Journal of Organometallic Chemistry, 160 (1978) 263—274

THE ACTIVATION OF TRANSITION-METAL CARBONYL CLUSTERS

BRIAN F.G. JOHNSON, JACK LEWIS * and DAVID PIPPARD
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received July 20th, 1978)

Summary

Methods by which the reactivity of transition-metal osmium carbonyl clusters may be modified are explored.

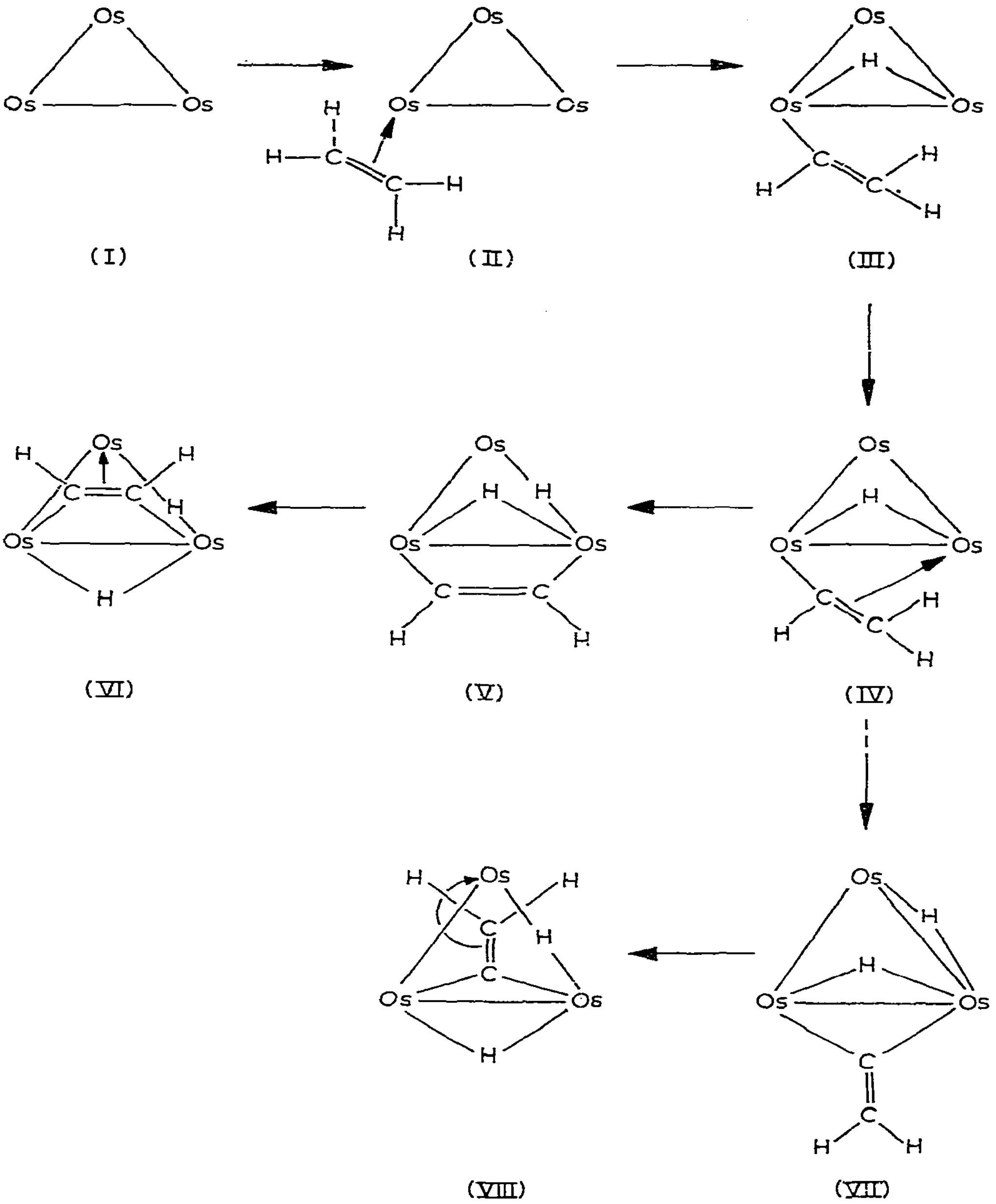
In this paper we consider the methods by which the reactivity of transition-metal carbonyls may be modified. We follow two main themes: (1) the activation of carbonyl clusters by methods which have allowed the isolation of a number of previously inaccessible reaction intermediates, and (2) the modification of the reactivity of cluster systems by the introduction of "blocking" groups or ligands.

1. The activation of carbonyl cluster compounds

A major problem encountered in studies of the series of cluster carbonyls $Os_3(CO)_{12}$, $H_4Os_4(CO)_{12}$, $Os_5(CO)_{16}$ and $Os_6(CO)_{18}$ is the comparatively drastic conditions required to bring about chemical reactivity with substrates such as ethylene. Consider, for example, the reaction of $Os_3(CO)_{12}$ with ethylene outlined in Scheme 1 [1]. The carbonyl undergoes reaction with ethylene to produce the two isomeric complexes VI and VIII of molecular formula $H_2Os_3(CO)_9C_2H_2$. The probable reaction pathway is also outlined in Scheme 1 but none of the proposed intermediates II—V or VII have been isolated from this reaction because of the vigorous conditions necessary to induce it. Similar difficulties have been encountered with the chemistry of $Os_6(CO)_{18}$. Reaction with ethylene produces the hexa-nuclear complexes $Os_6(CO)_{16}(CMe)_2$ and $Os_6(CO)_{16}C(C_2Me_2)$ in small yield [2]. Again intermediates are not observed and the reaction is complicated by the large range of other minor products produced under the forcing conditions employed.

---

* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

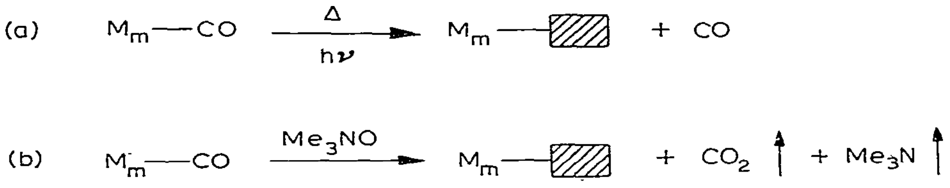


Scheme 1. Reaction of $Os_3(CO)_{12}$ with C_2H_4.

The major problem lies in the reluctance of these systems to undergo ligand-exchange reactions either via a CO dissociation step or a metal—metal bond cleavage associative step. This is emphasised by studies of ^{13}CO exchange. Systems such as $Co_4(CO)_{12}$ readily undergo ^{13}CO exhange under moderate conditions over moderately short periods of time. In contrast, exchange with $Os_3(CO)_{12}$ requires several days at 80° C and under the same conditions exchange with $Os_6(CO)_{18}$ is negligible [3]. There is some debate as to the mechanism of exchange or substitution in these clusters, but there is a growing body of evidence to suggest that both exchange and substitution occur via an associative, Os—Os bond-break mechanism. Reaction with ligands such as ethylene is, therefore, understandably slow under moderate conditions of temperature and pressure. Exchange under more vigorous conditions is known to lead to the stable $H_2Os_3(CO)_9C_2H_2$ derivatives (see Scheme 1). Consequently milder methods of reaction were sought. We may illustrate this by considering the following classes of reaction which create a vacant coordination site about the metal cluster system: (i) CO displacement; (ii) ligand—metal redox systems; (iii) metal—metal bond cleavage.

(i) CO displacement

In Scheme 2 we illustrate two methods by which a coordinatively unsaturated species, such as "$Os_3(CO)_{11}$" may be generated. Method (a), thermal or photolytic ejection of CO is known to be unfavourable (see above); method



Scheme 2. Methods of production of $Os_3(CO)_{11}$ from $Os_3(CO)_{12}$.

(b), the removal of CO as CO_2 by oxidation with Me_3NO is an easily carried out procedure and has led to a convenient source of many, hitherto rather inaccessible, derivatives. Some examples are given in Scheme 3. By this route we have prepared in good yields the mono-substituted ethylene derivatives $Os_3(CO)_{11}$·C_2H_4 [4]. The probable molecular structure of this complex is given in Fig. 1. To our knowledge this is the first example of an ethylene molecule bonded directly to a cluster in the Chatt—Dewar manner. The potential offered by this method is obviously enormous and further work on the $H_4Os_4(CO)_{12}$ and Os_6-$(CO)_{18}$ systems have revealed a rich vein of synthetic cluster chemistry [5].

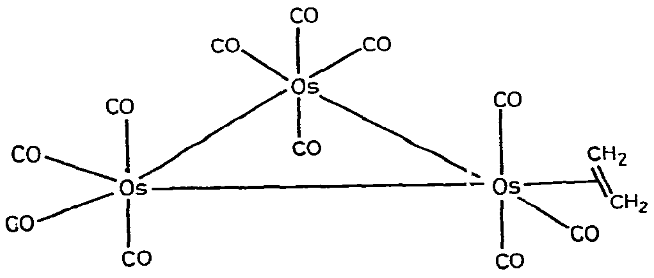
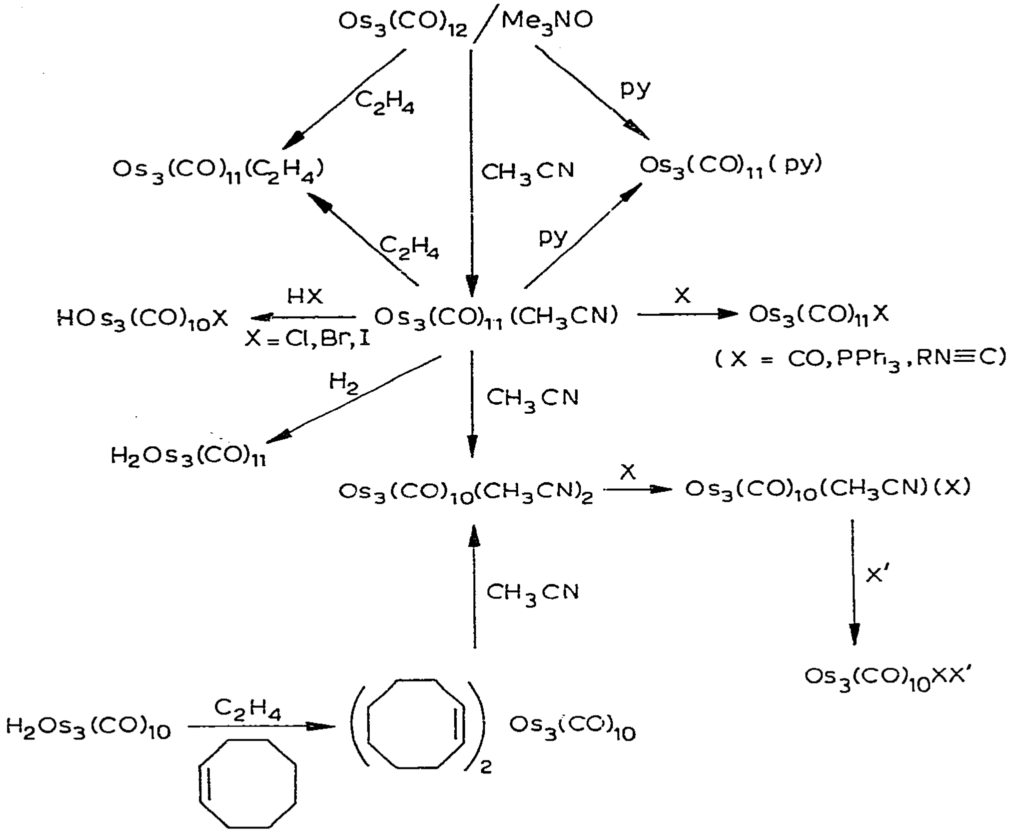


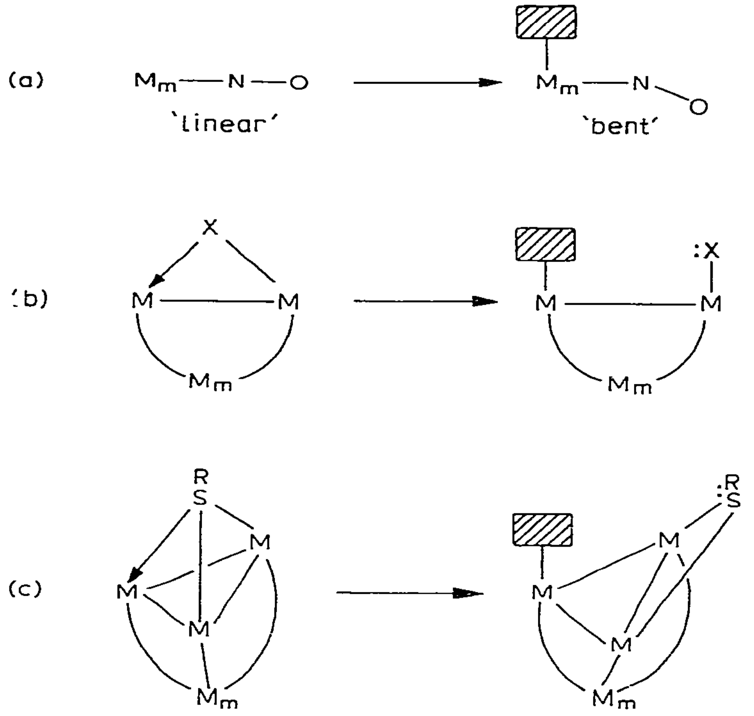
Fig. 1. Probable molecular structure of $Os_3(CO)_{11}C_2H_4$.



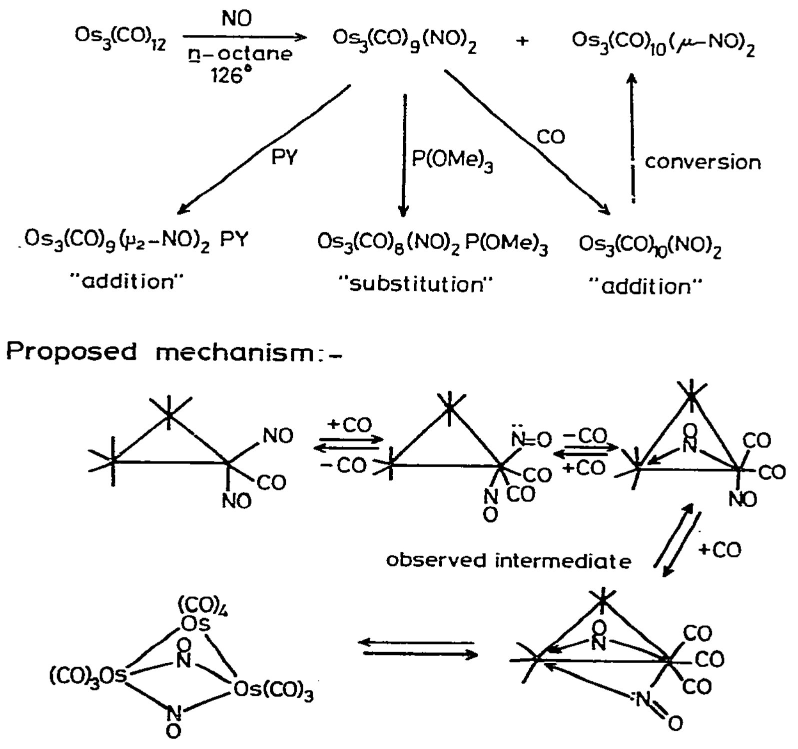
Scheme 3. Reaction of Me_3NO with $Os_3(CO)_{12}$.

(ii) Ligand—metal redox systems

In Scheme 4 is illustrated an alternative approach. We offer three of many possible examples. In method (a) we refer to a mechanism commonly applied to monometal nitrosyl complexes. The nitrosyl ligand may function formally as a three electron donor (NO^+) with a linear bonding mode or as a one electron donor (NO^-) with a bent (~120°) M—N—O arrangement. Conversion of an M^{n+}—N^+—O system to $M^{(n+2)+}$—$N^{(-)}$—O system has two effects. First, it increases the metal oxidation state by two and secondly, it generates a vacant coordination site. We have recently synthesised the new dinitrosyl cluster $Os_3(CO)_{10}(NO)_2$ which has been shown to possess the quasi-$Os_3(CO)_{12}$ molecular structure (Fig. 2) [6]. This complex which is prepared from the direction reaction of nitric oxide with $Os_3(CO)_{12}$ in n-octane at 126°C (Scheme 5) readily undergoes reaction with additional electron-pair donors such as CO, $P(OR)_3$, and pyridine. According to the nature of the ligand employed either simple CO substitution occurs to generate $Os_3(CO)_9(L)(NO)_2$ (L = $P(OMe)_3$) or addition to produce the complex $Os_3(CO)_{10}L(\mu_2\text{-}NO)_2$ (L = py) of the type first observed by Collman and Norton [7]. Possible mechanisms for these reactions are also given in Scheme 5 and are considered to involve $\overset{+}{N}O \rightleftharpoons \overset{-}{N}O$ interconversions about the Os_3 cluster unit.



Scheme 4.



Scheme 5. Preparation and some reactions of $Os_3(CO)_9(NO)_2$.

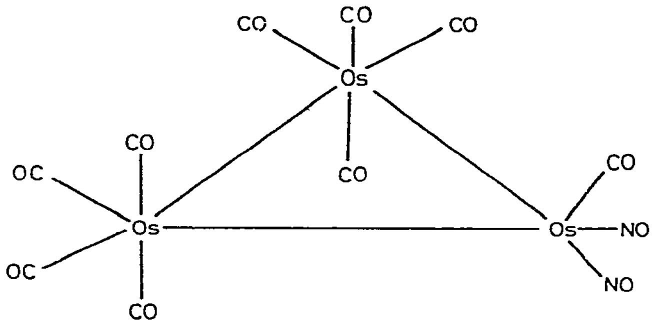
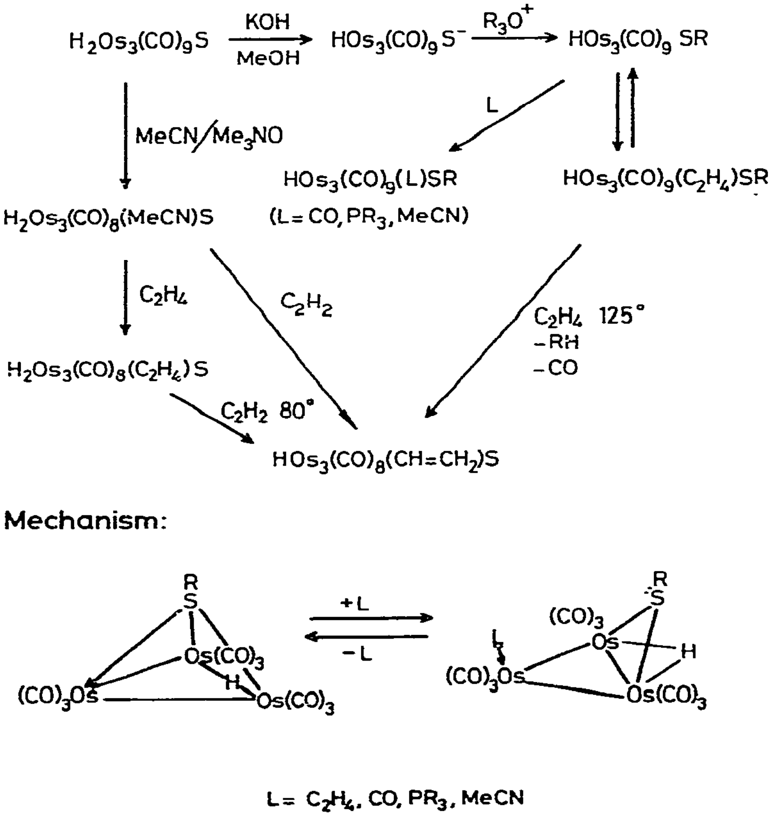


Fig. 2. The probable structure of $Os_3(CO)_9(NO)_2$.

(b) A group X, for instance a halogen, may function as a three-electron donor when present as a bridging group but as a one-electron donor when combined to one metal centre. The simple act of bridge-opening creates a vacant coordination site on one metal atom. We have invoked behaviour of this sort to explain the stereospecific incorporation of ^{13}CO in the complexes of composition $Os_3(CO)_{10}X_2$ [8].



Scheme 6. Preparation and reactivity of $HOs_3(CO)_9SR$ (R = Me or Et).

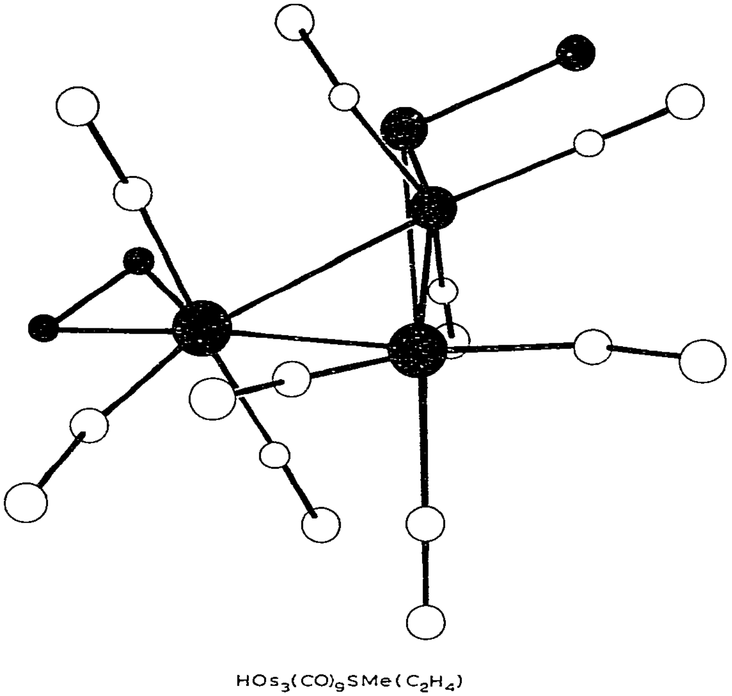


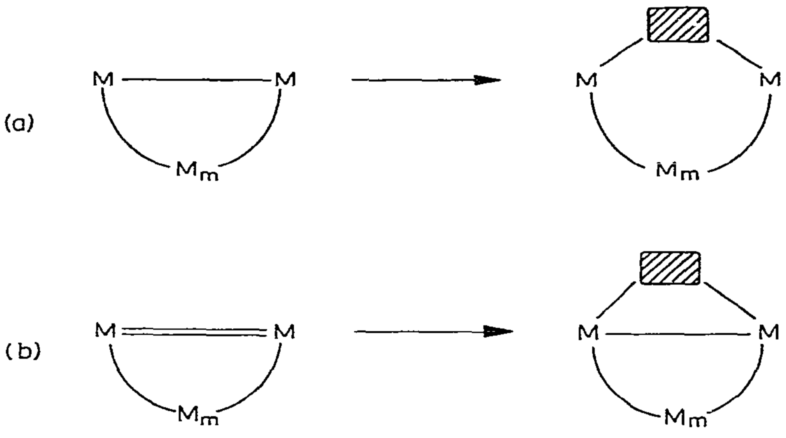
Fig. 3. Probable structure of $HOs_3(CO)_9SMe(C_2H_4)$.

(c) A related precess to (b) may be considered to occur when in place of a ligand spanning two metal atoms as a three-electron donor we now consider a ligand such as the SR group which may span three metal atoms and function as a five electron-donating species. Again, in a manner similar to (b), a vacant coordination site is created by the ligand moving away from the cappedsystem thereby creating a vacant coordination site on one metal atom.

We have recently carried out a series of reactions which have fulfilled this promise [9]. They are given in Scheme 6. Treatment of $H_2Os_3(CO)_9S$ with KOH/MeOH produces the anionic complex $[HOs_3(CO)_9S]^-$ which on treatment with R_3O^+ (R = Me or Et) generates the complex $HOs_3(CO)_9SR$ containing an SR group capping three Os atoms. This undergoes a facile reaction with C_2H_4, CO, or PR_3. For L = C_2H_4, the molecular structure has been established by X-ray analysis and is shown in Fig. 3 [10]. The "folding-back" of the SR ligand is clearly observed, as is the coordinated C_2H_4 ligand. This complex readily undergoes loss of C_2H_4 to regenerate the original $Os_3(CO)_9SR$ but, in the presence of C_2H_4 (to minimise C_2H_4 dissociation), conversion to the vinyl complex $HOs_3(CO)_8(CH{=}CH_2)S$, is observed. This reaction clearly parallels that described in Section 1. The vinyl complex may also be produced via reaction of Me_3NO with $H_2Os_3(CO)_9S$, again illustrating the versatility of that particular reagent.

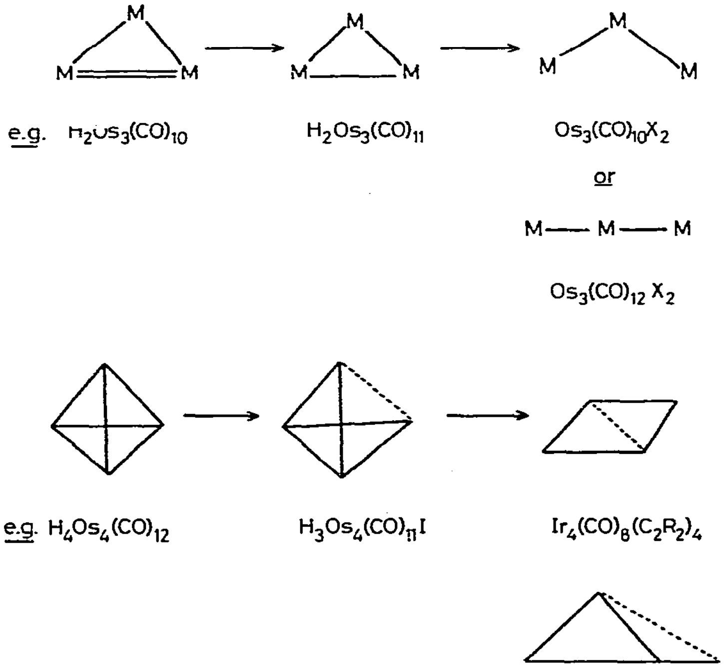
(iii) Metal—metal bond cleavage

Finally in Scheme 7 are illustrated two additional alternatives. These are



Scheme 7. Activation via metal—metal bond opening.

based on the idea that vacant coordination sites may be generated by the cleavage of metal—metal bonds. In case (b) we illustrated a double bond → single bond interconversion. The reaction of a coordinatively unsaturated species (46e as opposed to 48e species) such as $H_2Os_3(CO)_{10}$ parallels the oxidation—addition reactions so commonly observed for 16 electron systems. Thus, the unsaturated cluster, which in valence bond terms, requires a double bond along one edge of the Os_3 triangle readily undergoes reaction with electron-pair



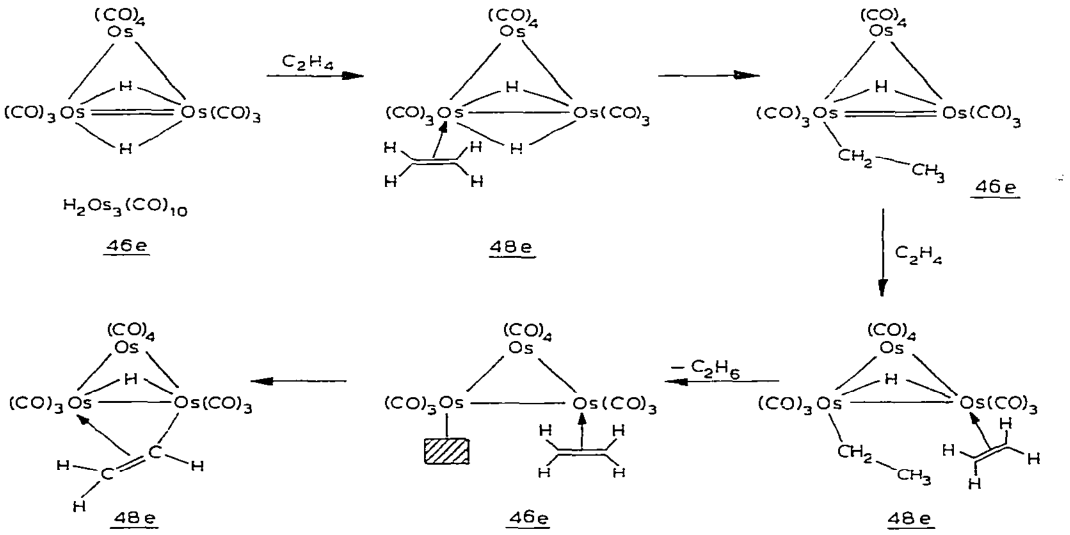
Scheme 8. Polyhedral interconversion for M_3 and M_4 clusters.

donors such as C_2H_2, CO or PR_3 to produce the electron-precise (48-electron) complexes $H_2Os_3(CO)_{10}(C_2H_4)$, $H_2Os_3(CO)_{11}$ or $H_2Os_3(CO)_{10}PR_3$. Such reactions occur under ambient conditions and may be viewed as saturating the double bond. Thus, activation of the cluster corresponds to the formation of one metal—ligand bond at the expense of one metal—metal bond (double → single). In the other example (a) we propose the cleavage of a single metal—metal bond as a method of generating unsaturation. As discussed above there is a view that clusters such as $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$ undergo substitution by an associative mechanism which requires metal—metal bond cleavage of this sort.

Clearly in a triangular system bond cleavage would lead initially to a "bent" molecule which may rearrange finally to a linear arrangement. For a tetrahedron the problem is slightly more complicated producing first a butterfly system but then either a square or triangle + 1 (Scheme 8). Thus, as the number of metal ions increases the number of polytopal arrangements or geometries also increases. This topic is discussed in detail elsewhere [11].

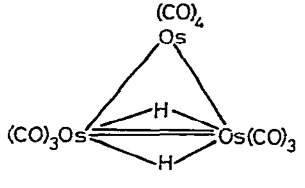
2. The effect of blocking groups on ligands

We have previously put forward the view that the driving force behind olefinic or acetylenic interactions with metal cluster systems may be associated with the interplay electron-precise ⇌ electron-poor. This is best illustrated by example and we have taken as a convenient system the reaction of ethylene with $H_2Os_3(CO)_{10}$ outlined in Scheme 9. As discussed in the previous section the initial step is cluster saturation leading to an electron precise (48 electron) system. The next step, H-migration to form an Os—C_2H_5 intermediate, generates a 46-electron system, also unsaturated; this in turn reacts with a second

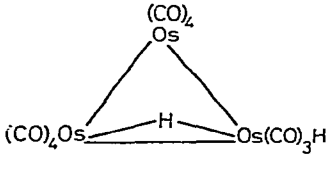


Scheme 9. The reaction of $H_2Os_3(CO)_{10}$ with C_2H_4.

molecule of ethylene to generate the 48 electron intermediate $HOs_3(CO)_{10}$-$(C_2H_5)(C_2H_4)$. Reductive elimination of ethane then occurs, a 46 electron system $Os_3(CO)_{10}(C_2H_4)$ is produced and in order to reach the stable 48 electron configuration oxidative addition of the olefinic C—H bond occurs to generate the thermodynamically stable product $HOs_3(CO)_{10}CH{=}CH_2$. Thus, the reaction sequence is governed by the 46 $\rightleftharpoons$ 48 electron interplay and also the ability of the cluster to expand its coordination sphere from 12 (as in $H_2Os_3(CO)_{10}$) to 13 as in $H_2Os_3(CO)_{10}C_2H_4$. The ability of the cluster to expand its coordination sphere in this way will also depend upon the clusters capabilities to accommodate the additional ligand (or substrate). For example, it is clear that in cluster compounds the H-ligand prefers to occupy bridging positions but given no other choice will adopt the terminal bonding mode. This is clearly illustrated by the two complexes $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{11}$. The molecular geometries of these two dihydrides have been established by X-ray crystallography (and neutron diffraction) [12,13] as:



$H_2Os_3(CO)_{10}$



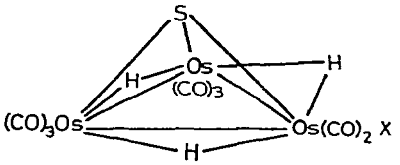
$H_2Os_3(CO)_{11}$

In this Section we will examine this theme in more detail. Our objectives are twofold: (i) can we induce a different type of substrate reactivity by modifying the cluster ligand geometry, and (ii) what is the effect of blocking cluster edges.

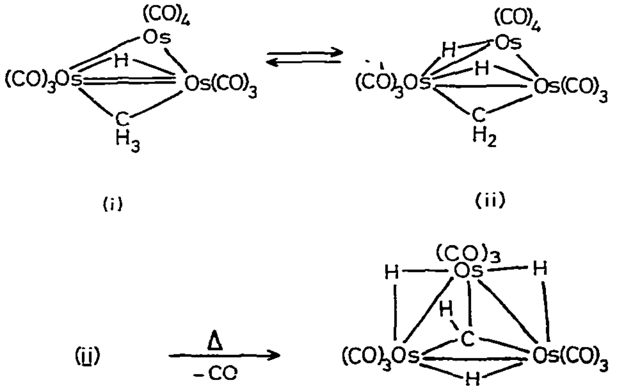
Consider Scheme 6. The complex $H_2Os_3(CO)_9S$ is conveniently prepared from the direct reaction of $Os_3(CO)_{12}$ with H_2S. The molecular structure of this complex has been established by X-ray analysis [14]. In essence it consists of a triangle of osmium atoms capped with a tridentate sulphur atom. There are three carbonyl groups per osmium atom and the hydrogens span two of the triangular edges. Simple electron-counting assuming the sulphur atom to donate 4 electrons indicates that this is 48 electron system.

Treatment of $H_2Os_3(CO)_9S$ in CH_2Cl_2/MeCN with Me_3NO leads to the formation of the complexes $H_2Os_3(CO)_8(MeCN)S$ and $H_2Os_3(CO)_8(Me_3N)S$ in yields of 50% and 10% respectively. A surprising feature of these compounds is their resistance to substitution. Only at elevated temperatures is the MeCN ligand, for example, replaced by C_2H_4. This is in marked contrast to $Os_3(CO)_{11}(MeCN)$ which undergoes substitution under very mild conditions. The ethylene complex $H_2Os_3(CO)_8(C_2H_4)S$ may be obtained from the reaction of $H_2Os_3(CO)_8$-(MeCN)S in cyclohexane with ethylene at 80° C. Unlike $Os_3(CO)_{11}(C_2H_4)$ which rapidly undergoes reaction to produce $HOs_3(CO)_{10}CH{=}CH_2$ under these conditions, this complex resists H-atom transfer and the ethylene remains bound in the Chatt—Dewar bonding mode. Reaction with acetylene yields the vinyl complex $HOs_3(CO)_8(CH{=}CH_2)S$. This reaction is reminiscent of the reaction of C_2H_2 with $H_2Os_3(CO)_{10}$ to produce $HOs_3(CO)_{10}(CH{=}CH_2)$ [15], but unlike that reaction the complex resists further C—H bond cleavage to produce $H_2Os_3(CO)_7(C{=}CH_2)S$. Clearly there is a remarkable increase in the stability of the ethylene and vinyl bonding modes in this sulphur containing system. Two explanations may be offered. First, that a steric constraint is imposed on the molecule by the S-capping and the H-bridges along each polyhedral edge; these H-bridges are known to have major steric requirements. Secondly, it would appear that the donating properties of the "soft" sulphur ligand stabilises the complex to substitution. The subtle changes in the bond enthalpies, M—C (σ), M—M and MCH_2—CH_2, are clearly of importance and may be employed to modify cluster reactivity.

The reactions of $H_2Os_3(CO)_8(MeCN)S$ with the diatomic molecules HX (X = H, Br or SH) have been examined. In all cases the product of this reaction is $H_3Os_3(CO)_8(X)S$:



Of special interest is the product $H_4Os_3(CO)_8S$ because with this complex three of the H-ligands adopt the preferential edge-bridging mode whereas the fourth choses to bind terminally. It would appear that, together with the S-capping, once each polyhedral edge of the metal polytope is involved in M—H—M bonds then further reaction is inhibited because this would necessitate a triple bridged-edge within the cluster. This facet has also been demonstrated rather neatly by Shapley [16] who has examined the chemistry of the bridged-methyl complex $HOs_3(CO)_{10}CH_3$:



He was able to demonstrate that, on the basis of ^{13}CO NMR studies, this complex, which possesses structure (i) undergoes inter-conversion to (ii) on the NMR time-scale. In doing so the second Os—Os edge is occupied by an H-ligand. On heating CO-ejection recurs presumably to produce the 46 electron system $H_2Os_3(CO)_8CH_2$ which then undergoes further C—H bond fission to produce $H_3Os_3(CO)_8CH$. This complex, which possesses 48 valence electrons and is therefore saturated, contains twelve ligands but no available polyhedral edge to accommodate additional hydride ligand and is therefore stabilised relative to the next product in the series $H_4Os_3(CO)_7C$. Other explanations are possible and have been given elsewhere.

The stability of the complexes $H_3Os_3(CO)_8(X)S$ is apparent from their resistance to CO-ejection. Thus, on heating in octane (125°C) for three hours CO removal and X bridge formation does not take place. In contrast, $HOs_3(CO)_{11}Br$ converts to $HOs_3(CO)_{10}Br$ after 5 minutes at 80°C:

$$H_3Os_3(CO)_8(X)5 \xrightarrow{\Delta} \text{No reaction}$$

$$HOs_3(CO)_{11}Br \xrightarrow{\Delta} HOs_3(CO)_{10}Br$$

The molecule $H_4Os_3(CO)_8S$ allows a comparison between the reactivities of a bridging and terminal hydride. Thus the complex undergoes reaction with ethylene only at high pressures to produce $H_2Os_3(CO)_8(C_2H_4)S$, in contrast to $H_2Os_3(CO)_{11}$ which is one of the few other reported clusters containing both M—H and M—H—M systems, is stable to CO ejection and does convert to a totally H-bridged system. The reaction presumably also leads to the formation of ethane and reflects the instability of terminal alkyl intermediates in clusters. Reaction with halogenated hydrocarbons, e.g. CCl_4 leads to the formation of the terminal M—X bond as is observed with mononuclear terminal hydrido complexes and markedly constrasts with the behaviour observed for M—H—M species.

The whole of this chemistry emphasises the influence of capping groups and saturation of edge bridging groups with H systems within clusters. This may play an important role in differentiating between the reactivity of alkenes and alkynes in metal cluster species as the former involve the formation of metal—hydrogen bridges whereas the latter may bond without this occurring.

References

1 see e.g. B.F.G. Johnson and J. Lewis, Pure Appl. Chem., 44 (1975) 43.
2 C.R. Eady, J.M. Fernandez, B.F.G. Johnson, J. Lewis, P.R. Raithby and G.M. Sheldrick, J. Chem. Soc. Chem. Comm., (1978) 421.
3 B.F.G. Johnson, J. Lewis, C.R. Eady and T.W. Matheson, unpublished results.
4 B.F.G. Johnson, J. Lewis and D. Pippard, J. Organometal. Chem., 145 (1978) C4.
5 B.F.G. Johnson, J. Lewis, M. Suss-Fink and K. Wong, unpublished results.
6 S. Bhaduri, B.F.G. Johnson, J. Lewis, D.J. Watson and C. Zuccarro, J. Chem. Soc. Chem. Commun., (1977) 477.
7 J.P. Collman, J.R. Norton, E. Dolcetti and W.T. Robinson, Inorg. Chem., 11 (1972) 382.
8 R.G. Bryan, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1977) 329.
9 D. Pippard, Ph.D. Thesis, Cambridge, 1978.
10 B.F.G. Johnson, J. Lewis, D. Pippard and P. Raithby, J. Chem. Soc. Dalton, in press.
11 R.F. Benfield and B.F.G. Johnson, J. Chem. Soc. Dalton, in press.
12 P.R. Raithby and G.M. Sheldrick, to be published.
13 M.R. Churchill and B.G. deBoer, Inorg. Chem., 16 (1977) 878.
14 B.F.G. Johnson, J. Lewis, P.R. Raithby and D. Pippard, J. Chem. Soc. Chem. Commun., in press.
15 M. Tachikawa and J.R. Shapley, J. Organometal. Chem., 124 (1977) C19; A.J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1974) 1415.
16 J. Shapley and R.B. Calvert, J. Amer. Chem. Soc., 99 (1977) 5225.