U.V. Photoelectron Spectral Studies on the Metal Carbonyl Cluster Compounds $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_6(CO)_{18}$

By Jennifer C. Green,* Elaine A. Seddon, and D. Michael P. Mingos

(Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR)

Summary The photoelectron spectra of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ have been recorded and shown to be consistent with the molecular orbital scheme proposed for such molecules; the first ionization energies of these compounds and that of $Os_6(CO)_{18}$ are compared with the work functions of the corresponding metals.

Much of the recent research on metal cluster compounds has originated from the belief that such compounds may provide reliable models for either the surface or the chemisorbed surface state of metals involved in heterogeneous catalytic processes, which are still incompletely understood despite the development of new analytical, structural, and spectroscopic techniques.[1] If metal cluster compounds are indeed reliable models then they should have electronic characteristics which resemble those of a metal surface. We now report for the first time some u.v. photoelectron spectral data on the metal carbonyl cluster compounds $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_6(CO)_{18}$ which provide detailed information on the electronic structures of these molecules and enable a comparison to be made between the first ionization energies of these molecular compounds and the work functions of the corresponding metal surfaces.

A simplified molecular orbital scheme (Figure 1) for the trinuclear clusters, $M_3(CO)_{12}$, which have an equilateral triangle of bonded metal atoms and D_{3h} symmetry, may be constructed by a combination of the frontier molecular orbitals of the individual $M(CO)_4$ fragments, which have C_{2v} local symmetry. The $M(CO)_4$ fragment has three filled orbitals which correspond approximately to the t_{2g} orbital set of an octahedral $M(CO)_6$ molecule, and at higher energies two singly occupied orbitals of a_1 and b_2 symmetry whose radial characteristics are such that they permit effective bonding with the corresponding orbitals of the other $M(CO)_4$ fragments in the triangle.[2] The similarity between these frontier orbitals and the frontier orbitals of the
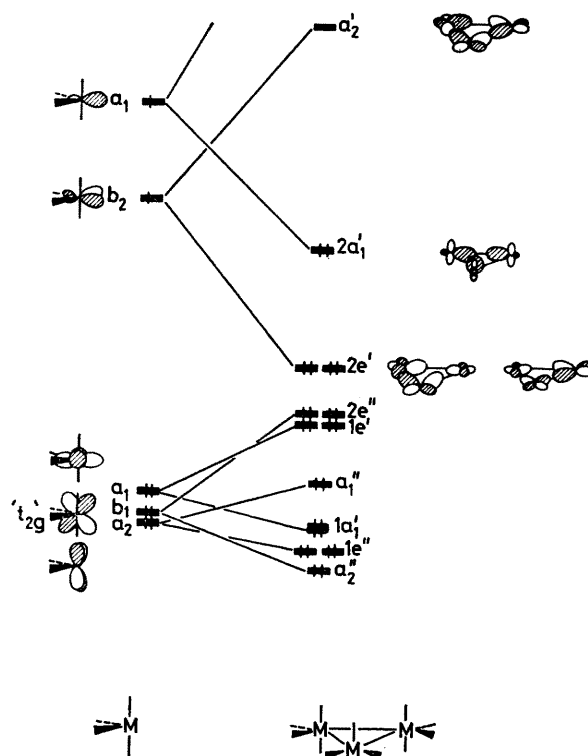

Figure 1. Molecular orbitals for $M_3(CO)_{12}$ (ref. 4).

methylene fragment (CH_2) has led to these fragments being described as isolobal[3] and suggests that the molecular orbitals of the $M_3(CO)_{12}$ molecule should closely resemble those of cyclopropane. The molecular orbital diagram for $M_3(CO)_{12}$ (Figure 1) is derived from the extended

Hückel calculations of Schilling and Hoffmann[4] which have indicated that the $2e'$ and $2a'$ molecular orbitals, which are responsible for the primary bonding interactions in the cluster, bear a strong resemblance to the Walsh molecular orbitals of cyclopropane,[5] but are inverted with respect to the latter. This arises because the a_1 orbital lies at lower energy than the b_2 orbital in methylene.[6] These calculations have also indicated significant interactions between the t_{2g} like orbitals of the $M(CO)_4$ fragments and suggest the possibility of mixing between these orbitals and the higher lying $2e'$ and $2a'$ orbitals.

In the photoelectron spectra of all three clusters the d-band lying between 7 and 11 eV is clearly separated from the bands characteristic of ionization of electrons mainly localized on the carbonyl ligands ($5\sigma + 1\pi$ at 13—16 eV: 4σ at 18 and 21 eV). In the He-II spectra the relative intensities of the various groups of bands correspond well with the values expected from orbital degeneracy. The He-I and He-II spectra of the d-band region are shown in Figure 2. For the $M_3(CO)_{12}$ species the intensity in this
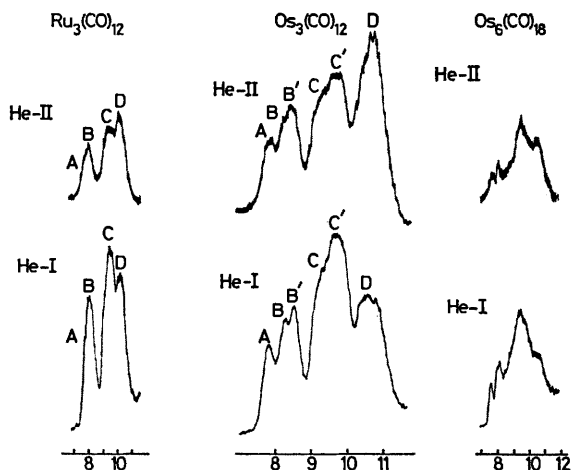

FIGURE 2. He-I and He-II photoelectron spectra of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Os_6(CO)_{18}$.

region can be divided between bands A+B and C+D, the relative areas being $1:2\cdot8$ He-I, $1:2\cdot9$ He-II $[Ru_3(CO)_{12}]$; $1:3$ He-I, $1:2\cdot65$ He-II $[Os_3(CO)_{12}]$. These relative areas strongly suggest that A and B account for 6 of the metal electrons whereas C and D account for 18 of them. This is compatible with band A and band B being ionizations from orbitals of a and e symmetry respectively. Consistent with this interpretation is the fact that band B shows spin-orbit

splitting in the osmium cluster compound. Band C shows an intensity loss in the He-II spectrum as expected from orbitals back bonding to CO relative to metal–metal bonding electrons.[7] Although the ratio $(A+B):(C+D)$ varies little on changing the ionizing radiation, from the band profiles it may be seen that band D shows a relative increase in intensity on increasing the photon energy. This is characteristic of a high metal content[7,8] for the orbital from which the ionization arises. This is consistent with the M.O. scheme proposed if interactions between the e' and a' orbitals of the frontier molecular orbitals and the t_{2g} like molecular orbitals are significant. In summary, the assignments made above confirm (within the limitations of Koopmans' theorem) that the highest occupied orbital is $2a'$ and not $2e'$ as anticipated by analogy with cyclopropane.

TABLE. Ionization energy data for metal carbonyl clusters (in eV).

	$Ru_3(CO)_{12}$		$Os_3(CO)_{12}$	$Os_6(CO)_{18}$
A	$7\cdot7^a$	A	$7\cdot83$	$7\cdot50$
B	$8\cdot0$	B	$8\cdot28$	$8\cdot09$
		B'	$8\cdot50$	$9\cdot47$
C	$9\cdot4$	C	$9\cdot24$	$10\cdot44$
		C'	$9\cdot60$	
D	$10\cdot1$	D	$10\cdot44$	

^{a} The error on these values is $\pm0\cdot2$ eV owing to spectral shift with time.

The data given in the Table for the bicapped tetrahedral cluster $Os_6(CO)_{18}$[9] indicate that the first ionization energy only decreases by $0\cdot3$ eV when the number of metal atoms is doubled. Furthermore, the observed ionization energies for the metal clusters are of the order of 3 eV higher than the work functions of the corresponding metals (Ru $4\cdot71$, and Os $4\cdot83$ eV[10]). Metal surfaces undergo only a small change in work function on chemisorption of carbon monoxide, for example, CO on platinum gives an increase of $0\cdot2$ eV.[11] Therefore, we conclude that although metal cluster compounds may provide a similar template effect to that proposed for surfaces their electronic characteristics differ significantly from those of surfaces in either their pure or chemisorbed states. Our limited observations also indicate that the cluster size would have to be much larger before their ionization energies would resemble the work function of the corresponding metal.

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