carbonyls of transition metals from groups 8-10, which may be taken as exemplary cases from the family of carbonyl clusters. The approach adopted here is to consider separately the electronic structure of the metal cluster and the polyhedral shell of ligands, before allowing the valence orbitals of these two fragments to hybridize. This is very convenient for exhibiting the similarities between these cluster species.

The discussion in section 3 can be summarized briefly by saying that the frontier MO's of the bare metal cluster of atomic s- and p-orbital parentage *plus a limited number of d-orbital parentage* contribute to the *cluster-ligand bonding*;[34] this theme will be explored in more detail in the following paper.[42] On the other hand the *electrons occupying the low-energy orbitals below the d-d* gap in the d band of the cluster compound are responsible for the *metal-metal bonding* in the metal cluster core. The principal difference between halides and chalcogenides on the one hand and carbonyls on the other is that, for the former, this d-d gap becomes the HOMO-LUMO gap of the cluster compound, whereas in the carbonyls the antibonding d orbitals weakly hybridized with tangential orbitals of the ligand polyhedron are also occupied, so their HOMO-LUMO gap is related to the s-d gap of the metal cluster (see Figures 1 and 4).

This description is consistent with the general principles[4,27-29,50] that govern bonding between transition-metal atoms with M-M bond lengths close to that found in the equilibrium structure of the bulk metals when the number of d electrons per atom is less than 10:

(i) Electrons occupying MO's of atomic d-orbital parentage produce a net attractive force between neighbouring metal atoms that accounts for the M-M bond energy.

(ii) Electrons occupying MO's of atomic s- and p-orbital parentage produce a net repulsive force between neighbouring metal atoms because those electrons are repelled by the cores of adjacent transition-metal atoms. In cluster compounds the main contribution of the metal atomic s and p orbitals is to the *unoccupied* antibonding cluster-ligand MO's; thereby the number of s and p electrons is kept low, being determined essentially by the d/s,p hybridization of levels below E_{HOMO} (cf. the bulk metals[28,29]). These principles do *not* apply in clusters of main-group elements ($N_d = 0$), or metals from group 11 (for which $N_d = 10$). Palladium is a borderline case because of the narrowness of its d band.[4,50]

The electronic structure of metal cluster compounds can be calculated by typical metal physics methods such as $X\alpha$ or the chemical pseudopotential method; such calculations lead to energy level schemes that seem broadly consistent with spectroscopic and other physical measurements.[2-4,9,10,12,13,16,17,37,43,45,49-51] Some recent extended Hückel parameterizations[11,38] are also consistent with this picture; however, earlier EH calculations that lead to "narrow" cluster d bands cannot be regarded as trustworthy as far as metal-metal bonding is concerned in metal cluster compounds at or near their equilibrium geometries.

The general bonding ideas presented in this paper should be applicable to transition-metal cluster compounds as a whole; in the following paper[42] I shall widen the discussion by examining the relationship of d-electron bonding in metal cluster compounds to the isolobal principle and the analogy with borane clusters.[41] The importance of the d-band levels for the electronic structure of metal cluster compounds has obvious implications for theories of cluster chemistry.

Acknowledgment. It is a pleasure to acknowledge helpful discussions with Prof. O. K. Andersen, Dr. A. J. Stone, Prof. K. Wade, and Dr. A. M. Woolley.

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(52) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confustion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(53) This is a big effect; the bond energy between transition-metal atoms is directly proportional to the d-band width (the energy separation of the lowest bonding MO and the highest antibonding MO originating from atomic d orbitals) and so a factor of 2 means that the bond energy is only half of what it ought to be. Obviously such a result cannot be taken seriously.

(54) For example, the calculations reported in ref 3 gave $E_{2\pi} \approx -8.2$ eV in the free CO molecule. This compares with the following metal s-orbital energies for the $d^{n-1}s^1$ configuration: Fe, -7.10 eV; Co, -7.33 eV; Ni, -7.54 eV; Ir, -11.36 eV; Pt, -11.50 eV.[3,46,47]

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Bonding in Transition-Metal Cluster Compounds. 2. The Metal Cluster-Borane Analogy

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Following the detailed discussion of the transition-metal cluster moiety $M_6(\mu_3\text{-}X)_8$ in the preceding paper, a more general account of the importance of the d electrons in transition-metal cluster chemistry is presented. The putative analogy with borane clusters (and their derivatives) is examined critically. Although an *isolobal* relationship exists between, e.g., BH and appropriate ML_n fragments (e.g. conical $Fe(CO)_3$), *this does not imply* that the BH and ML_n fragments behave in electronically similar ways when cluster formation occurs, even when structurally related clusters are formed. Nonidentical isolobal fragments have orbital differences that manifest themselves in interfragment resonance integrals and require a qualitative distinction to be drawn between the bonding modes and detailed electronic structures of (i) transition-metal cluster compounds and (ii) boranes, carboranes, and their metalla derivatives; an analysis developed in the electronic structure theory of transition-metal systems shows why this is the case. The isolobal principle and Wade's rules owe their generality and utility to being *symmetry-based* statements; the *energetics and details* of the electronic structure of cluster compounds however are a separate matter requiring appropriate methods of theoretical chemistry.

1. Introduction

In the preceding paper, a detailed account of the electronic structure of the transition-metal cluster moiety $M_6(\mu_3\text{-}X)_8$ was presented for X = chalcogen, halogen, and carbonyl ligands.[1] The approach used there was to analyze the orbitals for two fragments, the octahedral M_6 unit and the ligand polyhedron in the absence of the metal cluster core, before allowing the orbitals of the two parts to hybridize. Such an approach builds on recent studies of the electronic structure of transition metals[2-6] and exploits the

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relationship between clusters and the bulk metal. The resulting picture of bonding in metal cluster compounds in general can be summarized as follows: metal cluster MO's of mainly atomic s- and p-orbital parentage, plus a limited, but variable, number of d-orbital parentage, govern the cluster–ligand bonding, while the electrons occupying orbitals in the resulting d band of the cluster compound are responsible for the metal–metal bonding in the metal cluster core.

Such a description may seem surprising when it is recalled that a very popular rationalization of the structural systematics of metal cluster carbonyls, and even some of their chemistry, is based on a formal analogy with the boron hydrides, which, of course, have no d-electron participation in bonding; this approach leads to the skeletal electron pair model.[7-10] On the other hand, the d-electron-bonding model for the metal cluster gives a straightforward basis for the metal cluster ↔ metal surface analogy, which has also been exploited successfully in cluster chemistry. Thus it is important to consider whether, and to what extent, these different approaches can be reconciled. This is the topic of the present paper, which is organized as follows: In section 2 the discussion of the $M_6(\mu_3\text{-}X)_8$ moiety is completed by a brief account of the addition to it of terminal ligands. Then some aspects of the participation of the d-band levels in the bonding and chemistry of metal cluster compounds are described, and the chemical significance of d-band levels is emphasized. This provides the background for our discussion (section 3) of the isolobal principle,[7] and the putative analogy between metal cluster carbonyls and the boranes. Next, the formation of an octahedral metal cluster carbonyl from six $M(CO)_3$ fragments is discussed in section 4, and the paper concludes (section 5) with some general remarks about the theoretical chemistry of the isolobal principle.

2. The d Band in Metal Cluster Compounds

In the octahedral metal cluster there are 12 levels lying above the s–d gap and the s-orbital state $A_{1g}(1)$ (see Figure 1 in ref 1), which are frontier orbitals for the cluster because their energy is relatively low and they can be expected to give good overlaps with ligand orbitals. This suggests that octahedral M_6 cluster compounds may be expected to have 30 + 13 = 43 occupied valence MO's. A more accurate statement is that the bare octahedral M_6 cluster has 11 highly antibonding levels, which normally will have no involvement in cluster–ligand bonding, so that the cluster has *at most* $(6 \times 9) - 11 = 43$ MO's that can participate in the valence electronic structure of metal cluster compounds.[11-16] Of course this statement does not imply that the full set of 30 d-orbital levels of the octahedral metal cluster compound will be occupied nor does it imply that a valence electron count of 86 (=2 × 43) will be the general rule.

(a) Metal Clusters Based on the $M_6(\mu_3\text{-}X)_8$ Moiety. The $M_6(\mu_3\text{-}X)_8$ moiety is found as a fragment of larger cluster structures, and it is appropriate to complete the description of cluster compounds based on this fragment before widening the discussion. As is evident from the results in ref 1 (see Figures 1 and 4 there), there are relatively low-energy LUMO's below the p–p gap (specifically $A_{1g}(3)$, $E_g(3)$, $T_{1u}(4)$) that we have not involved in ligand bonding; because of their metal s- and p-orbital character these cluster MO's could be expected to overlap well with ligand orbitals. Six donor ligands in the exo positions have an octahedral arrangement and can provide orbitals that are very suitable for bonding to the cluster because they match precisely the symmetries of the available cluster MO's just identified; we thus expect favorable cluster–ligand interactions involving the cluster orbitals $A_{1g}(3)$, $E_g(3)$, and $T_{1u}(4)$, leading to six stable bonding molecular orbitals of mainly ligand character that are occupied and six unoccupied antibonding orbitals that are mainly metal s and p orbital in character. After the addition of these terminal ligands, the HOMO for the chalcogenides and halides remains just below or at the d–d gap, and the HOMO for the carbonyls remains at the top of the antibonding metal d levels, assuming that the terminal ligands are two-electron donors.

In the Chevrel phases, a chalcogen atom at a cube vertex in one $M_6(\mu_3\text{-}X)_8$ moiety serves as an exo-terminal ligand to a (tilted) neighboring M_6 cluster; this greatly increases the coordination of the chalcogen atoms and has important consequences for the electronic structure of Chevrel phase crystals. In the halides, exo ligands are either shared by pairs of M_6 clusters as in $Nb_6I_{11} \equiv [Nb_6(\mu_3\text{-}I)_8](I)_{6/2}$, or coordinate to give discrete species such as $Mo_6Cl_{14}^{2-}$. In carbonyls, the exo ligands are taken on to form discrete molecular species such as $Co_6(CO)_{14}^{4-}$ and $Co_4Ni_2(CO)_{14}^{2-}$.

Each ligand in the $M_6(\mu_3\text{-}X)_8$ structure is bonded to a triangular face of metal atoms and as a purely formal matter can be associated with three cluster–ligand bonding MO's; the terminal X ligands that can be added to this structure are each counted as contributing to one cluster–ligand bonding MO. By this counting scheme 30 MO's can be assigned formally to cluster–ligand bonding in the $M_6(\mu_3\text{-}X)_8X_6$ species, leaving a maximum of 13 MO's for the electrons associated with the metal cluster. As we have seen in ref 1, 12 of these lie below the "d–d" gap of the cluster compound and are strongly metal–metal bonding, and there is the much higher energy cluster orbital $A_{2g}(1)$ for which there is no ligand orbital of matching symmetry. In the chalcogenide and halide species the 30 "cluster–ligand bonding MO's" are derived from suitable metal cluster orbitals and the three atomic p orbitals contributed by each of the μ_3-ligands (24 orbitals in all), together with one p orbital contributed by each terminal ligand (6 orbitals in all). In carbonyls such as $Co_6(\mu_3\text{-}CO)_8(CO)_6^{4-}$, 14 cluster–ligand bonding MO's are derived from the carbonyl 5σ orbitals; however the origin of the remaining 16 cluster–ligand bonding MO's is less clear-cut because both the carbonyl 1π and 2π levels are involved in hybridization with the cluster. For the present discussion it will be sufficient to identify the metal orbitals that contribute to metal–ligand bonding (see below).

As seen in ref 1, the 30 cluster–ligand bonding MO's in the chalcogenide compounds lie below the d–d gap of the cluster compound, which is therefore likely to be the HOMO–LUMO gap; the energy level scheme for the halides is similar.[1] Thus the $A_{2g}(1)$ level is irrelevant in these compounds, and the other d-orbital levels above the d–d gap that are formally cluster antibonding can also be disregarded for electron-counting purposes; these species have a maximum of 24 electrons associated with the metal cluster core corresponding to a total of 42 occupied valence MO's for the cluster compound. This maximum number of metal electrons is found in a *discrete* halide cluster species, e.g. $Mo_6(\mu_3\text{-}X)_8(X)_6^{2-}$; such species obey the inert gas rule. There are no examples of discrete chalcogenide clusters with this structure.

When the clusters are linked together by bridging ligands much more variable electron counts are found; there are both halide and chalcogenide materials of this type. Electron-precise (24e) compounds have regular octahedral metal clusters and behave as electrical insulators, electron-deficient (<24e) materials have distorted octahedral metal clusters, and electron-rich materials (>24e) tend to exhibit metal cluster condensation.[17] When the

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clusters are close enough together to permit *intercluster* metal–metal interactions as in the Chevrel phases,[18–20] holes in the cluster d band are delocalized; the electron-deficient compounds behave electrically as metal at ordinary temperatures, and are remarkable high critical magnetic field superconductors at low temperatures. When the clusters are well separated by their bridging ligands (halides), holes in the d band are localized on the clusters, and such materials behave as electrical insulators; they may be either diamagnetic or paramagnetic.[17–21] When there are precisely 24 electrons associated with the metal cluster, as in the halide anions $Mo_6X_{14}^{2-}$, it is possible to speak of 12 classical bonds localized on the 12 edges of the octahedron. For other electron counts a precise match is not possible, and a localized bond picture has to be supplemented by the idea of resonance; for many purposes the MO picture is then preferable. Nevertheless the d^4 hybrid orbital construction that was described in ref 1 remains useful, not least because it helps to focus attention on the crucial role played by the metal d electrons in metal–metal bonding.[1]

The carbonyls derived from $M_6(\mu_3\text{-}CO)_8$ are discrete species such as $Co_6(\mu_3\text{-}CO)_8(CO)_6^{4-}$; these differ from the halide and chalcogenide species in that antibonding cluster d levels above the d–d gap, which are hybridized with the carbonyl π levels, *are occupied*, as is the purely metal cluster orbital $A_{2g}(1)$. The result is that the HOMO–LUMO gap is located at the s–d gap of the cluster carbonyl, and these carbonyls are 86 electron species. As already noted above, 14 of the 43 occupied valence MO's are derived from the carbonyl 5σ orbitals, and the remaining 29 MO's originate from the cluster d band as follows: 12 below the d–d gap responsible for metal–metal bonding, 16 above the d–d gap hybridized with the carbonyl π levels, and the cluster antibonding $A_{2g}(1)$ level, which cannot hybridize with the ligands. The "missing" state from the full set of 30 levels in the bare metal cluster "d band" is the $A_{2u}(1)$ level (d_{xy} parentage), which hybridizes strongly with the ligand orbitals and is, so to speak, swept up in energy into the unoccupied states of the cluster compound where it is the major contributor to an unoccupied cluster–ligand antibonding MO.

(b) $M_6(\mu\text{-}X)_{12}$ Clusters. The particular d-band levels of a metal cluster that are significantly destabilized by cluster–ligand bonding depend crucially on the structure of the ligand polyhedron and its orientation with respect to the metal cluster core, as well as the structure of the metal cluster itself of course. In the octahedral edge-bridged halides, $M_6(\mu\text{-}X)_{12}^{n+}$, the $d_{x^2-y^2}$ cluster levels $E_g(1)$ and $T_{2u}(1)$ (see Figure 1 in ref 1) are sufficiently strongly destabilized by their hybridization with the ligands that they are swept up in energy out of the d band. There then remain only eight d-orbital levels below the new d–d gap—$A_{1g}(2)$, $T_{2g}(1)$, $T_{1u}(1)$, and $A_{2u}(1)$ in order of increasing energy. With the group 5[39] metals Nb and Ta and $n = 2$, there are just enough electrons to make $A_{2u}(1)$ the HOMO of the cluster halide cation.[22,23] Metals to the right of group 5 in the periodic table do not form halides with this structure, presumably because their additional electrons would create a *small* HOMO–LUMO gap in the antibonding part of the d band, and this would not be expected to be stable against pseudo Jahn–Teller distortions.

Interestingly enough, we do find the M_6X_{12} species in the halides of Pt and Pd; since these are d^9s^1 metals, both the metal cluster and the 12 halogen ligands each contribute 60 valence electrons. There are 36 cluster–ligand bonding MO's, which we expect to be fully occupied, and so the remaining electrons are expected to occupy just 24 d-band levels, 8 below the d–d gap as in the group 5 metal halides, and 16 levels in the antibonding part of the d band up to the HOMO–LUMO gap of the compound. Presumably it is the $d_{x^2-y^2}$ level $A_{2g}(1)$ that is "lost" from the upper part of the cluster d band, destabilized by the edge-bridging ligands.

This account of Pt_6X_{12} is of course an extrapolation of what is known for the group 5 metals and needs to be checked by calculations of the type reported by Cotton et al.[22,23] It ignores the differences in orbital energies between group 5 and group 8–10 metals and says that the main distinction between the edge-bridged octahedral clusters of the metals of groups 5 and 8–10 is that the *antibonding* part of the cluster d band lying between the "d–d" gap and the "s–d" gap, which is known to be unoccupied in the former, is fully occupied in the latter. This is certainly consistent with the relatively long metal–metal bonds in the group 8–10 metal halides.[24]

(c) Carbonyl Addition Reactions. The idea that the cluster d band can be strongly modified by the ligand polyhedron offers a rationalization of some important cluster carbonyl chemistry. It is well-known that carbonyl ligands (and other ligands of course) can be added to or removed from a cluster carbonyl, without altering the total valence electron count, for example

$$Co_6(\mu_3\text{-}CO)_8(CO)_6^{4-} + :CO \leftrightarrow Co_6(CO)_{15}^{2-} + 2e^-$$

$$Co_6(CO)_{15}^{2-} + :CO \leftrightarrow Co_6(CO)_{16} + 2e^-$$

In passing from $Co_6(CO)_{14}^{4-}$ to $Co_6(CO)_{15}^{2-}$, or $Co_6(CO)_{15}^{2-}$ to $Co_6(CO)_{16}$, the total number of valence electrons remains unchanged but the number of cluster–ligand bonding MO's derived from the carbonyl 5σ orbitals is increased by one. Although the structure of $Co_6(CO)_{15}^{2-}$ is not derived from that of $Co_6(CO)_{14}^{4-}$ by simply adding on a carbonyl ligand to a vacant site, we know that fluxional motions of the carbonyl polyhedron do not disturb the main features of the electronic structure;[13,14,25] it seems reasonable therefore to assume that we can discuss the *initial* attack on a rigid $Co_6(CO)_{14}^{4-}$ ion and draw conclusions valid for $Co_6(CO)_{15}^{2-}$ without explicitly discussing the resulting structural modifications of the ligand polyhedron (and similarly for $Co_6(CO)_{15}^{2-} \leftrightarrow Co_6(CO)_{16}$). Steric considerations suggest that the initial attack by the ligand is directed at an *edge* of the metal octahedron and involves the overlap of the ligand's (radial) 5σ orbital with a suitable metal cluster orbital; from the example of the edge-bridged halides $M_6(\mu\text{-}X)_{12}$ just discussed, we see that the probable candidate is derived from the $d_{x^2-y^2}$ orbitals of the two metal atoms making up the edge.

The overlap of the carbonyl 5σ orbital with this localized d orbital leads to a strong bonding combination, which we expect to be mainly carbonyl 5σ, and an antibonding combination, which is mainly $d_{x^2-y^2}$. Initially both of the participant ligand and cluster orbitals are occupied, but since the total number of valence electrons is the same in the adduct as in the reactant carbonyl, we infer that the antibonding combination is sufficiently destabilized that it is energetically unfavorable for it to retain its two electrons. The net result is that an orbital is added to the low-lying set of cluster–ligand bonding orbitals, while one is lost from the occupied part of the d band of the cluster compound, leaving no overall change in the number of occupied valence MO's but a reduction of two in the charge on the cluster carbonyl. Thus the numbers of occupied d-band levels in $Co_6(CO)_{14}^{4-}$, $Co_6(CO)_{15}^{2-}$, and $Co_6(CO)_{16}$ should be 29, 28, and 27 respectively; these results are consistent with the discussions of Lauher[15] and Mingos,[11]

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although these writers made nothing of the participation of the cluster d band in cluster chemistry.

The above argument can obviously be generalized to cover other cluster carbonyl species and/or other ligands, and it follows that this sort of dynamic rearrangement of the d-band levels could be expected to occur wherever a ligand adds on to, or leaves, a cluster carbonyl without a concomitant change in the valence electron count. Transition-metal cluster carbonyls of given metal nuclearity commonly do have a fixed valence electron count; the existence of numerous examples of cluster carbonyls acting as sources or sinks for electrons (by taking on or losing ligands) points to the ease with which the cluster d band participates in the process described above. However more quantitative theoretical analysis of cluster chemistry on these lines will require (i) the results of accurate electronic structure calculations using methods capable of describing the cluster d band *and* (ii) appropriate experimental work, for example photoelectron spectroscopy and visible/UV absorption spectroscopy. At the moment the amount of such information is still rather limited.[34-37]

Since the metal cluster d band has been identified as playing an essential role in cluster chemistry, it is now appropriate to examine the description of metal cluster bonding that has emerged from an analogy between metal cluster compounds and isostructural boranes. This is the concern of sections 3 and 4.

3. Cluster Bonding and the Isolobal Principle

It is convenient to begin by reviewing briefly the bonding in borane polyhedra, which are clusters of BH units and H atoms disposed such that the BH bonds lie on radial directions from the polyhedron center. Each B atom can be equipped with two sp_z hybrids together with its p_x,p_y atomic orbitals. In a BH unit therefore, one of the sp_z hybrids is used for bonding with the H atom, and there remains one sp_z hybrid point toward the polyhedron center together with a pair of atomic p orbitals perpendicular to this, oriented tangentially with respect to the pseudospherical surface of the polyhedron. If we bring together *m* of these units into a *closo*-polyhedral structure, it follows from general arguments[9,13,14] that there will be $m + 1$ bonding MO's, and $2m - 1$ strongly antibonding MO's arising from the $3m$ atomic orbitals that participate in skeletal interactions. The octahedral borane cluster ($m = 6$) $B_6H_6^{2-}$, for example, has the electronic configuration

$$\underbrace{(A_{1g})^2(T_{1u})^6(E_g)^4}_{\text{6 B-H bonds}} \qquad \underbrace{(A_{1g})^2(T_{1u})^6(T_{2g})^6}_{\text{7 skeletal bonding orbitals}}$$

together with 11 highly antibonding MO's of symmetries E_g, T_{1u}, T_{1g}, and T_{2u}, which are unoccupied in the ground electronic state.

An exactly similar argument rationalizes the bonding in the *closo*-carborane clusters $C_2B_{p-2}H_p$ that are related to the *closo*-borane anions $B_pH_p^{2-}$, since BH and CH units can be described by similar sets of hybrid orbitals. Moreover it has become evident that a wide range of other atoms and groups can substitute for the BH or CH groups of boranes and carboranes. Neutral analogues of BH include $Fe(CO)_3$, $Co(\eta^5\text{-}C_5H_5)$, $Ni(PR_3)_2$, $BeNMe_3$, AlR, GaR, Sn, and Pb, all of which can function as sources of two electrons when required to contribute three atomic orbitals to cluster bonding. Units capable of taking the place of CH units in carborane clusters, and also functioning as sources of three electrons and three atomic orbitals, include $Co(CO)_3$, $Ni(\eta^5\text{-}C_5H_5)$, $Cu(PR_3)_2$, BCO, P, As, and Sb.[9,26] Of particular interest here is the fact that this chemical behavior is not restricted to the transition-metal *tricarbonyl* fragments $Fe(CO)_3$ and $Co(CO)_3$; $M(CO)_n$ (n = 2–5) fragments with suitable metals can all play a substitutional role in the formation of metallaboranes and metallacarboranes.

These aspects of cluster chemistry are rationalzed in terms of the *isolobal principle*:[27,28] fragments are said to be isolobal if they have equal numbers of frontier orbitals of similar symmetry, properties, energies, and extent in space. *Other things being equal*, the interactions between such fragments can be expected to issue in isostructural polyhedral clusters.[7,32] A conical $M(CO)_3$ fragment is regarded as being isolobal with a BH unit, in that it provides one unique ($sp_zd_{z^2}$) hybrid orbital pointing along the 3-fold axis away from the carbonyl ligands, and a pair of pd hybrid orbitals (p_xd_{xz} and p_yd_{yz}) as the counterparts of the radially oriented sp_z and tangential p_x and p_y orbitals of a BH unit. Of course, apart from the three orbitals participating in metal–ligand bonding and the "skeletal-bonding" orbitals just identified, the $M(CO)_3$ fragment also has three other d-orbitals (d_{xy}, $d_{x^2-y^2}$, d_{z^2}), but these apparently have a nonbonding role in metallaborane and metallacarborane clusters and could be treated separately from the chemical (skeletal) bonding as in the ligand field theory of mononuclear transition-metal complexes.[29]

This observation however should remind us of the importance of the *chemical context* when discussing fragments with different numbers and types of atomic orbitals. Although isolobal, a conical metal tricarbonyl fragment $M(CO)_3$, e.g. M = Fe, and BH are electronically similar in a functional sense only on two assumptions, namely that (a) three valence orbitals of the $M(CO)_3$ fragment must be "non–bonding" or nearly so and (b) the sets of (three) skeletal orbitals in BH and conical $M(CO)_3$ must interact with other fragments in a similar fashion. A priori, the validity of these assumptions is governed by the *local bonding environment* of the BH and $M(CO)_3$ fragments, i.e. *the chemical nature of the species with which they are to interact* and must be investigated case by case. While there are few grounds for concern in the case of metallaboranes and metallacarboranes, transition-metal cluster compounds formed exclusively from ML_n fragments stand out as being *qualitatively* different from other clusters as far as their electronic structure is concerned. Of course there are numerous similarities in *geometric* structure between transition-metal and main-group-element cluster compounds, and these have important implications for the division between bonding and antibonding *molecular orbitals* in such clusters.[13,14,24,25] However, as was shown in ref 1, the cluster bonding, and very likely the cluster chemistry, in transition-metal systems is dominated by the participation of the metal d orbitals in a way that, of course, is simply not possible in main-group-element cluster compounds.

One reason for the difference in electronic structure between borane clusters and transition-metal cluster compounds can be pinpointed quite precisely. The isolobal analogy requires that the frontier orbitals of isolobal fragments be similar in their symmetry properties and energetics; for example, ML_5, with a d^7 metal ion, and the conical CH_3 fragment, both have one electron in their HOMO's and have sets of frontier orbitals that appear similar to those of an approaching ligand (or fragment). More precisely the *outer parts* of their frontier orbitals appear similar so that their interactions with a *sufficiently distant* approaching ligand or fragment may be expected to be similar in closely related (but expanded) cluster structures. However the frontier orbitals *near to the nucleus* of the metal atom look very different from those of the methyl radical near the carbon nucleus, and this difference *is* important when bonding with other transition-metal–ligand fragments is considered. (This distinction applies to *any* transition-metal–ligand fragment and an "isolobal" partner formed from main-group elements.) This is one reason why isostructural clusters may be built up from isolobal fragments yet be electronically dissimilar in the sense described in these papers.

It cannot be emphasized too strongly that, in a molecular orbital model, the chemical bonding between atoms is determined by the size of the resonance integrals, $\int d\tau\ \phi_i^*\ \hat{H}\ \phi_j$ of the orbitals ϕ_i and ϕ_j on the participating atoms under the one-electron molecular Hamiltonian, $\hat{H}$. Uncritical belief in *overlap* integrals, $\int d\tau\ \phi_i^*\phi_j$, as even a qualitative guide to estimating resonance integrals, and hence bonding, throughout the periodic table, is to be subject to

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3 hybrids for ligand bonding

$$\left.\begin{aligned} \phi_1 &= \frac{1}{\sqrt{2}}\left(s - p_z\right) \\ \phi_2 &= \frac{1}{\sqrt{2}}\left(-p_x + d_{xz}\right) \\ \phi_3 &= \frac{1}{\sqrt{2}}\left(-p_y + d_{yz}\right) \end{aligned}\right\} \quad \text{metal-ligand antibonding m.o.'s}$$

3 "skeletal" hybrids

$$\phi_4 = \frac{1}{\sqrt{2}}\left(s + p_z\right) \qquad \text{radial}$$

$$\left.\begin{aligned} \phi_5 &= \frac{1}{\sqrt{2}}\left(p_x + d_{xz}\right) \\ \phi_6 &= \frac{1}{\sqrt{2}}\left(p_y + d_{yz}\right) \end{aligned}\right\} \quad \text{tangential}$$

3 "atomic" orbitals

$$\left.\begin{aligned} \phi_7 &= d_{z^2} \\ \phi_8 &= d_{x^2-y^2} \\ \phi_9 &= d_{xy} \end{aligned}\right\} \quad \text{the "}t_{2g}\text{" set of octahedral } M(CO)_6$$

Figure 1.

a crude fallacy. As far as d-electron interactions are concerned, overlap arguments are not reliable, and are not necessary.[1,3,25,30,32] The magnitude of the resonance integral $\int d\tau\, \phi_d^{A*}\, \hat{H}\, \phi_{d'}^{B}$ involving d orbitals ϕ_d^A and $\phi_{d'}^B$ on two adjacent transition-metal atoms A and B, at separation distances close to that found in the equilibrium bulk metals, is *determined by the nature of the d orbitals near the nuclei of the metal atoms A and B and is not related to overlap.*[3,25] This idea may sound completely counterintuitive in a chemical context, but is is a well-established result in the electronic structure theory of transition-metal systems[3] that is supported by detailed computational studies and mathematical analysis, and a *credible* discussion of transition-metal cluster bonding has to take account of it.

We are thus lead to the important conclusion that the *geometric* similarites of metal and nonmetal polyhedral cluster compounds *do not entail* similarities in the details of their bonding and electronic structure, although, as mentioned above, isostructural clusters may be expected to have similar *molecular orbital energy level* schemes (Wade's rules) because of symmetry-based factors discussed by Stone and others.[7,8,11,13-16,25] I shall return to this important idea in section 5.

4. The Cluster Bonding of $M(CO)_3$ Fragments

(a) The Borane Analogy. After the cautionary remarks in section 3, it is now appropriate to give a more detailed account of what can be expected when six $M(CO)_3$ fragments combine to form an octahedral metal cluster carbonyl; an example would be the hypothetical process of forming $Os_6(CO)_{18}^{2-}$ from six $Os(CO)_3$ fragments. The isolobal analogy between $M(CO)_3$ and BH suggests that the nine valence atomic orbitals of the metal atom should be grouped into three sets of hybrid orbitals as shown in Figure 1; these orbitals are the d^2sp^3 hybrids of an octahedral $M(CO)_6$ complex together with its "t_{2g}" set of crystal field d orbitals. The hybrids in Figure 1 refer to a $M(CO)_3$ fragment frozen in the geometry it inherits from the octahedral $M(CO)_6$ species, not the isolated $M(CO)_3$ molecule. The lowest orbitals in energy are the "t_{2g}" set of atomic d orbitals, which cannot be involved in cluster bonding to any significant extent if $M(CO)_3$ is to be electronically similar to BH; ligand field analysis tells us that these levels are only weakly perturbed by the carbonyl ligands.[29] The next three orbitals are the skeletal hybrids derived from the analogy with the BH unit; the radial orbital, ϕ_4, has the same symmetry as the d_{z^2} orbital, ϕ_7, and may hybridize with it, while the pd hybrids, ϕ_5 and ϕ_6, are tangential to the pseudospherical surface on which the apices of the M_6 octahedron lie. Finally because the interaction between ligand and metal orbitals is rather heteropolar, the set ϕ_1, ϕ_2, and ϕ_3 can be taken as a basis for the metal–ligand *antibonding* molecular orbitals; the corresponding bonding combinations, equal in number, resemble closely the ligand 5σ orbitals and have energies lower than any of the orbitals listed in Figure 1.

We now imagine a process in which six of these prepared $M(CO)_3$ fragments are brought together from a large separation into a cluster structure, in such a way that the metal atoms define a regular octahedron at all times. The *initial* driving force toward cluster formation from the fragments arises from the favorable overlaps of the metal s- and p-orbital contributions to the skeletal hybrids because the d-orbital interactions can certainly be neglected at *large separations* of the fragments. In this region of *weak* interaction, conical $M(CO)_3$ is electronically similar to BH, and the resulting distribution of the developing MO's for the cluster carbonyl can be obtained easily from the borane analogy. The low-lying atomic d orbitals $\{\phi_7, \phi_8, \phi_9 \times 6\}$ interact only weakly and form a narrow band of 18 d-electron levels, while the metal–ligand antibonding orbitals of the cluster carbonyl develop smoothly from the set $\{\phi_1, \phi_2, \phi_3 \times 6\}$. Correspondingly there are 18 metal–ligand bonding orbitals at energies below the d-electron levels. The final, and crucial, point is that the set of skeletal orbitals $\{\phi_4, \phi_5, \phi_6 \times 6\}$ can be taken to develop as in the analogous case of octahedral $B_6H_6^{2-}$; i.e., 7 strongly bonding and 11 highly antibonding cluster orbitals result from the interactions between the 18 skeletal orbitals of the fragments. The conclusion is, therefore, that 18 M–CO bonding orbitals, 18 d-electron levels and 7 skeletal bonding levels are separated by an energy gap from the remaining (18 + 11) higher energy (metal–carbonyl antibonding, skeletal antibonding) orbitals. If we make this gap the HOMO–LUMO gap, there results an 86-electron species corresponding to the electrons occupying these 43 low-lying levels.

The discussion so far has referred only to the *weakly interacting fragments at large separations*; we must now attempt to describe the electronic structure of the cluster carbonyl $M_6(CO)_{18}$ *at, or close to, its equilibrium separation.*

The "obvious" account of the bonding in the equilibrium structure according to the borane analogy is as follows: as the fragments come together into the equilibrium structure of $M_6(CO)_{18}$, the energy gap between the 7 skeletal bonding and 11 highly antibonding levels continues to increase, as in (BH) × 6 → $B_6H_6^{2-}$, with the radial, a_{1g}, molecular orbital being the most strongly bonding. The "atomic" d orbitals finally develop into a narrow-cluster d band of 18 levels, while the bonding and antibonding metal–ligand orbitals of the fragments are relatively little changed by the process of cluster carbonyl formation. In this view, which seems to be the conventional inorganic chemistry description,[9-16] the stability of the cluster carbonyl is due to the electrons occupying 7 skeletal bonding orbitals, and for this reason the octahedral metal cluster carbonyl is said to have "7 skeletal bond pairs of electrons". This idea has been extended to give a general classification of metal cluster carbonyls that is analogous to the classification of the borane polyhedra in terms of skeletal bond pairs. However, as has also been noted in the literature,[9-11,15] this description may be purely formal because of the difficulty in actually identifying the molecular orbitals associated with the skeletal bond pairs. Before giving the resolution of this paradox in terms of the d-electron-bonding model, it is appropriate to interrupt the discussion of the $M_6(CO)_{18}$ cluster and review some general theoretical arguments that are pertinent here.

(b) General Theoretical Results for Transition-Metal Systems. The elegant analysis of Stone[13,14] has shown that when *m* sets of valence s, p, and d atomic orbitals are placed in a *closo*-polyhedral arrangement on the surface of a sphere, we can expect there to result $7m + 1$ relatively low-lying molecular orbitals and $2m - 1$ higher energy MO's, subject to certain assumptions about the resonance integrals between the atomic orbitals. The octahedron is a closo polyhedron with $m = 6$, and we may therefore expect an octahedral arrangement of ML_n fragments to lead to $7 \times 6 + 1 = 43$ occupied MO's. The octahedral metal chalcogenide and halide clusters discussed in the preceding paper[1] and in section 2 of this paper show, however, that the utilization of the maximum number (43) of low-lying MO's is not an invariable rule, although it is found empirically to be generally valid for numerous octahedral metal cluster carbonyls of the group 8–10 metals. This variation in behavior is due to the fact that the d band of an octahedral transition-metal cluster, with nearest-neighbor distances comparable to those found in the bulk metal, cannot be treated as an undifferentiated block of 30 levels. Rather, because of the considerable interaction between the d orbitals, it has an important gap dividing it into two groups of energy levels, 13 + 17, and this gap may be utilized as the precursor of the HOMO–LUMO gap of cluster compounds that have less than 43 occupied valence levels. Halides and chalcogenides are distinguished from carbonyls by this difference in valence electron count.

There are two general theoretical arguments that suggest that the hybrid orbitals of the metal–ligand fragments are likely to be strongly affected in the process of metal cluster compound formation; first, the full set of fragment orbitals has numerous degeneracies (and near degeneracies), and second, electron correlation effects are known to be more severe in transition-metal systems than with main-group elements.[25] For our purposes we need to recognize that the main consequence of electron correlation is that, for metal–metal nearest-neighbor distances comparable to that found in the bulk metal *and* in the presence of the carbonyl polyhedron encasing the metal cluster, we can expect the s and p electrons to give rise to only a weakly attractive or even repulsive force between adjacent transition-metal atoms. The large bonding potential due to the very favorable overlaps of valence s and p orbitals at these distances can be cancelled out by the electron–electron repulsion energy between valence s and p electrons and the s- and p-electron density in the *cores* of adjacent metal atoms. This is more important in metal cluster compounds than in the bare metal cluster because of the *confinement* of the metal valence electron density by the ligand polyhedron. This effect can be seen in the recent LMTO (Xα-like) calculations of Nohl et al. on Mo_6 clusters;[17] in a bare metal cluster the $A_{1g}(1)$ bonding molecular orbital arising from the overlap of metal s orbitals usually lies embedded in the lower part of the d band. However when the metal cluster is enclosed in a Watson sphere, which in effect is a simulation of the confinement by a ligand polyhedron, they find that the $A_{1g}(1)$ orbital rises *above* the s–d gap of the metal cluster. The net bonding interaction between the metal atoms is due to the partially filled d band of the cluster. There is also experimental information that is relevant to a discussion of bonding and electronic structure in metal cluster carbonyls; for example, photoelectron spectroscopy reveals the *occupied* d-electron levels in hexanuclear metal cluster carbonyls as extending over 3–4 eV.[31,34–37] The most straightforward explanation for such observations of course is that there is considerable interaction between the d orbitals of the cluster.

For these experimental and theoretical reasons, one ought not to expect to find such a simple correlation between the fragment hybrid orbitals and the molecular orbitals of the cluster carbonyl in its final, equilibrium geometry, as was sketched in section 4(a). In the process of bringing transition-metal carbonyl fragments together to form cluster carbonyls (or other isolobal ML_n fragments), we ought to have recognized the possibility of a dynamic readjustment of the hybridization of the atomic orbitals that contribute to each fragment orbital so that the proportion of *occupied* metal s and p orbitals is kept as low as possible. Thus as ML_n fragments come together adiabatically (in the sense of the Born–Oppenheimer approximation) energy levels of different symmetries are expected to cross, while levels of the same symmetry obey the "noncrossing rule" and have "avoided crossings".[33] The most we should expect of the metal cluster–borane analogy is that the electronic structure of e.g. a hexanuclear octahedral metal cluster compound $(ML_n)_6$, with ML_n isolobal to BH, remains the same as described in section 4(a), at least qualitatively. Here, qualitatively means that even though the relative ordering of energy levels must be expected to change as the fragments come together, there is still the prediction that the HOMO–LUMO gap falls at the same electron count. Thus for $6M(CO)_3 \rightarrow M_6(CO)_{18}$ the prediction is that a substantial energy gap can be maintained between levels 43 and 44 (taking the most stable metal–carbonyl bonding orbital to be level 1).

Type of fragment orbital			Irreducible Representations in O_h
hybrids for ligand bonding	$6 \times \phi_1$	$\rightarrow$	$a_{1g}(3) + e_g(4) + t_{1u}(5)$
	$6 \times \phi_2, 6 \times \phi_3$	$\rightarrow$	$t_{1u}(4) + t_{2g}(3) + t_{1g}(2) + t_{2u}(3)$
"skeletal" hybrids	$6 \times \phi_4$	$\rightarrow$	$a_{1g}(2) + e_g(3) + t_{1u}(3)$
	$6 \times \phi_5, 6 \times \phi_6$	$\rightarrow$	$t_{1u}(2) + t_{2g}(2) + t_{1g}(1) + t_{2u}(2)$
"atomic" orbitals (the "t_{2g}" sets)	$6 \times \phi_7$	$\rightarrow$	$a_{1g}(1) + e_g(2) + t_{1u}(1)$
	$6 \times \phi_8$	$\rightarrow$	$a_{2g}(1) + e_g(1) + t_{2u}(1)$
	$6 \times \phi_9$	$\rightarrow$	$a_{2u}(1) + e_u(1) + t_{2g}(1)$

Figure 2.

On the other hand, the actual contribution of each kind of atomic orbital to the molecular orbitals of the cluster compound is governed by the *energetics* of the interaction process; a quantitative description must be based on accurate calcuations of course, but if we want a qualitative picture, it is reasonable to require it to be in accordance with general theoretical results now known for bonding in transition-metal systems and relevant experimental data for these compounds (photoelectron spectroscopy, visible/UV spectroscopy). The conventional inorganic discussion, modeled on borane clusters, does not meet these criteria.

(c) Orbital Correlations for $M_6 + (CO)_{18}$, $M_6(CO)_{18}$ and $6 \times M(CO)_3$. With these general remarks in mind the discussion can now return to the specific case of $M_6(CO)_{18}$; perhaps the most helpful way of presenting this discussion is by giving the likely correlations between the orbitals of the six separated $M(CO)_3$ fragments with (a) the orbitals of the separated M_6 cluster and $(CO)_{18}$ polyhedron and (b) the metal cluster carbonyl in its equilibrium structure. Using the character table for the point group O_h,[38] we can classify the orbitals in Figure 1 according to the irreducible representations of this group; the result is given in Figure 2. Note that the symmetries of the M–CO bonding orbitals are the same as those of the set $\{\phi_1, \phi_2, \phi_3 \times 6\}$. The possible correlations between the orbitals of the $M(CO)_3$ fragments and the octahedral M_6 cluster are strongly restricted by the group-theoretical selection rules that enable us to consider each of the numerous irreducible representations separately; for example, any combination of s, p_z, and d_{z^2} orbitals can only belong to the representations a_{1g}, e_g, and t_{1u} in this point group.

Octahedral metal clusters and their compounds have 11 highly antibonding MO's, which may be taken to correlate with 11 of the "skeletal" hybrids (Figure 1), exactly as in the borane case; the formal relationship between the remaining 7 MO's can also be identified with some certainty. These correlations are listed in Figure 3a. Both $T_{1u}(1)$ and $T_{2g}(1)$ are expected to contribute to the metal–metal bonding in the cluster carbonyl, but $A_{1g}(1)$ is not, as is the case for the metal cluster. There are fairly definite correlations between the "t_{2g}" sets of d orbitals on the fragments and the M_6 cluster d band, as shown in Figure 3b. According to the discussion in ref 1 the seven levels underlined in Figure 3b fall below the d–d gap of the metal cluster and contribute to metal–metal bonding, while the other eleven levels lie in the antibonding part of the d band and in $M_6(CO)_{18}$ are modified by hybridization with both the 1π and 2π levels of the carbonyl ligands. Finally inspection of Figure 1 in ref 1, and Figure 2 here, shows that there is a straightforward correlation of the $M(CO)_3$ fragment hybrids denoted as "metal–ligand antibonding" with the 12 frontier orbitals of the metal cluster that lie above the s–d gap and the 6 levels in the metal cluster d band; see Figure 3c.

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(38) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley-Interscience: New York, 1971.

(39) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

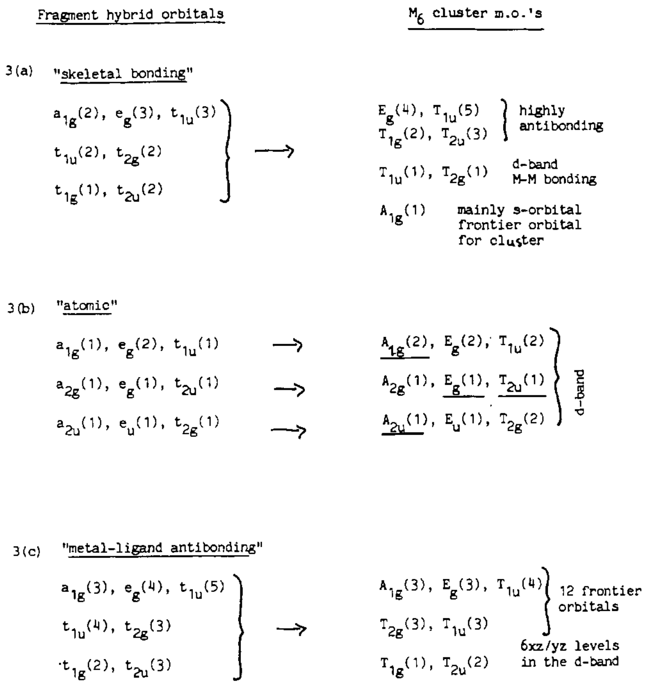

Figure 3.

Comparison of Figure 3a,b with Figure 1 in ref 1 shows that the "skeletal" hybrids ϕ_5, and ϕ_6 and the "atomic" ("t_{2g}") d orbitals ϕ_7 and ϕ_8 give rise to the 12 M–M bonding orbitals that can be related to 12 localized bonds on the edges of the metal octahedron (using the d^4 hybrid orbital construction—see section 3(c) in ref 1) together with their antibonding partners, which hybridize to varying extents with ligand π orbitals. Thus in the *strong interaction region* close to, or at, the equilibrium structure, there is a breakdown of the classification of the fragment hybrid orbitals as either "skeletal" or "atomic", and the isolobal analogy with BH can no longer be taken literally.

There is also a further aspect of Figure 3 that needs discussing. The interaction between the metal cluster and the 18 lone-pair (5σ) orbitals of the carbonyl polyhedron gives rise to 18 metal–carbonyl bonding orbitals and their antibonding partners. The conclusion to be drawn from the discussion of cluster compound formation given in ref 1 is that the metal–ligand *antibonding* orbitals may be assumed to have significant metal orbital character and to be sufficiently far above the d band of the cluster carbonyl that they are not occupied in the ground electronic state. The metal cluster energy levels $A_{1g}(1)$ and $A_{1g}(3)$ are both expected to participate strongly in metal–ligand bonding because of their metal s- and p-orbital character; accordingly from this point of view, we expect *two* "metal–ligand antibonding" orbitals of A_{1g} symmetry. However reference to Figure 2 shows only *one* fragment orbital of symmetry a_{1g} in the set $\{6 \times \phi_1, \phi_2, \phi_3\}$ that is formally associated with the metal–ligand antibonding orbitals of the cluster carbonyl; the only other suitable orbital of a_{1g} symmetry originates from the "skeletal bonding" hybrid ϕ_4. Here we have a real difference in assignments; the borane analogy suggests that a_{1g} (ϕ_4) will be strongly skeletal bonding (as in $B_6H_6^{2-}$), while the metal physics view of cluster compound formation suggests that this orbital may well end up *above* E_{HOMO}! What is needed to settle this point is an accurate calculation.

5. Theoretical Chemistry of the Isolobal Principle

I have attempted in this second paper to give a critical discussion of the putative analogy between the bonding in borane and carborane clusters (and their metalla derivatives) and the bonding in transition-metal cluster compounds that is suggested by the fact that BH fragments and appropriate metal carbonyl fragments are isolobal. Isolobal arguments are used in several ways. Firstly, and mainly, by identifying isolobal fragments, an a posteriori rationalization of the occurrence of structurally similar clusters can be given, and this has brought coherence to a large body of chemical data.[7] In addition, these arguments have considerable value as aids to the design of synthetic pathways for cluster species.[32] In the latter case, we recognize that while isolobal similarities between fragments are frequently suggestive of the final issue, they by no means entail it. The considerable differences between electronic structures of transition-metal and main-group-element cluster compounds, however, suggest that the isolobal principle should *not* be used in discussion of cluster bonding in metal clusters, even if originated from fragments isolobal with say BH or CH.

The isolobal principle[7,27,28] allows that between the orbitals of nonidentical fragments there *are* differences; the chemical significance of such differences must, therefore, be evaluated. As explained in our earlier discussion (section 4), the capacity these differences have for affecting the final outcome is not a property of a fragment alone, rather it depends on the chemical context, i.e. the interactions with other fragments. In practice, only fragments coming from transition-metal compounds are problematic.

This is consistent with previous accounts; for example, Stone writes, "This prompts a cautionary remark about isolobal mapping. There is no guarantee that a synthesis based on a correlation between the isolobal nature of two groups, (e.g. $RhCl(CO)_2$ and CH_2) will result in products with similar structures".[32] Just so. Stone goes on to identify kinetic and thermodynamic factors as being responsible for the lack of a priori certainty about the result of a synthesis suggested by isolobal arguments.[32] However, whereas kinetics and thermodynamics are aspects of the physical chemistry of a reaction mixture (matter on a macroscopic scale), the isolobal principle itself is wholly concerned with a microscopic comparison between the electronic structures of molecular fragment species. An appreciation of the successess and failures of applications of the isolobal principle can, therefore, be based purely on electronic structure considerations; the consequence of this new point of view is that differences in the electronic structure of nonidentical isolobal fragments are seen, *and actually must be seen, there being nothing else*, as the cause of breakdowns in isolobal mappings. There is also the further advantage that while qualitative electronic structure arguments can be used to identify factors affecting the energetics of the interactions between the fragments as they come together into a cluster structure, an analogous discussion in terms of kinetics and/or thermodynamics is scarcely feasible for chemical systems of this complexity. From the theoretical point of view, analysis of the *failures* of isolobal mappings in terms of electronic structure is likely to be as helpful to our understanding of the isolobal principle, as discussion of its successes.

The *isolobal principle*,[7] is widely appreciated as one of the most valuable generalizations in modern inorganic chemistry. However, because the analysis presented in these two papers shows that the cluster bonding in transition-metal cluster compounds is dominated by the metal d electrons, something that is obviously not possible for nonmetal cluster species, the reader may feel that the justification for using isolobal arguments in transition-metal cluster chemistry has, in some way, been undermined. I do not believe such a conclusion is warranted even if the theory described here raises questions as to how the isolobal principle (which works!) should be understood.

The isolobal principle is a *symmetry-based* statement about separated cluster fragments, which assumes little about the details of their interactions in actual clusters; equally, conclusions about the details of cluster bonding *cannot* be validly drawn from (symmetry) arguments of this type—such information can only come from explicit investigation of the energetics of the interactions between the fragments in the equilibrium geometry of the cluster.

The critical insight is this. When confronted by a complex physicochemical problem, the way forward is to search for a *simple soluble problem* that preserves the *essential* symmetry aspects (more generally, invariances) of the true problem, with the aim of connecting the soluble problem to the true problem by a process that does not break the symmetry. This very general concept in theoretical work was illustrated by the example in section 4, and its application to clusters in general is summarized here.

(a) The Simple Soluble Problem—a Set of Fragments. (i) The cluster is divided up into separated fragments that are frozen in the geometry they possess in the equilibrium geometry of the cluster. (ii) The number of electrons is held fixed. (iii) The fragments are brought together by rigid motions that preserve the point-group symmetry of the equilibrium geometry of the final cluster. Then perturbation theory suggests that *weakly interacting isolobal fragments* will indeed have qualitatively similar interactions and energy level diagrams; the symmetry of the ground electronic state and the numbers of occupied and unoccupied levels (or the relative position of the HOMO–LUMO gap) are not altered by the interaction.

(b) The True Problem—the Cluster in Its Equilibrium Geometry. As the fragments are brought together, we expect to reach a region where strong interfragment interactions take place. By exploiting features (i), (ii), and (iii) of the soluble problem (section 5a) that are conserved, we may derive a qualitative understanding of the cluster at, or near, its equilibrium geometry. The results of such arguments are Wade's rules,[8–10] which describe the number of bonding and antibonding *molecular orbitals* in the cluster, and *the likely position of the HOMO–LUMO gap*. These rules may be justified by symmetry-based arguments such as those of Stone,[13,14] which, however, do *not* tell us the details of the atomic orbital composition of the cluster MO's. The success of Stone's model can be understood when it is appreciated that the overall *near-spherical symmetry* of most clusters discussed in these terms is a powerful constraint on the distribution of energy levels (as between bonding and antibonding) as the fragments come together. Implicit in this isolobal argument is the *assumption* that the interfragment interactions leave (i), (ii), and (iii) basically unaltered or, in other words, that the geometric and electronic symmetry adopted by the cluster at equilibrium is determined by the initial weak interaction of the separated isolobal fragments; this is the principle that underlies the use of isolobal mappings in synthetic studies.[32] The *details* of the electronic structure of main-group-element and transition-metal cluster compounds is a quite separate issue that should not be mixed up with the isolobal argument and must be determined by recourse to the methods of theoretical chemistry.

6. Conclusions

Two principal ideas required for an account of the electronic structure of transition-metal cluster compounds have been developed in detail in these two papers: (i) The metal d electrons play a crucial role in the bonding between transition-metal atoms in low oxidation states at separation distances comparable to those found in the bulk metals.

(ii) The d band of a transition-metal cluster is significantly affected by its ligand polyhedron when cluster compound formation occurs, and may be further modified in the compound's subsequent chemistry.

This second conclusion is actually in agreement with earlier (extended Hückel) accounts of cluster carbonyls[11,15] to the extent that the participation of a limited number of cluster d-band levels in cluster–ligand bonding was correctly identified (see especially Lauher's comments on $M_3(CO)_{12}$ and $M_4(CO)_{12}$ clusters[15]). Since the frontier orbitals of a metal cluster include *all* the low-energy cluster MO's of s- and p-orbital parentage, the extended Hückel model offers no explanation for the metal–metal bonding in the cluster. However by retaining the parts of these EH discussions that refer to cluster ligand bonding (which is largely controlled by the overall near-spherical symmetry of the cluster[13–15]), and making use of recent results from transition-metal physics, one can give a consistent account of both cluster–ligand *and* metal–metal bonding in transition-metal cluster compounds. It is expected that the account given here can be usefully applied to transition-metal cluster chemistry; it is already known to be consistent with the physical properties of these materials.[17,23,31,34–37]

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Kinetics and Mechanisms of the Reduction of *trans*-Dihalogenotetracyanoplatinate(IV) Complexes by Inorganic Anions[†1]

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The stoichiometries and kinetics of the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ (X = Br, Cl) by SCN^-, $S_2O_3^{2-}$, CN^-, and SO_3^{2-} in aqueous solution have been examined at 25 °C, $\mu = 0.10$ M, pH 2–8. These reactions are described in terms of a mechanism that involves an X^+ transfer from platinum complex to the reducing anion. $Pt(CN)_4^{2-}$ is the platinum product in all the reactions studied. Reductions of *trans*-$Pt(CN)_4X_2^{2-}$ by SCN^- and of *trans*-$Pt(CN)_4Cl_2^{2-}$ by $S_2O_6^{2-}$ are first order in Pt(IV) complex, first order in reducing anion, and zero order in H^+. Reductions of *trans*-$Pt(CN)_4X_2^{2-}$ by CN^- and SO_3^{2-} are first order in Pt(IV) complex, first order in reducing anion, and inverse first order in H^+. Rate ratios of k_{Br}/k_{Cl} for the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ by SCN^-, I^-, CN^-, and SO_3^{2-} were found to be nearly constant. The implication of the constant ratio is discussed.

Introduction

The interest in inner-sphere electron-transfer mechanisms for Pt(II)-assisted substitution on Pt(IV) complexes[2] has prompted our study of the reduction of Pt(IV) complexes by several inorganic substrates. We have reported that the reduction of *trans*-$Pt(CN)_4Br(OH)^{2-}$ and $Pt(CN)_4Br(H_2O)^-$ by inorganic anions proceeds via an inner-sphere Br^+-transfer mechanism.[3] The trans ligand, i.e. OH^- or H_2O, has a profound influence on the reaction rate. In this paper we report the results of studies of the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ (X = Br, Cl) by SCN^-, $S_2O_3^{2-}$, SO_3^{2-}, and CN^-. The purpose is to extend our understanding of the reductive-elimination reactions of Pt(IV) complexes.

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