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Preliminary communication

UV PHOTOELECTRON SPECTRAL STUDIES OF CARBONYL-HYDRIDO-CLUSTERS AND THE DEVELOPMENT OF A TOPOLOGICAL BONDING MODEL

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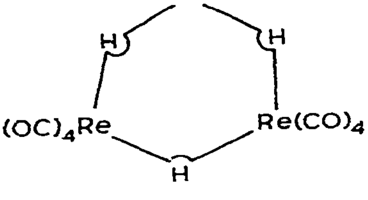
Summary

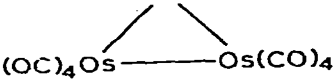
The UV PES of $Re_3(CO)_{12}H_3$, $Os_4(CO)_{12}H_4$ and $Os_3(CO)_{10}H_2$ have been interpreted essentially in terms of a localised three centre two electron $M\overset{H}{\frown}M$ bond model, and this description has been generalised into a topological approach similar to that developed for boranes.

The study of hydrido-cluster compounds of the transition metals has important implications for defining the nature of metal-hydrogen interactions on metal surfaces and in "interstitial" hydrides [1], but to date such studies have been limited to X-ray and neutron studies in the solid state [2]. In this communication we report the first gas phase UV photoelectron spectral studies on hydrido-carbonyl cluster compounds, which can be interpreted in terms of an essentially localised bonding scheme for the three centre M—H—M bond.

A comparison of the He-I photoelectron spectra of $Re_3(CO)_{12}H_3$ (I) and $Os_3(CO)_{12}$ (II), which are isoelectronic, is given in Figures 1a and 1b.



(I)



(II)

Both spectra show bands in the 13—16 eV region, which can be associated with ionizations from molecular orbitals constituted primarily from 5σ and 1π CO ligand orbitals [3].

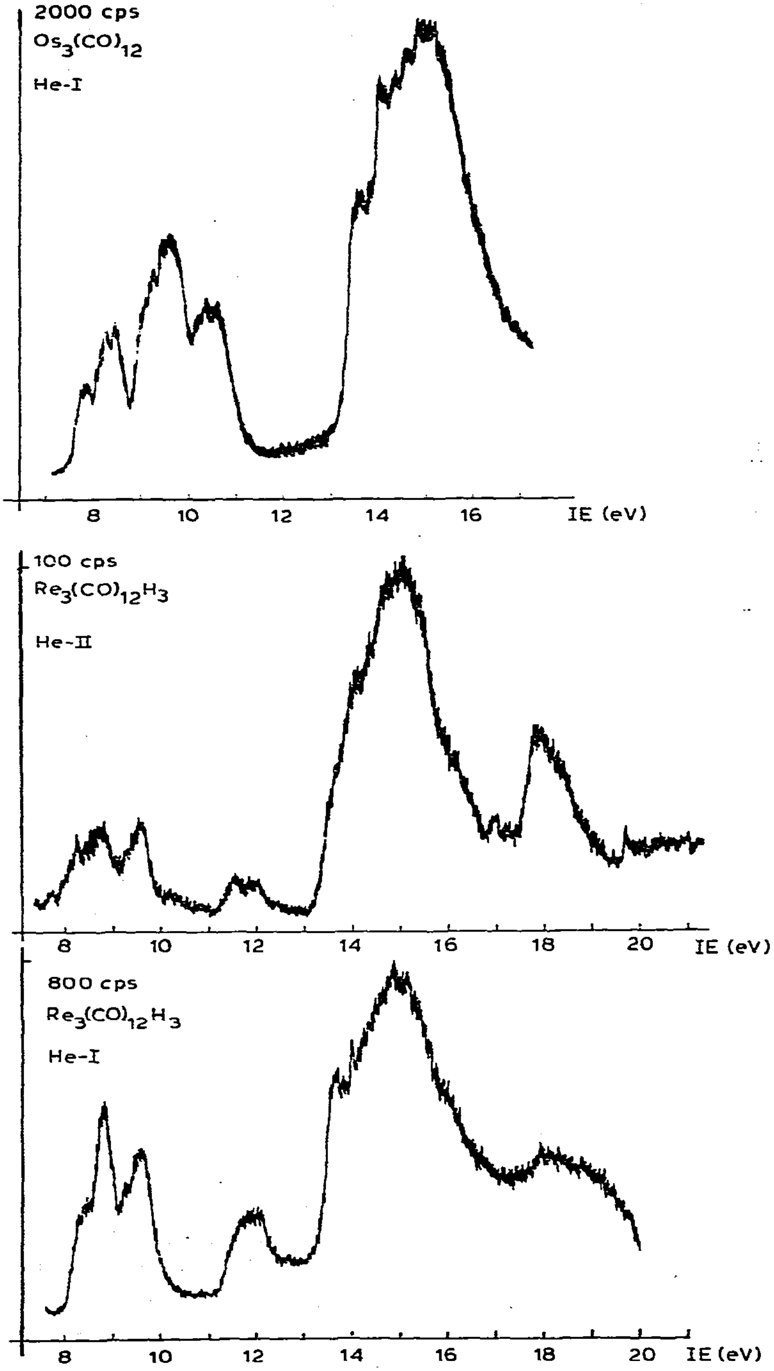


Fig. 1. He-I spectrum of $Os_3(CO)_{12}$ and the He-I and He-II spectra of $Re_3(CO)_{12}H_3$.

In addition bands at 8.45—9.60 eV for $Re_3(CO)_{12}H_3$ and 9.24—10.44 eV for $Os_3(CO)_{12}$ can be assigned to ionizations from metal-CO backbonding molecular orbitals which are derived from the t_{2g} set of the parent octahedral metalcarbonyl fragments, by analogy with other mono- and bi-nuclear carbonyl complexes, e.g. $Re_2(CO)_{10}$ [4]. The ionizations at 7.83 and 8.33 eV in $Os_3(CO)_{12}$, which have been assigned to the Walsh like metal-metal molecular orbitals of a_1' and e' symmetry [5], are absent in $Re_3(CO)_{12}H_3$ and are replaced by a new broad band at ca. 12 eV, which we assign to the three-centre $\mathrm{Re}\overset{H}{\frown}\mathrm{Re}$ bonds. Similar bands have been observed in the range 11.9—12.7 eV for the hydridocarbonyl cluster compounds $Os_3(CO)_{10}H_2$ and $Os_4(CO)_{12}H_4$ suggesting that the $\mathrm{M}\overset{H}{\frown}\mathrm{M}$ bonds are essentially of a localised nature. The solid state He-II spectrum of $Ir_4(CO)_{12}$ [6] which is isoelectronic with $Os_4(CO)_{12}H_4$ shows no ionization bands in this region. The importance of the metal—metal bonding in addition to metal—hydrogen bonding in this class of compound has also been inferred from neutron diffraction studies, and Bau has proposed that the bridging hydrogen bond be represented as in (III) by analogy with boranes [2].

(III)

The comparison of the He-I and He-II spectrum of $Re_3(CO)_{12}H_3$ (cf. Figures 1b and 1c) shows a large decrease in intensity of the band at ca. 12 eV suggesting that $\mathrm{Re}\overset{H}{\frown}\mathrm{Re}$ bonds are localised predominantly on the hydrogen atom rather than the metal atoms, since the ionization cross-section of a hydrogen 1*s* orbital is known to drop considerably between He-I and He-II wavelengths [7].

The presence of the metal-hydrogen ionizations in a window of the metal carbonyl UV photoelectron spectrum not only has assisted the present valence study, but also could have significant implications for the study of metal-surfaces involved in catalytic reactions of CO and H_2. In such cases the identification of metal-hydrogen in addition to metal-carbonyl bonds could considerably assist identification of molecular species on the surface.

The support for the three-centre two electron bond concept for $\mathrm{M}\overset{H}{\frown}\mathrm{M}$ bonds provided by photoelectron and crystallographic studies, suggests the development of a topological treatment of metal-hydrido clusters analogous to that proposed by Lipscomb [8] for boranes, B_pH_{p+q}. Such a development is particularly germane in view of the isolobal nature of $M(CO)_3$ and B-H fragments and the structural implications derived from this principle [9]. For the cluster $\{M(CO)_3\}_pH_q$ the isolobal principle suggests that each $M(CO)_3$ fragment contributes three orbitals and n electrons for skeletal bonding (where n = number of metal valence electrons – 6). Furthermore, the following common two-electron bond types can be defined for hydrido-cluster compounds:

s three centre M-H-M bonds

t three centre $M\overset{M}{\overset{|}{\text{———}}}M$ bonds

y two centre M—M bonds

x four centre $M{-}H\langle{}^{M}_{M}$ bonds

It follows from the electron requirements for these bonds and the full utilization of metal orbitals (which is equivalent to assuming the 18 electron rule) that it is possible to derive the equations of balance given in Table 1 for neutral and charged cluster compounds. The resultant equations are very similar to Lipscomb's *styx* formulae [8] but differ in the important sense that the identity of the metal atom is left as a variable defined by n, which is specified for actual examples.

TABLE 1

EQUATIONS OF BALANCE FOR HYDRIDO-CLUSTER COMPOUNDS

$\{M(CO)_3\}_pH_q$		$\{M(CC)_3\}_pH_q^{z+}$	
$(x = q - s,\ t = (3-n)p - q - x,\ 2y = np - q - 2t)$		$(x = q - s,\ t = (3-n)p + z - q - x,\ 2y = (np - z) - q - 2t)$	
Examples (*styx* numbers in brackets)[a]			
$Ru_4H_4(CO)_{12}$	(4020)	$Re_4H_6(CO)_{12}^{2-}$	(6000)
$Re_4H_4(CO)_{12}$	(0004)		
$Ru_6H_2(CO)_{18}$	(0232)		
	(1321)		
	(2410)		
$\{M(CO)_4\}_pH_q$[b]		$\{M(CO)_4\}_pH_q^{z+}$	
$(x = q - s,\ t = (2-n)p - q - x,\ 2y = np - q - 2t)$		$(x = q - s,\ t = (2-n)p + z - q - x,\ 2y = (np - z) - q - 2t)$	
Examples			
$Re_2(CO)_8H_2$	(2000)	$Re_3H_2(CO)_{12}^{-}$	(2010)
$Mn_3(CO)_{12}H_3$	(3000)	$Re_3H(CO)_{12}^{2-}$	(1020)

[a] The sum of the *styx* numbers is equal to the number of skeletal electron pairs which defines the metal polyhedral skeleton. [b] Each $M(CO)_4$ fragment contributes two orbitals and 6-number of metal valence electrons for skeletal bonding (i.e. it is isolobal with BH_2).

For example, in $\{Re(CO)_3\}_4H_4$, $p = 4$, $q = 4$ and $n = 1$ giving rise to the following equations of balance: $x = 4 - s$, $t = 8 - 4 - x$, $2y = 4 - 4 - 2t$, and the unique solution $s = 0$, $t = 0$, $y = 0$ and $x = 4$, i.e. all four bridging hydrogen atoms triply bridged. In contrast, for $\{Ru(CO)_3\}_4H_4$, $p = 4$, $q = 4$ and $n = 2$ and the equations of balance lead to the alternative unique solution: $s = 4$, $t = 0$, $y = 2$ and $x = 0$, i.e. four edge bridging hydrogen atoms.

Therefore, this topological treatment clearly distinguishes the different geometries of $Re_4(CO)_{12}H_4$ and $Ru_4(CO)_{12}H_4$ as determined by crystallographic studies [10]. Table 1 also illustrates the extension of this methodology to charged hydrido-clusters and those with empirical formula $\{M(CO)_4\}_pH_q$. For many of the smaller cluster compounds the equations of balance lead to unique solutions such as those above, however, in common with boranes there are alternative solutions possible for the higher homologues, see $Ru_6H_2(CO)_{18}$ in Table 1 for example. The relationship of these possibilities to the fluxional behaviour of the hydrido cluster compounds is currently being explored.

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