

# Cluster Compounds of the Platinum Metals

## CONSIDERABLE POTENTIAL AS INDUSTRIAL CATALYSTS

By Brian F. G. Johnson

University Chemical Laboratory, Cambridge, England

*In recent years metal cluster compounds with large numbers of metal atoms in the molecule have been prepared and characterised. The intermediate role of such clusters between monometal co-ordination compounds and metal surfaces is apparent, and is of great importance in studies of surface reactions for use in catalytic and other industrial processes. Investigation of the modification of the behaviour of carbon monoxide and simple organic ligands on co-ordination to such "metal fragments" is consequently one of the most rapidly expanding areas of chemical research.*

In recent years a remarkable growth has occurred in the knowledge of cluster compounds which contain transition metal ions. The number of known compounds of this type has increased several fold and the information about simple substances such as the binary carbonyls of ruthenium and osmium,  $M_3(CO)_{12}$  ( $M = Ru$  or  $Os$ ), has expanded greatly. The reason for this growth is to be found largely in the awakened interest in metal-metal bonds initiated by Professors Lewis and Cotton and the late Sir Ronald Nyholm, and also the development of instrumental, spectroscopic methods of structure characterisation. Chief among these are the availability of high resolution mass spectrometers, more rapid methods of X-ray structure analysis, and the advent of nuclear magnetic resonance (NMR) instruments capable of examining nuclei other than  $^1H$ ,  $^{19}F$  and  $^{31}P$ . An additional factor is the potential usefulness in industry of some of the compounds, in particular carbonyl clusters of rhodium which have proved to be effective catalysts for the production of ethylene glycol from carbon monoxide and hydrogen. Still a third stimulus is the expectation that the chemistry of small transition metal

clusters should prove to be valuable in providing information about the reactions of small molecules, for example carbon monoxide, hydrogen, oxygen, olefins and acetylenes, with the surfaces of macroscopic crystals used in heterogeneous catalysis.

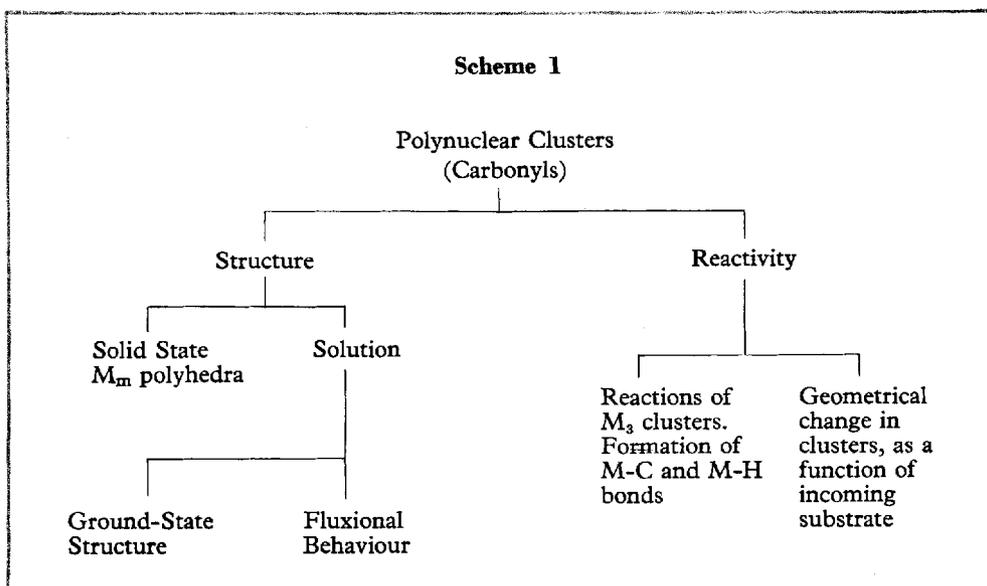
In this review we shall emphasise this latter point. For the most part we shall illustrate our general arguments by examples of our own work on the carbonyls of ruthenium and osmium. However, it must be appreciated that these arguments will also apply to clusters formed by elements throughout the transition-metal block. We will examine the chemistry of polynuclear clusters according to Scheme 1 and concentrate mainly on clusters containing carbonyl (CO) ligands.

### Structure

#### Solid State

Consider collections of metals  $M_m$ . These may be conveniently separated into the following three overlapping classes. Clusters, where  $m$  is between 3 and 50; microcrystallites, where the upper range of  $m$  reaches several hundreds; and macroscopic crystals, where  $m$  extends towards infinity.

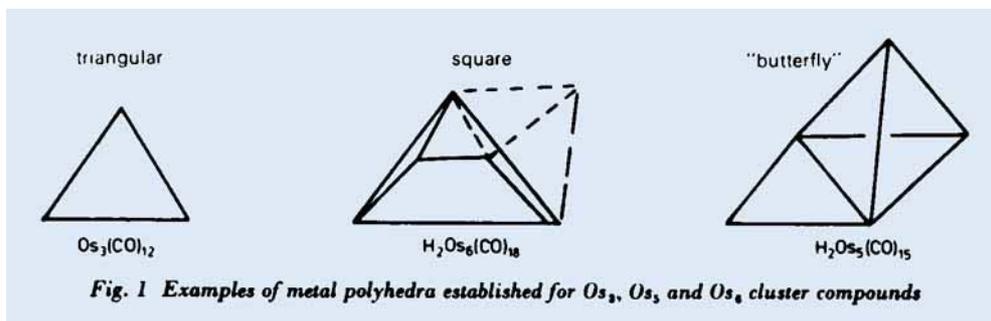
At one time there was the general view that



in terms of structure there was a steady progression from a single metal ion, where  $m=1$ , to the macroscopic crystal with  $m=\infty$ . The arrangement of the metal ions was essentially the same irrespective of whether there were few, say 13, or many metal ions present. Microcrystallites and clusters, in the absence of ligands, were merely fragments of the bulk metal structure. This idea has been questioned particularly by Burton who has argued—and his arguments are apparently well supported by experimental evidence—that microcrystallites do not necessarily have close-packed arrangements of metal atoms, that is corresponding to hexagonal close packing or cubic close packing, but may in

some cases be based on pentagonal symmetries. Clearly then there could be a major discontinuity in the build-up of macroscopic crystals which, of course, possess close-packed arrangements of metal atoms.

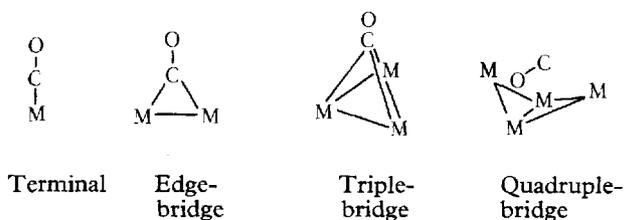
Geometry apart, recent calculations have led to the conclusion that even for relatively small clusters, where  $m=8$  or 12, there is a remarkable similarity of electronic structure for these and those of highly crystalline metals. In essence band theory may also apply to small aggregates of metals. However, caution must be exercised here particularly in view of the proposed geometrical changes, and much further work in this area is essential.



Irrespective of these two aspects it is clear that clusters, microcrystallites, and macroscopic crystals have in common the faces, for example,  $M_3$  (triangular),  $M_4$  (square planar) or  $M_4$  (butterfly), which they present on the outside surface. In Figure 1 we illustrate these faces as they are found in known transition metal cluster compounds.

It is conceivable therefore that by studying the mode of behaviour of small molecules with such cluster faces, information leading to a better understanding of surface reactivity may be obtained about:

- (a) The bonding modes adopted by these molecules with triangular (111), square planar (110) and similar metal ion arrangements, and their consequent chemistries.
- (b) The energies of interconversion of one bonding mode to another. For example, it is known that in metal carbonyl clusters the CO ligand may bond in at least four different ways, shown below.



Other bonding modes will almost certainly be discovered. These modes parallel those considered for the interaction of CO with metal surfaces and clearly some idea of the energy necessary to convert one mode to another is of importance.

- (c) Whether or not the metal cluster geometry is itself sensitive to the reacting species. For many years there has been the implicit assumption that the geometry of the cluster species is insensitive to reactions on its surface. This may not be true, however, even for some reactions with microcrystallites and macroscopic crystals.

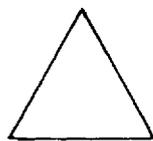
- (d) The chemistry, catalytic and otherwise, of the metal cluster.

At this stage it is important to realise that in our discussions of cluster reactivity we have two extremes to consider. First, we can have a "naked" cluster. That is to say a cluster which has no ligands associated with it and sits in an inert matrix. This is in reality a very difficult situation to reach. Secondly we can have the more conventional cluster species  $M_mL_n$ , in which the metallic cluster is surrounded by donor ligands L. Clusters of this type can themselves be separated out into:

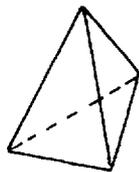
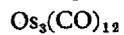
- (i) Low-valent clusters. In these the metal ions are assumed to be in the zero-valent, or less, oxidation state and are commonly found for  $L = CO, PR_3$  and so on.
- (ii) High-valent clusters. In this class L is a ligand such as  $Cl^-$  or  $O^{2-}$ . The so-called "naked clusters" supported in  $O^{2-}$ -containing matrices will almost certainly be of this type.

Clusters of type (i) are in general terms the more easily studied. Certainly these are potential homogeneous catalysts and are clearly important in reactions involving, for example, the activation of CO (Fischer-Tropsch). For these clusters, which, for  $m=3$  to 13, form cage like polyhedra (tetrahedra, octahedra, etc.), the effect of the peripheral ligands L is very important. They can exert an electronic influence. Consider the tetrahedral carbonyl  $Ir_4(CO)_{12}$ . It has been shown that on reaction with triphenylphosphine, substitution of up to three CO groups by  $Ph_3P$  can occur. The remarkable feature of this reaction, however, is that the rates of substitution increase dramatically in the order  $3rd > 2nd > 1st$ . Substitution has been shown to occur on separate metal ions and substitution on the first iridium atom labilises a CO group on the iridium atom adjacent to it. They can also exhibit steric constraints. Most simple carbonyl containing

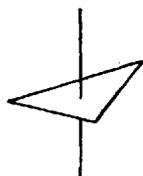
Scheme 2



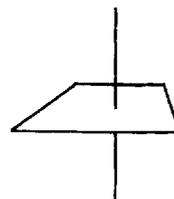
Equilateral Triangle



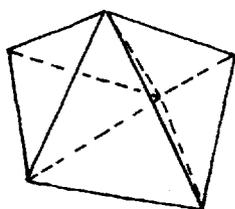
Tetrahedron



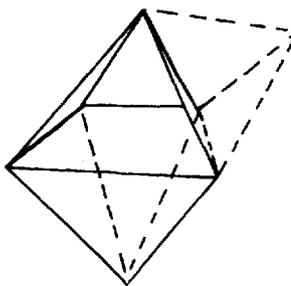
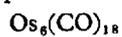
Trigonal Bipyramid



Octahedron



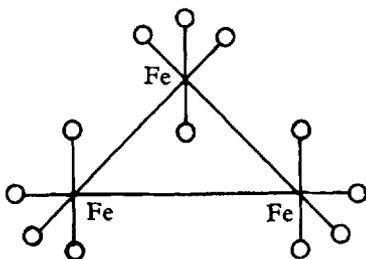
Bicapped Tetrahedron



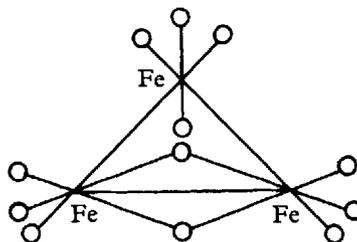
Monocapped Octahedron



Scheme 3

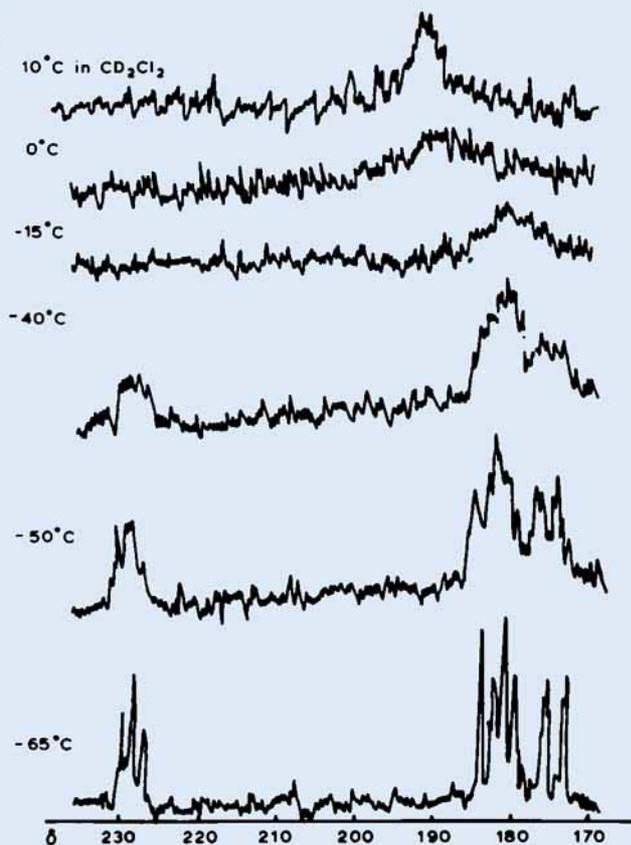


$\text{Fe}_3(\text{CO})_{12}$  : proposed non-bridged form

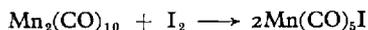
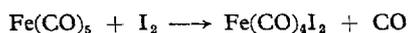


$\text{Fe}_3(\text{CO})_{12}$  : bridged form observed in solid

**Fig. 2** The carbon-13 NMR spectra of  $Rh_4(CO)_{12}$  over the temperature range  $-65$  to  $+10^\circ C$



species undergo reaction with the iodide ion to produce a metal iodide species, for example:



The hexanuclear carbonyl,  $Os_6(CO)_{18}$ , is different. This carbonyl reacts with  $I^-$  (and other anions) to produce the dianion  $[Os_6(CO)_{18}]^{2-}$  in quantitative amounts and iodine is liberated. Here we believe that the eighteen carbonyl groups effectively shield the  $Os_6$  nucleus from attack. Iodide attack therefore occurs at the CO ligand leading to an electron transfer reaction through an incipient CO-bridge. This serves to illustrate a common problem found for carbonyl clusters namely that in many reactions the rate determining step is CO-dissociation, to expose the  $M_m$  cluster, and this is often sluggish.

Much structural information is now available for carbonyl compounds and a wide variation in metal polyhedra have been found. Some are shown in Scheme 2.

### Solution

It has been known for some time that in solution at least, some carbonyl clusters undergo a structural change. Notable in this respect is  $Fe_2(CO)_{12}$  which is known to possess two carbonyl bridges in the solid (Scheme 3) but there is little evidence to support their presence in solution. This has been interpreted in terms of fluxional behaviour. In solution, where the CO ligands are removed from the constraints of the lattice, migration of the CO ligands about the  $Fe_2$  triangle occurs generating species with and without CO-bridges. The energy of activation for this

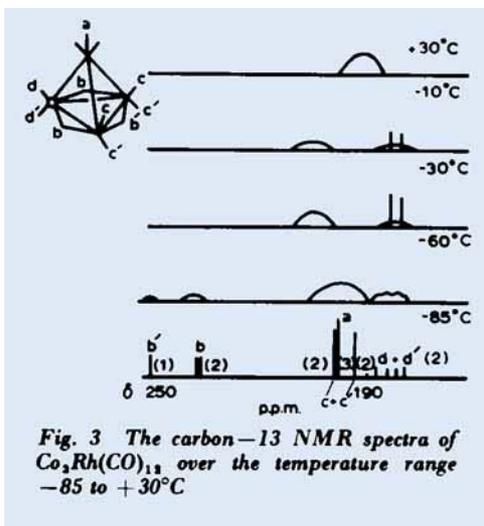


Fig. 3 The carbon-13 NMR spectra of  $\text{Co}_3\text{Rh}(\text{CO})_{12}$  over the temperature range  $-85$  to  $+30^\circ\text{C}$

process has been estimated to be  $<5$  kcal/mol and the non-bridged species are considered to dominate in solution.

For some carbonyls it has been found possible to deduce ground-state geometries in solution from  $^{13}\text{C}$  NMR studies of isotopically  $^{13}\text{C}$  enriched species. For these compounds, which may also exhibit fluxional behaviour, activation energies for CO migration must be in excess of 5 kcal/mol. We will consider the following three examples, each of which illustrates a different aspect of CO-fluxionality.

**$\text{Rh}_4(\text{CO})_{12}$ .** The  $^{13}\text{C}$  NMR spectra for this species (70 per cent  $^{13}\text{C}$  enriched) over a range of temperatures are shown in Figure 2. At low temperatures the spectrum is totally compatible with the observed solid state structure exhibiting three doublets in the intensity ratio 3 : 3 : 3 and one triplet of intensity 3. The appearance of the triplet clearly identifies the CO group as a bridge spanning two rhodium nuclei ( $^{103}\text{Rh}$  100 per cent,  $S = \frac{1}{2}$ ). As the temperature is raised, all signals collapse uniformly until at  $40^\circ\text{C}$  only a well resolved quintet is observed indicating that all CO groups are seeing four equivalent rhodium nuclei, in other words the twelve CO ligands are rapidly migrating around the  $\text{Rh}_4$  cluster. An activation energy of  $\sim 12$  kcal/mol has been calculated for this process.

**$\text{Co}_3\text{Rh}(\text{CO})_{12}$ .** In the solid the complex has a structure related to that of  $\text{Rh}_4(\text{CO})_{12}$ . The  $^{13}\text{C}$  NMR spectrum at low temperature is consistent with this geometry, however, in contrast to  $\text{Rh}_4(\text{CO})_{12}$ , as the temperature is raised two types of fluxional behaviour become apparent. At the intermediate temperature of  $-30^\circ\text{C}$  all but two CO groups, namely those bound terminally to the rhodium atom (Figure 3), undergo interchange. This has the effect of equilibrating the two CO groups. At high temperatures all CO groups become equivalent and are clearly migrating over the whole  $\text{Co}_3\text{Rh}$  cluster. The intermediate behaviour is of interest because it shows that CO-migration preferentially follows a course which enables bridges to be in association with the rhodium atoms at all times.

**$\text{Os}_6(\text{CO})_{18}$ .** The remarkable feature of this molecule is the presence of three different types of osmium atoms, Figure 4. Osmium(1) is six-co-ordinate being adjacent to three osmium atoms and three CO groups. Osmium(2) is seven-co-ordinate and osmium (3) eight. This is clearly apparent from the  $^{13}\text{C}$  NMR. At low temperatures the spectrum is as expected for this geometry (Figure 4) with three sets of signals  $[\text{A} + \text{A}']$ ,  $[\text{B} + \text{B}']$  and  $[\text{C} + \text{C}']$ . Each set consists of two signals in the ratio of 2 : 1 corresponding to the two CO environments about each

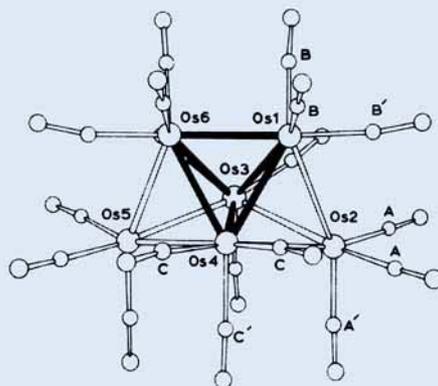


Fig. 4 The molecular structure of  $\text{Os}_6(\text{CO})_{18}$

osmium atom. As the temperature is raised, these latter signals collapse giving rise eventually to three single signals. In this case equilibration occurs about each independent osmium atom and there is no evidence for CO transfer from one osmium to another in the temperature range examined. The effect of co-ordination number and electronic differences from one osmium to another is very dramatic.

These three examples serve to show that ground state geometries may be accessible for carbonyl clusters in solution, and that a variety of fluxional processes are available.

## Reactivity

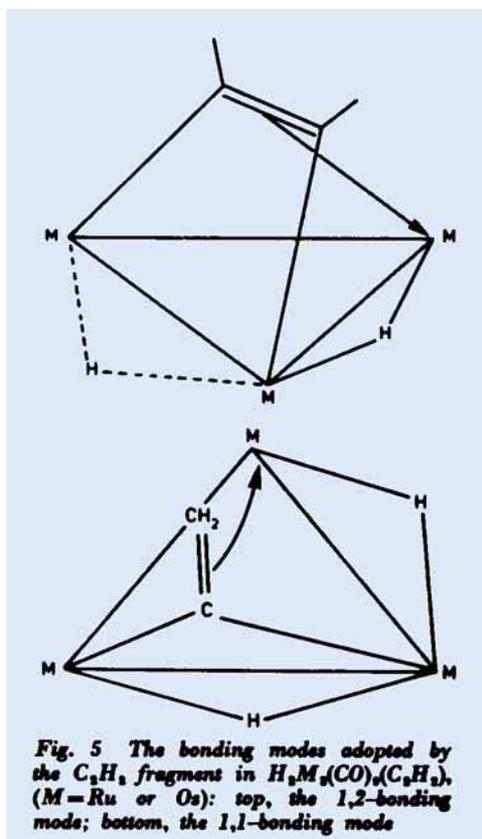
### Triangular Clusters

The triangular clusters of ruthenium and osmium have been the most widely studied. This is largely due to their availability. Consider the reaction established for  $M_3(CO)_9$ , Scheme 4, with  $H_2$ ,  $C_2H_4$  and  $C_2H_2$ .

On reaction of  $M_3(CO)_9$  ethylene undergoes C-H bond cleavage to produce  $M_3$ -hydrido species containing either a  $C:CH_2$  or a  $CH:CH$  unit. In an alternative reaction sequence  $Os_3(CO)_9$  reacts first with  $H_2$  to produce  $H_2Os_3(CO)_9$  which will then react with  $C_2H_2$  to give first  $HOs_3(CO)_9(CH:CH_2)$  which on heating generates one of the products of the reaction of  $C_2H_4$  with  $Os_3(CO)_9$ .

Hydrogenation of  $H_2Os_3(CO)_9(C:CH_2)$  occurs not only on the  $C:CH_2$  fragment but also on the  $Os_3$  triangle to produce a species containing a CMe fragment bound symmetrically to the metal triangle. In contrast, reduction of  $H_2Os_3(CO)_9(CH:CH)$  liberates olefin and forms the tetranuclear cluster  $H_4Os_4(CO)_9$ . The bonding modes of the various  $C_2$  fragments are shown in Figure 5.

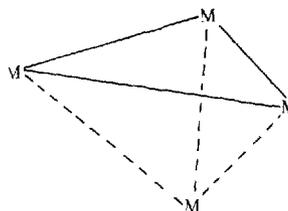
These observations are important not only for the intrinsic interest in cluster chemistry but also because they provide some insight into the bonding modes that olefins might adopt on contact with metal, or related, surfaces. They certainly provide evidence of bonding modes not previously contemplated by the chemist interested in heterogeneous



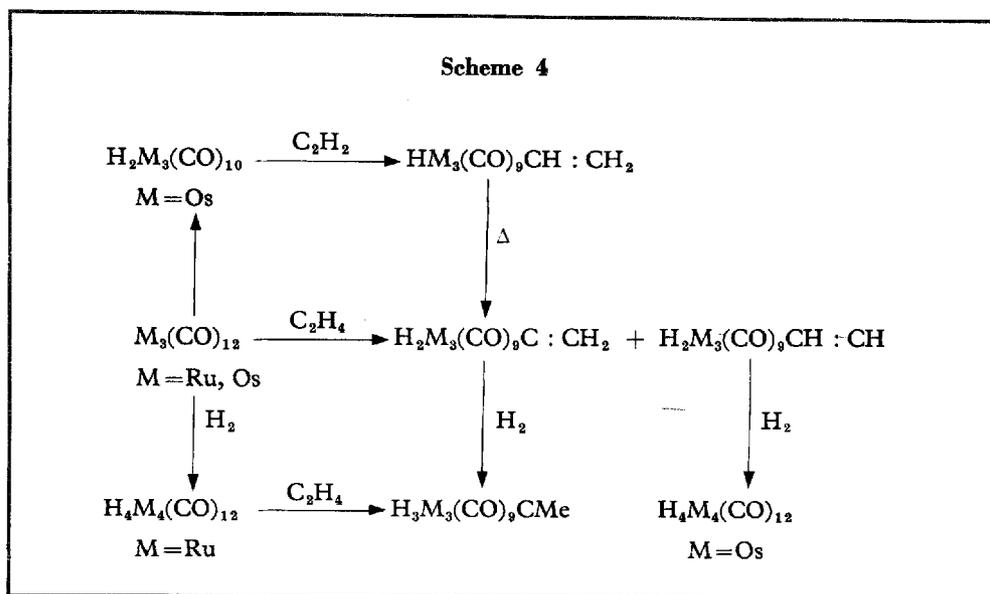
catalysis. It is also interesting to note that on reaction with  $Os_3(CO)_9$ , ethylene undergoes C-H bond cleavage whereas if  $H_2$  is present hydrogenation to  $C_2H_6$  occurs.

Similar behaviour has been noted for a wide range of substituted olefins and acetylenes, and also a variety of cyclic systems.

A tetranuclear cluster might intuitively be expected to behave similarly since it merely consists of four triangular faces. Alternatively, it could be considered as an  $M_3$  triangle in association with an additional metal:

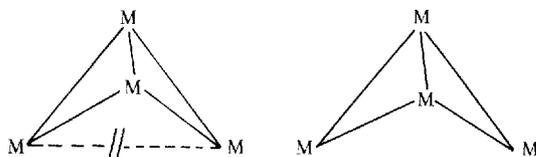


Clearly this additional metal ion will exert



some influence on the metal triangle. Some reactions of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and  $\text{H}_4\text{Os}_4(\text{CO})_{12}$ , two readily available tetrahedral clusters, are shown in Scheme 5.

There are two observations of note. First  $\text{H}_4\text{Os}_4(\text{CO})_{12}$  undergoes reactions which differ from those of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ . With  $\text{C}_2\text{H}_4$  the osmium cluster retains its tetrahedral geometry whereas the ruthenium compound undergoes cluster fragmentation to yield among other products,  $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CMe}$ . With cyclic olefins the ruthenium cluster again undergoes structural rearrangement to give clusters based on the butterfly arrangement of four metal atoms. This is simply derived from the tetrahedron by a bond-break mechanism:

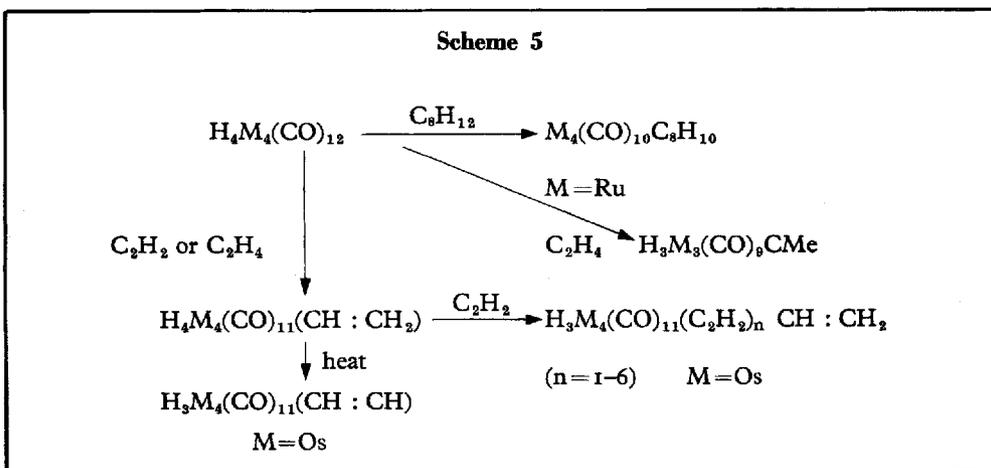


The osmium compound again retains its tetrahedral configuration and in general terms gives products similar to those derived from linear

olefins. Interestingly the same product is obtained irrespective of whether the reacting substance is an olefin or acetylene. In contrast to the  $\text{M}_3$  system, on heating the vinylic derivations  $\text{HM}_4(\text{CO})_{11}(\text{CH} : \text{CH}_2)$ , C-H bond cleavage to give the 1,2 disubstituted olefin derivative only and none of the 1,1 disubstituted complex. Finally, and again in contrast to the behaviour of the  $\text{M}_3$  system,  $\text{H}_3\text{Os}_3(\text{CO})_{11}(\text{CH} : \text{CH}_2)$  undergoes acetylene insertion into the Os-C bond to generate linear polymers. Clearly the effect of the additional M is to modify the reactivity of the  $\text{M}_3$  triangle.

#### Geometrical Changes in Clusters

There are available a number of theories which permit the rationalisation of cluster geometrics. None are totally successful but the Effective Atomic Number (E.A.N.) rule and the approach put forward by Wade have proved to be especially useful. The E.A.N. rule works very well for clusters with five metals or less, while Wade Theory may be more generally applied. Wade Theory very

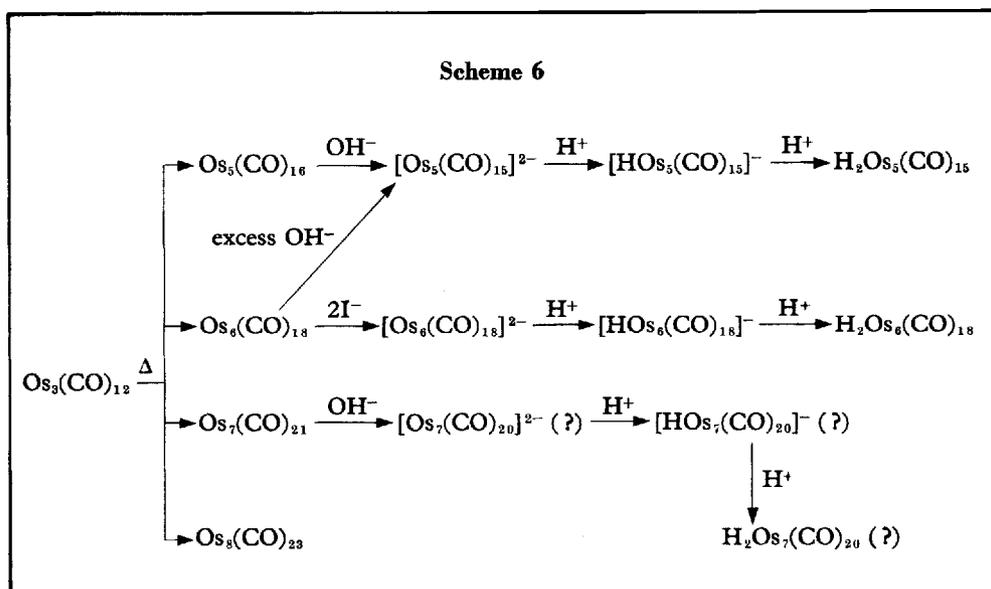


satisfactorily accounts for the bicapped tetrahedral geometry adopted by  $\text{Os}_8(\text{CO})_{18}$  but even more successful was the prediction that on reduction to  $[\text{Os}_6(\text{CO})_{18}]^{2-}$  the geometry should change to regular octahedron. In essence Wade Theory says that cluster shape is a function of the number of electron pairs available for cluster bonding irrespective of the source of these electrons, that is charge or ligand.

Recently we were able to produce a series

of new binary carbonyls of osmium by the pyrolysis of  $\text{Os}_3(\text{CO})_{12}$  in a sealed tube. The structures of all these carbonyls, which are based on  $\text{Os}_5$ ,  $\text{Os}_6$ ,  $\text{Os}_7$  and  $\text{Os}_8$  units, have been established. These in turn undergo reaction with base ( $\text{OH}^-$ ) to produce anionic species, for example  $[\text{Os}_5(\text{CO})_{15}]^{2-}$ , which react with  $\text{H}^+$  to produce hydrido-clusters. These reactions are summarised in Scheme 6.

Consider  $\text{Os}_5(\text{CO})_{16}$  which has been shown by single crystal X-ray analysis to possess a



trigonal bipyramidal arrangement of five osmium atoms. Treatment with base produces  $[\text{Os}_5(\text{CO})_{15}]^{2-}$ , which also has a trigonal bipyramidal geometry in keeping with Wade Theory, and reacts with acid ( $\text{H}^+$ ) to form first  $\text{HOs}_5(\text{CO})_{15}^-$  and then  $[\text{H}_2\text{Os}_5(\text{CO})_{15}]$ . The structure of the latter species, established by X-ray analysis, is an edge-bridged tetrahedron. Since the three species  $\text{Os}_5(\text{CO})_{16}$ ,  $[\text{Os}_5(\text{CO})_{15}]^{2-}$  and  $\text{H}_2\text{Os}_5(\text{CO})_{15}$  have the same number of electrons, similar geometries might have been expected. The observed change clearly emphasises the effect of the incoming ligands, in this case  $\text{H}_2$ . Similar behaviour is found for the  $\text{Os}_6$  series. Thus  $[\text{Os}_6(\text{CO})_{18}]^{2-}$  has a regular octahedral geometry whereas  $\text{H}_2\text{Os}_6(\text{CO})_{18}$  has a mono-capped square base pyramidal arrangement. Such changes cannot possibly be restricted to hydrido-species and other ligands will play

a similar role. The implications of these results are important. They lead us to suggest that in the course of chemical reaction it is unrealistic to expect the cluster geometry to remain intact. It could be argued that similar changes might occur in surface reactions and there is growing evidence to support this.

## General Conclusions

In this review we have attempted to point out the various points of interest in cluster chemistry. Two points of significance have emerged from our more recent studies. First the bonding modes adopted by small molecules on contact with clusters are far more numerous than previously supposed from a simple comparison with monometal systems. Secondly, there is growing evidence that clusters may undergo facile structure exchange on contact with substrate.

## Platinum Monoxide

The nature of a platinum surface exposed to the air we breathe is, as Oscar Wilde said of truth, rarely pure and never simple. The metal will almost certainly be covered with a more or less continuous, adherent, and protective film of an oxide or mixture of oxides of platinum. Depending on the previous history of the surface—whether it has been heated since it was formed, the temperatures to which it was raised, the rates of heating and cooling, and the chemical composition of the atmosphere—the film may consist of  $\text{PtO}_2$ ,  $\text{Pt}_3\text{O}_4$ , possibly  $\text{PtO}$ , or a mixture of these with inclusions of fine platinum particles. All this is to say nothing of possible contamination by sulphur compounds and O-H complexes.

The constitution of the surface is of more than academic interest for it largely determines the nature and extent of its catalytic activity at low temperatures up to, perhaps, a few hundreds of degrees centigrade. The erratic behaviour of early platinum catalysts for igniting domestic gas fires and burners was undoubtedly due to the variable composition of the platinum surface films.

It is thus of interest that the existence of PtO as a constituent of these films—for some

time a matter of controversy—has recently been established and its electron diffraction and X-ray diffraction spectra recorded. The work, carried out by M. and A. Hecq at the State University at Mons in Belgium, is reported in *J. Less-Common Metals*, 1977, **56**, (1), 133–136.

Films of PtO, stable at room temperature, were formed by reactive sputtering by an electrical discharge in a mixture of 10 per cent oxygen and 90 per cent argon at a pressure of  $10^{-1}$  to  $10^{-2}$  torr, using a platinum target. The technique was devised by the authors for studying oxide films on tin, and it is believed that the oxide is formed in the plasma as neutral particles and that these are then collected on the substrate.

In these experiments, a current density of  $0.3 \text{ mA/cm}^2$  was used at 2000V and the PtO deposited on the substrate at 200°C. Films 400Å thick were formed at a rate of 35 Å/min. The films decompose on heating to 400°C in argon.

As a result of this work, it should be possible more certainly than heretofore to establish quantitatively the presence of PtO whenever it may occur on the surfaces of platinum catalysts.

J. C. C.