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Invited review

Reflections on osmium and ruthenium carbonyl compounds

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Abstract

The development of transition metal cluster chemistry is traced from the early discoveries of metal–metal bonded systems through to some recent developments made in the area of high nuclearity osmium and ruthenium cluster carbonyls. Emphasis is placed on developments made in the physical techniques used to establish the structures of the cluster complexes in the solid state and in solution. Recent developments in synthetic methods which lead to "rational" cluster synthesis are described, and the electron counting rules used to rationalise the observed structures of carbonyl clusters are reviewed. New high nuclearity cluster structures are described, and emphasis is placed on the ability of these systems to undergo reversible redox chemistry without the metal frameworks rearranging. This contrasts the situation observed for low nuclearity clusters, and illustrates the potential of the higher nuclearity clusters to act as electron sinks.

Keywords: Osmium; Ruthenium; Carbonyl; Cluster

This papers is dedicated to Joseph Chatt, who made a major contribution to our knowledge and understanding of organometallic compounds of the transition elements. He commenced his studies in this area immediately after the 1939–45 War, when much of the scientific development that arose from research during the wartime period was just beginning to impact on the chemical community. In particular, the increase in the range and versatility of instrumentation led to the investigation of new areas of chemistry that were not possible previously. This led to the burgeoning of inorganic chemistry as a significant discipline. Prior to this the main emphasis in chemistry had been in the areas of organic and physical chemistry and in some Departments of Chemistry in British universities there was no one even qualified to teach inorganic chemistry.

Chatt was one of the small group of workers who established inorganic chemistry as a major discipline within the subject. The following discussion is an attempt to illustrate some of the significant changes within chemistry by outlining the developments that occurred in the area of metal carbonyl compounds, with particular reference to the problems associated with the polynuclear carbonyl of osmium and ruthenium.

It is interesting to reflect that prior to 1955, the knowledge of metal carbonyl compounds was primarily restricted to simple mononuclear species or to polynuclear compounds of relatively low molecularity. In particular, the stability of compounds containing metal–metal bonds was considered to be low. Thus, Sidgewick and Bailey [1], in discussing the structures of the compounds $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$, considered conformations that did not involve the presence of metal–metal bonds, and maintained the inert gas configuration for the metal centres by donation of extra electrons from the carbonyl oxygen atoms in an isocarbonyl bonding mode (see Fig. 1). The stability of transition metal compounds that contained metal–metal bonding was considered to be low by analogy with the behaviour of the heavier p-block elements where the stability of element–element bond in a group decreases with increasing atomic number. It was therefore assumed that there would be a similar decrease in stability of metal–metal bonds on descending a triad of the transition

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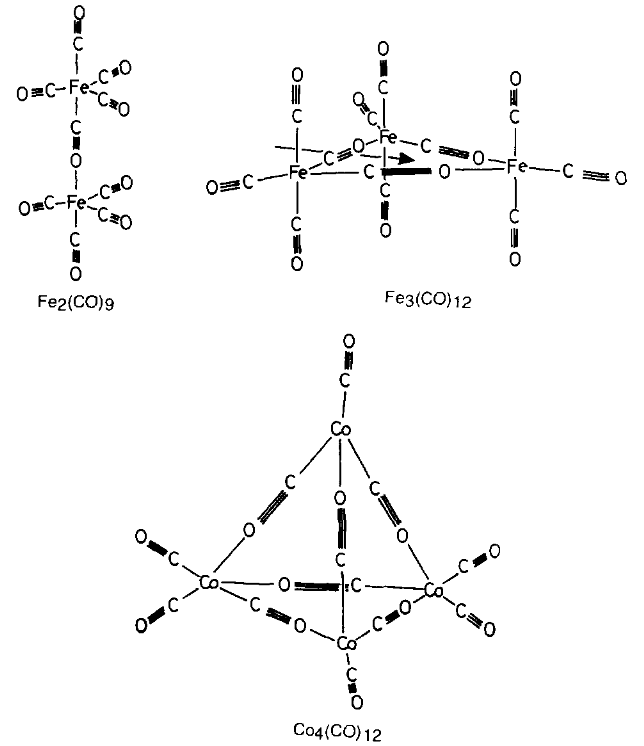


Fig. 1. Proposed structure of metal carbonyls without metal–metal bonds.

elements and hence that compounds containing such bonds would not be stable, particularly for the heavier elements.

In marked contrast to this, it was found that for the transition elements the stability of metal–metal bonding increased on descending the Periodic Table. Table 1 gives the thermochemical data for the energies of the metal–metal bond in a series of carbonyl derivatives.

The difference between the transition elements and the non-transition elements is even more graphically illustrated in a comparison of the s block for the non-transition and transition elements. The bond energies of the diatomic molecules are given in Table 2. If the bonding is restricted to the overlap of s orbitals, then both potassium and copper dimers involve the overlap of the $4s^1$ orbitals. From the data it is clear that there is a significant increase in the bond energy for copper relative to potassium. This also applies to the corresponding $5s^1$ and $6s^1$ pairs. In addition, there is a decrease in the bond energies of the diatomic molecules on descending the group for the s-block elements, as observed for the p-block elements. In contrast, for the transition elements there is an increase in the bond energies with an increase in atomic number, and in the case of gold the bond energy of the diatomic molecule exceeds the values for all the halogens except chlorine.

Table 1
Bond energies of metal–metal bonds in metal carbonyls (kJ mol^{-1})

Metal	Bond energy	Metal	Bond energy	Metal	Bond energy
Mn	67	Fe	80	Co	92
Tc	–	Ru	117	Rh	112
Re	128	Os	130	Ir	130

Table 2
Bond energies of diatomic molecules (kJ mol^{-1})

Metal	M_2	M_2^+	Metal	M_2	M_2^+
Li_2	101	140			
Na_2	69	93			
K_2	50	82	Cu_2	196	221
Rb_2	47	69	Ag_2	160	
Cs_2	38	59	Au_2	220	

It is also interesting that for these molecules there is an increase in the bond energy on removal of an electron to give the cation $[M_2]^+$. For the s-block elements this has been associated with the decrease in inner core repulsion on forming the cation [2]. In the case of the transition elements, the only datum available is for the copper dimer. The bond energy was also found to increase on formation of the cationic dimer; in this case there is the possibility of a contribution from the higher 4p orbitals to the bonding as the energy separation from the 4s orbital will decrease on formation of the cationic species. It is therefore possible from these data to assume that the formation of high-nuclearity clusters may occur for the transition elements and involve bonding with the copper, silver and gold triad. In the case of this group of elements, there may be significant variation in the bonding behaviour depending on the availability of the p orbitals, which may reflect changes in the charge on these metal centres.

Two of the problems that were encountered in the early studies of metal carbonyl compounds were in the analysis of the compounds and the determination of the molecular mass. Shortly after his isolation of the first metal carbonyl compound, $Ni(CO)_4$, Mond and extended his studies to give the corresponding iron carbonyl, $Fe(CO)_5$. This was found to produce, on standing, another carbonyl that was initially formulated as $Fe_2(CO)_7$. This was later correctly analysed by Jones and Dewar [3] as $Fe_2(CO)_9$. Similarly, a number of the carbonyls of both ruthenium and rhodium were initially incorrectly formulated on the basis of their analysis. The molecularity of some of the early isolated polynuclear carbonyls were also incorrectly assigned on the basis of the molecular mass data. This was due to the low solubility of the compounds in the normal organic solvents used for molecular mass determination. Thus, Dewar and Jones [4] showed that an oxidation product of iron carbonyl was a complex $[Fe(CO)_4]_n$. The molecular mass data however, gave values of n in the region of 20 rather than the correct figure of 3, owing to the low solubility of the compound in the common solvents used for molecular mass determination.

The power of X-ray crystallography was of major importance in establishing the molecularity and correct formulation of a number of these derivatives. Thus, the compounds of rhodium isolated by Hieber, and formulated as $[Rh(CO)_3]_n$ and $[Rh_4(CO)_{11}]$, were shown by Dahl and co-workers [5] to be $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$, respectively, by determination of their X-ray structures. Mason and Rae [6] also established, by X-ray crystallography, that the ruthenium carbonyl originally isolated by Mond was $[Ru_3(CO)_{12}]$.

The recent developments in the area of higher nuclearity clusters have been very much dependent on the new separation methods available, such as thin-layer chromatography, the more rapid determination of X-ray structure and the advent of modern technical development in mass spectrometry. Problems that would have been difficult if not impossible to solve only a couple of decades ago are now often soluble in a matter of days. Thus, even in 1950, X-ray structures took months if not years to solve. The same structures, with modern instrumentation and computing facilities, can often be determined within a few days. Mixtures of compounds that were produced in reactions that might have taken days to separate by classical methods can now be separated in minutes using chromatographic techniques. Molecular mass measurements that often required large quantities of compound, and encountered particular difficulty in the case of ionic species, can now be rapidly carried out with very small quantities of compound by modern mass spectrometric methods. This has reduced the time-scale for the determination of the composition and structure of low molecularity compounds, say below a nuclearity of eight, to a matter of days, if the appropriate instrumentation is available.

Another important development in instrumentation was in the area of vibrational spectroscopy. The early studies in carbonyl chemistry utilized infrared spectroscopic data very heavily as this was one of the first forms of spectroscopy to become available and was easily applied to this range of compounds. The clear region of the spectrum in which the carbonyl infrared absorption occurred led to the rapid application of this approach to the analysis of both structure via symmetry arguments and electronic changes within molecules due to variation in the carbonyl stretching frequencies observed. This approach was further enhanced with the advent of Fourier transform infrared instrumentation and the use of laser sources in Raman spectroscopy. These developments have allowed a more rapid assimilation of spectroscopic data. In particular, the introduction of laser sources has revolutionized the use of Raman spectroscopy, and the high polarizability of metal–metal bonds makes the technique particularly suited to the study of cluster complexes and compounds containing metal–metal multiple bonds.

Perhaps the other most important development has been in the application of NMR spectroscopy, particularly that utilizing the higher magnetic fields now available and the multinuclear capabilities. This has allowed for detailed studies to be made not only in the area of structural identification but also in many aspects of the kinetics of these carbonyl systems. Many of the compounds show a high degree of fluxionality, and the mobility of ligand groups over the metal cluster core has been established in solution. There is evidence from solid-state NMR experiments that fluxionality can also occur in the solid.

However, the range of compounds that can now be studied is again becoming limited by the type of instrumentation that is available. Thus, for the metal carbonyl clusters the limit appears to be reached in the range of 30 metal atoms for crystallography, whereas mass spectrometric methods can establish molecular masses into the hundreds of metal atoms. We are therefore now in the position of needing to develop new approaches to determine the detailed structure of this class of compounds. Methods such as electron microscopy have recently been employed in an attempt to solve this problem, and this technique has been applied to molecules of high nuclearity, in the range 100–500 metal units, with some success [7]. With the ease of recognition and identification of metal clusters using the above techniques, the preparation of many of the carbonyl cluster compounds was found to be relatively simple, although the controlled synthesis is still one of the major synthetic problems in this field. Initially the two major approaches employed were the redox condensation reactions used to prepare a range of carbonyl clusters of rhodium [8] and thermal pyrolysis methods employed for the preparation of carbonyl clusters of osmium and ruthenium [9]. Both of these methods have been employed to give a wide range of compounds. Although the nature of the product could not be predicted, they did lead to a range of complexes that allowed the basic method of handling and investigating of this class of compound to be established.

$$Rh_4(CO)_{12} + [Rh(CO)_4]^- \rightarrow [Rh_x(CO)_y]^{n-}$$

$$Os_3(CO)_{12} \rightarrow Os_5(CO)_{16} + Os_6(CO)_{18} + Os_7(CO)_{21} + Os_8(CO)_{23}$$

In the case of the osmium carbonyl preparation, the conversion into the higher nuclearity clusters was very high (90% or greater), but the product distribution was critically dependent on the temperature of the thermolysis. In the reaction the formation of metal–metal bonds in the production of the higher cluster units is at the expense of metal carbonyl bonds. The reactions proceed with the evolution of carbon monoxide, and entropy terms will therefore play an important role in these reactions. The formation of the metal clusters will be favoured by increase in temperature.

Recently, more controlled methods of synthesis have been developed. Two such methods involve the use acetonitrile derivatives of the carbonyl clusters and cation–anion condensation reactions. It was found possible to incorporate acetonitrile into the carbonyl clusters of both osmium and ruthenium by oxidation of the metal carbonyl group with amine oxide in the presence of acetonitrile as a solvent [10]. The resulting substituted compounds were stable, but in contrast to the metal carbonyl group the acetonitrile group could be readily replaced under mild conditions. A variety of nucleophiles such as phosphines, arsines and unsaturated organic molecules including alkenes and alkynes give substituted derivatives in high yield. This group of compounds have been of considerable use as synthetic intermediates for the production of a wide range of products that can be synthesized in high yields. Thus the use of metal nucleophiles to displace the acetonitrile ligands may be used to produce either mixed metal species or to increase the nuclearity of the metal cluster unit if the anion is derived from the same metal.

$$\text{M–CO} + \text{R}_3\text{NO} \xrightarrow{\text{CH}_3\text{CN}} \text{M–(CH}_3\text{CN)} + \text{CO}_2 + \text{R}_3\text{N}$$

$$\text{Os}_x(\text{CO})_y(\text{CH}_3\text{CN}) + [\text{Os}(\text{CO})_4]^{2-} \rightarrow [\text{Os}_{x+1}(\text{CO})_z]^{2-}$$

$$\text{Os}_x(\text{CO})_y(\text{CH}_3\text{CN}) + [\text{M}(\text{CO})_n]^{m-} \rightarrow [\text{Os}_x\text{M}(\text{CO})_p]^{m-}$$

$\text{M} = \text{Fe, Ru, Co}$

The alternative approach that has proved very successful is the use of ionic condensation reactions. The reaction of a neutral carbonyl cluster with reducing agents such as Na–Hg, K–Ph$_2$CO or BH$_4^-$ gives the corresponding carbonyl anions in high yield [11].

$$\begin{array}{cccc} \text{Os}_5(\text{CO})_{16} & \text{Os}_6(\text{CO})_{18} & \text{Os}_7(\text{CO})_{21} & \text{Os}_8(\text{CO})_{23} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \text{Os}_5(\text{CO})_{15}^{2-} & \text{Os}_6(\text{CO})_{17}^{2-} & \text{Os}_7(\text{CO})_{20}^{2-} & \text{Os}_8(\text{CO})_{22}^{2-} \end{array}$$

These anions may the be treated with a variety of cationic species to produce substituted derivatives in good yields. This has been found to be a very good method for the incorporation of the copper, silver and gold derivatives into cluster units by using cationic species such as [Cu(CH$_3$CN)$_4$]$^{2+}$ or Ph$_3$PAuCl–Tl$^+$ [12] and for arene or cyclopentadiene derivatives of the osmium or the ruthenium groups via the cations [(arene)M(CH$_3$CN)$_3$]$^{2+}$ and [(Cp)M(CH$_3$CN)$_3$]$^+$ (M = Os,Ru) [13].

$$\text{Os}_7(\text{CO})_{20}^{2-} + \text{Et}_3\text{PAuCl} \rightarrow [\text{Et}_3\text{PAu}]_2\text{Os}_7(\text{CO})_{20}$$

$$\text{Os}_5(\text{CO})_{15}^{2-} + [(\text{arene})\text{Os}(\text{CH}_3\text{CN})_3]^{2+} \rightarrow (\text{arene})\text{Os}_6(\text{CO})_{15}$$

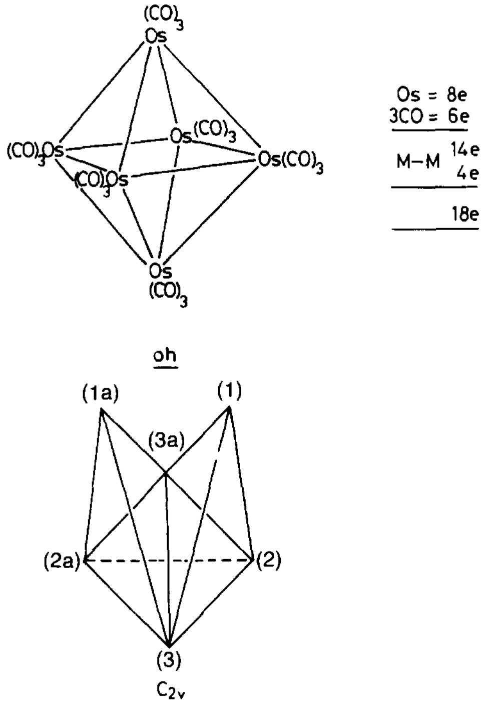


Fig. 2. Top, octahedral structure for Os$_6$(CO)$_{18}$ (O$_h$); bottom, C_{2v} structure for Os$_6$(CO)$_{18}$.

One particular aspect of the chemistry of these derivatives that was of obvious interest was the structure of these carbonyl clusters, particularly for nuclearities greater than four. One of the first structural determinations made was that for the compound Os$_6$(CO)$_{18}$ [14]. In terms of the currently held views on the bonding in metal carbonyl derivatives, the major structural requirement was that each metal attains the electronic configuration that of the next inert gas. This involves the filling of the 5d, s and 3p orbitals in the valence band, the nine orbitals, each containing two electrons, leading to the so called 18-electron rule. For Os$_6$(CO)$_{18}$ this may be simply fulfilled by a structure of the type shown in Fig. 2 (top) involving an octahedron of osmium atoms. At each metal centre the 18 electrons may be attained by donation of six electrons from the three carbonyl groups and the formation of four metal bonds.

The actual structure of the complex is shown in Fig. 2 (bottom) and involves an octahedron of osmium atoms having only C_{2v} symmetry. This may be viewed as a central tetrahedron of osmium atoms, two faces of which are capped by further osmium atoms. The structure has three carbonyl groups associated with each metal and there are three different environments for the osmium atoms. Os(1) and Os(1a) are bonding to three other osmium atoms, whereas Os(2) and (2a) are bonded to four and Os(3) and (3a) to five. The 18-electron configuration around each metal centre may then be attained from the six electrons for each metal from the three carbonyl groups, the eight electrons associated

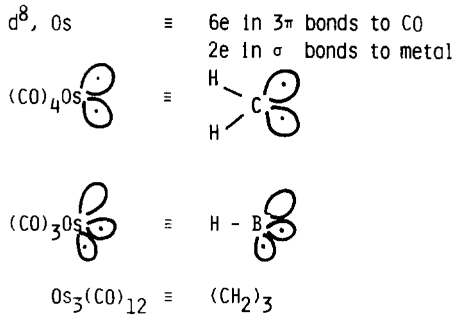


Fig. 3. Frontier orbitals for $Os(CO)_3$ and BH.

with the osmium electron configuration (d^8) and the requirement to obtain four electrons from metal bonding.

For Os(2) centres this may be readily accomplished by the formation of four two-electron bonds to the four osmium atoms to which it is coordinated. For the Os(1) centres, however, there is clearly only the possibility of obtaining three electrons by the equivalent bonding to the three metal atoms coordinating to the atom whilst for the Os(3) an equivalent bonding pattern would lead to an excess of electrons. A suggestion is that the electron in equivalency between the two sites is resolved by the formation of a two-electron donor bond from Os(3) to Os(1). This will lead to a polar bonding pattern for the metal framework that is illustrated in Fig. 5. The molecule is thus a homonuclear species that has a heteropolar metal framework. This will clearly be reflected in the chemical reactive of this and related compounds. A similar bonding mode has also to be

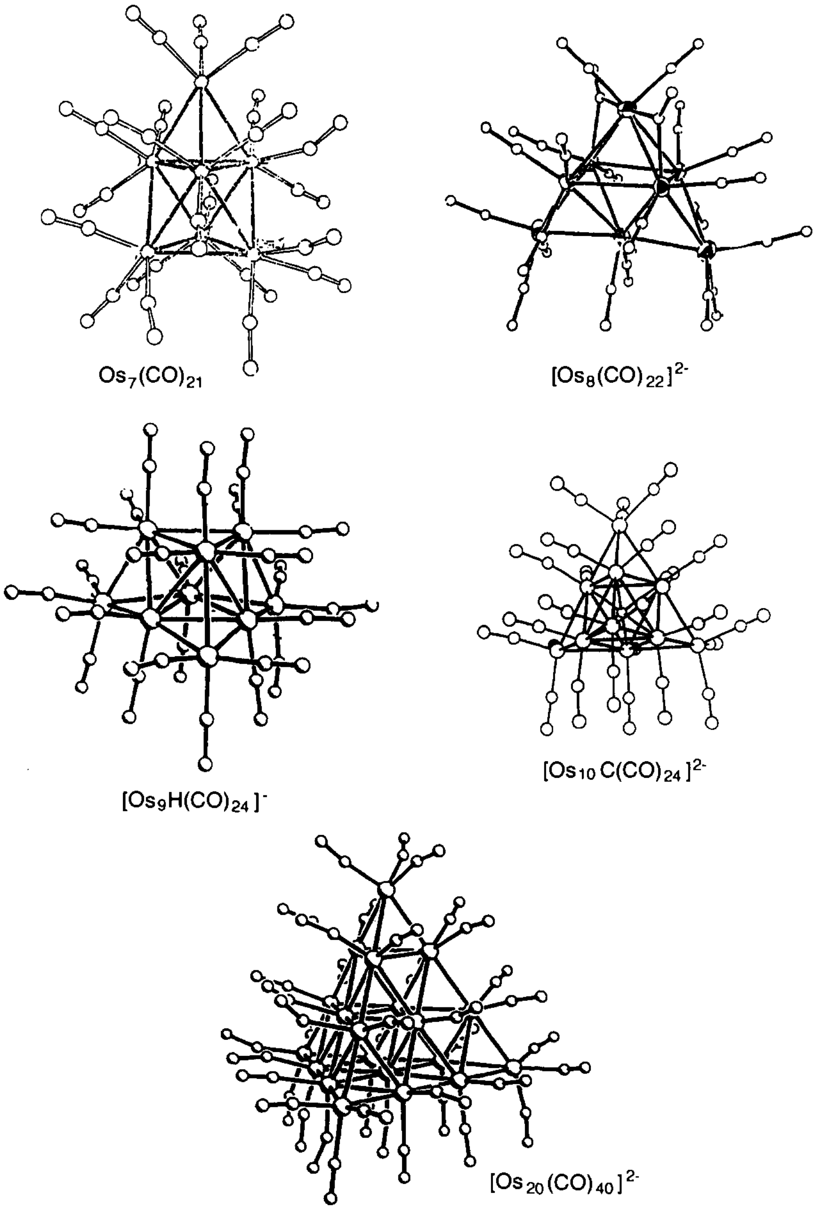


Fig. 4. Capped octahedral osmium clusters.

assumed for all complexes that involve the capping of a triangular face of a metal cluster unit by the $Os(CO)_3$ group.

The rationalization of the structure of $Os_6(CO)_{18}$ and related compounds came from the observation of the equivalence of the outer orbitals of $Os(CO)_3$ and BH by Wade. These are depicted Fig. 3. For the $Os(CO)_3$ group of the 14 electrons in the valency shell, 12 are considered to be associated with the carbonyl groups, with six in the σ-bonding orbitals and six in the π orbitals. This utilizes six of the nine metal bonding orbitals. This leaves two electrons in the remaining three metal orbitals. This orbital pattern has then a close resemblance to the three frontier orbitals associated with the BH group. Wade applied the electron counting system developed for boron hydride systems and was able to predict correctly the structure of $Os_6(CO)_{18}$ and related compounds. It is important to recognize that this orbital distribution assumes a high π-acidity of the carbonyl groups and the dominance of this in determining the structure of these compounds. The replacement of the carbonyl group by less π acidic groups may lead to a different frontier orbital structure and hence the potential breakdown of the Wade approach.

For the boron hydride systems the compounds considered were found to have the same or fewer vertices than the polyhedra predicted by the theory. For the carbonyl compounds of the transition elements it was often found that there was an excess of atoms over the number required to satisfy the polyhedra predicted. Mingos [15] suggested a simple solution to this by noting the compatibility of the empty three orbitals of the $Os(CO)_3^{2+}$ with the orbitals on a triangular face of a polyhedra metals predicted by the Wade approach. This was referred to as a "capping" of the polyhedra by the $Os(CO)_3^{2+}$ group. Thus the structure predicted for $Os_6(CO)_{18}$ was based on a trigonal bipyramid of metals associated with the $[Os_5(CO)_{15}]^{2-}$ and the structure obtained by a capping of one of the triangular faces with the $Os(CO)_3^{2+}$ to give the observed structures. Fig. 4 illustrates the wide range of osmium carbonyl cluster molecules that are observed and may be rationalized in terms of the capping of an octahedron of osmium atoms, the basic unit predicted for all these molecules by the Wade theory.

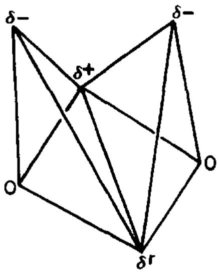


Fig. 5. Bonding in $Os_6(CO)_{18}$.

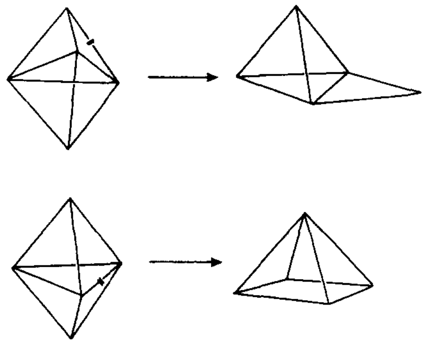


Fig. 6. Alternative structures obtained by clearing different edges in a trigonal bipyramid.

We may consider the chemistry of some of these compounds in terms of this structural approach. One of the most dramatic cases is the behaviour of five coordinated metal systems, as typified by $Os_5(CO)_{16}$ and $[Os_5(CO)_{15}]^{2-}$. The structure for both of these species is based on a trigonal bipyramidal arrangement of metal as predicted by the Wade theory. The detailed bonding involves donor bonding from the equatorial osmium atoms to the "electron-deficient" apical atoms and hence the charge distribution equivalent to that shown in Fig. 5 for $Os_6(CO)_{18}$. Reaction with a nucleophile would then be expected to occur at the electron deficient apical osmium atoms. Indeed, reaction with a variety of nucleophiles has been shown to occur [16] with addition to the apical atoms to give a structure in which one of the metal bonds of the initial trigonal bipyramid has been broken, leading to an edged bridged tetrahedral arrangement as shown in Fig. 6. In the case of the trigonal bipyramid there are two ways in which metal bond breaking can occur, to give either the edge-bridged tetrahedron or the square-based pyramid as indicated in Fig. 6. In terms of the Wade approach, the predicted structure would be the square-based pyramid, whereas the actual structure is the alternative edge-bridged tetrahedron consistent with the electronic properties that may be anticipated from the presence of a metal-donor bond.

On heating, many of these compounds lose carbon monoxide to revert to the trigonal bipyramidal metal arrangement, but the nucleophile then substitutes at the equatorial rather than the apical metal position. This reflects the fact that the π-bonding capacity of the nucleophile is generally lower than that of carbon monoxide and substitution at the equatorial atoms will therefore enhance the electron density at the metal centre by reduction in the π requirement of the ligand grouping. This will then maximize the possibility of donation to the apical atoms via the donor bonding mechanism. For $Os_5(CO)_{16}$ it is possible to extend this metal bond breaking by reaction with carbon monoxide under slight pressure to give as the ultimate product $Os_5(CO)_{19}$ which has a "bow-tie" structure as shown in Fig. 7a and corresponds to the breaking of three of the metal bonds in the initial molecule.

The corresponding reaction also occurs for $Os_6(CO)_{18}$ [17] and in this case the intermediate molecules can be identified. The X-ray structure of the final product $Os_6(CO)_{21}$ has not been obtained but various phos-

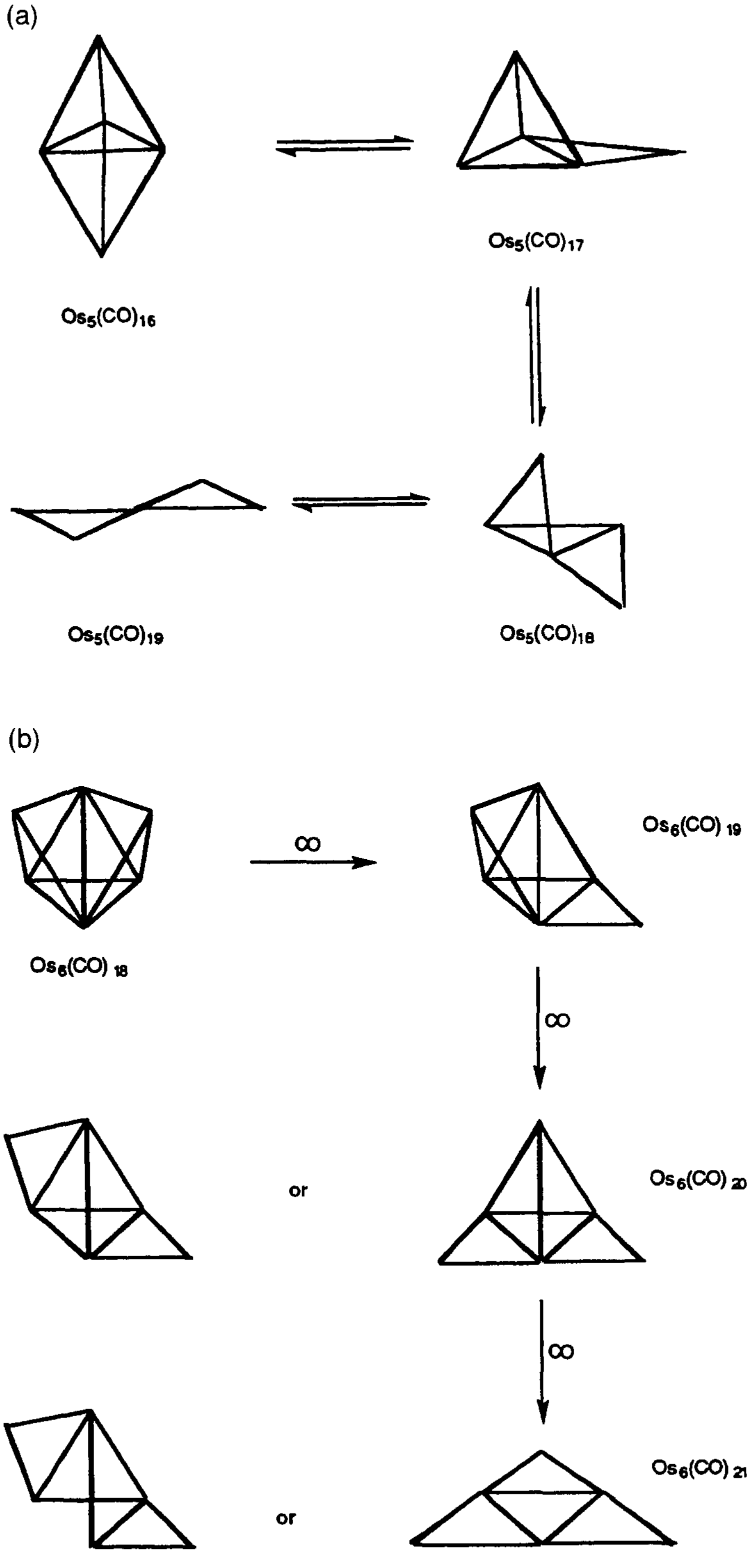


Fig. 7. Sequential breakdown of (a) $Os_5(CO)_{16}$ leading to the formation of $Os_5(CO)_{19}$ and (b) $Os_6(CO)_{18}$ leading to the formation of $Os_6(CO)_{21}$.

phine-substituted derivatives have been reported, and illustrate the planar nature of the array of metal atoms of these structures, (Fig. 7b). This group of molecules once again do not have the structures that might be expected from the application of Wade's rules but may be rationalized in terms of addition to the donor metal bonds within these systems.

$$Os_6(CO)_{18} \rightarrow Os_6(CO)_{19} \rightarrow Os_6(CO)_{20} \rightarrow Os_6(CO)_{21}$$

An interesting series of molecules that have recently been synthesized involve the replacement of carbonyl groups by arene groups. The substitution of carbonyl groups by arene ligands in the five-coordinate osmium atoms in $Os_5(CO)_{16}$ cannot readily be accomplished by direct reaction. However, the compounds can be synthesized starting with a tetranuclear osmium anion such as $[Os_4(CO)_{13}]^{2-}$ and treating this with an arene-substituted osmium cation such as $[(C_6H_6)Os(CH_3CN)_3]^{2+}$ to give the substituted complex $Os_5(CO)_{13}(C_6H_6)$ [18]. By use of the corresponding ruthenium cation, the related mixed osmium–ruthenium complex can be prepared. For the osmium compound only one isomer was obtained, with the arene-substituted metal centre in the equatorial position, consistent with the weaker π acidity of the arene group relative to carbon monoxide. For the mixed osmium–ruthenium reaction, two isomers were isolated, corresponding to replacement at both apical and equatorial sites. The isomer involving substitution at the apical atom, however, was unstable and isomerism to the equatorial compound occurred on standing. This isomerization of the mixed metal compounds implies that the apical–equatorial isomerization occurs via a metal framework rearrangement rather than by movement of the ligand group over the metal polyhedra.

The corresponding Os_6 metal arene compounds can be prepared in a similar way from the arene cations and the related Os_5 anion, $[Os_5(CO)_{15}]^{2-}$. In the case of substitution at $Os_6(CO)_{18}$ there are three potential metal centres to consider, corresponding to three different metal environments shown in Fig. 2. In terms of the electronic effects discussed above, the preference for substitution should be Os(3) > Os(2) > Os(1), whereas in terms of steric interaction the reverse order should apply, namely Os(1) > Os(2) > Os(3), as the metal connectivities of the metal centres are 3, 4 and 5, respectively. Substitution occurs at the Os(2) centre with benzene is used as the arene, but at Os(1) when toluene is used, consistent with the higher steric interaction expected with toluene. Interestingly, with the toulene compound there is a carbonyl group bridging between the Os(1) and Os(2) centres [19]. This may occur because of the lower π acidity of the arene group. It is possible to write a structure for $Os_6(CO)_{18}$ which does not involve the metal donor bonding described above by invoking a similar bridging carbonyl from the Os(3) to the Os(1) centre. However, the presence of a bridging carbonyl group from the Os(3) centre would reduce the number of electrons and orbitals that can be involved in the π bonding between the terminal carbonyl groups and the Os(1) metal centre. If this is considered to be of major importance for the bonding of the carbonyl groups to the metal (and it is essentially the basis for the success of the Wade's rules in accounting for the structure of the carbonyl cluster compounds), then the donor bonding structure would be the preferred bonding mode for $Os_6(CO)_{18}$, whilst the bridging carbonyl is preferred for the toluene-substituted compounds, consistent with the lower π-acidity.

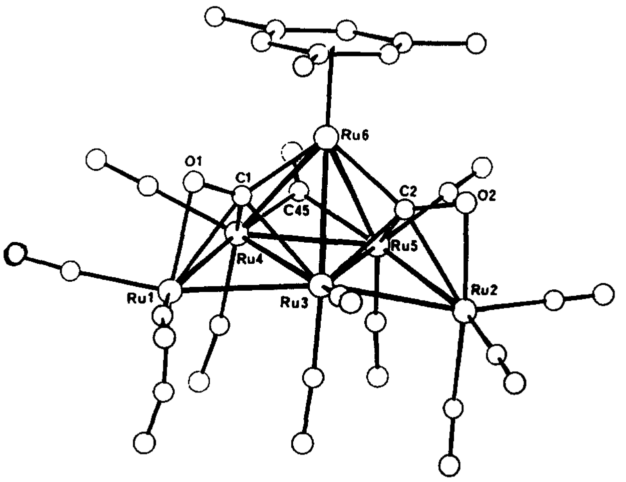
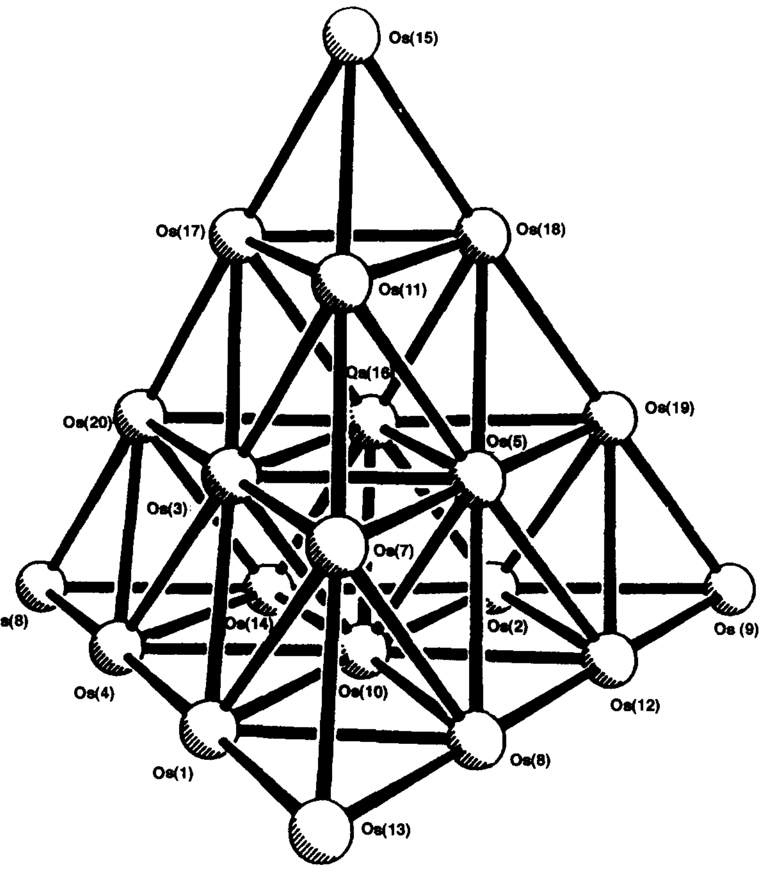


Fig. 8. Structure of $Ru_6(CO)_{15}$(mesitylene).

Recently, a related ruthenium arene derivative has been isolated in the reaction of mesitylene with ruthenium carbonyl [20]. The parent $Ru_6(CO)_{18}$ cluster has never been isolated, but the complex obtained in the above reaction was the arene-substituted complex $Ru_6(CO)_{15}$(mesitylene), the structure of which is shown in Fig. 8. This compound shows a number of very interesting features. The presence of the methyl groups in the arene will increase the donor properties of the ligand whilst increasing the steric problems. From the structure shown in Fig. 8, it is clear that substitution has occurred at the Ru(3) centre, consistent with the high donor nature of the ligand. The steric strain in the system has been been alleviated by the opening of the metal cage by the breaking of two metal–metal donor bonds and the donation of the electron from the oxygen of the three-centre carbonyl groups to the electron-deficient metal centres. This molecule thus illustrates the presence of the rare isocarbonyl bonding mode suggested by Sidgwick. This may be associated, in part, with the high electron density on the oxygen of the carbonyl group due to the three-centre metal bonding of the carbon atom of the carbonyl group. It perhaps significant that this structural form has been observed for a ruthenium compound and may reflect the weaker metal–metal bond-strength of ruthenium relative to osmium.

As stated above, one consequence of the Wade approach to the bonding in this class of compounds is that the addition or removal of electrons from a cluster system should lead to a change in the metal polyhedron. In general, redox behaviour for systems in which there is a change in the stereochemistry at the metal centre leads to irreversible electrochemical behaviour. Thus, cyclic voltammetric studies on the $Os_6(CO)_{18} \rightleftharpoons [Os_6(CO)_{18}]^{2-}$ system shows that the redox properties are irreversible, consistent with the different structures of the two molecules.

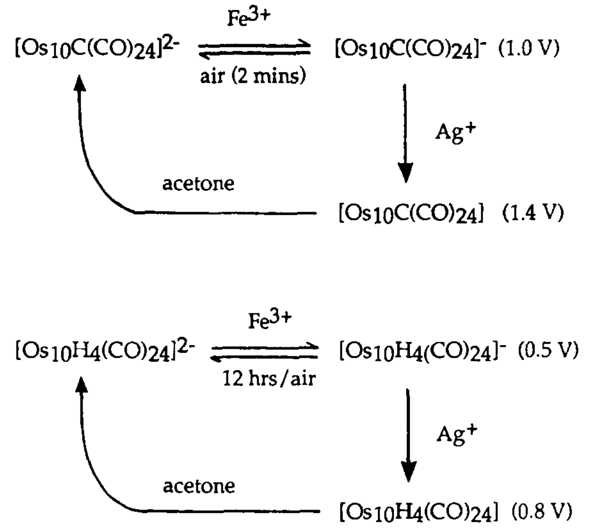
For some of the higher cluster compounds of osmium it has been established that there is reversible redox behaviour. Some data for the ions $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_{10}H_4(CO)_{24}]^{2-}$ are given in Scheme 1; all the reactions were found to reversible. It is obvious that there is ready oxidation and reduction of these two anions, with the hydrogen derivative being more susceptible to oxidation. For higher cluster systems this behaviour is even more pronounced. Thus, for the anion $[Os_{20}(CO)_{40}]^{2-}$ it is possible to a obtain a range of oxidation states corresponding to the species M^{2+} to M^{4-}. Although only the structure of the M^{2-} has been determined the infrared spectra of a series of the ions is given in Table



Cavity type	Number of Cavity	Average Os-Os Distances (Å)
Tetrahedral 1	4	2.785 (5)
Tetrahedral 2	6	2.747 (3)
Tetrahedral 3	1	2.676 (8)
Octahedral	4	2.746 (4)

The metal core geometry of the $[Os_{20}(CO)_{40}]^{2-}$ anion.

Fig. 9. Structure of the $[Os_{20}(CO)_{40}]^{2-}$ dianion.



Scheme 1. Oxidation potentials for Os_{10} dianions (potential relative to $FeCp_2$)

3 and indicates from similarity in the number and intensity of the bands that the symmetry of the various molecules is the same. The variation in the frequencies may be associated with the change in the charge of the molecules. The structure of the ion $[Os_{20}(CO)_{40}]^{2-}$ has been shown to be tetrahedral (Fig. 9) [21]. This is a structure that cannot be accounted for in terms of Wade's rules. There are three metal environments in the molecule corresponding to the four vertices, six edges and four faces of the tetrahedron. The carbonyl distributions between these points are three, two and one, respectively. For the face-centred metals with only one carbonyl group per metal centre, two of the metal d orbitals, lying in the tetrahedral face, will not be able to bond to the carbonyl group but can be involved in bonding between metal centres within the metal framework. Thus the necessity to maintain the 18-electron configuration around the metal centres to satisfy the bonding requirements of the carbonyl group need no longer apply. It is therefore possible for the number of electrons associated with the metal framework to vary; this will probably be reflected in variations within the bond lengths within the metal tetrahedral core, and may be viewed essentially as a "breathing" of the tetrahedral core with variation in the electron occupation. As for the higher nuclearity clusters, the ratio of carbon monoxide to metal decreases with increase in cluster size, as the metal carbonyl bonds are replaced by metal–metal bonds. Thus the dominance of the bonding requirements of the carbonyl groups which controls the electronic structure of the lower cluster compounds will become less evident. The appearance of redox behaviour without major structural changes in the higher cluster units is therefore not surprising.

Table 3
IR spectra of osmium carbonyls

Compound	ν(CO) (cm^{-1})	
$Os_{20}(CO)_{40}$	2068(m)	2031(s)
$[Os_{20}(CO)_{40}]^{-}$	2059(m)	2019(s)
$[Os_{20}(CO)_{40}]^{2-}$	2045(m)	2002(s)
$[Os_{20}(CO)_{40}]^{3-}$	2033(m)	1988(s)
$[Os_{20}(CO)_{40}]^{4-}$	2023(m)	1978(s)

The presence of reversible redox behaviour has also been detected in the planar phosphine-substituted compounds of $Os_6(CO)_{21}$ (see Fig. 7b). These compounds also do not obey Wade's rules. Three of the metals, in the edges of the triangular structure, bond to two carbonyl groups as occurs in some of the higher cluster compounds and the possibility of redox behaviour becomes possible. Mingos [15] carried out a molecular orbital analysis of this system and accounted for the redox behaviour in terms of variation in the occupation of the highest energy occupied molecular orbitals which are essentially metal in character. The variation in the oxidation states were associated with changes in the bond lengths of the metal framework.

It therefore appears that the higher carbonyl cluster compounds will have a much richer oxidation chemistry, and show a more interesting variation in the chemistry, than their lower cluster counter parts. Thus whilst the lower cluster anions readily react with electrophilic reagents such as cationic species, the higher cluster derivatives very often involve redox behaviour as electrophilic reagents are also potential oxidants (and correspondingly nucleophiles potential reducing agents). Thus whilst $[Ph_3PAu]NO_3$ will readily react with a range of anionic osmium polynuclear carbonyls [22], up to $[Os_9(CO)_{24}]^{2-}$, to give the triphenylgold-substituted products, the corresponding reactions with $[Os_{10}H_4(CO)_{24}]^{2-}$ lead to oxidation of the cluster to the neutral species.

It is clear that the development of the chemistry discussed above depends on the application of a wide range of modern instrumental techniques. The position in the carbonyl cluster field is one in which the present approaches are proving to be limited for the higher cluster complexes and clearly new approaches are to be sought. However, the chemistry that has been disclosed by these studies indicates that there is rich potential, and there appears to be a gradual change within these series from the chemistry dominated by that applicable to simple carbonyl systems to that for higher cluster systems that involve a variety of interrelated redox states and a final transition to "metallic" behaviour.

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