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THEORETICAL AND STRUCTURAL STUDIES ON ORGANOMETALLIC CLUSTER MOLECULES

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ABSTRACT. The development of topological rules for hydrido-metal cluster compounds, similar to those proposed by Lipscomb for boron hydrides, is shown to be a direct consequence of the multicentre bonding in bridged hydrido-metal bonds. Evidence for this localised view of the bonding has been obtained from U.V. photoelectron spectral studies of the hydrido-carbonyl cluster compounds $Re_3(CO)_{12}H_3$, $Os_4(CO)_{12}H_4$ and $Os_3(CO)_{10}H_2$. The bonding in interstitial hydrido- cluster compounds, e.g. $Co_6(CO)_{15}H^-$, is also discussed in relation to the unusual chemical shift observed for the hydrido-ligand in this class of compound. Theoretical and preparative studies on metal centred cluster compounds, particularly of gold, are also discussed.

A number of key structural determinations in the 1960's laid the foundations of our present understanding of the geometries of metal-hydrogen bonds in mononuclear transition metal complexes. X-ray investigations (Refs. 1-3) showed hydrogen to be a stereochemically active ligand occupying a distinct coordination site and two important neutron diffraction studies (Refs. 4 & 5) established that the M-H bond has a length of 1.6-1.7Å. More recently, X-ray and neutron studies on polynuclear metal cluster compounds with bridging hydrido- ligands particularly by Bau, Churchill, Dahl, Williams and their coworkers (Ref.6) has resulted in a clearer definition of the geometric characteristics of the bridged metal-hydrogen bond and the suggestion that such bonds closely resemble the three centre two electron bond which has been established for the bridging hydrogen bonds in boranes (Ref. 7). The nature of this interaction and its proposed representation are illustrated below in (1).

(1)

The suggestion of a two-electron three-centre bond for $M\overset{H}{\smile}M$ suggests the development of a topological treatment of metal-hydrido-cluster compounds analogous to that proposed by Lipscomb (Ref. 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 (Ref. 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 = number of three centre M-H-M bonds;

t = number of three centre $M\overset{M}{\frown}M$ bonds;

y = number of two centre M-M bonds; and

x = number of four centre $M{-}H\begin{array}{l}\diagup M\\ \diagdown M\end{array}$ bonds.

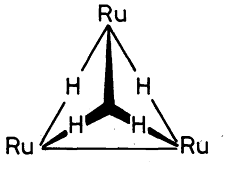
It follows from the electronic requirements for these bonds and the full utilization of metal valence orbitals (which is equivalent to assuming the 18 electron rule) that it is possible to derive the equations of balance given in Table I, for neutral and charged cluster compounds. The resultant equations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

For example, in $\{Re(CO)_3\}_4H_4$, because p = 4, q = 4 and n = 1 the following equations of balance pertain

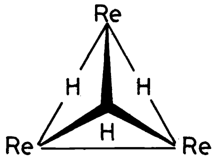
$$\begin{aligned} x &= 4 - s \\ t &= 8 - 4 - x \\ 2y &= 4 - 4 - 2t \end{aligned}$$

and give rise to the unique solution S = 0, t = 0, y = 0 and x = 4; i.e. all four hydrogen ligands are triply bridged. In contrast, for $\{Ru(CO)_3\}_4H_4$ p = 4, q = 4, and n = 2 and the three equations of balance lead to the alternative unique solution; s = 4, t = 0, y = 2 and x = 0, i.e. four edge bridging hydrogen ligands.

Therefore this topological treatment clearly distinguishes the different geometries of $Re_4(CO)_{12}H_4$ and and $Ru_4(CO)_{12}H_4$ inferred from crystallographic analyses and illustrated below (Ref. 10).



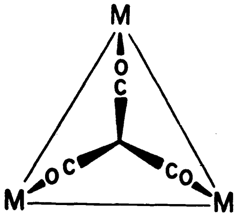
Edge Bridging



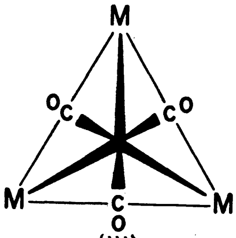
Face Bridging

These compounds provide a particularly striking example of the way in which electronic effects govern the placement of hydrido- and carbonyl ligands around the metal cluster, because steric considerations must be almost identical for two such closely related compounds. Table I also illustrates the extension of this methodology to charged hydrido- cluster compounds 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 $Ru_6(CO)_{18}H_2$ in Table I for example. The relationship between these alternative solutions and the fluxional behaviour of this class of cluster compound is currently being investigated.

The usefulness of such a simple model for classifying the structures of hydrido- carbonyl cluster compounds and exploring possible reaction intermediates is evident, but inherent in its assumptions are certain limitations which have to be recognised. Most serious of all is its implicit assumption that the 18-electron rule will be followed. In complexes such as $Ni_4H_3(\eta\text{-}C_5H_5)_4$, where the 18-electron rule is not followed, it is necessary to perform detailed molecular orbital calculations in order to account for its ground state electronic properties. Such calculations based on the extended Hückel approximation have recently been reported (Ref. 10) and have accounted for the paramagnetism of this hydrido- cluster. This type of calculation has also proved useful for understanding the electronic factors responsible for the very different conformations of the carbonyl ligand in $Re_4(CO)_{12}H_4$ (II) and $Ru_4(CO)_{12}H_4$ (III) illustrated below.



(II)



(III)

TABLE I

Equations of balance for hydrido-cluster compounds

$\{M(CO)_3\}_p H_q$	$\{M(CO)_3\}_p H_q^{z+}$
$x = q-s$	$x = q-s$
$t = (3-n)p-q-x$	$t = (3-n)p+z-q-x$
$2y = np-q-2t$	$2y = (np-z)-q-2t$

Examples (styx numbers in brackets)*

$Ru_4H_4(CO)_{12}$	(4020)	$Re_4H_6(CO)_{12}^{2-}$	(6000)
$Re_4H_4(CO)_{12}$	(0004)		
$Ru_6H_2(CO)_{18}$	(0232) (1321) (2410)		

$\{M(CO)_4\}_p H_q$**	$\{M(CO)_4\}_p H_q^{z+}$
$x = q-s$	$x = q-s$
$t = (2-n)p-q-x$	$t = (2-n)p+z-q-x$
$2y = np-q-2t$	$2y = (np-z)-q-2t$

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)

* The sum of the styx numbers is equal to the number of skeletal electron pairs which defines the metal polyhedral skeleton.

**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).

Recently, Dr. J. C. Green and myself have completed the first U.V. photoelectron spectral measurements on hydrido-metal carbonyl cluster compounds and have thereby provided additional evidence for the three-centre $M\overset{H}{\frown}M$ bonding model proposed above (Ref. 11).

A comparison of the He-I photoelectron spectra of $Re_3(CO)_{12}H_3$ and $Os_3(CO)_{12}$, which are isoelectronic, is given in Figures 1a and 1b. Both spectra show bands in the 13 - 16eV region, which can be attributed to ionizations from 5σ and 1π CO ligand molecular orbitals. In addition bands at 8.45 - 9.60eV for $Re_3(CO)_{12}H_3$ and 9.24 - 10.44eV for $Os_3(CO)_{12}$ can be assigned to ionizations from metal-CO back bonding orbitals, which are derived from the t_{2g} set of the parent octahedral metal carbonyl fragments by analogy with other mono- and bi-nuclear carbonyl complexes, e.g. $Mo(CO)_6$ and $Re_2(CO)_{10}$. The ionizations at 7.83 and 8.33eV in $Os_3(CO)_{12}$, which have been assigned to the Walsh-like metal-metal bonding molecular orbitals of a_1' and e' symmetry (Ref. 11) (see Figure 2) are absent in $Re_3(CO)_{12}H_3$ and are replaced by a new broad band at ca 12eV, which is attributed to the three-centre Re—H—Re bonds. Similar bands have been observed in the range 11.9 - 12.7eV for the hydrido- cluster compounds $Os_3(CO)_{10}H_2$ and $Os_4(CO)_{12}H_4$ suggesting that the M–H–M bonds are essentially of a localised nature.

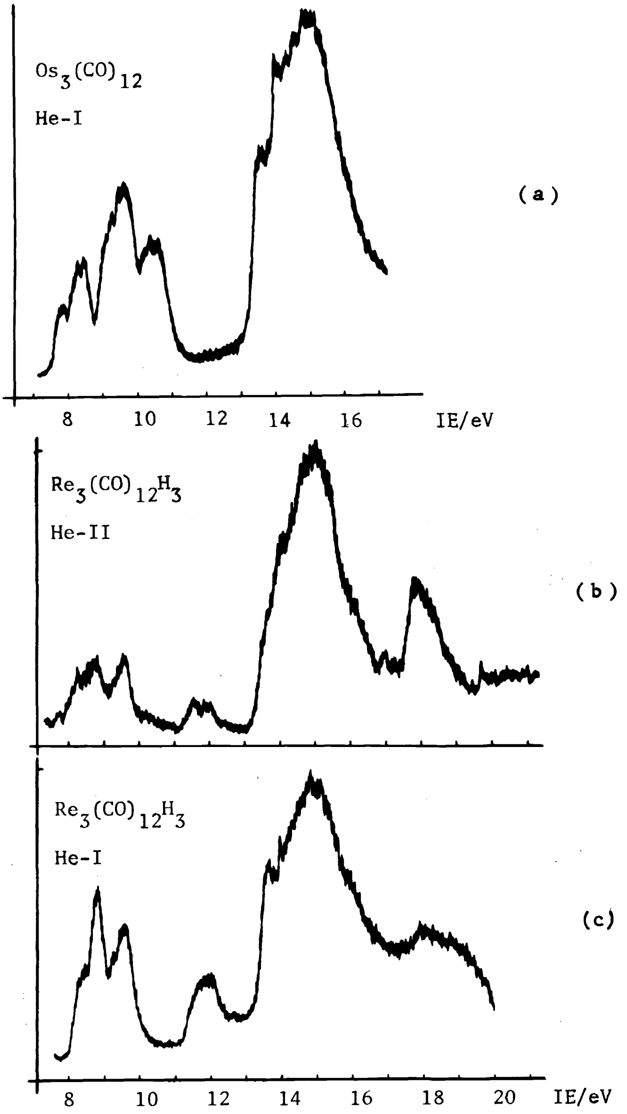


Figure 1. He-I spectrum of $Os_3(CO)_{12}$ and the He-I and He-II spectra of $Re_3(CO)_{12}H_3$.

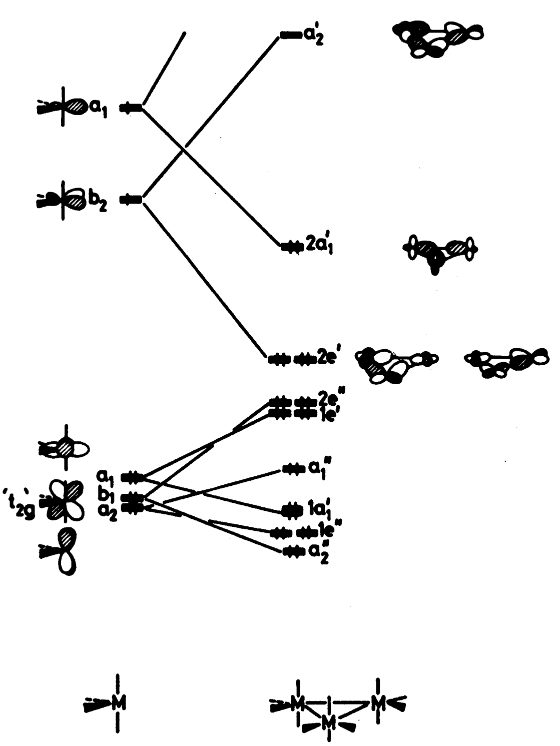
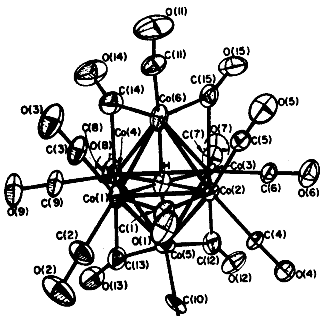


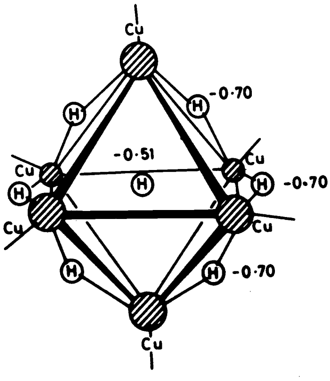
Figure 2. Molecular orbitals for $Os_3(CO)_{12}$ (Ref. 10)

A comparison of the He-I and He-II spectra of $Re_3(CO)_{12}H_3$ (c.f. Figures 1b and 1c) shows a large decrease in intensity of the band at *ca* 12eV in the latter. This suggests that the M—H—M bond, as illustrated in (I) above, is localised predominantly on the hydrogen atom rather than the metal atoms, since the ionization cross section of a hydrogen 1s orbital is known to drop considerably between He-I and He-II wavelengths (Ref. 11).

The recent characterisation by neutron diffraction techniques of the $[Co_6(CO)_{15}H]^-$ ion (IV), has shown it to have a hydrido- ligand located right at the centre of the metal polyhedron (Ref. 12). The unusual ^{1}H chemical shift reported for the hydrido- ligand in this complex (-13ppm) prompted us to complete a molecular orbital calculation on the hypothetical, but related, ion $[Cu_6H_7(PH_3)_6]^+$, derived from the known cluster $Cu_6H_6(PPh_3)_6$ by the addition of an "interstitial" hydride ligand. This compound was chosen as a model because it provided an internal comparison between edge bridging and the "interstitial" hydrogen ligands.



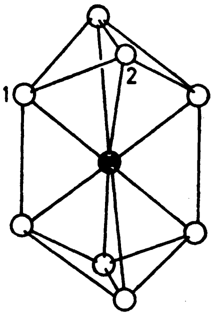
(IV)



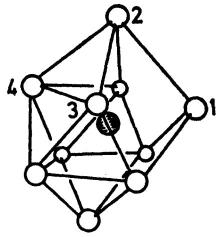
(V)

The computed atomic charges in this ion shown in (V) suggest little difference in the electron density on the peripheral and central hydrogen ligands, and therefore the unusual chemical shift of the latter is unlikely to be a consequence of the multicentre bonding between it and the octahedron of metal atoms. One may speculate that the observed down field shift might originate from second order paramagnetic effects arising from low lying excited states in the cluster. Similar down field shifts have been reported for the internal protons in 16-annulene and have been rationalised in the same manner (Ref. 13).

Interstitial bonding is not limited to hydrogen and the incorporation of carbon, nitrogen and even other metal atoms into the centre of the clusters has been an important feature of recent developments in cluster chemistry. An analysis of the bonding in gold cluster compounds of the type illustrated in (VI) and (VII) showed (Ref. 14) that in common with the hydrogen ligand the central gold atom utilises primarily its 6s orbital in its interactions with the peripheral gold atoms. An effect which is illustrated effectively in Figure 3 by the large stabilisation of the A_g orbital in $Au_9(PPh_3)_8^{3+}$.



(VI)



(VII)

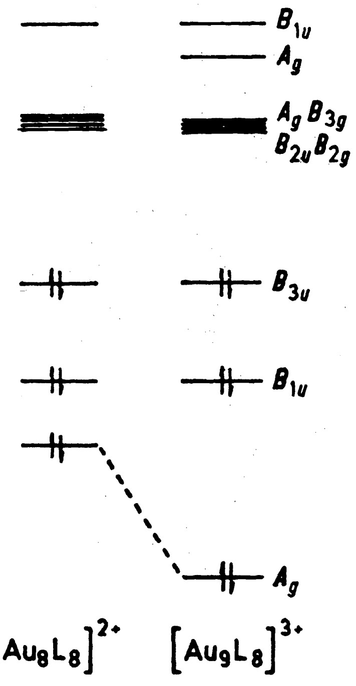


Figure 3. A schematic illustration of the interaction of the 6s orbital of the central gold in $Au_9(PPh_3)_8^{3+}$ with the orbitals of the peripheral atoms.

The molecular orbital analysis of the gold cluster compounds also led to a number of interesting predictions, for example, that the cluster compound $[Au_{13}(PPh_3)_{12}]^{5+}$ has the correct electronic requirements to stabilise a centred icosahedral geometry. We have sought to verify some of these predictions by initiating a programme of research to establish new synthetic routes to gold cluster compounds. We have found that the compound Ti(Toluene)$_2$, first prepared by Dr. Malcolm Green and his coworkers, is a most useful general reagent for the synthesis of gold cluster compounds according to the following scheme:

$$AuCl(PPh_3) \xrightarrow[\text{2. EtOH/NaX}]{\text{1. Ti(Toluene)}_2/C_6H_6} [Au_8(PPh_3)_8](BF_4)_3,\ [Au_{11}(PPh_3)_8Cl_2]PF_6$$

$$AuCl(PMePh_2) \xrightarrow[\text{2. EtOH/NaX}]{\text{1. Ti(Toluene)}_2/C_6H_6} \begin{array}{l} Au_{12}(PMePh_2)_8Br_6 \\ [Au_{13}(PMePh_2)_8Cl_4]BF_4 \\ [Au_{13}(PMePh_2)_{10}Cl_2](PF_6)_3 \end{array}$$

These compounds are still being investigated and characterised by X-ray crystallographic techniques. For this class of compound the latter are not trivial in view of the high molecular weights and large unit cell volumes.

The use of the more conventional reducing agent $NaC_{10}H_8$ with $AuI(PPh_3)$ has led to the isolation of the dimeric gold compound $Au_2(PPh_3)_2$ according to the following equation:

$$2AuI(PPh_3) + 2NaC_{10}H_8 \longrightarrow Au_2(PPh_3)_2 + 2NaI + 2C_{10}H_8$$

The result of the X-ray crystallographic analysis on crystals of this compound (Ref. 15) has confirmed the presence of the Au-Au metal-metal bond (see Figure 4). This gold complex is isoelectronic with the ubiquitous mercurous halides Hg_2X_2 which have been known for almost a century. The gold complex differs in an important structural sense, however, the P-Au-Au-P atom sequence adopts a trans-bent geometry rather than the linear sequence which would have been predicted from the mercurous structures.

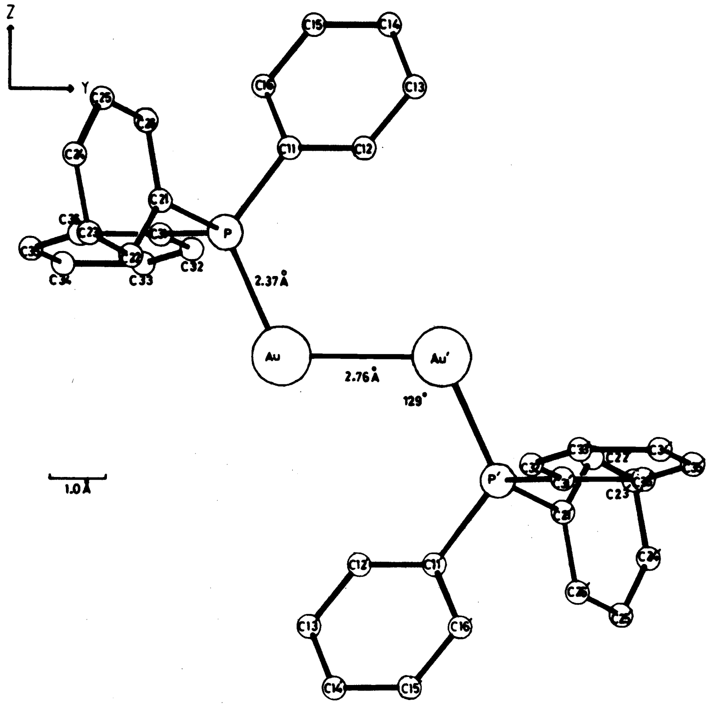


Figure 4. Molecular structure of $Au_2(PPh_3)_2$

A detailed examination of the structure suggests that the distortion in the gold complex may arise from weak supplementary interactions between the gold atoms and ortho-hydrogens of the phenyl rings in the solid state.

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