The Role of Bridging Carbonyls in Metal Cluster Compounds

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The bonding in clusters containing bridging carbonyl groups is analysed using a fragment molecular approach and the reasons for the more widespread occurrence of this co-ordination mode in clusters of the lighter transition metals are discussed.

The stoicheiometries and metal polyhedra observed in transition metal carbonyl clusters[1] have been rationalised from a molecular orbital viewpoint by numerous workers[2-5] and are now well documented. Such analyses have been less successful
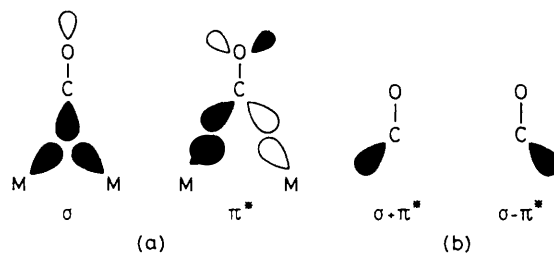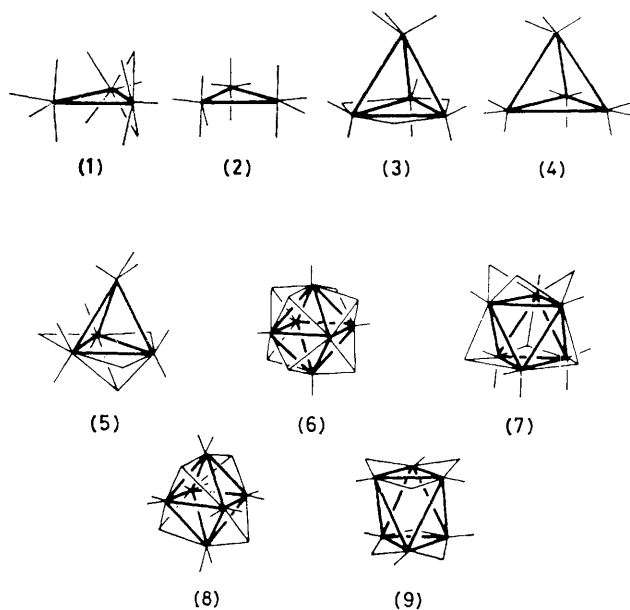
Figure 1. (a) An illustration of the bonding in an M–(μ-CO)–M system. The ligand HOMO interacts with an in-phase combination of metal orbitals whilst one component of the π^* LUMO's interacts with an out-of-phase combination of metal orbitals. (b) The bridging CO ligand effectively provides two orbitals of σ-symmetry with respect to metal–ligand bonding.

in understanding the finer details of cluster geometry: for example why $Fe_3(CO)_{12}$ (1) and $Os_3(CO)_{12}$ (2) have different geometries as do $Co_4(CO)_{12}$ (3) and $Ir_4(CO)_{12}$ (4).

Johnson[6,7] has argued that the structural differences between (1) and (2) and between (3) and (4) are determined by the ability of the metal polyhedron to fit into a close-packed arrangement of carbonyl ligands. Although steric effects are undoubtedly important in cluster chemistry,[8] the analysis presented here suggests that the difference may be at least in part electronic in origin.

The bonding in clusters containing terminal carbonyl ligands only is readily analysed in terms of the isolobal analogies[9] between CH_{n-2} and $M(CO)_n$ fragments. The presence of bridging carbonyls has generally been glossed over in the past. As shown in Figure 1(a) a bridging carbonyl ligand is effectively isolobal with methylene[10] as illustrated by the isostructural and isomorphous nature of $Os_3(CO)_{11}(CH_2)$[11] and $Fe_3(CO)_{12}$ (1). From a localised viewpoint [see Figure 1(b)] the μ_2-CO and μ_2-CH$_2$ ligands can be considered to provide two orbitals of σ-symmetry with respect to metal–ligand bonding, each of which contains one electron. In a similar fashion a μ_3-carbonyl ligand can be considered to furnish three localised hybrid σ-orbitals and to be isolobal with CH$^+$.

The usual form of the isolobal analogy assumes that the orbitals of an ML_n fragment consist of n M–L σ-bonding MO's, three non-bonding MO's (the remnants of the t_{2g} set in an octahedral ML_6 complex), and $6 - n$ frontier orbitals. Hoffmann[9] has pointed out however that the isolobal analogy is not a one-to-one mapping and that the t_{2g} set, although less directional than the frontier orbitals, may still become involved in the bonding. In this case the isolobal nature of the fragment is determined by the number of electrons in the t_{2g} and frontier orbitals. Thus a d^6 ML_5 fragment is isolobal with a d^8 ML_4 fragment and hence with CH_2.

The tendency to utilise the t_{2g} orbitals in bonding will decrease from iron to osmium. In the case of ruthenium and osmium the remnants of the t_{2g} set are strongly stabilised by π-bonding with the terminal carbonyl ligands, whereas the more contracted nature of the 3d orbitals in iron makes them less effective in π-bonding. Furthermore the formation of a larger number of M–L σ-bonds is favoured for the lighter element because each individual bond is weaker than for the heavier

congeners and because there is a greater p–d mixing in the case of iron where the orbitals are closer in energy.

Thus $Fe_3(CO)_{12}$ can be considered to consist of two d^6 square pyramidal $Fe(CO)_3(L')_2$ fragments (where L' represents a one electron σ-donor ligand equivalent to half a bridging carbonyl ligand) and one d^8 C_{2v} $Fe(CO)_4$ fragment, whereas the heavier elements form trinuclear clusters based on three of the latter d^8 ML_4 fragments.

Fragments such as d^9 $M(CO)_3$ and d^7 $M(CO)_2(L')_2$, which are isolobal with CH, will form tetrahedral clusters. Iridium preferentially forms d^9 $M(CO)_3$ fragments, in which π-bonding is maximised, accounting for the structure of $Ir_4(CO)_{12}$, whilst cobalt and rhodium form clusters with one such $M(CO)_3$ fragment and three d^7 $M(CO)_2(L')_2$ fragments in which the σ-bonding capability is maximised. Replacing carbonyl ligands by triphenylphosphine, which is a poorer π-acceptor, destabilises the remnants of the t_{2g} set and should encourage the formation of a larger number of σ-bonds. Interestingly the structure of $Ir_4(CO)_{10}(PPh_3)_2$ is analogous to that of $Co_4(CO)_{12}$, with three bridging carbonyl ligands.

Triply bridging carbonyl ligands may be treated in a similar fashion so that the structure of $Fe_4(CO)_{13}^{2-}$, (5), may be derived from one d^9 $Fe(CO)_3^-$ fragment and three d^5 $Fe(CO)_2(L')_2$-$(L'')^{1/3-}$ fragments (where L'' represents a 2/3 electron donor equivalent to one third of a μ_3-carbonyl ligand). The latter d^5 ML_5 fragment is isolobal with CH and a regular tetrahedral geometry results.

Higher nuclearity clusters are also amenable to a similar analysis. For example $Co_6(CO)_{14}^{4-}$, (6), is composed of d^4 $Co(CO)(L'')_4^{1/3-}$ fragments. Such d^4 ML_5 fragments are isolobal with d^8 $M(CO)_3$ and BH fragments. In $Co_6(CO)_{15}^{2-}$, (7), there are three C_{3v} trigonal pyramidal d^6 $Co(CO)(L')_2(L'')^{1/3-}$ fragments and three C_{2v} d^6 $Co(CO)_2(L'')_2^{1/3+}$ fragments. Such fragments are isolobal with BH and an octahedral cluster again results. Six C_{2v} d^6 $Rh(CO)_2(L'')_2^{1/3+}$ fragments also occur in $Rh_6(CO)_{16}$, (8). Finally in $Ni_6(CO)_{12}^{2-}$, (9), there are six T-shaped d^8 $Ni(CO)(L')_2$ fragments, which are formally isolobal with BH and an octahedral cluster again results. Although the T-shaped fragment provides three orbitals for skeletal bonding, the two derived from the t_{2g} set are less effective in bonding than the third, which is a d–p hybrid. This accounts for the fact that the metal polyhedron actually defines a trigonal antiprismatic structure, in which the octahedron is elongated along a C_3 axis.

This idea of treating bridging carbonyls as ligands which furnish two or three σ-donor orbitals appears to provide a satisfactory way of rationalising the different geometries adopted by transition metal cluster compounds within the framework of fragment molecular orbital theory. The approach has

been successfully applied to other, larger, clusters and this will be discussed in a succeeding publication.

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