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THE BONDING CAPABILITIES OF TRANSITION METAL CLUSTERS

IV *. THREE CLASSES OF CARBONYL CLUSTER COMPOUNDS **

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Summary

A new classification scheme for transition metal carbonyl cluster compounds is proposed. Class I clusters are defined as those which use all available Cluster Valence Molecular Orbitals, CVMOs, Class II cluster compounds have *s* and *p* CVMOs vacant and Class III clusters have vacant *d* CVMOs. In general the earlier transition elements to the left of the transition metal series will have more of a tendency to form Class III cluster compounds, while the later transition elements to the right of the transition series will tend to form Class II compounds. The more common Class I cluster compounds will be favored by the central Group VIII metals such as Rh. Only the Class I clusters will follow the Polyhedral Skeletal Electron Pair analogy between main group and transition metal clusters and will exhibit the "magic numbers" of Cluster Valence Electrons, CVEs.

The high-nuclearity carbonyl cluster compounds of Chini and his coworkers [1,2] exhibit a fascinating variety of structures and form. The metal cores are intermediate in size between the two extremes of the single metal atoms of mononuclear transition metal compounds and the effectively infinite lattices of crystallites of bulk metals. Chemists generally have a firm theoretical understanding of these two extremes, but the chemical, structural and bonding relationships between the extremes and the intermediate clusters are not so well developed. Our goal has been the formulation of a unified theory of bonding which will allow one to explain and predict the chemistry of these varied chemical systems [3—5]. We wish to present here a further elaboration of the ideas we have put forward previously and to formulate the hypothesis that there are

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* For part III see ref. 8.

** Dedicated to the memory of Professor Paolo Chini.

three fundamental classes of transition metal carbonyl cluster compounds.

Transition metal atoms have 9 valence atomic orbitals and thus tend to form stable organometallic compounds with precisely 18 valence electrons. When metal atoms cluster together to form discrete aggregates and ultimately an infinite lattice the 9 atomic orbitals of each metal atom evolve into first Cluster Valence Molecular Orbitals, CVMOs, and finally into the band structure of the bulk metal, Figures 1 and 2.

The *d* orbitals have relatively small overlaps and form a rather narrow *d* band. The *s* overlaps are greater so the *s* band is wide and overlaps the *d* band. The *p* orbitals also have large overlaps and form a wide band which is forced to higher energies by mixing with the lower *s* and *d* bands. Mixing actually occurs between all of the orbitals and the identification of discrete bands is only a convenient formulism. The states of orbitals of a bulk metal which lie at or below the Fermi energy, E_F, are occupied by electrons. The number of occupied valence orbitals per metal atom of the lattice is of interest and has been determined by both experimental and theoretical means. Data derived from the spontaneous magnetic moments of the ferromagnetic Group VIII metals Fe, Co and Ni and their alloys [6] suggest that for these metals there are roughly 5.3 occupied valence orbitals per metal atom. Iron, with fewer electrons, has more singly occupied states than do Co and Ni which have more doubly occupied states. Published theoretical analyses are in general agreement and suggest that the composition of these 5.3 valence orbitals is about 4.8 *d* and 0.5 *s* with little if any *p* contribution. The heavier Group VIII metals are not so well understood, but we will make the rather drastic but seemingly useful assumption of

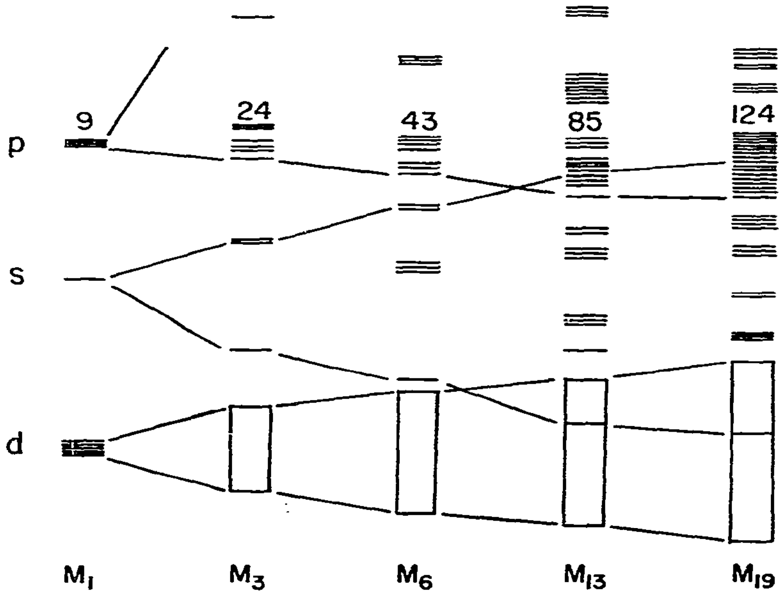


Fig. 1. The evolution of the atomic orbitals of a single metal atom into the Cluster Valence Molecular Orbitals (CVMOs) of M_3, triangular, M_6 octahedral, M_{13} cube octahedral, and M_{19} octahedral clusters. The number of CVMOs for each cluster is shown.

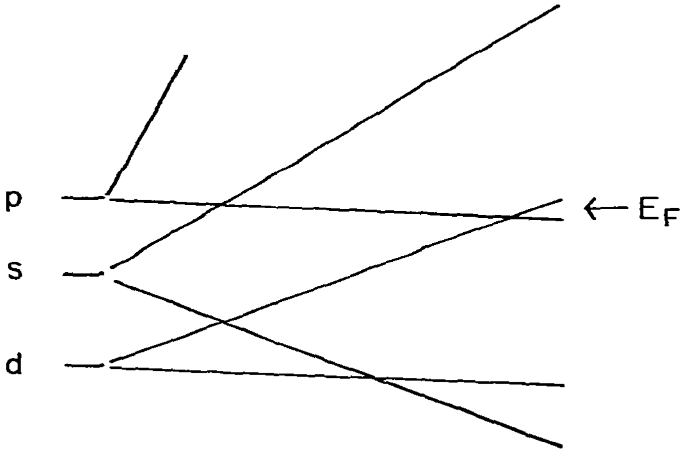


Fig. 2. A qualitative extension of Fig. 1, showing the final band structure of a typical metal. The arrow indicates the Fermi energy, E_F, which is the upper energy bound of the filled states.

a rigid band model and assume that the number of 5.3 occupied valence states is correct for the heavier Group VIII metals as well.

Thus we have the extremes of a single metal atom with 9 important valence orbitals in an isolated environment and single metal atom with 5.3 valence orbitals in an infinite lattice enviroment. What then is the relationship between these two extremes and what do they tell us about the intermediate clusters? Is there a relatioship between the 18 electron rule and the rigid band model of a bulk metal? One relationship can be found by examining the energies envolved.

For a typical transition metal atom the highest filled orbital is an *s* orbital and the ionization potential which corresponds to the removal of an *s* electron is about 7 or 8 eV. The *p* orbitals, which are not occupied but which are important for ligand bonding, lie higher at —4 to —5 eV. These values correspond roughly to the observed values of 4 to 5 eV for the Fermi energies, E_F, of most bulk metals. The highest orbitals of chemical significance, the *p* orbitals of a single atom, thus have energies comparable to the highest valence orbitals of the bulk. It is our basic hypothesis that this same energy upper bound on the orbitals of chemical interest exists for the intermediate clusters as well.

The orbital structures of a few representative clusters are shown in Figure 1. We identify those orbitals at or below the energy of the *p* orbitals of a single atom as Cluster Valence Molecular Orbitals, CVMOs. They are the orbitals which are suitable for containing metal electrons or for serving as ligand acceptor orbitals. Those orbitals lying significantly above the *p* level are termed High Lying Antibonding Orbitals, HLAOs, and can neither contain metal electrons nor serve as ligand acceptor orbitals.

The precise number of CVMOs of a given cluster is a function of the geometry of the cluster and in turn determines the stoichiometry of ligand bonding to the cluster. A cluster with a given number of CVMOs will form a stable cluster compound with precisely twice that number of Cluster Valence Electrons, CVEs, Table 1. This directly corresponds to the preference of a single atom with 9 atomic orbitals for 18 valence orbitals. Using this method we have deter-

TABLE 1

BONDING CAPABILITIES OF TRANSITION METAL CLUSTERS [3,4] [a]

Geometry	N	$9N$	HLAO	CVMO	CVE	CVMO/N
Monomer	1	9	0	9	18	9.0
Dimer	2	18	1	17	34	8.5
Trimer	3	27	3	24	48	8.0
Tetrahedron	4	36	6	30	60	7.5
Trigonal Bipyramid	5	45	9	36	72	7.2
Octahedron	6	54	11	43	86	7.17
Square Antiprism	8	72	15	57	114	7.13
Tetrahedron	10	90	20	70	140	7.0
Cube Octahedron	13	108	23	85	170	6.54
Octahedron	19	171	47	124	248	6.53
Tetrahedron	20	180	53	127	254	6.35

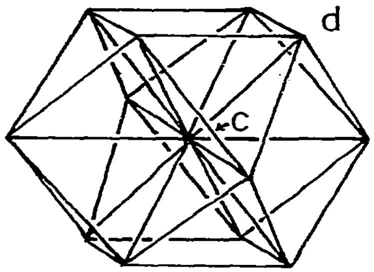
[a] N is the number of atoms; $9N$ is the number of atomic orbitals; HLAO is the number of High Lying Antibonding Orbitals; CVMO is the number of Cluster Valence Molecular Orbitals; CVE is the number of Cluster Valence Electrons.

mined CVMO numbers for a wide variety of metal cluster geometries. The observed stoichiometries of most known cluster compounds are in agreement with the predicted values. Recently Ciani and Sironi [7] have published calculations based upon our methods for about 100 additional cluster geometries.

Clusters versus bulk metals

As clusters grow larger one would expect an increasing similarity to the bulk. One good measure of this is the ration CVMO/N which is the number of CVMOs per metal atom of a cluster. For a single metal atom this ratio is 9.0 and it drops to a value of 6.54 for a cube-octahedral cluster, Table 1. This ratio continues to drop for even larger clusters, but very slowly reaching values less than 6.0 only for cluster with hundreds of atoms [8].

A localized analysis [4] of the number of CVMOs assigned to individual metal atoms of a given cluster shows that metal atoms with high numbers of nearest neighbors have fewer CVMOs than do metal atoms with fewer nearest neighbors. For example the interior atom, c, of the cube-octahedral cluster, I, contributes 5.67 CVMOs to the cluster, whereas the surface atoms, d, contribute 6.61 CVMOs. The interior atom has all 12 nearest neighbors of a cubic-



(I)

close packed atom, while the surface atoms have only 5 nearest neighbors. The orbital compositions for the CVMOs on each atom are 4.88 *d*, 0.65 *s*, and 1.08 *p* for the d atoms and 4.74 *d*, 0.42 *s*, and only 0.51 *p* for the interior atom c. This simply means that the interior atom needs fewer Cluster Valence Electrons, CVEs, for stability than does a surface atom.

The 5.67 CVMOs of the central atom c correspond approximately to the 5.3 occupied states of a bulk metal. The number is higher due mainly to the 0.51 *p* orbital contribution. This *p* contribution is not important in bulk metals since occupied states with significant *p* character would be of high energy compared to the *s* and *d* states. In a cluster the *p* contribution does have chemical significance, however, and can not be neglected. The CVMOs with *p* character are available for ligand bonding and a cluster compound will not be stable if any low lying orbitals are vacant. Surface atoms of clusters and of metal crystallites have higher *p* orbital contributions and correspondingly much higher ligand bonding capabilities [4].

Polyhedral skeletal electron pair theory

One of the most successful approaches for the prediction of cluster compound geometries and stoichiometries has been the Polyhedral Skeletal Electron Pair (PSEP) theory developed by Wade and Mingos [9,10]. The theory consists of a series of empirical rules which predict the number of skeletal electron pairs for a polyhedron of a given geometry. One of the most useful aspects of the rules is the recognition that a polyhedron of metal atoms has the same basic number of skeletal electron pairs as an isostructural main group cluster. The numbers of Cluster Valence Electrons are also related. For example the octahedral carborane cluster $C_2B_4H_6$ has 26 CVEs, corresponding to the 86 CVEs of the octahedral metal cluster $Co_6(CO)_{16}$. The 60 additional CVEs are needed to fill the 6 sets of Co *d* orbitals. The stoichiometries predicted for small clusters by the Wade and Mingos rules are generally in good agreement with the results of our semiemperical MO procedures [3,4,8].

The basis for the close relationship between the stoichiometries of main group and transition metal clusters is due to the fundamental role of the *s* and *p* orbitals. This was first pointed out by Mingos who found that there was an exact correspondence between the number and symmetries of the antibonding *s* and *p* orbitals of main group clusters and the High Lying Antibonding Orbitals of transition metal clusters [11]. The bonding and nonbonding orbitals of *s* and *p* character also correspond, thus the electron counts are directly related.

One important corrollary to the PSEP theory is that no HLAO of a transition metal cluster can be primarily of *d* character; otherwise the main group analogy would not work. In other words no orbital which formally belongs to the *d* band of a cluster can be so destabilized by metal—metal antibonding interactions such that it can neither contain metal electrons nor serve as ligand acceptor orbital. The point is fundamental to the derivation of the classification scheme we present below.

A classification scheme for carbonyl cluster compounds

The procedures and rules discussed above apply to the vast majority of carbonyl cluster compounds. The stoichiometries of most cluster compounds can be predicted. It is not difficult, however, to find examples for which the procedures do not work.

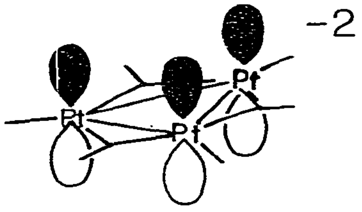
The most obvious exceptions are the many carbonyl clusters of platinum which tend to be electron deficient. Another significant group of exceptions are clusters which require the assignment of multiple bonds in order to satisfy the electron count. We feel that it is important to have a better understanding of how these exceptions relate to the norm and how our "Cluster Rigid Band" model may be extended to include the exceptions as well. To do this we propose the following classification scheme for carbonyl cluster compounds. Certain aspects of the scheme will apply to other types of metal compounds as well.

Class I clusters

The Class I cluster are those which obey the rules, all available CVMOs are used and the number of CVEs is precisely as predicted. All orbitals with energies at or below the p level of a free atom are used. Most known carbonyl cluster compounds are of this type. The familiar "magic numbers" of CVEs are found. Examples would include, $[Fe_3(CO)_{12}]$ with 48 electrons, $[Co_4(CO)_{12}]$ with 60 electrons and $[Rh_6(CO)_{16}]$ with 86 electrons. The diagrams in Figures 1 and 2 and the PSEP rules apply and indeed were derived for Class I cluster.

Class II clusters

Platinum generally forms carbonyl cluster compounds which are electron deficient. Those CVMOs of pure p character often are not used and the CVE count is lower than predicted. The simpliest known examples are Pt_3 clusters such as $[Pt_3(CO)_6]^{2-}$ with 44 CVEs and $[Pt_3(PPh_3)_3(CO)_3]$ with only 42 CVEs. The unused CVMOs in both cases are p_z orbitals which are perpendicular to the molecular plane.

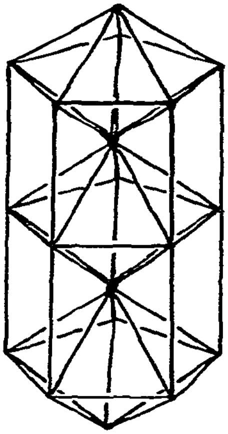


(II)

In the 42 electron cluster all three p_z orbitals remain vacant, while in the 44 electron clusters one weakly bonding CO π^* stabilized CVMO of a_2'' symmetry, II, is used [3].

In a more complicated example the ion $[Pt_{19}(CO)_{22}]^{4-}$ is a unique cluster, III, synthesized by Chini which has five-fold symmetry [12]. Applying our normal procedures we found that the cluster has 123 CVMOs [13]. This predicts

246 CVEs, but only 238 are actually found ($19 \times 10 + 22 \times 2 + 4 = 238$). There must be four unused CVMOs. A detailed analysis of our results indicates that the vacant and unused CVMOs consist of e_2' and e_2'' sets made up of tangental p orbitals, IV. These orbitals are bonding between adjacent Pt atoms of the five-membered rings with the e_2' set centered upon the central ring and the e_2'' set centered upon the outer rings. These orbitals are not of the proper symmetry to interact with the donor CO orbitals and are too high in energy to contain electrons.



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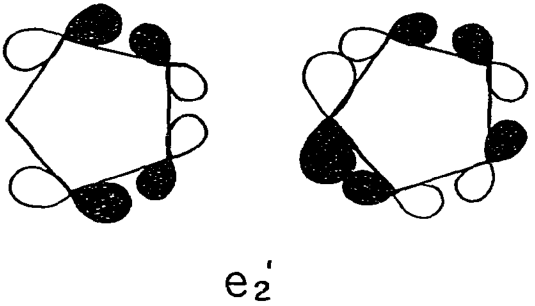


(IV)

The general picture which emerges from this analysis is that Pt clusters will tend to form stable electron deficient compounds with unused CVMOs of pure p character. Those p orbitals which can form hybrid CVMOs with s character will be used. For example in the Pt_3 clusters there are three formally p in plane CVMOs utilized for ligand bonding.

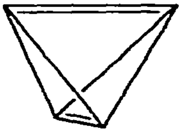
There are examples of similar electron deficient clusters with other elements near platinum in the periodic table. Gold in particular forms many electron deficient phosphine clusters such as octahedral clusters of the type $[Au_6L_6]^{2+}$. These clusters have only 76 CVEs instead of the predicted 86. Mingos has shown that there are several unused CVMOs of p and even s character in such clusters [14].

The observed electron deficient cluster compounds of platinum and gold are not surprising when it is noted that mononuclear 16 electron Pt and 14 electron Au compounds are common. The electron deficiencies of the Class II clusters are due to the fact that the valence p and to a lesser extent the s orbitals lie at increasingly higher energies with respect to the valence d orbitals as one moves to the right along the transition series. Class II clusters can be defined as those clusters which are electron deficient due to vacant s and p CVMOs. They will be found most commonly for the heavier Group VIII metals and the Group IB metals. Class II clusters can not obey the PSEP rules because not all of the available s and p orbitals are used. The diagrams of Figures 1 and 2 need to be modified for Class II clusters by increasing the splitting between the s and p orbitals versus the d band.

Class III clusters

Fewer examples of cluster compounds belonging to Class III are known but more should be found in the future. Class III clusters are electron deficient also, but for a different reason. In Class III clusters there are CVMOs of *d* character which are not used while the available *s* and *p* CVMOs are utilized. This is a violation of the corollary to the PSEP theory as discussed above. The stoichiometries of Class III clusters do not agree with predictions, but can in most cases be explained by the invocation of multiple bonds between the metal atoms.

A good example of a Class III cluster the compound $[Re_4(CO)_{12}H_4]$. This compound has only 56 CVEs instead of the expected 60 as in $[Ir_4(CO)_{12}]$. As Hoffmann [15] has pointed out in $[Re_4(CO)_{12}H_4]$ the highest formally *d* CVMOs, an orbital set of *e* symmetry in the T_d point group, are vacant. The highest *d* CVMOs of any cluster are always metal—metal antibonding. The electron deficiency has been accounted for in this compound by considering resonance forms with formal double bonds between adjacent pairs of Re atoms, V.



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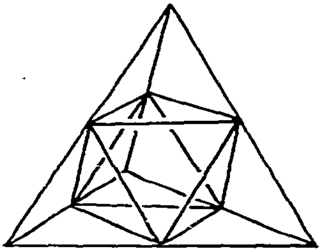

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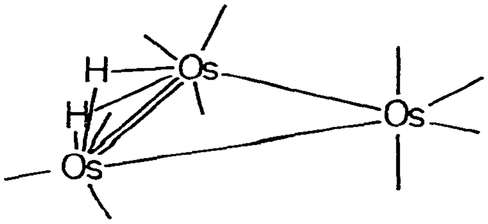

(VII)

Another more recent example from the Lewis groups [16] is the Os cluster $[Os_{10}C(CO)_{24}]^{2-}$, VI, which has a ten atom tetrahedral structure with the carbide ligand in the central octahedral hole. Our calculations [3] and those of Ciani and Sironi [8] indicate the presence of 70 CVMOs requiring 140 CVEs for a Class I cluster. The observed $[Os_{10}C(CO)_{24}]^{2-}$ cluster only has 134 CVEs and is thus formally electron deficient by 6 electrons. A detailed examination of our MO calculations again suggests that the highest formal *d* CVMOs, in this case a triply degenerate t_2 set, are empty and unused. The three orbitals are again metal—metal antibonding. The fact that Os can form Class III clusters is further exemplified by the well known 46 electron $Os_3H_2(CO)_{10}$ cluster, VII, which formally has a double bond.

The nature of the electron deficiencies in Class III clusters are in direct contrast to the Class II deficiencies. The Class II clusters have empty *s* or *p* CVMOs, while the Class III clusters have empty *d* CVMOs. The explanation is, however, essentially the same. On the left side of the transition series the relative energies of the *s* and *p* orbitals are lower with respect to the *d* orbitals than they are for the metals on the right hand side of the transition series. A Group VIII metal such as Rh just happens to be in the middle and forms mostly Class I clusters.

Mononuclear analogues of Class III clusters are known. A simple example would be the 12 electron compound hexamethyltungsten. Very common are compounds with two metal atoms bound by formal multiple metal—metal bonds. Such species as the Cotton [17] quadruply bonded dimers are good examples of compounds with *d* orbitals so destabilized by metal—metal antibonding interactions that they can neither contain metal electrons nor serve as ligand acceptor orbitals.

Many more large Class III carbonyl clusters should be synthesized in the future particularly for metals of the Cr, Mn and Fe triads. For some such clusters the formal assignment of multiple bonds may be meaningful, but for other cases such as $[Os_{10}C(CO)_{24}]^{2-}$ a delocalized picture would seem to be more useful. The PSEP analogy with main group clusters will not work for a Class III cluster, because there are vacant *d* orbitals. The diagrams in Figure 1 and 2 should show less of a splitting between *s* and *p* versus the *d* levels for Class III clusters.

Conclusions

There are three classes of transition metal carbonyl clusters. Class I Clusters use all available CVMOs, Class II clusters have vacant *s* and *p* CVMOs, and Class III clusters have vacant *d* CVMOs. In general the earlier transition metals to the left in the transition series will have more of a tendency to form Class III cluster while the later transition metals to the right of the transition series will tend to form Class II clusters. The more common Class I clusters will be favored by the central Group VIII metals such as Rh.

Extensions of the classification to other chemical systems should be possible, but certain obvious difficulties will be encountered. Mixed metal clusters containing metals of different electronic character do not fit the scheme well; an Fe—Au cluster would be an example. Ligands other than CO or simple phosphines also present difficulties. The Ni cyclopentadienyl clusters of Dahl [18] need to be treated as Class I clusters with weak field ligands [13]. Class II and Class III clusters may be expected to have a more interesting reaction chemistry because they are not saturated. Intermediates in the reactions of the more common Class I cluster compounds may be Class II or Class III clusters depending upon the metal.

Finally we need to consider the possibilities which should be encountered for truly large metal cluster compounds. One interesting fact that emerges is that Pt Class II clusters become Class I if they grow large enough. Very large clusters have CVMO/*N* ratios which approach 6.0. This means that there are no CVMOs of pure *p* character and clusters may form Class I clusters. The largest Chini cluster, the $[Pt_{38}(CO)_{44}H_4]^{-2}$ anion, with a CVMO/*N* ratio of 6.23, appears to be a Class I Pt carbonyl cluster. In fact though it may be found that the largest clusters which are ever isolated may turn out to be Class II or

Class III clusters simply because they require fewer ligands on a crowded surface than a Class I cluster of the same geometry.

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