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Aspects of Ruthenium and Osmium Cluster Chemistry [and Discussion]

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Aspects of ruthenium and osmium cluster chemistry

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In this paper, we survey the synthesis, structure and bonding of a series of cluster carbonyl compounds of ruthenium and osmium containing from three to ten metal atoms. Members of this series include neutral, anionic hydrido and carbido clusters, all of which are derived from their $[M_3(CO)_{12}]$ parent. In general, the synthesis of these compounds involves the pyrolysis of either $[M_3(CO)_{12}]$ or, with osmium, some higher nuclearity cluster. The mechanism by which these reactions occur is believed to involve the formation of highly unstable, unsaturated derivatives. Many of these clusters contain frameworks of metal atoms that may be regarded as fragments of close-packed metallic arrangements; others may be regarded as examples of tetrahedral growth patterns. They exhibit a new and diverse chemistry, much of which may now be understood in terms of simple bonding arguments.

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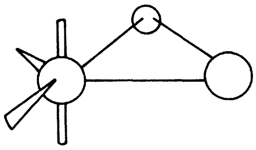

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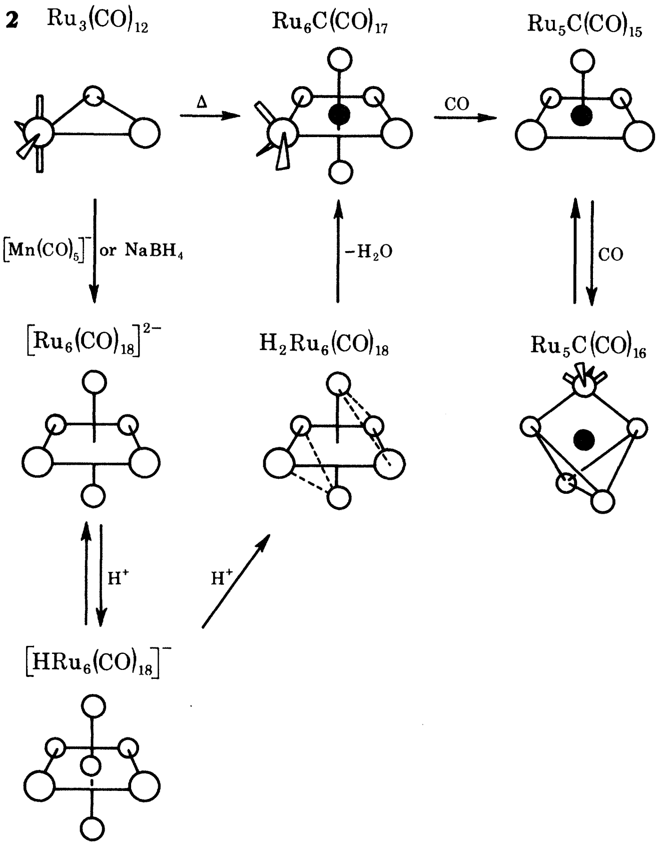

Figure 1. The molecular structure of $Os_3(CO)_{12}$.

Figure 2. Some reactions of $Ru_3(CO)_{12}$ to produce hexaruthenium and pentaruthenium clusters.

INTRODUCTION

In this paper we shall consider the preparation, structure and some chemical properties of cluster carbonyl compounds of both ruthenium and osmium. In figure 1 is illustrated the structure of triosmium dodecacarbonyl, which is the parent of the clusters that we wish to discuss. In this structure, which was originally established by X-ray analysis by Corey & Dahl (1962), the three osmium atoms define an equilateral triangle with three Os–Os distances of *ca.* 288 pm. This distance, which is similar to that of the closely related compound $Ru_3(CO)_{12}$,

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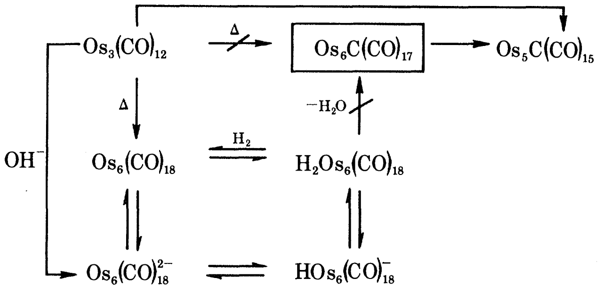

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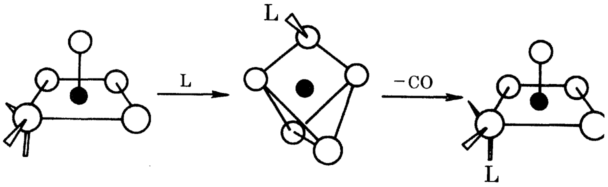

FIGURE 3. Some reactions of $Os_3(CO)_{12}$ to produce hexaosmium and pentaosmium clusters.

FIGURE 4. Possible mechanism of CO substitution in $Ru_5C(CO)_{15}$.

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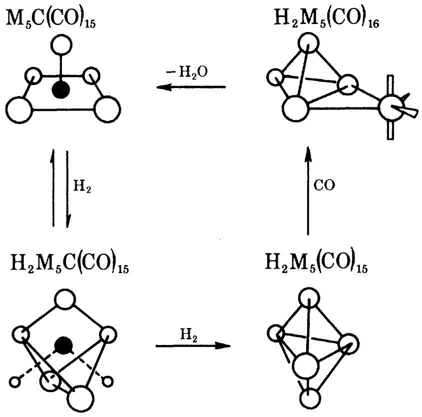

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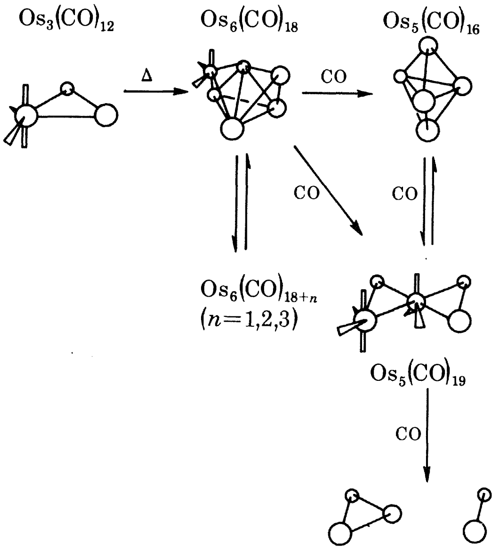

FIGURE 5. The reaction of $Ru_5C(CO)_{15}$ with H_2.

FIGURE 6. Formation and subsequent carbonylation of $Os_6(CO)_{18}$.

is now commonly taken as corresponding to an Os–Os single bond. It is worth noting that within the higher clusters, Os–Os distances ranging from about 260 to 300 pm are observed, and there is no simple relation between bond length and bond multiplicity in systems of this type.

In figure 2 are outlined some of the simple reactions that $Ru_3(CO)_{12}$ will undergo. Several years ago we (Johnson *et al.* 1975) demonstrated that, on pyrolysis, $Ru_3(CO)_{12}$ underwent polymerization and CO_2 ejection to produce $Ru_6C(CO)_{17}$, which has been shown to consist of an octahedron of ruthenium atoms with a central, interstitial carbon atom. More recently we have established that on treatment with CO under moderate pressure and temperature cleavage occurs and the pentanuclear carbide $Ru_5C(CO)_{15}$ and $Ru(CO)_5$ are produced (Farrar *et al.* 1981*b*). This pentanuclear carbide reacts, in turn, with more CO to form the unstable adduct $Ru_5C(CO)_{16}$ (Johnson *et al.* 1982). This adduct almost certainly possesses a wing-tipped butterfly structure with an exposed semi-interstitial C atom, by analogy with the structure that we have established for the more stable adduct $Ru_5C(CO)_{15}MeCN$ (Johnson *et al.* 1982), prepared by the direct reaction of $Ru_5C(CO)_{15}$ with MeCN. In an alternative sequence the dianion $Ru_6(CO)_{18}^{2-}$ has been produced from the reaction of $Ru_3(CO)_{12}$ with base; protonation of this dianion produces first $[HRu_6(CO)_{18}]^-$ and then $H_2Ru_6(CO)_{18}$ (Jackson *et al.* 1979*a*). We find that on heating, water is apparently ejected from this dihydride to provide a second route to $Ru_6C(CO)_{17}$. The corresponding reactions of $Os_3(CO)_{12}$ (figure 3) follow a different

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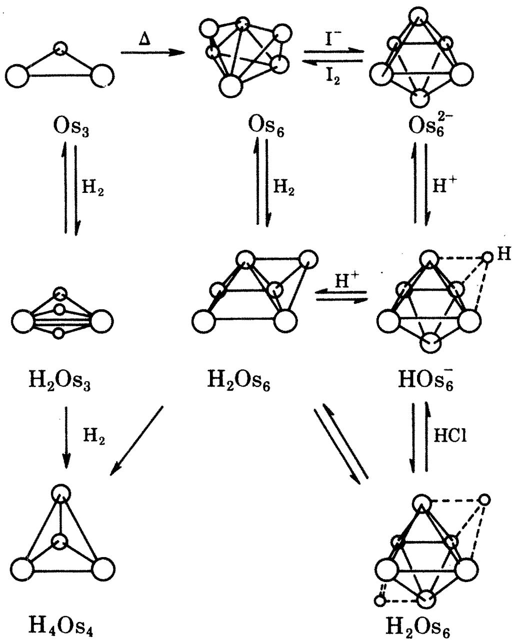

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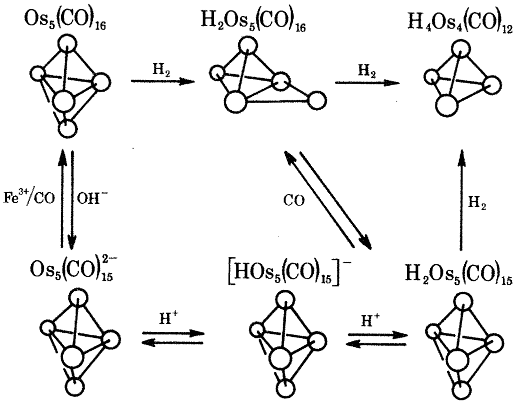

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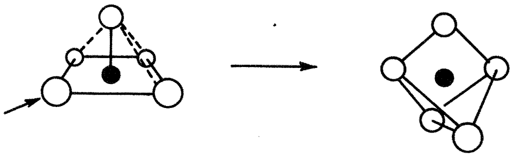

Figure 7. The reactions of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ with H_2.

Figure 8. Formation of pentaosmium and tetraosmium hydrido clusters.

Figure 9. Nucleophilic addition to $M_5C(CO)_{15}$.

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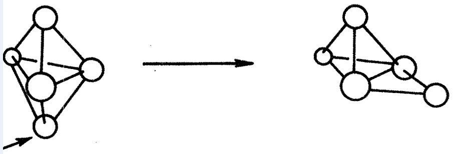

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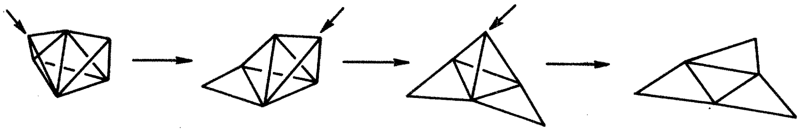


12

$$Os_6(CO)_{18} \xrightarrow{L} Os_6(CO)_{18}L_n$$

Figure 10. Nucleophilic addition to $Os_5(CO)_{16}$.

Figure 11. Nucleophilic addition to $Os_6(CO)_{18}$.

Figure 12. Addition of ligand L to $Os_6(CO)_{18}$ (L = CO or $P(OMe)_3$; n = 1–4).

course and although varying yields of $Os_5C(CO)_{15}$ (Jackson *et al.* 1980) may be produced from the pyrolysis of $Os_3(CO)_{12}$, $Os_6C(CO)_{17}$ has not been characterized.

The pentanuclear carbides, $M_5C(CO)_{15}$, undergo CO substitution reactions with a range of ligands L to produce $M_5C(CO)_{15-n}L_n$. Almost certainly the mechanism of these reactions is that shown in figure 4. Intermediates of the type $M_5C(CO)_{15}L$ have been fully characterized (see above). Of special note is the reaction of $Ru_5C(CO)_{15}$ with H_2 (figure 5) to produce first $H_2Ru_5C(CO)_{15}$ and then $H_2Ru_5(CO)_{15}$ and (possibly) methane. Further reaction with CO regenerates $Ru_5C(CO)_{15}$ (Johnson *et al.* 1982). Carbonylation of $Os_6(CO)_{18}$ (figure 6) produces $Os_5(CO)_{16}$ and the new binary carbonyls $Os_5(CO)_{19}$, with a bow-tie metal skeleton, and $Os_6(CO)_{20}$ (Farrar *et al.* 1981*d*). Reaction of H_2 with $Os_6(CO)_{18}$ or $Os_5(CO)_{16}$ generated several hydrido species, but in all cases $H_4Os_4(CO)_{12}$ is eventually produced (figures 7 and 8).

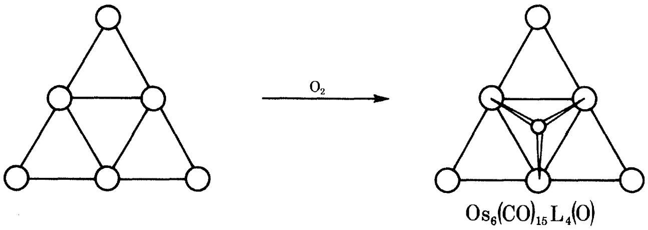
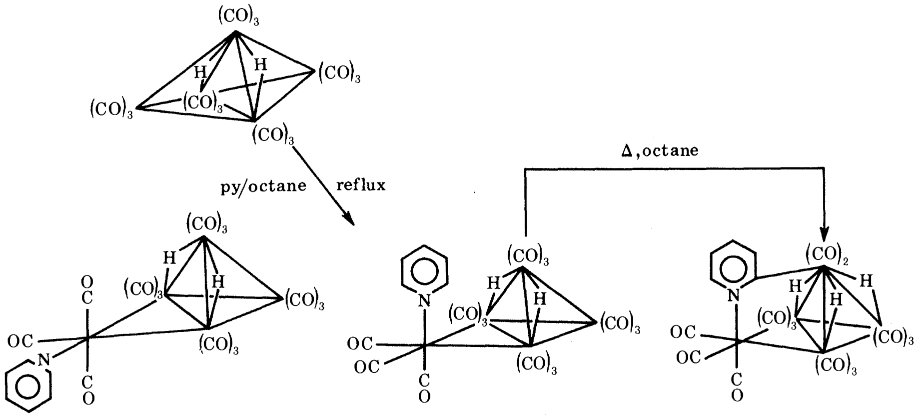


FIGURE 13. Reaction of raft-like clusters $Os_6(CO)_{17}L_4$ with dioxygen.



addition product A: $H_2Os_5(CO)_{15}(py)$

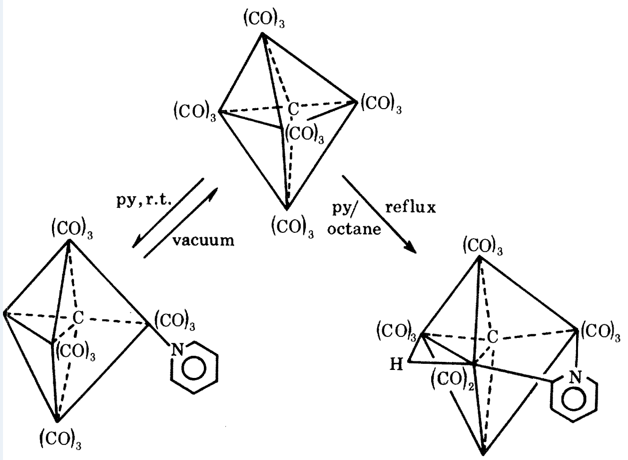
addition product B: $H_2Os_5(CO_{15})(py)$

orthometallation product: $H_3Os_5(CO)_{14}(NC_5H_4)$

FIGURE 14. Reactions of $H_2Os_5(CO)_{15}$ with pyridine (py).

The mechanism of nucleophilic attack on these clusters has not been determined with certainty. However, because the clusters may be regarded as electron-deficient, possible reaction pathways (summarized in figures 9, 10 and 11) would involve addition to the least coordinatively saturated metal atom. For $Os_6(CO)_{18}$ the addition of successive molecules of $P(OMe)_3$ leads to the systematic opening of the bicapped tetrahedral unit, with attack occurring at each unsaturated metal in turn, to produce the planar Os_6 (figures 12 and 13) (Goudsmit *et al.* 1982). The compound $Os_6(CO)_{17}[(P(OMe)_3]_4$ has been shown to react with O_2 to produce $Os_6(CO)_{15}$-$[P(OMe)_3]_4[O]$. Similar nucleophilic additions occur when $H_2Os_5(CO)_{16}$, $Os_5C(CO)_{15}$ or $Os_6(CO)_{18}$ are reacted with pyridine. Here the initial addition is followed by C–H bond cleavage (figures 14, 15 and 16).

Attack of base (OH^-) on $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ or $Os_8(CO)_{23}$ brings about the removal of



ddition product:
$Os_5C(CO)_{15}(py)$

orthometallation product:
$HOs_5C(CO)_{14}(NC_5H_4)$

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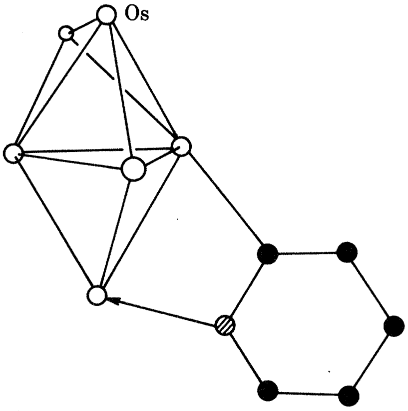

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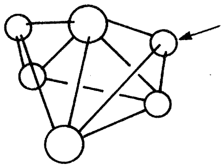

FIGURE 15. Reaction of $Os_5C(CO)_{15}$ with pyridine (py).

FIGURE 16. Arrangement of osmium and ligand anions in $HOs_6(CO)_{16}(C_5H_4N)$.

FIGURE 17. Os_6 core in $Os_6(CO)_{18}$.

8

$$Os_6(CO)_{18} \xrightarrow{OH^-} Os_6(CO)_{18}(OH)^- \xrightarrow{OH^-} Os_6(CO)_{18}(OH)_2^{2-} \xrightarrow{OH^-} Os_5(CO)_{15}^{2-} + Os(CO)_3(OH)_3^-$$

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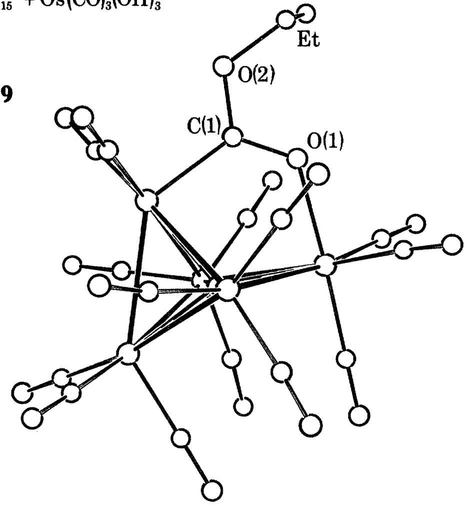

FIGURE 18. Addition of OH^- to $Os_6(CO)_{18}$.

FIGURE 19. Molecular structure of $HOs_5C(CO)_{14}(COOEt)$.

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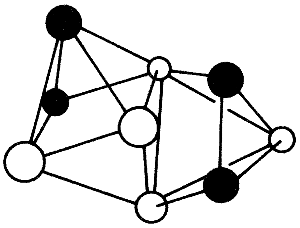
$$Os_5(CO)_{15} \xrightarrow{C_2R_2} Os_5(CO)_{15}(C_2R_2)_2 + \text{others}$$



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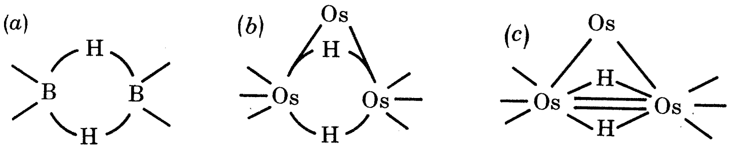

FIGURE 20. Preparation and structure of the organometallic cluster $Os_5(CO)_{15}(C_2R_2)_2$.

FIGURE 21. Bonding picture for $H_2Os_3(CO)_{10}$: (*b*) analogous to B_2H_6 (*a*); (*c*) the alternative viewpoint.

an $Os(CO)_3$ capping unit (figure 17), and here successive nucleophilic addition occurs at the same Os atom (figure 18). $Os_5C(CO)_{15}$ undergoes reaction with ROH in which both nucleophilic addition to a coordinated CO and donation from the so-formed RCO_2 unit to the cluster occurs. The structure of one such derivative (R = Et) is shown in figure 19.

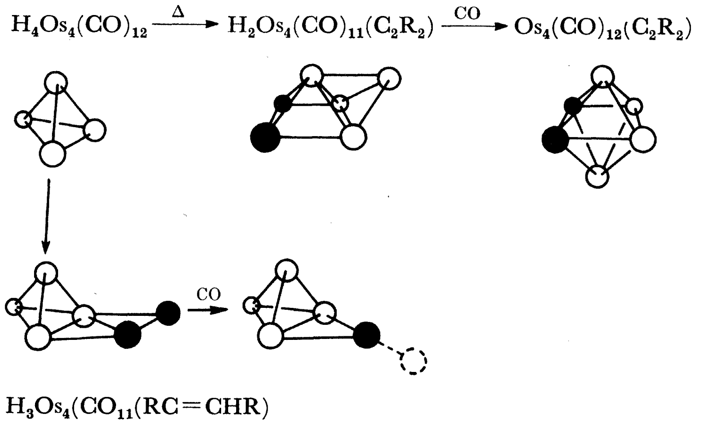

FIGURE 22. Reactions of $H_4Os_4(CO)_{12}$ with alkynes (R_2C_2) to produce tetraosmium organometallic clusters.

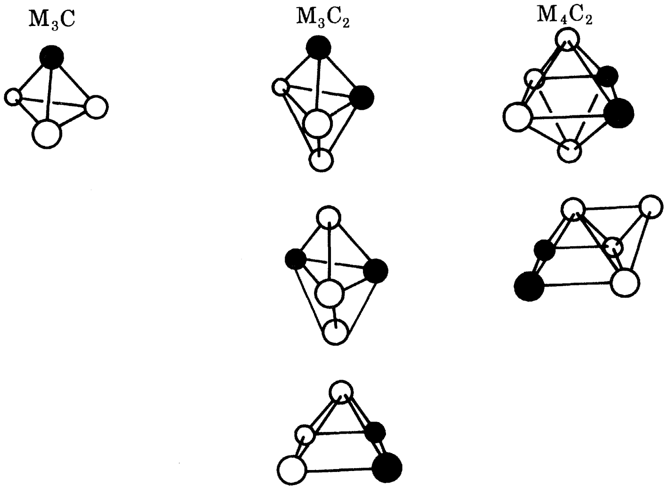

FIGURE 23. Organo-osmium clusters based on M_3C, M_3C_2 and M_4C_2 units.

tetrahedron ⟶ monocapped tetrahedron ⟶ bicapped tetrahedron
$H_4Os_4(CO)_{12}$ $[Os_5(CO)_{15}]^{2-}$ $Os_6(CO)_{18}$

FIGURE 24. Tetrahedral growth pattern exhibited by osmium clusters.

O_h octahedron ⟶ monocapped octahedron ⟶ bicapped octahedron
$[Os_6(CO)_{18}]^{2-}$ $[Os_7(CO)_{21}]^{2-}$ $[Os_8(CO)_{22}]^{2-}$

↓

tetracapped octahedron $[Os_{10}C(CO)_{24}]^{2-}$ ⟵ tricapped octahedron '$[Os_9(CO)_{24}]^{2-}$'

FIGURE 25. Growth pattern towards c.c.p. exhibited by osmium clusters.

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The similarity between the metal clusters and the boranes is further illustrated by the reactions that they undergo with alkenes and alkynes. Again the reaction pathways are similar to those described above, with initial attack occurring at capping atoms. The structure of $Os_5(CO)_{13}(C_2R_2)_2$ (figure 20) is clearly derived from the trigonal bipyramidal $H_2Os_5(CO)_{15}$ (Farrar *et al.* 1981*c*). This idea of electron-deficiency may be extended to include hydrido-clusters as shown in figure 21, the cluster $H_2Os_3(CO)_{10}$ being more appropriately regarded as having a reaction pattern in keeping with that of B_2H_6. Following this idea that reactions are induced by the opening of three-centre, two-electron Os–H–Os bonds, the behaviour shown by

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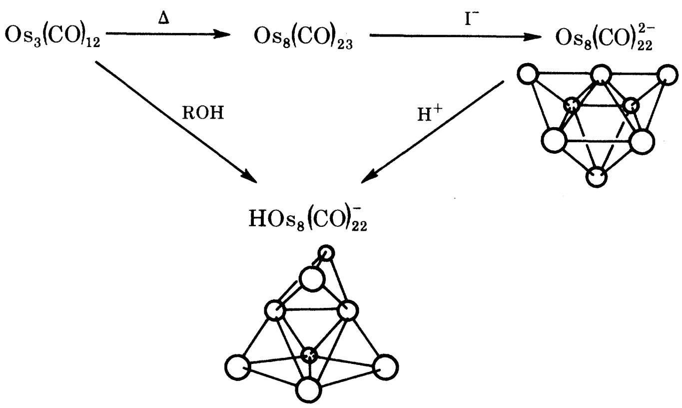

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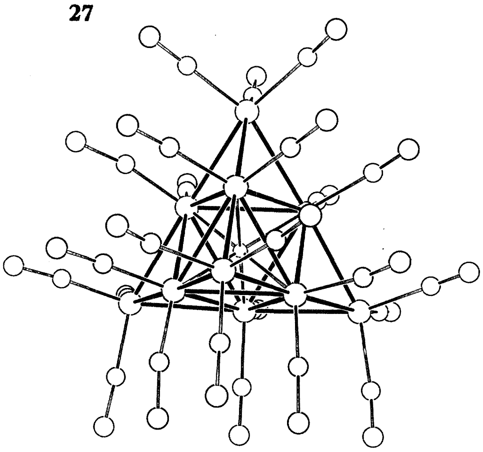

FIGURE 26. Preparation and structure of $[Os_8(CO)_{22}]^{2-}$ and $[HOs_8(CO)_{22}]^-$.

FIGURE 27. Molecular structure of the cluster dianion $[Os_{10}C(CO)_{24}]^{2-}$, emphasizing the close-packed sheath of CO ligands.

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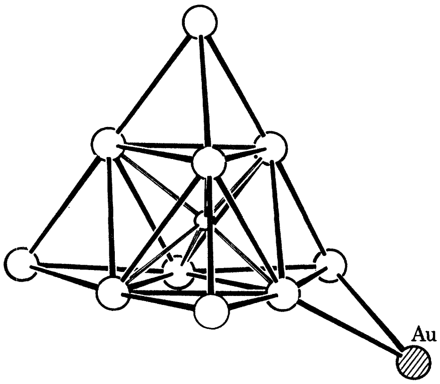

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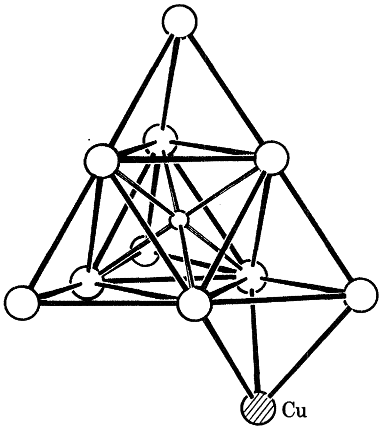


FIGURE 28. Metal geometry observed in the mixed cluster $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$.

FIGURE 29. Metal geometry observed in the mixed cluster $[Os_{10}C(CO)_{24}Cu(NCMe)]^-$.

$H_4Os_4(CO)_{12}$ is readily understood (figure 22) (Johnson *et al.* 1980). Here, octahedral or monocapped square based prismatic geometries are observed in keeping with the view that a CR group is isoelectronic and isolobal with $Os(CO)_3^-$. Other polyhedra based on Os_3C and

Os_3C_2 units may be derived similarly (figure 23). The reactions of $Os_6(CO)_{18}$ are similar, but under the conditions employed expected intermediate compounds have not been observed (Eady *et al.* 1978).

The polyhedral forms adopted by various Os_m fragments fall into two distinct types; those showing the fused tetrahedral growth pattern exemplified by $H_4Os_4(CO)_{12}$, $Os_5(CO)_{15}^{2-}$ and $Os_6(CO)_{18}$ (figure 24), and those exhibiting progressive growth towards c.c.p. (figure 25), $Os_6(CO)_{18}^{2-}$, $Os_7(CO)_{20}^{2-}$, $Os_8(CO)_{22}^{2-}$ and $Os_{10}C(CO)_{24}^{2-}$ are good examples. Other related molecules based on Os_7 and Os_9 units are clearly related to the former. The factors that influence the geometry adopted are not clear. The geometries of the two isoelectronic species

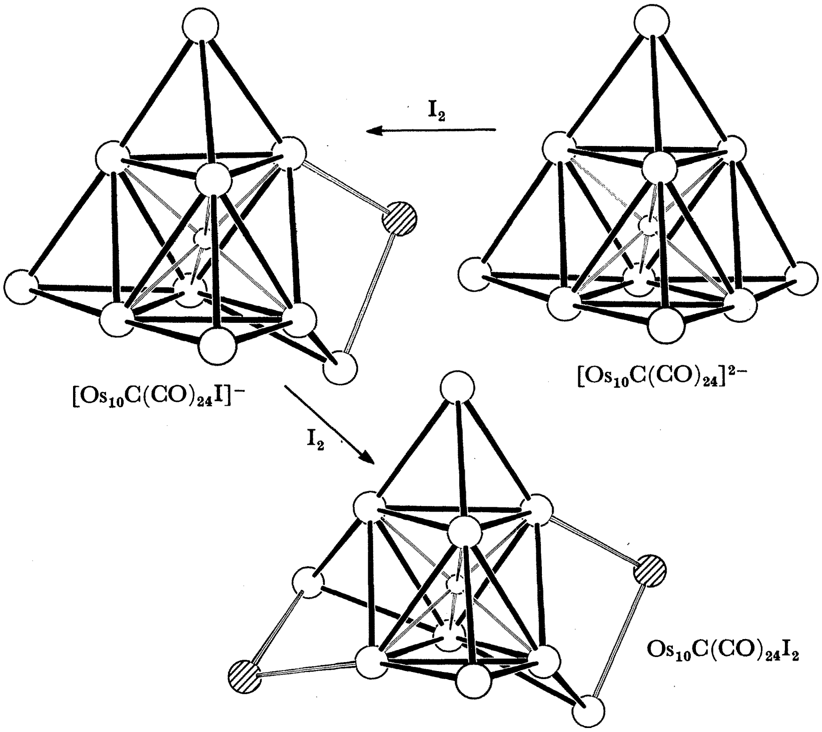
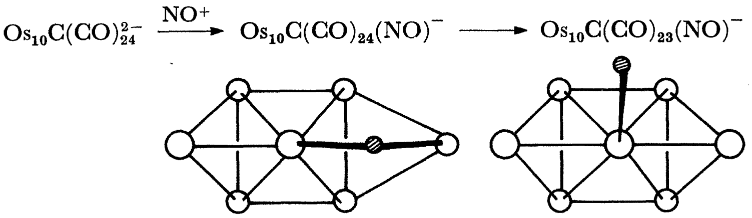


FIGURE 30. Products of the reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with I_2.



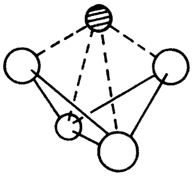
$$Os_{10}C(CO)_{24}^{2-} \xrightarrow{NO^+} Os_{10}C(CO)_{24}(NO)^- \longrightarrow Os_{10}C(CO)_{23}(NO)^-$$

FIGURE 31. Preparation and structure of the nitrosyl cluster compounds $[Os_{10}C(CO)_{24}(NO)]^-$ and $[Os_{10}C(CO)_{23}(NO)]^-$.

$Os_8(CO)_{22}^{2-}$ and $HOs_8(CO)_{22}^-$ reflect this problem (figure 26). It is possible that the steric bulk of the ligands is important; the inclusion of additional ligands (e.g. H) clearly affects the overall symmetry of the species. Thus the addition of H^+ to the outer ligand sheath of $Os_{10}C(CO)_{24}^{2-}$

(figure 27) would clearly have a marked effect on ligand distribution. In fact an interstitial compound is produced, with the H-ligand occupying a tetrahedral site.

Work now in progress has established that growth along one path or the other may be achieved by the choice of the appropriate bridging or capping atoms. Two examples are shown in figures 28 and 29. These compounds were prepared by the reaction of the appropriate electrophile (e.g. $AuPPh_3^+$) with $Os_{10}C(CO)_{24}^{2-}$. An extensive array of such compounds have now been prepared.



32

$$HRu_3(CO)_{11}^- \xrightarrow{NO^+} HRu_3(CO)_{10}(NO) \xrightarrow{\Delta} H_nRu_4(CO)_{12}N \quad (n = 1,\ 2 \text{ or } 3)$$

$$H_3Os_4(CO)_{12}^- \xrightarrow{NO^+} H_3Os_4(CO)_{12}(NO) \xrightarrow{\Delta} HOs_4(CO)_{12}N$$

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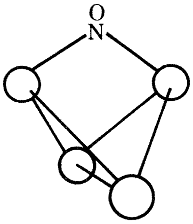

FIGURE 32. Preparation of nitrosyl and nitrido cluster compounds of Ru and Os.

FIGURE 33. The $Os_4(NO)$ arrangement in $H_3Os_4(CO)_{12}NO$.

$$\begin{tikzcd}
H_4Os_4(CO)_{12} \arrow[r] & {[H_3Os_4(CO)_{12}]^-} \arrow[r, "NO^+", "MeCN"'] \arrow[d, "NO^+"', "CH_2Cl_2"] & {[H_3Os_4(CO)_{12}(MeCN)_2]^+} \arrow[d, shift left] \\
 & H_3Os_4(CO)_{12}NO \arrow[d, "\Delta"', "-H_2O"] & H_2Os_4(CO)_{12}(MeCN)_2 \arrow[u, shift left] \arrow[d, shift left] \\
 & HOs_4(CO)_{12}N & {[HOs_4(CO)_{12}(MeCN)_2]^-} \arrow[u, shift left]
\end{tikzcd}$$

FIGURE 34. Reactions of the anionic cluster $[H_3Os_4(CO)_{12}]^-$ with NO^+ to produce either $H_3Os_4(CO)_{12}NO$ or $[H_3Os_4(CO)_{12}(MeCN)_2]^+$.

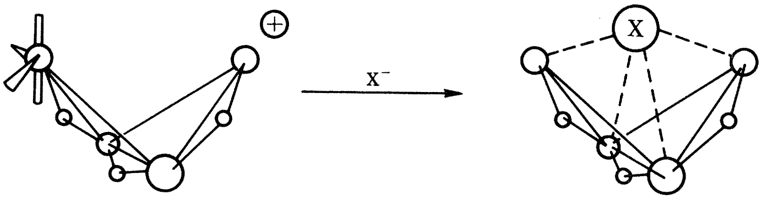

FIGURE 35. Reaction of the cationic cluster $[H_3Os_4(CO)_{12}(MeCN)_2]^+$ with X^- (e.g. Cl^-).

The site of electrophilic attack in cluster species has not been explored in any detail. We have examined some reactions of H^+, I^+, NO^+ and anionic metallic reactants (see above). The reaction of $Os_{10}C(CO)_{24}^{2-}$ with H^+ was discussed earlier, with I^+ the sequence of reactions shown in figure 30 was established (Farrar *et al.* 1981*a*). Very recently we have observed that the same dianion reacts with NO^+ to produce first $Os_{10}C(CO)_{24}(\mu_2\text{-}NO)^-$ and then $Os_{10}C(CO)_{23}(\mu_1\text{-}NO)^-$ (see figure 31). Because the attack of NO^+ directly at a metal atom might be expected to bring about CO loss directly and produce a terminally bound NO species, it is tempting to speculate that attack occurs directly on an Os–Os bond. Other examples of NO^+ addition include the reaction with $H_3Os_4(CO)_{12}^-$ to form either $H_3Os_4(CO)_{12}NO$ (figures 32 and 33) or $[H_3Os_4(CO)_{12}(MeCN)_2]^+$ (figure 34). The former contains a butterfly of four Os atoms with a multibridging NO ligand, and the latter an unsupported butterfly of four osmium atoms. As expected the latter is extremely reactive, combining with a wide variety of reagents X^- to produce capped butterfly compounds (figure 35).

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Discussion

D. M. P. MINGOS (*Inorganic Chemistry Laboratory, University of Oxford, U.K.*). I was most interested to note in Dr Johnson's talk his recent synthesis and structural characterization of an example of a planar 'raft' cluster based on six metal atoms, because independently we have made a theoretical study of the electronic requirements for the stabilization of such cluster compounds. The development of a bonding model for such capped clusters represents an extension of the 'capping principle' that we developed several years ago to account for the skeletal electron requirements for capped polyhedra (Mingos 1972; Forsyth & Mingos 1977). The $Os(CO)_4^{2+}$ fragment of C_{2v} symmetry is isolobal with CH_2^{2+} and therefore its bonding capabilities are set by a pair of outpointing hybrid orbitals of a_1 and b_2 symmetry, which are ideally located to enable this fragment to form bonds to a pair of metal atoms and thereby generate a triangular bridge. Therefore from the triangular cluster it is possible to generate the series of bridged

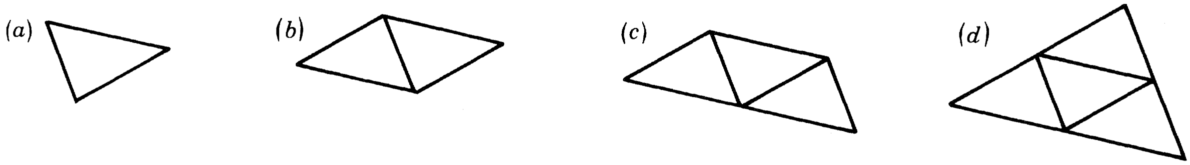

FIGURE D1. Bridged species: (*a*) 48 valence electrons ($Os_3(CO)_{12}$); (*b*) 62 valence electrons ($Re_4(CO)_{16}^{2-}$); (*c*) 76 valence electrons; (*d*) 90 or 92 valence electrons ($Os_6(CO)_{17}(PR_3)_4$).

species shown in figure D1. The last member in the series has been described as a 'raft cluster' by Dr Johnson. According to the capping principle, the formation of such bridges does not affect the number of bonding molecular orbitals of the parent cluster unless the orbitals of the capping atoms introduce a linear combination of orbitals whose symmetry is not matched by those of the bonding skeletal molecular orbitals of the parent. Since the parent triangular cluster is characterized by a total of 48 valence electrons, it follows that the clusters above will be characterized by a total of $48+14m$ valence electrons, where m is the number of bridging $Os(CO)_4$ fragments. The 14 valence electrons per $Os(CO)_4$ fragment are just sufficient to occupy the four Os–CO bonding molecular orbitals and the three non-bonding orbitals of the $Os(CO)_4$ fragment. $Os_3(CO)_{12}$ (48 valence electrons), $Re_4(CO)_{16}^{2+}$ (62 valence electrons) and $Os_6(CO)_{17}(P(OMe)_3)_4$ (90 valence electrons: the compound reported by Dr Johnson) provide examples of (*a*), (*b*) and (*d*) above. This principle can also be applied to open triangular clusters and for example account for the electron count in 'bow-tie clusters'.

It might also be of interest to add that the calculations that we have completed on the raft clusters suggest the presence of a low-lying molecular orbital of a_2' symmetry, which suggests the occurrence of 92-electron clusters in addition to the 90-electron clusters reported. Furthermore, this orbital is antibonding with respect to the metal atoms in the inner triangle and bonding between these metal atoms and the bridging metal atoms, a prediction that could be confirmed by structural studies on related 90-electron and 92-electron clusters.

A detailed account of this work will be presented in a publication by D. G. Evans and myself.

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