})_{10}(t\text{BuNC})\text{AuPEt}_3$ , in a similar manner to the reaction of  $t\text{BuNC}$  with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  to yield  $\text{H}_2\text{Os}_3(\text{CO})_{10}(t\text{BuNC})$ . However many of the wide range of reactions observed for  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with acetylenes, azides, and diazo compounds do not seem to occur with the gold complexes (diazo methane does react to yield

an unstable complex). However it has been noted that substitution of a carbon monoxide by phosphine e.g. as in  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ , leads to a considerable decrease in reactivity towards all these classes of reagents. This decrease in reactivity in both the phosphine substituted and the gold phosphine complexes may be associated with steric factors making the osmium-osmium bond less accessible for attack.

Pyrolysis of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  in refluxing octane leads to the formation of high clusters, particularly of  $\text{H}_2\text{Os}_5(\text{CO})_{15}$  and  $\text{H}_4\text{Os}_4(\text{CO})_{12}$ . The phosphine gold adducts  $(\text{R}_3\text{PAu})\text{H}_2\text{Os}_3(\text{CO})_{10}$  also yield the clusters  $\text{H}_3\text{Os}_4(\text{CO})_{12}\text{AuPR}_3$  and  $\text{H}_2\text{Os}_5(\text{CO})_{15}\text{AuPR}_3$ , (R = Ph, Et) under similar conditions; the products being identical to those obtained by the preparative methods discussed above.

As stated above the complex  $[\text{H}_2\text{Os}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$  exists in two isomeric forms, initially we believed this to be similar to that observed in the  $[\text{H}_3\text{M}_4(\text{CO})_{12}]^-$  systems M = Ru, Os. A recent X-ray structure of one of these isomers has however identified a new structural form. (See Fig. 17), in which there is a direct bond between the gold atoms (2.80 Å), and the gold atoms appear to be bonded to the osmium tetrahedron to produce a molecule reminiscent of  $\text{Os}_6(\text{CO})_{18}$ .

The chemistry of these gold-osmium adducts, although as yet only studied in a preliminary way indicates comparison with the homonuclear clusters, and implies a higher stability than observed for other heteronuclear complexes of osmium and ruthenium.

As stated above, extensive studies have been carried out on the carbonyls,  $\text{M}_3(\text{CO})_{12}$ , M = Ru, Os, with a wide variety of reagents. It is perhaps of interest to conclude this lecture by briefly contrasting the behaviour observed with the related chemistry for mononuclear species and the work reported here for the higher polynuclear complexes.

For the trinuclear compounds, particularly with organic ligands, many new bonding modes of the ligand groups have been observed from those recorded for mononuclear complexes. In particular the ligand group often donates many more electrons to the bonding in these complexes than observed in mononuclear compounds; thus ethylene contributes six electrons in the complex  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{H}_4)$  via breaking of C-H bonds, whilst in mononuclear complexes, two electron addition from the ethylene group is the normally observed bonding mode. For the trinuclear complexes bonding of a ligand group often also occurs to more than one metal centre even with hydrogen the most common bonding mode involves two metal centres (edge bridging), or three (face bridging). This obviously implies a potentially different chemistry for the trinuclear complexes to that established in the vast studies of mononuclear systems and emphasises the necessity for a comparative extensive study of the chemistry of the trinuclear systems.

In contrast the preliminary studies that have been carried out on the higher nuclearity complexes seem to indicate very similar bonding patterns for the ligand groups to that observed in the trinuclear species; possibly reflecting the common feature of the metal triangulated face in the majority of the structures of the high nuclearity cluster compounds. The presence of more than one of these triangular faces also allows the possibility of more groups bonding in the higher cluster units. However perhaps of more significance for the higher nuclear clusters is the presence of a larger number of metal-metal bonds within the metal framework allowing for an extensive chemistry involving fission of metal bonds. The primary chemistry reported for the trinuclear complexes involves substitution of the carbonyl groups in the coordination here. Attack on these compounds appears to occur in many instances via a primary attack at the metal centre with the breaking of a metal metal bond followed by ejection of the carbonyl group and the reformation of the metal metal bond implying a different mechanistic pathway to substitution reaction observed in mononuclear species. For the higher nuclear clusters the ejection of the carbonyl group does not necessarily occur and a main feature of the chemistry appear to be electron addition to the cluster with the concomitant change in the stereochemical arrangement of the metal atoms within the framework due to the breaking of metal-metal bonds. For the higher clusters (nuclearity greater than four), the possibility of a variety of different stereochemical forms are possible, reflecting the facility to break different metal bonds within the molecular framework. For the higher cluster the presence of metal-metal donor bonds leads to a further variation in the reactivity pattern as the induced polarity of this bonding mode enhances the potential reactivity. The natural extension of this concept to heteronuclear systems offer a further variation in chemical reactivity, particularly if this involves the use of metals with incomplete valency shells such as Gold. The overall future of the chemistry of this area is impossible to predict at this early stage in its development, but the marked variation in bonding to that observed for mononuclear compounds must reflect a new dimension in this as yet sparsely studied area of chemistry.

We should like to acknowledge the many collaborators that have participated in this work. Without their efforts and enthusiasm little of this would have been accomplished. In particular we should like to mention the major contributions of Dr P R Raithby and Dr M McPartlin whose patience and expertise in the X-ray studies have been paramount in the establishment of these studies.

TABLE 1. Carbido-carbonyl complexes of ruthenium and osmium

Ru	Os	Ru	Os
<i>NUCLEARITY : PENTANUCLEAR</i>		<i>NUCLEARITY : HEXANUCLEAR</i>	
$\text{Ru}_5\text{C}(\text{CO})_{15}$	$\text{Os}_5\text{C}(\text{CO})_{15}$	$[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$	
$\text{Ru}_5\text{C}(\text{CO})_{15}\text{MeCN}$	$[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$	$\text{H}_2\text{Ru}_6\text{C}(\text{CO})_{16}$	
$[\text{Ru}_5\text{C}(\text{CO})_{15}\text{X}]^-$ , $[\text{HRu}_5\text{C}(\text{CO})_{15}\text{X}]$ , X = Cl, Br, I	$\text{HOS}_5\text{C}(\text{CO})_{14}[\text{PO}(\text{OMe})_2]$	$[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{HSEt})_3]$	
$\text{Ph}_3\text{PAuRu}_5\text{C}(\text{CO})_{15}\text{Cl}$	$\text{HOS}_5\text{C}(\text{CO})_{13}[\text{PO}(\text{OMe})\text{OP}(\text{OMe})_2]$	$\text{Ru}_6\text{C}(\text{CO})_{15}(\text{MeCH}=\text{CH})_2$	
$\text{Ru}_5\text{C}(\text{CO})_{15-n}\text{L}_n$ n = 1-2, L = $\text{PPh}_3$ , $\text{PEt}_3$ , $\frac{1}{2}$ diphos	$\text{HOS}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_4\text{N})$	$\text{Ru}_6\text{C}(\text{CO})_{14}(\text{arene})$ , Arene = $\text{C}_6\text{H}_6$ , $\text{MeC}_6\text{H}_5$ , 1:3 $\text{MeC}_6\text{H}_4$ 1:3:5 $\text{Me}_3\text{C}_6\text{H}_3$	
$\text{H}_2\text{Ru}_5\text{C}(\text{CO})_{13}(\text{diphos})$		$\text{Ru}_6\text{C}(\text{CO})_{13}\text{L}_4$ , L = $\text{P}(\text{OMe})_3$	
<i>NUCLEARITY : HEXANUCLEAR</i>		<i>NUCLEARITY : HIGHER NUCLEAR CLUSTER</i>	
$\text{Ru}_6\text{C}(\text{CO})_{17}$	$\text{H}_2\text{Os}_6\text{C}(\text{CO})_{16}$	$\text{H}_4\text{Ru}_7\text{C}(\text{CO})_{16}\text{Se}_4$	$\text{H}_2\text{Os}_7\text{C}(\text{CO})_{19}$
$\text{Ru}_6\text{C}(\text{CO})_{16}\text{L}$ , L = $\text{PPh}_3$ , $\text{P}(\text{C}_6\text{H}_4\text{F})_3$ , $\text{AsPh}_3$			$\text{Os}_8\text{C}(\text{CO})_{21}$
$[\text{Ru}_6\text{C}(\text{CO})_{16}\text{CO}_2\text{Os}_3\text{H}(\text{CO})_{11}]^-$	$\text{Os}_6\text{C}(\text{CO})_{16}(\text{MeC}_2\text{Me})$		$[\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$
$[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{CO}_2\text{Me})]^-$			$[\text{HOS}_{10}\text{C}(\text{CO})_{24}\text{I}]^-$
			$\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2$

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