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HETEROPOLAR HOMONUCLEAR METAL—METAL BONDING IN CLUSTERS *

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Summary

The presence of donor metal to metal bonds is reviewed for polynuclear complexes of osmium. The general nature and reactivity of these systems is considered and illustrated by the electrophilic character of the complex $Os_6(CO)_{18}$. The potential importance of this in catalytic reactions involving clusters is considered.

The Effective Atomic Number Rule (EAN) has been a very useful means of rationalising the molecular formulae of the simple binary carbonyls and complexes of the later transition elements in low oxidation states. Essentially this rule implies that all the available valency orbitals are filled in these complexes, i.e. 5*d*, 1*s* and 3*p*, and has been rationalised in terms of providing the maximum π-bonding capacity for a given set of ligand groups, or reflecting the overall spherical symmetry resultant from this electronic configuration. In order to accommodate structures which involve more than one metal, it is often necessary to imply direct bonding between the metal centres, and the short intermetallic distances found in X-ray structural determinations normally reflect this potential bonding mode, with an equal electron contribution from each metal centre, as in a covalent bond. However, when structures involving a number of metal atoms are considered, it is often not possible to maintain the EAN rule at each metal centre by utilising this simple covalent metal—metal bonding scheme. This may be viewed as a breakdown of the EAN rule in higher metal clusters. Alternatively, a donor two-electron bond from one metal centre to another may be envisaged as resulting in the maintenance of the EAN rule at each metal centre. This is effectively an extension of the normal bonding pattern exhibited in mononuclear complexes to polynuclear species. This bonding mode was first postulated by Mills and Hock [1] to explain the bonding in the binuc-

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* Dedicated to Joseph Chatt on the occasion of his 65th birthday.

lear complex $Fe_2(CO)_6[C_4Me_2(OH)_2]$ obtained in the reaction of iron carbonyl with but-2-yne. The overall structure is given in Fig. 1. Normal electron counting procedures involve the metal centre Fe(2) with the requisite ten electron count of the EAN rule, whilst for Fe(1), without the involvement of a metal—metal bond a count of eight electrons is derived. Mills suggested a two-electron donation from the Fe(2) to Fe(1) centres, consistent with the relatively short Fe—Fe distance of 2.49 Å in the molecule.

As implied above, the assumption of a two-electron donor bond maintains the use of all the valence *d*, *s* and *p* orbitals on each metal centre, and the concept is consistent with the short metal—metal distances observed in those complexes where bonding of this nature has been postulated. The localisation of the bonding to specific bonds in the case of the higher nuclearity species is not possible. The alternative view of these molecules as electron deficient would correspond to the utilisation of only part of the *d*, *s* and *p* orbital manifold, and generally it is considered that as the *p* orbitals of the metal are less energetically favourable for bonding that only partial occupation of these occurs. For the d^8 configuration, osmium(0), iridium(I), platinum(II), the *sp* separation in the free ion increases rapidly from ~3 to ~12 eV. The potential availability of the *p* orbitals therefore decreases with increasing oxidation state and as observed for mononuclear species, the possibility of stable structure not employing all the *p* orbitals at each metal centre may occur. Conversely it seems therefore that for the lower oxidation states there is a much greater probability of all the orbitals being utilised and the "electron deficient" behaviour observed in these species may be associated with the presence of this donor bonding scheme.

As in mononuclear species this type of bonding should imply a difference in polarity between the metal centres. Thus for the iron complex mentioned above (Fig. 1) the polarity would be $\overset{\delta+}{\mathrm{Fe}}(2) \rightarrow \overset{\delta-}{\mathrm{Fe}}(1)$. This difference in polarity has been suggested as a cause for the semi-bridged carbonyl bonding of the C—O^a to metal Fe(1) by Cotton [2]. Such a polarity difference between metal centres must also reflect a greater potential chemical reactivity within molecules containing this bonding mode. In heteronuclear species where bond polarity exists because of differences in electronegativity between the different metals bound to each other we have observed marked enhancement in chemical reactivity. Thus the two complexes $H_3CoOs_3(CO)_{12}$ [3] and $H_4Os_4(CO)_{12}$ [4] vary considerably in

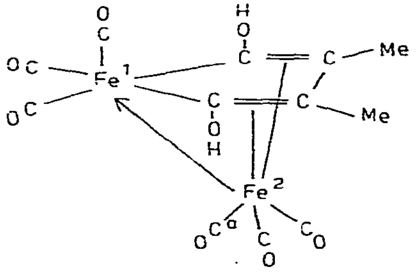


Fig. 1.

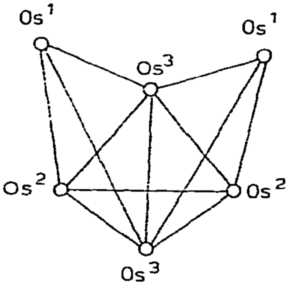


Fig. 2.

reactivity; the cobalt—osmium complex is stable to disproportionation, but in contrast to the homonuclear osmium species the cobalt substituted derivative is rapidly attacked by air. This contrasts with the inert Rh—Co carbonyl species $Rh_xCo_{(4-x)}(CO)_{12}$ [5], which although chemically stable readily disproportionates to the constituent homonuclear species, as would be consistent with the smaller differences in electronegativity between cobalt and rhodium.

The presence of a donor—metal bond has also been recognised in heteronuclear metal systems, e.g. $(PhP)Cp(CO)_2Mn[Fe(CO)_3]_2$ [6]. Not surprisingly this system proves to be very reactive, undergoing ready fission of the Mn—Fe bond with nucleophilic addition to the iron centre with a variety of nucleophiles. Interestingly, these reactions are found to be reversible and are postulated as model compounds for catalytic systems.

We have observed similar chemical reactivity for those polynuclear species of osmium where two-electron donation from one metal centre to another is required to maintain the EAN rule. Thus if we consider the structure of the molecule $Os_6(CO)_{18}$ (Fig. 2) a two-electron donor bond is postulated between the Os(3) and Os(1) centres. For all osmium carbonyl species in which the "capping" of the metal polyhedron occurs by a $M(CO)_3$ group, a bond of this type must be involved to maintain the EAN rule, e.g., $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$. As implied above, the assumption of a two-electron donor bond is consistent with the short metal—metal distances observed in $Os_6(CO)_{18}$ and $Os_7(CO)_{21}$.

The general chemistry of $Os_6(CO)_{18}$ does reflect the presence of this donor bond and the potential electron deficiency of the metal centres. The complex readily reacts with a variety of nucleophiles to lead in addition to substitution normally observed in carbonyl complexes, to addition reactions. For the latter class, the addition of two electrons to the metal cluster unit leads to a change in the geometry of the metal polyhedron. The chemistry of $Os_6(CO)_{18}$ will be used to illustrate the chemistry of systems containing this heteropolar bonding scheme. The chemical reactions may be classified into four basic types, although overlap does occur between the various groups: (a) substitution, (b) cluster fragmentation, (c) cluster reduction, and (d) solvent addition, (b, c and d relate to the electron deficient nature of these complexes).

(a) Carbonyl substitution

Substitution may be achieved in two ways, either by the pyrolysis of $Os_6(CO)_{18}$ in the presence of substrate, as for example in eq. 1 [7] or by the generation of

$$Os_6(CO)_{18} \xrightarrow[CH_2=CH_2]{\Delta} Os_6(CO)_{16}(CCH_3)_2 \qquad (1)$$

a reactive intermediate species (via CO loss by treatment with Me_3NO) followed by direct attack of the substrate, as in eq. 2 [8]. This latter reaction also illustrates the process of orthometallation which often occurs in the reactions of such cluster species with organic substrates.

$$Os_6(CO)_{18} \xrightarrow[\text{(ii) pyridine}]{\text{(i) } Me_3NO} HOs_6(CO)_{16}(C_5H_4N) \qquad (2)$$

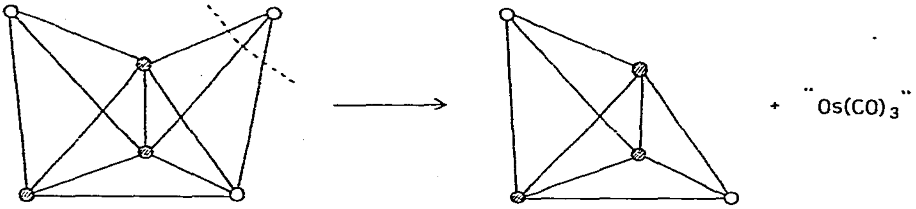
(b) Cluster fragmentation

The action of strong bases on metal carbonyl complexes to yield carboxylate anions via CO loss is well-known and has been applied by Chini et al. [9] to the production of high nuclearity cluster carboxylate anions. However, the treatment of $Os_6(CO)_{18}$ with hydroxide, methoxide or a concentrated solution of cyanide ions leads to cluster fragmentation and the production of $[Os_5(CO)_{15}]^{2-}$ in virtually quantitative yield, as shown in eq. 3. This type of reaction also occurs for the higher clusters $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$, where similar treatment

$$\underset{(S = 6)}{Os_6(CO)_{18}} \xrightarrow[\text{MeoH}]{OH^-} \underset{(S = 6)}{[Os_5(CO)_{15}]^{2-}} + \text{“}Os(CO)_3\text{”} \qquad (3)$$

leads to the anions $[Os_6(CO)_{18}]^{2-}$ and $[Os_7(CO)_{20}]^{2-}$, respectively. These observations have been rationalised [10] in terms of the removal of a "capping" $Os(CO)_3$ group via primary attack at a donor metal—metal bond. The neutral Os_6, Os_7 and Os_8 clusters each have the fundamental polyhedron based on the requisite number of skeletal electron pairs (S) capped by one or more $Os(CO)_3$ groups. The removal of an electron deficient capping group then generates the electron precise anion based on the next lower metal cluster unit. The structural changes involved in reaction 3 are represented in Scheme 1.

SCHEME 1



In contrast to the above clusters, $Os_5(CO)_{16}$ has a structure based on the fundamental polyhedron (a trigonal bipyramid) for $S = 6$ which is an electron precise system. This is reflected in its chemistry since treatment with strong base effects simple CO loss and the production of the equally electron precise anion $[Os_5(CO)_{15}]^{2-}$.

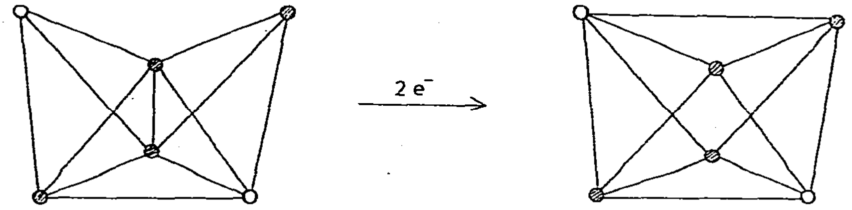
Thus, in the cluster fragmentation process, the primary attack is at the metal—metal bonds of the electron deficient capping group with an extensive opening-out of the cluster framework and ultimate elimination of the capping "$Os(CO)_3$" group.

(c) Cluster reduction

$Os_6(CO)_{18}$ may be reduced heterogeneously by the action of activated zinc ($K/ZnCl_2$) to yield the anion $[Os_6(CO)_{18}]^{2-}$, but in order to avoid separation difficulties, it is much more convenient to effect this reaction in solution by the use of iodide, nitriles, a very dilute solution of cyanide, or pyridine. The addition of the electron pair to the cluster via these donor groups is accompanied by the transformation of the capped trigonal bipyramidal arrangement of $Os_6(CO)_{18}$

($S = 6$) into the regular octahedral arrangement of $[\mathrm{Os_6(CO)_{18}}]^{2-}$ ($S = 7$). This is illustrated in Scheme 2. Both species have the same number of metal—metal bonds and again, for this process to occur, attack at the metal—metal bonds and a general opening out of the cluster is envisaged.

SCHEME 2



The reduction reaction has been studied kinetically for both iodide [11] and propionitrile [12], using dichloromethane as (inert) solvent.

Reduction by iodide follows the rate law shown in eq. 4 and the simplest mechanism proposed (eq. 5 and 6) involves a pre-equilibrium association between the iodide and the cluster followed by rate-determining attack of a second iodide ion. The required rate expression (eq. 7) reduces to the experimentally observed form (eq. 8) at low iodide concentration. Iodine is indeed observed and under such conditions $[\mathrm{Os_6(CO)_{18}}]^{2-}$ may be obtained in yields >90%. No clearly discernible infrared spectrum for a reaction intermediate is noticed.

$$k_{\mathrm{obs}} \propto [\mathrm{I^-}]^2 \qquad (4)$$

$$\mathrm{Os_6(CO)_{18}} + \mathrm{I^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Os_6(CO)_{18}I}]^- \qquad (5)$$

$$[\mathrm{Os_6(CO)_{18}I}]^- + \mathrm{I^-} \xrightarrow[\text{slow}]{k_2} [\mathrm{Os_6(CO)_{18}}]^{2-} + \mathrm{I_2} \qquad (6)$$

$$\text{Rate} = \frac{k_1 k_2 [\mathrm{Os_6(CO)_{18}}][\mathrm{I^-}]^2}{k_{-1} + k_2[\mathrm{I^-}]} \qquad (7)$$

$$k_{\mathrm{obs}} = \frac{k_1}{k_{-1}} k_2 [\mathrm{I^-}]^2 \qquad (8)$$

Similar kinetic studies on the reaction with propionitrile reveal the following rate law (eq. 9). The generalised mechanism (eq. 10—12) leads to the rate expression of eq. 13, by the application of stationary state or pre-equilibrium approaches, in agreement with the experimentally observed form (eq. 9).

$$k_{\mathrm{obs}} \propto [\mathrm{RCN}]^3 \qquad (9)$$

$$\mathrm{Os_6(CO)_{18}} + \mathrm{RCN} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Os_6(CO)_{18}(RCN)} \qquad (10)$$

$$\mathrm{Os_6(CO)_{18}(RCN)} + \mathrm{RCN} \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Os_6(CO)_{18}(RCN)_2} \qquad (11)$$

$$\mathrm{Os_6(CO)_{18}(RCN)_2} + \mathrm{RCN} \xrightarrow[\text{slow}]{k_3} [\mathrm{Os_6(CO)_{18}}]^{2-} + \text{“}(\mathrm{RCN})_3\text{”} \qquad (12)$$

$$\text{Rate} = K_1 K_2 k_3 [\mathrm{Os_6(CO)_{18}}][\mathrm{RCN}]^3 \qquad (13)$$

(d) Solvent addition

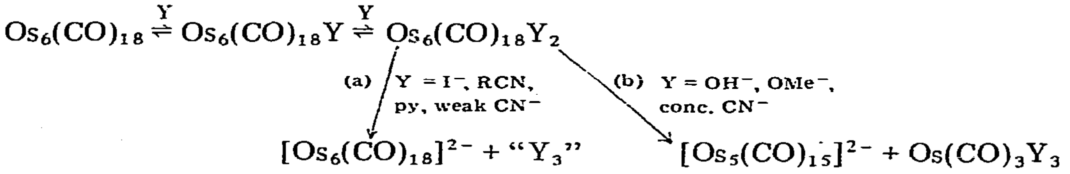
$Os_6(CO)_{18}$ readily dissolves in well-established "inert" solvents such as alkanes, dichloromethane, chloroform and carbon tetrachloride to give stable (ca. days) solutions which exhibit a "normal" infrared spectrum in the carbonyl stretching region, designated a Type A spectrum. Coordinating solvents such as tetrahydrofuran, acetone, ethylacetate, nitromethane and diethyl ether produce a modified spectrum, Type B. The removal of these solvents merely regenerates $Os_6(CO)_{18}$; thus no stable adducts are isolable. In contrast, the dissolution of $Os_6(CO)_{18}$ in acetonitrile or propionitrile leads to the ultimate formation of $[Os_6(CO)_{18}]^{2-}$ within a few hours for acetonitrile and only a matter of minutes for propionitrile at room temperature. Low temperature and mixed solvent experiments demonstrate a sequence of three distinct infrared spectra prior to the formation of $[Os_6(CO)_{18}]^{2-}$, according to eq. 14 in which the first two steps only are reversible. Again, attempts to isolate the intermediate species lead only to the recovery of

$$\text{Type A} \rightleftharpoons \text{Type B} \rightleftharpoons \text{Type C} \rightarrow [Os_6(CO)_{18}]^{2-} \qquad (14)$$

$Os_6(CO)_{18}$. A similar sequence is observed when $Os_6(CO)_{18}$ is dissolved in pyridine, $[Os_6(CO)_{18}]^{2-}$ being the final product of reaction.

From the above studies we propose that both the reduction and fragmentation reactions proceed according to the general Scheme 3.

SCHEME 3



$$Os_6(CO)_{18} \overset{Y}{\rightleftharpoons} Os_6(CO)_{18}Y \overset{Y}{\rightleftharpoons} Os_6(CO)_{18}Y_2$$

$$\text{(a) } Y = I^-, \text{RCN, py, weak } CN^- : \quad Os_6(CO)_{18}Y_2 \rightarrow [Os_6(CO)_{18}]^{2-} + \text{“}Y_3\text{”}$$

$$\text{(b) } Y = OH^-, OMe^-, \text{conc. } CN^- : \quad Os_6(CO)_{18}Y_2 \rightarrow [Os_5(CO)_{15}]^{2-} + Os(CO)_3Y_3$$

The first two stepwise additions of Y in the reduction sequence have been shown to be reversible (Y = RCN, pyridine) while the second- and third-order dependence on [Y] for $Y = I^-$ and Y = RCN, respectively, merely reflect differences in the kinetic parameters.

Using this scheme, cluster fragmentation would proceed with the expulsion of an anionic species of the type $[Os(CO)_3Y_3]^-$, Y = OH, OMe, CN; complexes $[Os(CO)_3X_3]^-$ (X = Cl, Br, I) are well characterised species [13]. As yet, $[Os(CO)_3Y_3]^-$ has not been positively identified as the other product from fragmentation of the cluster.

From the observation that weak CN^- solutions produce $[Os_6(CO)_{18}]^{2-}$ exclusively, while progressively stronger solutions give increasing yields of $[Os_5(CO)_{15}]^{2-}$, routes (a) and (b) are envisaged as competitive steps, rather than alternative pathways, which are under kinetic control.

The role of the intermediate complex $Os_6(CO)_{18}Y_2$ in this scheme would then be vital and the extent of the bond weakening to the capping group, i.e., the extent of cluster opening, would determine the final outcome of reaction. This, in turn, clearly depends on the nature of Y. A simple representation of $Os_6(CO)_{18}Y_2$ is given in Fig. 3. As already suggested, the greater the opening out of the structure, the more likely cluster fragmentation would appear to be. The observations can be rationalised very easily in terms of these ideas, where

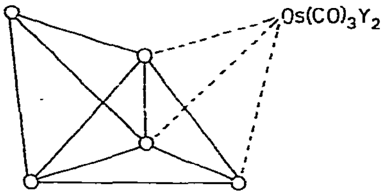


Fig. 3.

strong bases (OH$^-$, OMe$^-$) stretch metal—metal bonds sufficiently to result in cleavage of a fragment, but where less basic substrates (RCN, I$^-$, pyridine) merely weaken metal—metal bonds just enough to allow reorganisation within the structure.

In a complementary way, it is noted that these strong bases are not easily oxidised, whereas iodide, nitriles and pyridine all have much lower oxidation potentials. In the latter cases, the exact nature of such "oxidised" products of nitriles and pyridine is as yet unknown although the formation of I_3^- is predicted. The appearance of iodine in the reduction of $Os_6(CO)_{18}$ by iodide may be explained by reaction 15.

$$I_3^- \rightarrow I_2 + I^- \qquad (15)$$

Conclusions

We believe that the attack of nucleophiles at the donor metal—metal bond and resultant opening-out of cluster geometries during reaction plays a vital role in the determination of the ultimate course of reaction. This has been effectively illustrated for $Os_6(CO)_{18}$, which contains the heteropolar bonding scheme previously described. Further, this molecule is thermally stable but disproportionates upon treatment with a number of substrates. The generality of this approach will no doubt be tested further, but we already have considerable supporting evidence that the chemistry of the molecules $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ also exhibits such heteropolar bonding. It is obvious that this type of interaction must allow the inclusion of donor groups in the coordination sphere of the polynuclear complex, which as with mononuclear complexes, may play a primary role in any catalytic processes involving polynuclear adducts.

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