

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.

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