General Discussion

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General discussion

M. B. Hall (*Department of Chemistry, Texas A & M University, U.S.A.*). The chemistry of $H_2Os_3(CO)_{10}$ resembles that of an alkene because both have an empty, low-lying π* orbital, which accepts electrons from an attacking nucleophile. However, the similarity of the unoccupied orbital does not imply a similarity of the occupied orbitals. Molecular orbital calculations and photoelectron spectra (Sherwood & Hall, *Inorg. Chem.* (in the press); Green, Mingos & Seddon, *Inorg. Chem.* **11**, 1619 (1981)) suggest that the bonding within the H_2Os_2 unit is best described as two three-centre, two-electron Os–H–Os bridging bonds similar to those in B_2H_6. Although the analogy with diborane is closer than that with ethylene, it is not completely accurate. Our calculations show that the H bridges stabilize some of the orbitals involved in Os to CO π backbonding and that this stabilization leads to some net, direct Os–Os bonding in addition to the Os–H–Os bridging bonds.

J. C. Green (*Inorganic Chemistry Laboratory, University of Oxford, U.K.*). The general form of the photoelectron spectrum of a metal carbonyl compound containing a metal–metal bond consists of the lowest ionization energy bands (7.4–9 eV) resulting from ionization of metal–metal bonding electrons followed by bands associated with metal d electrons involved in backbonding to the carbonyl ligands (9–11 eV) (Green *et al.* 1981). This is illustrated in figure 1 by the p.e. spectrum of $Os_3(CO)_{12}$. Thus the metal–metal bonding electrons are the easiest to remove from the cluster.

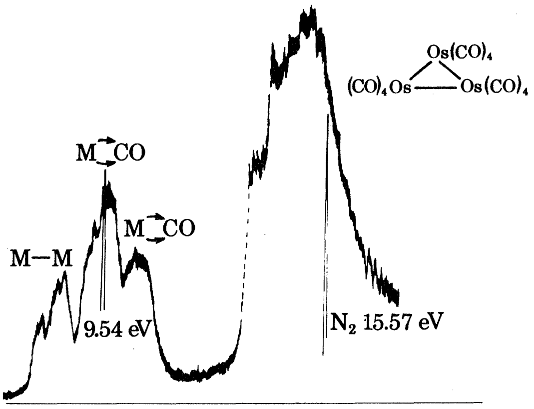

Figure 1

When, in an isoelectronic compound, an M–M interaction is replaced by an M–H–M bridge, the ionization band previously due to the M–M bond is absent and is replaced at considerably higher ionization energy (11.5–13 eV) by another band, which may be associated with ionization of the two electrons binding the M–H–M bridge. Both the high binding energy of these bands and their intensity characteristics indicate a considerable degree of localization on the hydrogen atom. This type of spectrum is illustrated by the p.e. spectrum of $Re_3H_3(CO)_{12}$ (figure 2).

In compounds where both M–M and M–H–M bonds are present, both types of band are found in their characteristic regions, indicating that bonding in this mixed type of cluster is fairly localized. If this type of cluster were to be subjected to electrophilic attack, such as oxidation by iodine, as Dr Mays described in his paper, that attack would be predicted to centre round the most easily removed electrons, namely the M–M bond rather than the more tightly bound M–H–M electron pair.

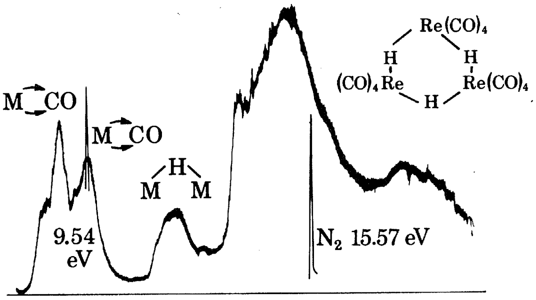

FIGURE 2

We may conclude that the role of heteroatoms is twofold. They not only provide electrons necessary for binding the cluster but they also have the capacity to stabilize markedly the cluster bonding orbitals.

Reference

Green, J. C., Mingos, D. M. P. & Seddon, E. A. 1981 *Inorg. Chem.* **20**, 2595.