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## The Bonding Capabilities of Transition Metal Clusters

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**Abstract:** The bonding capabilities of various transition metal clusters and the resulting stoichiometries of transition metal cluster compounds have been estimated, based upon extended Hückel calculations of the isolated metal clusters. It has been found that the molecular orbitals of each cluster may be readily divided into two classes: the high lying antibonding orbitals (HLAOs) and the cluster valence molecular orbitals (CVMOs). Only the CVMOs are suitable energetically for ligand bonding or for containing metal electrons. Each cluster of a given size and geometry has a particular number of CVMOs which may be used for reliable predictions of compound stoichiometries. A wide range of cluster geometries with up to 15 atoms has been explored including common geometries such as the tetrahedron and octahedron found for known cluster compounds, as well as other less conventional geometries for which there are no known examples.

Transition metal cluster compounds lie at the focus of two converging lines of study. Synthetic chemists are continually preparing new cluster compounds of increasing nuclearity and complexity,<sup>1,2</sup> while at the same time chemists concerned with catalysis are devoting more study to the important roles of small metal clusters or particles as the active sites in heterogeneous catalysts.<sup>3,4</sup> Clusters have also been used as models for bulk metals and metal surfaces. This interrelationship becomes more evident when one considers the high nuclearity clusters prepared by Chini and co-workers,<sup>1</sup> clusters which greatly resemble small fragments of bulk metals. Indeed the metal cores of nearly all known organometallic clusters can be considered to be derived from a bulk close packed structure.

Theories of bonding within metal cluster compounds are still primitive. Theoretical analyses have been of necessity primarily of a qualitative nature owing to the complexity of the problem.

Discrete cluster compounds have been approached with varying degrees of success by various empirical rules including the quite successful polyhedral skeletal electron pair theory developed by Wade and Mingos.<sup>5,6</sup> A few semiempirical LCAO-MO treatments have also been applied to specific systems.<sup>7,8</sup> The bonding within bare metal clusters, primarily as models for surface and bulk metal phenomena, has also been examined. Included are numerous LCAO-MO calculations<sup>9-11</sup> as well as a number of more sophisticated X- $\alpha$  calculations.<sup>12</sup>

In our studies we have also made semiempirical LCAO-MO calculations for a number of bare metal clusters, but our objectives have been slightly different from those of previous studies. We are not particularly concerned with the electronic properties of a bare metal cluster itself, but are instead concerned with certain aspects of its chemistry. We wish to answer

**Table I.** Rh-Rh Overlaps at 2.69 Å

	$\sigma$		$\pi$		$\Delta$
s-s	0.2219	x-x	0.1160	xy-xy	0.0133
s-z	-0.2950	x-xz	-0.0840		
s-z <sup>2</sup>	0.1148	xz-xz	-0.0656		
z-z	-0.3730				
z-z <sup>2</sup>	0.1527				
z <sup>2</sup> -z <sup>2</sup>	0.0809				

the questions: What is the total bonding capacity of a small metal cluster? How many ligands can a small cluster potentially bond? To answer these questions, we have examined the valence molecular orbitals of various bare metal clusters and have estimated the number of such orbitals available for ligand bonding.

Once we understand the bonding capabilities of small clusters with approximately 15 or fewer atoms, it may be possible to use our same model to explore the bonding capabilities of larger clusters or small metal particles. Certain aspects of the model may also apply to metal surfaces, but any such extrapolations must be made with care.

**Mononuclear Complexes.** Before considering clusters of metal atoms, it is appropriate to briefly review a few general principles governing the bonding of ligands to isolated transition metal atoms. Transition metals have nine valence atomic orbitals, one s, three p, and five d orbitals. These nine atomic orbitals are used by the metal either as acceptor orbitals or for containing nonbonded electrons. This is the basis of the well-known 18-electron rule formulated originally by Sidgwick,<sup>13</sup> which is obeyed by the vast majority of low-valent organometallic complexes. There are, of course, exceptions to the 18-electron rule even among organometallics. The most obvious examples are d<sup>8</sup> square planar 16-electron complexes, which are common for the platinum metals. In these complexes the p<sub>z</sub> orbital is not used; it remains nonbonding and empty. The group 1B metals also form numerous compounds in which the p orbitals are not fully utilized. Gold(I), for example, forms primarily two-coordinate 14-electron complexes.

These deviations from the 18-electron rule found for the platinum metals and the copper triad are often said to be due to the large s to p promotion energies found for the free atoms.<sup>14,15</sup> As one moves across a given row of the transition series toward the heavier elements, the d and s energy levels drop more quickly than do the p levels, thus increasing the s to p promotion energies. It appears that the bonding capacity of a given metal is quite dependent upon the relative energy level of its p orbitals. Any destabilization of the p orbitals will cause them to be less available for ligand bonding.

In transition metal clusters the energy levels of the p orbitals are also important and are influenced greatly by metal-metal interactions. It is the central hypothesis of this study that any significant destabilization of the p orbitals within a transition metal cluster with respect to their level in the free metal atoms will cause them to be unavailable for ligand bonding and that this is the most important factor in determining the bonding capacity of a small transition metal cluster.

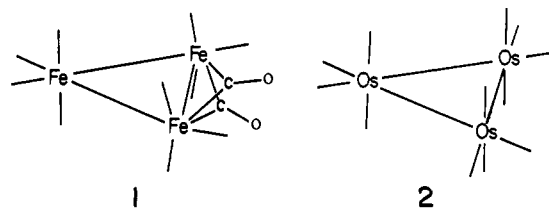
**Calculation Method.** The qualitative molecular orbital arguments presented in this paper are based on extended Hückel calculations<sup>16</sup> performed on bare clusters of rhodium atoms. The details of the calculations may be found in the Appendix. The actual results are not very sensitive to the parameters used and are primarily determined by the symmetries and nodal patterns of the orbitals. Thus, the qualitative results may be used with confidence for metals other than rhodium.

The most important consideration for evaluating the interactions of two metal atoms are the orbital overlaps. For two Rh atoms at a distance of 2.69 Å, which is the distance in the

bulk metal,<sup>17</sup> and the distance used throughout this study, the calculated overlaps are listed in Table I. It can be seen that the largest overlaps involve the s and p orbitals and that the pure d-d overlaps are small. This means that the largest interactions between the metal atoms will be between the s and p orbitals and not the d orbitals. Stated another way, the d band within a cluster will have a smaller energy spread than the s and p bands.

**Metal Clusters.** The number and variety of well-characterized transition metal clusters are constantly increasing. Clusters with from 3 to 6 metal atoms are now quite common and larger clusters with up to 18 metal atoms have been prepared. Generally, cluster compounds may be divided into two broad classes on the basis of ligand types. The largest class are those with soft "organometallic" type ligands such as carbon monoxide and phosphines. Most of these clusters contain group 8 metals. The second class of clusters includes the earlier transition metals as well as group 8 metals. The metal atoms often have high oxidation states and the ligands are typically halides, sulfides, or oxides. This class will not be considered here.

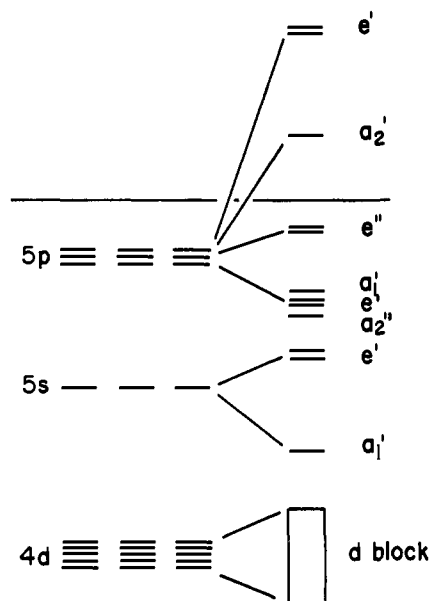
**Three-Atom Clusters.** The simplest clusters are those with three metal atoms arranged in the form of an equilateral triangle. There are hundreds of such triangular clusters known, many of which have been structurally characterized. The most studied compounds of this type are the M<sub>3</sub>(CO)<sub>12</sub> (M = Fe, Ru, Os) clusters.<sup>18</sup> These clusters and other closely related analogues adopt a wide variety of structures, which have the same basic triangular metal core, but have differing arrangements of their ligands. The solid-state structures of two of these compounds are shown below (1, 2).



Most, but not all, clusters are fluxional molecules in which the individual CO ligands rapidly interchange positions intramolecularly. Often there is no one arrangement of ligands about the central metal core which is greatly preferred energetically over all others.<sup>19</sup> Indeed Johnson has recently proposed<sup>20</sup> that the most important factors determining the ligand structural arrangement are the van der Waals interactions between the individual ligands and not their interactions with the metal core. It is readily apparent that the individual ligands are interacting with the three-atom cluster as a whole and not just with the individual metal atoms.

Although the ligand geometries of three metal clusters are quite variable, their stoichiometries are not. As has been recognized for a number of years, each individual transition metal cluster of any given structure will characteristically form complexes with a particular electron count. This idea of a characteristic valence can be explained for the simplest clusters by the 18-electron rule. For larger clusters the method runs into difficulties and a molecular orbital method is required. We believe that for a consistent and proper understanding a molecular orbital approach should be applied to the small clusters as well.

To properly analyze the bonding of the ligands to the three-metal aggregate one must first determine the molecular orbital structure of the bare metal cluster. A molecular orbital interaction diagram for a D<sub>3h</sub> triangular cluster is shown in Figure 1. The strongest interactions are between the s and p orbitals due to their higher overlaps (Table I). There is, of course, mixing between orbitals of the same symmetry, meaning that certain lower lying "d" molecular orbitals ac-

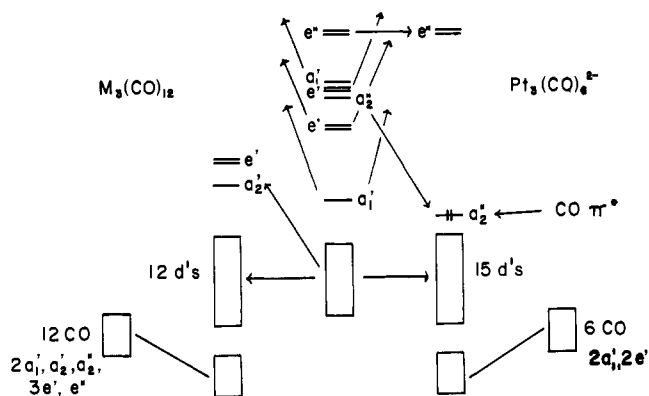


**Figure 1.** An interaction diagram for a  $M_3$  cluster. The atomic orbitals of the three metal atoms are shown separately on the left side and the resultant molecular orbitals of the  $M_3$  cluster are shown on the right side. The horizontal line separates the CVMOs from the HLAOs.

tually have significant amounts of s and p character. Since a single metal atom has 9 valence atomic orbitals we are required to form 27 molecular orbitals for the three metal atoms. An examination of the interaction diagram reveals, however, that three high-lying molecular orbitals, an  $e'$  set and an  $a_2'$ , are significantly destabilized owing to their highly antibonding character. Since these three cluster molecular orbitals are considerably higher in energy than the p orbitals of the individual metal atoms, we may apply our qualitative hypothesis that these three orbitals are too high in energy to contain nonbonding electrons and are too high to serve as ligand acceptor orbitals. Thus, a three-metal cluster does not have 27 molecular orbitals available, only 24. These 24 molecular orbitals will be termed cluster valence molecular orbitals (CVMOs). The three high-energy orbitals will be termed high lying antibonding orbitals (HLAOs). If all 24 CVMOs are used as ligand acceptor orbitals or for containing nonbonded electrons, the cluster will have 48 cluster valence electrons (CVEs). A three-atom transition metal cluster has a definite preference for 48 CVEs in the same manner that a single metal atom prefers 18 valence electrons.<sup>21</sup>

The great majority of organometallic three-atom clusters do have 48 cluster valence electrons. The previously mentioned  $M_3(\text{CO})_{12}$  clusters are examples. The compound  $\text{Fe}_3(\text{CO})_{12}$  has three  $d^8$  Fe atoms and 12 two-electron donor ligands for a total of 48 electrons. Another example<sup>19,22</sup> of a 48-electron cluster is the cyclopentadienylcobalt cluster,  $\text{Co}_3(\text{C}_5\text{H}_5)_3(\text{CO})_3$ , which has three  $d^8$  Co(I) atoms, three two-electron donors, and three six-electron donors also totaling 48. Traditionally, each of these compounds is said to have three metal-metal bonds.

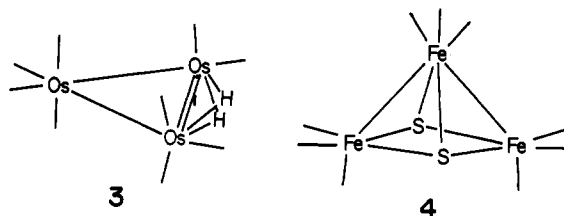
A detailed analysis of the bonding in a  $M_3(\text{CO})_{12}$  cluster shows how the 24 CVMOs are used to form stable complexes. Figure 2 shows an interaction diagram of the symmetric  $D_{3h}$  isomer, **2**, based on an extended Hückel calculation. The CO ligands are divided into two classes, the six in-plane equatorial ones which form group donor orbitals of  $a_1'$ ,  $e'$ ,  $a_2'$ , and  $e'$  symmetries, and the out-of-plane axial ligands which form group donor orbitals of  $a_1'$ ,  $e'$ ,  $a_2''$ , and  $e''$  symmetries. As is the case for a mononuclear complex the principal acceptor orbitals of the three metal atom core are the orbitals of primarily s and p character. These metal orbitals of symmetries



**Figure 2.** Interaction diagrams for  $M_3(\text{CO})_{12}$  and  $\text{Pt}_3(\text{CO})_6^{2-}$  cluster compounds.

$a_1'$ ,  $e'$ ,  $a_2''$ ,  $e'$ ,  $a_1'$ , and  $e''$  interact with ligand donor orbitals of similar symmetries to form the normal bonding and antibonding combinations. Three orbitals from the d block must also be used, the lone  $a_2'$  orbital and a hybrid  $e'$  set. This leaves 12 CVMOs of the d block which can precisely contain the 24 d electrons. The actual ordering of the filled orbitals within the cluster is greatly influenced by interactions with the  $\pi^*$  orbitals of the CO ligands. The analysis presented here is for the  $D_{3h}$  arrangement of the CO ligands because the high symmetry makes the analysis much simpler. We have also performed calculations for other ligand geometries and have found similar bonding patterns. The energy differences between different isomers as calculated by the extended Hückel method do not seem to be meaningful since the actual energy surface is quite complex and is dependent upon the precise positional parameters of all 27 of the atoms involved. In particular, the interligand interactions are difficult to interpret. It is, however, always possible to find a match between the symmetries of the CVMOs and the symmetries of any chemically reasonable arrangement of ligand orbitals. This is true simply because there is a wide variety of CVMO symmetries to choose from.

There are examples which do not have 48 cluster valence electrons. In most such cases the three metals atom core deviates considerably from  $D_{3h}$  symmetry. Thus, the cluster  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  (**3**) has only 46 electrons and has two normal length Os-Os bond distances and one short Os-Os distance,<sup>23</sup>



classically assigned as a double bond. On the other hand, the cluster  $\text{Fe}_3\text{S}_2(\text{CO})_9$  (**4**) has 50 electrons, an excessive number, and is assigned only two Fe-Fe bonds.<sup>24</sup>

One group of three-atom clusters is electron deficient with less than the expected 48 electrons, but retains the basic  $D_{3h}$  geometry. These are clusters of platinum and palladium which typically have 44 or 42 cluster valence electrons.<sup>25,26</sup> The most important example is the 44-electron cluster  $\text{Pt}_3(\text{CO})_6^{2-}$  (**5**), synthesized by Chini.<sup>25a</sup> Figure 2 shows a molecular orbital

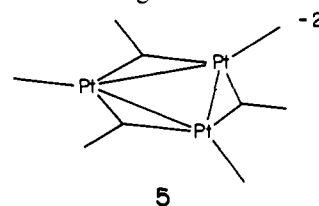




Table II. Bonding Capabilities of Transition Metal Clusters<sup>a</sup>

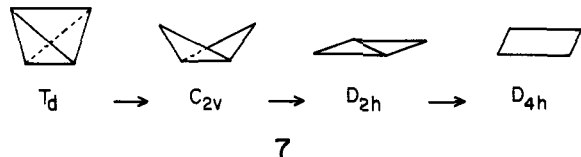
geometry	<i>N</i>	9 × <i>N</i>	HLAB	CVMO	CVE	CVMO/ <i>N</i>	example
monomer	1	9	0	9	18	9.0	Ni(CO) <sub>4</sub>
dimer	2	18	1	17	34	8.5	Fe <sub>2</sub> (CO) <sub>9</sub>
trimer	3	27	3	24	48	8.0	Os <sub>3</sub> (CO) <sub>12</sub>
tetrahedron	4	36	6	30	60	7.5	Rh <sub>4</sub> (CO) <sub>12</sub>
butterfly	4	36	5	31	62	7.75	Re <sub>4</sub> (CO) <sub>16</sub> <sup>2-</sup>
square plane	4	36	4	32	64	8.0	Pt <sub>4</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>8</sub>
trigonal bipyramid	5	45	9	36	72	7.2	Os <sub>5</sub> (CO) <sub>16</sub>
square pyramid	5	45	8	37	74	7.4	Fe <sub>5</sub> (CO) <sub>15</sub> C
bicapped tetrahedron	6	54	12	42	84	7.0	Os <sub>6</sub> (CO) <sub>18</sub>
octahedron	6	54	11	43	86	7.17	Ru <sub>6</sub> (CO) <sub>17</sub> C
capped square pyramid	6	54	11	43	86	7.17	Os <sub>6</sub> (CO) <sub>18</sub> H <sub>2</sub>
edge shared bitetrahedron	6	54	11	43	86	7.17	
pentagonal pyramid	6	54	10	44	88	7.33	
trigonal prism	6	54	9	45	90	7.5	Rh <sub>6</sub> (CO) <sub>15</sub> C <sup>3-</sup>
capped octahedron	7	63	14	49	98	7.0	Rh <sub>7</sub> (CO) <sub>16</sub> <sup>3-</sup>
pentagonal pyramid	7	63	14	49	98	7.0	
capped trigonal prism	7	63	12	51	102	7.29	
bicapped octahedron	8	72	17	55	110	6.88	
triangular dodecahedron	8	72	16	56	112	7.0	
square antiprism	8	72	15	57	114	7.13	Co <sub>8</sub> (CO) <sub>18</sub> C <sup>2-</sup>
bicapped trigonal prism	8	72	15	57	114	7.13	
cube	8	72	12	60	120	7.5	Ni <sub>8</sub> (PC <sub>6</sub> H <sub>5</sub> ) <sub>6</sub> (CO) <sub>8</sub>
tricapped octahedron	9	81	18	63	126	7.0	
tricapped trigonal prism	9	81	17	64	128	7.11	
capped square antiprism	9	81	16	65	130	7.22	
capped cube	9	81	15	66	132	7.33	
tetrahedron	10	90	20	70	140	7.0	
bicapped cube	10	90	19	71	142	7.1	
bicapped square antiprism	10	90	19	71	142	7.1	
truncated trigonal bipyramid	12	108	28	80	160	6.67	
icosahedron	12	108	23	85	170	7.08	
cube octahedron	12	108	23	85	170	7.08	
truncated hexagonal bipyramid	12	108	23	85	170	7.08	
icosahedron	13	117	32	85	170	6.54	
cube octahedron	13	117	32	85	170	6.54	
truncated hexagonal bipyramid	13	117	32	85	170	6.54	Rh <sub>13</sub> (CO) <sub>24</sub> H <sub>3</sub> <sup>2-</sup>
face centered cube	14	126	36	90	180	6.43	
rhombic dodecahedron	14	126	30	96	192	6.86	
rhombic dodecahedron	15	135	39	96	192	6.40	

<sup>a</sup> *N* is the number of atoms; 9 × *N* is the number of atomic orbitals; HLAB 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.

are all equivalent and form group donor orbitals of symmetries  $a_1$ ,  $t_2$ ,  $e$ ,  $t_1$ , and  $t_2$ . Nine of the *s* and *p* type CVMOs are used as acceptor orbitals along with a  $t_1$  set from the *d* block. This leaves 17 orbitals of the *d* block plus an  $a_1$  *sp* hybrid available for containing the 36 electrons.

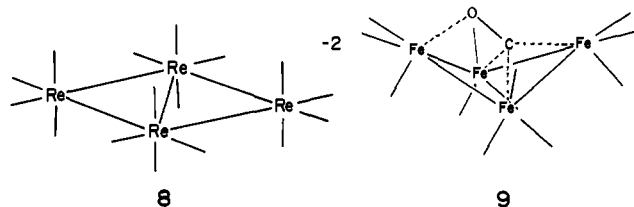
Another interesting cluster which happens to have full  $T_d$  symmetry is the Ni<sub>4</sub>(CO)<sub>6</sub>(PR<sub>3</sub>)<sub>4</sub> (R = CH<sub>2</sub>CH<sub>2</sub>CN).<sup>28</sup> Each phosphine ligand is bound to a single nickel atom and lies on a threefold axis, while each CO ligand bridges two of the nickel atoms, one on each edge of the tetrahedron. The phosphine and CO donor orbitals form group donor orbitals of symmetries  $a_1$  and  $t_2$  and of  $a_1$ ,  $t_2$ , and  $e$ , respectively (Figure 4). This is a perfect match for the symmetries of the CVMOs of primarily *s* and *p* character. The 20 *d* block orbitals are filled with the 40 *d* electrons. Again the *s* and *p* block orbitals are the principal acceptor orbitals.

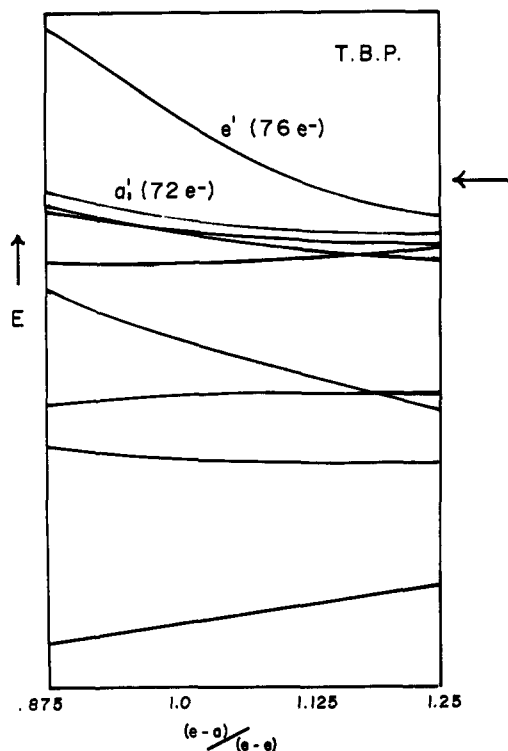
If one edge of a tetrahedron is lengthened, **7**, the resulting structure has the butterfly geometry with  $C_{2v}$  symmetry. The structure may also be folded flat with  $D_{2h}$  symmetry. At an intermediate geometry (dihedral angle of 70.53°) the structure



may be regarded as an octahedron with two missing vertices. Classically this breaking of one edge of a tetrahedron would correspond to adding two electrons to the antibonding orbital which corresponds to the two-electron bond along that edge of the tetrahedron. Our calculations (Figure 3) show the equivalent phenomena. As the edge is opened up by increasing the dihedral angle between the two halves of the butterfly, one of the high-lying antibonding orbitals of the tetrahedron drops in energy and the CVMO number is increased from 30 to 31. This means that the butterfly structures should indeed have two more electrons, 62, than the tetrahedron which prefers 60 electrons. A further deformation of the flat butterfly structure to a square planar structure,  $D_{4h}$ , results in a further increase of the CVMO number from 31 to 32.

There are only a few known clusters with these nontetrahedral geometries. The anion Re<sub>4</sub>(CO)<sub>12</sub><sup>2-</sup> (**8**) is a 62-electron ion with the  $D_{2h}$  butterfly geometry.<sup>29</sup> The  $C_{2v}$  folded butterfly geometry is exemplified by the anion Fe<sub>4</sub>(CO)<sub>13</sub>H<sup>-</sup> (**9**).<sup>30</sup> This



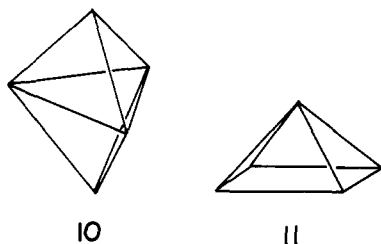


**Figure 5.** A correlation diagram showing the molecular orbitals of regular and distorted trigonal bipyramidal  $M_5$  clusters. The  $(e-a)/(e-e)$  ratio is the ratio of the equatorial-axial bond distances to the equatorial-equatorial bond distances. In a regular bipyramid this ratio is 1.0. The arrow indicates the level of the p orbitals in a free atom; thus the CVM0 cutoff would be slightly higher.

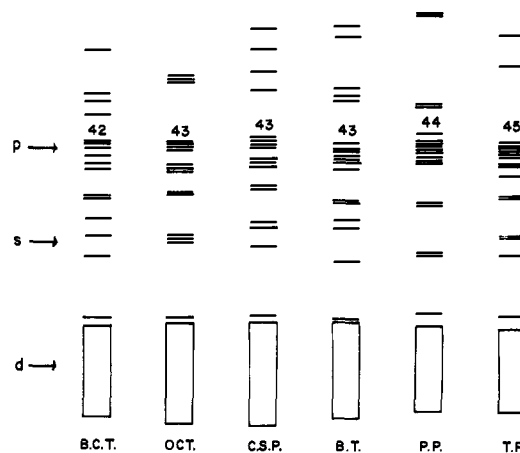
example is a particularly important one because at first glance it would appear to be a 60-electron cluster, which would have a tetrahedral geometry. Four  $d^8$  Fe atoms plus 14 two-electron donor ligands equal 60 electrons. The actual molecular structure reveals, however, that one of the CO ligands has an unusual bridging geometry such that not only is the C atom of the CO ligand within bonding distance of the metal core, the O atom is also. Thus, one CO ligand is acting as a four-electron donor and not a normal two-electron donor and the overall cluster does have 62 electrons.

The  $C_{2v}$  cluster  $Pt_4(CO)_5(PPhMe_2)_4$  is another example of an electron-deficient platinum compound since it has the  $C_{2v}$  butterfly geometry, but only 58 electrons.<sup>31</sup> Surprisingly, there is a platinum(II) cluster which obeys the electron counting rule for square planar geometry. The compound  $Pt_4(O_2CCH_3)_8$  has four Pt atoms in a square plane with each acetate ligand bridging an edge and with each O atom bound to one Pt atom.<sup>32</sup> The total number of electrons is thus 64 as expected for 32 CVM0s.

**Five-Atom Clusters.** There are two compact close-packed structures available for five-atom clusters, the trigonal bipyramid, **10**, and the square pyramid, **11**. The MO energy

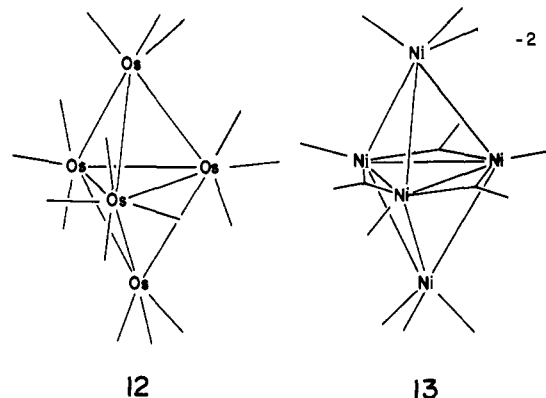


levels calculated for the trigonal bipyramid are shown in Figure 5. The regular trigonal bipyramid is predicted to have 36 CVM0s and should thus have 72 CVEs. An example is the



**Figure 6.** The molecular orbitals of various  $M_6$  clusters. The number of CVM0s is indicated for each geometry (B.C.T., bicapped tetrahedron; O.C.T., octahedron; C.S.P., capped square pyramid; B.T., edge shared bitetrahedron; P.P., pentagonal pyramid; and T.P. trigonal prism).

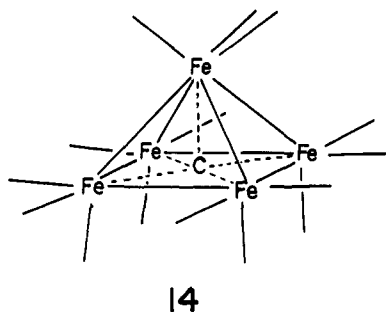
compound  $Os_5(CO)_{16}$  (**12**), which is a 72-electron cluster with a trigonal bipyramid core of Os atoms.<sup>33</sup> Interestingly there are a number of 76-electron trigonal bipyramidal clusters also. These are anionic species which have a  $Ni_3(CO)_6^{2-}$  fragment capped on each side by  $Ni(CO)_3$  or  $M(CO)_5$  ( $M = Cr, Mo,$  or  $W$ ) fragments.<sup>34,35</sup> The resulting clusters  $Ni_5(CO)_{12}^{2-}$ , **13**,



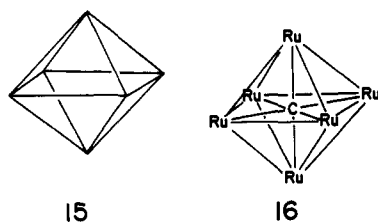
and  $Ni_3M_2(CO)_{16}^{2-}$  have elongated trigonal bipyramidal geometries. In the  $Ni_5(CO)_{12}^{2-}$  anion, for example, the equatorial-equatorial ( $e-e$ ) nickel-nickel bond distances are 2.36 Å while the equatorial-axial ( $e-a$ ) distances average 2.81 Å, about 20% longer.<sup>34</sup> To explore this distortion in detail we have calculated MO energy levels for a series of elongated trigonal bipyramids. The ( $e-e$ ) bond distances were fixed at the standard value of 2.69 Å, while the ( $e-a$ ) bond distances were varied. The calculated energy levels are plotted in Figure 5 as a function of the distance ratio  $(e-a)/(e-e)$ . The most important variation is the lowering in energy of an  $e'$  set of acceptor orbitals as the cluster is elongated. In the regular trigonal bipyramids the  $e'$  set is highly antibonding, too high in energy to be used for ligand bonding, and there are 36 CVM0s. In the elongated structure the  $e'$  set drops in energy and the number of CVM0s is thus increased to 38. This is in agreement with the observed stoichiometries. The known 72-electron clusters have the regular geometry while the 76-electron anionic clusters mentioned above are elongated.

The square pyramidal cluster geometry is represented by a lone compound  $Fe_5(CO)_{15}C$  (**14**).<sup>36</sup> This cluster is also an example of a carbide cluster in which the interstitial hole of the cluster is occupied by a C atom. The number of CVEs is predicted to be 74 and this is achieved by summing the 40 Fe d electrons, 30 from the CO ligands and the 4 electrons from the

interstitial C atom. We will have more to say about carbide clusters when we discuss six-atom clusters.



**Six-Atom Clusters.** By far the most common geometry for six-atom clusters is the octahedron, **15**, a close-packed structure.<sup>1,2</sup> There are many such clusters, the majority of which have 86 CVEs. This number is significant because a simple analysis based on 12 two-electron bonds between the metal atoms would predict that there should be 84 electrons. For all cluster polyhedra which have been mentioned previously, a simple analysis based on the assignment of metal-metal bonds to each edge predicts the correct electron count. A molecular orbital analysis of an Rh<sub>6</sub> octahedral cluster shows that of the 54 metal MOs, 11 orbitals and not 12 are highly antibonding orbitals (Figure 6). This means that there are 43 CVMOs and not 42. The importance of the 11 HLAOs in the octahedral case was first recognized by Mingos,<sup>7</sup> who presented an analysis of the bonding within the compound Co<sub>6</sub>(CO)<sub>16</sub>.<sup>37</sup> This Co cluster has 16 two-electron donors which use 16 of the 43 CVMOs. The remaining 27 orbitals contain the 54 d electrons.



At this point it is useful to consider the bonding within the carbide cluster compounds since there are a number of octahedral metal clusters with a C atom in the center of the octahedral hole. The structures are quite similar to bulk metal carbides which also are found to have C atoms in octahedral holes of close-packed metal atoms. Specific examples of octahedral carbide clusters are Ru<sub>6</sub>(CO)<sub>17</sub>C (**16**)<sup>38</sup> and Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>,<sup>39</sup> both have 86 CVEs. The 43 CVMOs of a bare Rh<sub>6</sub> octahedron are indicated in Figure 7. The symmetries of the highest CVMOs happen to be t<sub>1u</sub> and a<sub>1g</sub>, identical with the symmetries of the s and p orbitals of the interstitial C atom. The C atom's orbitals interact with all metal orbitals of t<sub>1u</sub> and a<sub>1g</sub> symmetries, but the most important interactions are with the highest CVMOs. These orbitals are destabilized and become highly antibonding as the corresponding metal-carbon bonding orbitals are formed. This means that the addition of the C atom does not lead to an increase in the number of CVMOs. The seven-atom cluster Rh<sub>7</sub>C has 86 CVMOs identical in number with the 86 CVMOs of the octahedron of metal atoms alone. The net effect of the C atom is an exchange of four filled low-lying CVMOs for four higher lying acceptor orbitals. Thus, in the cluster Ru<sub>6</sub>(CO)<sub>17</sub>C the Ru<sub>6</sub>C core has 52 electrons including 48 from the Ru atoms and 4 from the C atom. The remaining 34 electrons are supplied by the 17 CO ligands yielding the desired total of 86 CVEs.

Other close-packed structures of six metal atoms are possible. One such geometry is the capped square pyramid. In this structure the capping atom sets on a triangular face of the

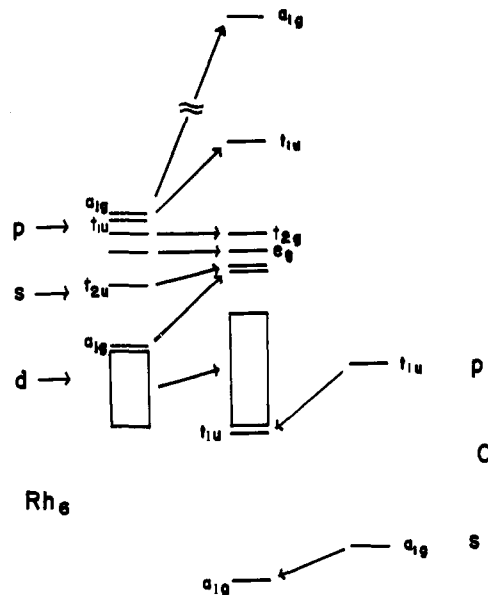
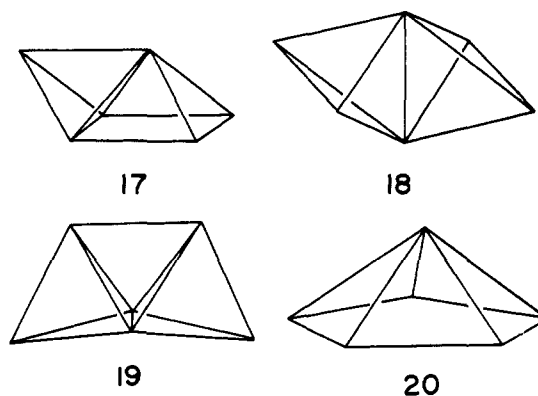


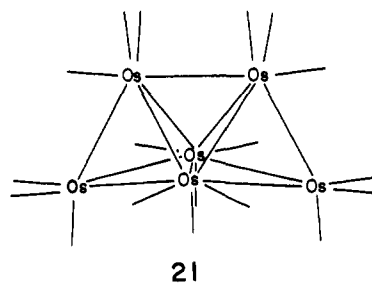
Figure 7. An interaction diagram for a Rh<sub>6</sub> cluster. The CVMOs of the Rh<sub>6</sub> cluster are on the left and the atomic orbitals of the interstitial C atom are on the right.

square pyramid; if the capping atom set on the square face, an octahedron would be the result. The capped square pyramid, **17**, also has 43 CVMOs. The only known example is the 86-



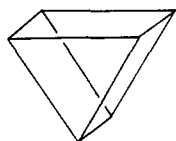
electron compound Os<sub>6</sub>(CO)<sub>18</sub>H<sub>2</sub>.<sup>40</sup> The reasons for the preference of only this one cluster for the nonoctahedral geometry are not clear. A third close-packed geometry, the edge shared bitetrahedron, **18**, also has 43 CVMOs. There are no known examples.

The cluster Os<sub>6</sub>(CO)<sub>18</sub> (**21**) is an example of a cluster with a bicapped tetrahedron core, **19**.<sup>41</sup> The bicapped tetrahedron can be considered to be locally close-packed but cannot be part



of a periodic close-packed lattice. As shown in Figure 6, there are 42 CVMOs in agreement with the stoichiometry of Os<sub>6</sub>(CO)<sub>18</sub>, an 84-electron species. We have also investigated the pentagonal pyramid, **20**, and found it to have 44 CVMOs. No examples are known, but when found, they should have 88 CVEs.

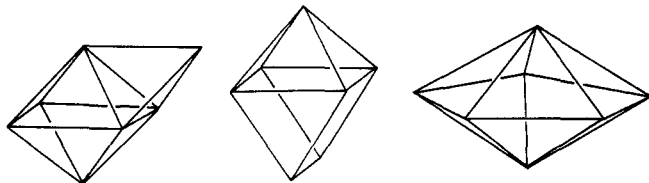
The Rh carbide cluster anion  $\text{Rh}_6(\text{CO})_{15}\text{C}^{2-}$  has a trigonal prismatic structure, **22**.<sup>42</sup> The trigonal prism is a very open



22

structure meaning that there are fewer close metal-metal contacts than there are in the close-packed structures. Thus there are fewer HLAOs and a greater number of CVMOs, 45 vs. 43 for the octahedron. In the  $\text{Rh}_6(\text{CO})_{15}\text{C}^{2-}$  anion the bonding of the interstitial C atom is similar to the octahedral case. In the  $D_{3h}$  point group the orbitals of the C atom are of symmetries,  $a_1'$ ,  $e'$ , and  $a_2''$ . These orbitals interact with four cluster CVMOs of similar symmetries yielding low-lying bonding orbitals and four high-lying antibonding orbitals. The total number of CVMOs for the seven-atom  $\text{Rh}_7\text{C}$  cluster is thus also 45. The interstitial carbon atom does not change the number of CVMOs, only the number of electrons.

**Seven-Atom Clusters.** For seven atoms the most likely geometries are the capped octahedron, **23**, the capped trigonal prism, **24**, and the pentagonal bipyramid, **25**. The capped oc-



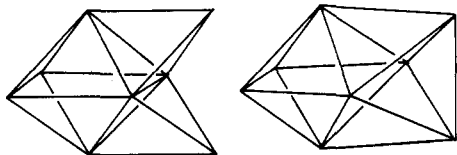
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tahedron is the only geometry observed to date. Calculations suggest that there are 49 CVMOs and that such clusters should have 98 CVEs. This agrees with the stoichiometry of the known anion  $\text{Rh}_7(\text{CO})_{16}^{3-}$ , which has a capped octahedral geometry.<sup>43</sup> A capped trigonal prism should have 51 CVMOs and should thus have 102 CVEs. The pentagonal bipyramid is an interesting case because the calculations indicate that a regular structure with all edges equal has 49 CVMOs and that cluster compounds should have 98 CVEs. Wade's theory would predict an electron count of 100 based on an analogy with the borane anion  $\text{B}_7\text{H}_7^{2-}$ , a 30-electron species.<sup>5</sup> The two-electron difference occurs because in the case of the  $\text{Rh}_7$  aggregate there is a significant interaction between the two axial atoms. These two atoms are only 2.88 Å apart if all the nearest-neighbor distances are 2.69 Å. One result of this interaction is a highly antibonding orbital of  $a_2''$  symmetry which corresponds to a filled orbital in the  $\text{B}_7\text{H}_7^{2-}$  anion. Our calculations also suggest that elongation of the pentagonal bipyramid will lead to an increase in the CVMO number to 50.

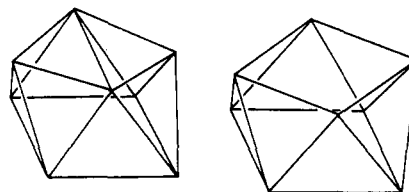
**Eight-Atom Clusters.** There are only a few known eight-atom clusters but it is an interesting case because there are a number of possible polyhedra closely related to each other which can be interconverted with only small movements of the vertices.<sup>44</sup> Of these the most compact structure is the close-packed bicapped octahedron. There are three possible isomers, each of which is indicated to have 55 CVMOs. A slight distortion of one of the isomers, **26**, leads to the triangular dodecahedron, **27**. The dodecahedron has  $D_{2d}$  symmetry and 56



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CVMOs. A slight distortion of the dodecahedron leads in turn to the bicapped trigonal prism, **28**, which has 57 CVMOs. A further distortion results in a square antiprism, **29**, which also

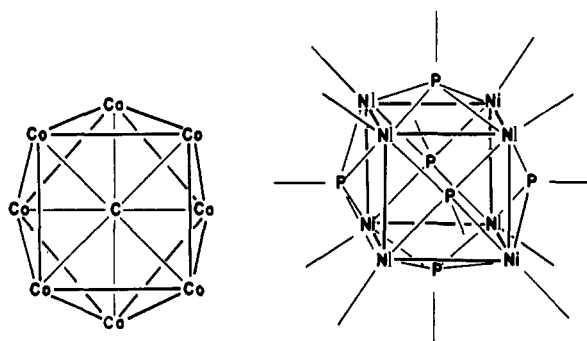


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has 57 CVMOs. The only example of any of these structures is the anion  $\text{Co}_8(\text{CO})_{18}\text{C}^{2-}$  (**30**), which has 114 electrons and a geometry midway between a square pyramid and a trigonal prism.<sup>45</sup>

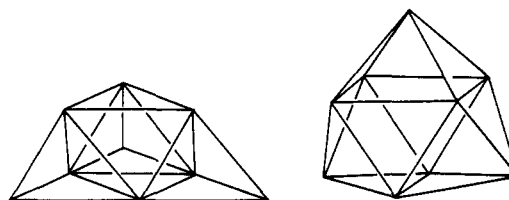
The one remaining important eight-atom polyhedron is the cube, which is a very open structure with fewer close metal-metal interactions and thus a greater number of CVMOs, 60. The one good example of such is the 120-electron compound  $\text{Ni}_8(\text{PC}_6\text{H}_5)_6(\text{CO})_8$  (**31**).<sup>46</sup>



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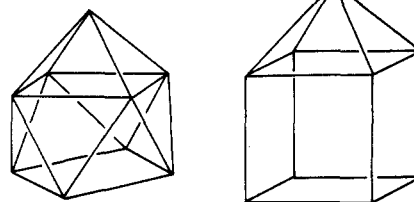
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**Clusters with Nine or More Atoms.** For these larger metal clusters there are only a couple of known examples, but more will undoubtedly be synthesized in the future. We have investigated a few of the more symmetrical geometries. For nine metal atoms, possible structures include the  $C_{3v}$  tricapped octahedron, **32**, with 63 CVMOs, the  $D_{3h}$  tricapped trigonal prism, **33**, with 64, the  $C_{4v}$  capped square antiprism, **34**, with 65, and the capped cube, **35**, with 66. For ten atoms the tetrahedron, **36**, has 70 CVMOs while the  $D_{4d}$  bicapped square antiprism, **37**, and the  $D_{4h}$  bicapped cube, **38**, each have 71 CVMOs. For 12 atoms the truncated trigonal bipyramid has 80 CVMOs, **39**.



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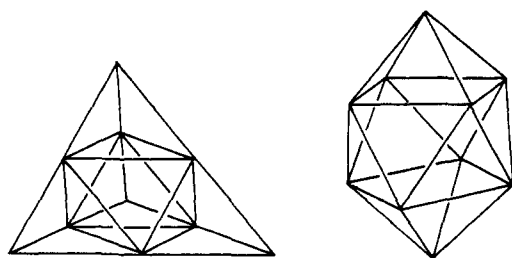
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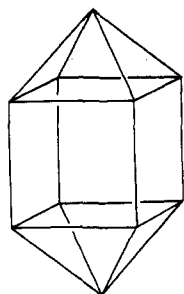
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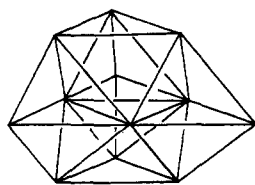


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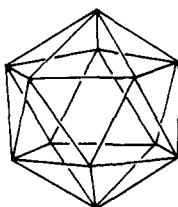


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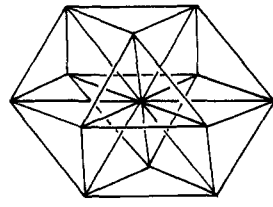


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There are two very symmetrical polyhedra with 12 vertices, the icosahedron with  $I_h$  symmetry, **40**, and the cube octahedron with  $O_h$  symmetry, **41**. The cube octahedron represents the

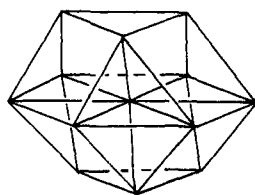


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fundamental coordination unit within a cubic close-packed lattice. The corresponding fundamental coordination unit within a hexagonal close-packed lattice is the 12-vertex truncated hexagonal bipyramid of  $D_{3h}$  symmetry, **42**. A 12-atom



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cluster which has one of these three geometries has an interstitial hole large enough to contain a 13th atom. In the  $O_h$  and  $D_{3h}$  geometries the center to vertex distance is equal to the distance between vertices. In the icosahedron the center to vertex distance is about 5% shorter. The MO energy levels for two of the three  $Rh_{12}$  clusters are shown in Figure 8. All three have 85 CVMOs. The addition of an additional Rh atom at the center of the polyhedra results in 13-atom clusters. The bonding of this additional interstitial Rh atom is very similar to the bonding of the carbon atom in the carbides which were discussed earlier. The nine atomic orbitals of the central Rh atom interact with CVMOs of appropriate symmetries and nine new bonding orbitals and nine new highly antibonding orbitals are formed. The number of CVMOs thus remains 85 for all three  $Rh_{13}$  structures. Chini has prepared the anion  $Rh_{13}(CO)_{24}H_3^{2-}$  which has an  $Rh_{13}$  core with the  $D_{3h}$  geometry.<sup>47</sup> In agreement with the calculations, the anion has

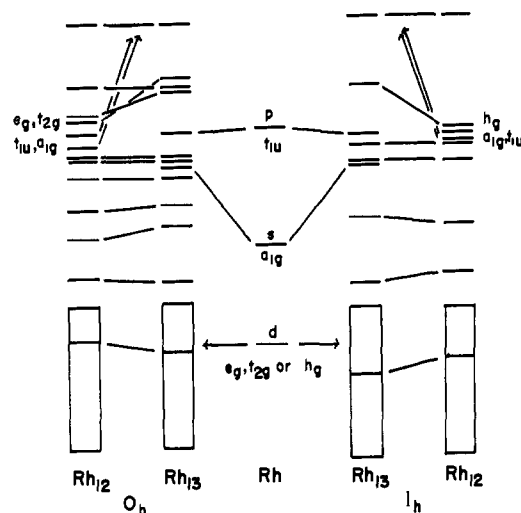


Figure 8. Interaction diagrams for  $I_h$  and  $O_h$   $Rh_{13}$  clusters. Each diagram shows the interactions of the central Rh atom with the outer  $Rh_{12}$  shell.

116 electrons from the Rh atoms, 48 from the CO ligand, and 6 from the hydride ligands yielding a total of 170 CVEs.

Possible 14-atom structures include two that have  $O_h$  symmetry, the cubic close-packed, face-centered cube with 90 CVMOs and the rhombic dodecahedron which represents the fundamental coordination unit within a body-centered cubic lattice. This rhombic dodecahedron has an interstitial hole which can accommodate a 15th atom. Calculations suggest that both the 14- and 15-atom clusters have 96 CVMOs and that a cluster compound with such a geometry should have 192 CVEs.

**Saturation, Compactness, and Future Extensions.** A transition metal cluster of a given geometry has a certain predictable number of CVMOs. If the number of CVEs is equal to twice the number of CVMOs, then the cluster may be said to be electronically saturated. A cluster with a deficiency of CVEs will be electronically unsaturated. With certain metals, such as platinum or the group 1B metals, the unsaturated cluster may actually be stable. With other metals unsaturated clusters can be expected to show unusual reactivity. Such a cluster would in general readily react with any additional ligands to achieve the proper number of CVEs. In the absence of additional ligands, the metal core of the cluster might isomerize to a different geometry with the proper number of CVMOs or one of the existing ligands might bind in an unusual manner such that more of its electrons are formally donated to the metal. An example is seen in the cluster  $Fe_4(CO)_{13}H^-$ , which has a butterfly geometry and one unusual dihapto carbonyl ligand which acts as a four-electron donor.<sup>30</sup>

Throughout this paper a great deal of emphasis has been placed on whether or not a given metal geometry was close packed. Close-packed structures such as the octahedron can be said to be "compact" and have many close metal-metal interactions. They thus resemble the bulk metal more closely than do clusters with "open" geometries such as the trigonal prism or cube. This idea of compactness or "bulk metal similarity" is a difficult one to quantify but one measure is the number of CVMOs per metal atom. For the most compact structures this ratio will be low and for the more open structures it will be high. For example, for an eight-atom structure, the bicapped octahedron has the lowest ratio, 6.88, while the ratio for the cube, 7.5, is the highest. Of all geometries considered, the one which shows the most compactness or bulk metal similarity is the 15-atom rhombic dodecahedron with a ratio of 6.40. On the other hand, a single metal atom has a ratio of 9 and is not very similar to a bulk metal.

Table III. Rh Parameters

	$H_{ii}$ , eV	exponent	
Rh 5s	-8.0	2.135	
Rh 5p	-4.5	2.10	
Rh 4d	-12.5	$\zeta_1 = 4.29$	$C_1 = 0.5807$
		$\zeta_2 = 1.97$	$C_2 = 0.5685$

The conclusions set forth in this paper are qualitative, but seem to be in good agreement with empirical observations. It remains to be seen how far the results may be extended to other systems. The model can be applied with some confidence to small (less than 15 metal atoms) clusters with geometries other than those considered here. For large clusters with more than 15 atoms the basic ideas should remain valid, but it will become increasingly more difficult to make quantitative predictions, because the energy bands tend to become a continuum. This makes the judgment as to which orbitals are suitable energetically to serve as acceptor orbitals somewhat arbitrary. Also, with larger systems questions regarding "surfaced localized" molecular orbitals vs. "interior localized" orbitals become more important. Ligand acceptor orbitals must be localized on the surface of a cluster. For the small systems considered here this is not a problem because all atoms are effectively surface atoms.

A number of general points may, however, be applicable to larger clusters and perhaps in some respects to surfaces. The first major point is that the principal acceptor orbitals in transition metal clusters are of s and p character. These orbitals are quite important and cannot be ignored. Second, it should be recognized that a bare cluster of metal atoms is an unsaturated and very reactive molecule which will accept electrons from any available ligands. Theoretical studies which investigate the bonding of a *single* ligand with an aggregate of metal atoms must be evaluated with care because they will invariably show very strong bonding and perhaps will show misleading ligand geometries. This is due to the fact that it usually requires many ligands, not just one, to satisfy the bonding requirements of a cluster. Third, it appears that interstitial atoms do not greatly affect the number of available CVMOs, but merely supply electrons. Fourth, the number of available CVMOs per metal atom is dependent upon the cluster geometry. This will mean that in larger clusters metal atoms with geometrically distinct environments will have different bonding capacities. For example, the bonding capacity of a corner atom will be greater than that of a close-packed surface atom. Fifth, while most group 8 metals can be expected to follow the rules outlined here, clusters of platinum and group 1B metals are more likely to be stable with fewer than the predicted number of ligands.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Preliminary program development was supported by the Research Foundation of the State University of New York.

## Appendix

All calculations were performed using Hoffmann's extended Hückel scheme utilizing the weighted  $H_{ij}$  formula.<sup>16</sup> Rhodium was chosen as the representative element for all calculations, since it is the centermost group 8 element and because there are many known Rh cluster compounds of high nuclearity. The parameters used are listed in Table III. For each cluster geometry the nearest-neighbor distances were fixed at 2.69 Å, which is the Rh-Rh distance in the bulk metal. As explained in the text of this paper the molecular orbitals calculated for a given cluster geometry can be divided into two classes, the high lying antibonding orbitals, HLAOs, and the cluster va-

lence molecular orbitals, CVMOs. Orbitals which are significantly destabilized from the energy of the p orbitals of a single atom are considered to be HLAOs. This division is a qualitative one, but for most cluster geometries there is a clear energy separation. In general the division is made on the following basis. The Rh 5p  $H_{ij}$  value used is -4.50 eV so any cluster molecular orbital which has an energy significantly (usually more than 0.5 eV) higher than -4.50 eV is considered to be highly antibonding. In almost all cases considered there is a significant energy gap of at least 1.0 eV which clearly separates the HLAOs from the CVMOs which are either bonding or essentially nonbonding with respect to the p orbitals of a free atom. This energy gap is not very sensitive to the parameters used in the calculation. This is due to the fact that the antibonding character of the HLAOs is determined by the nodal patterns and symmetry of the cluster orbitals and is not a function of the energy parameters. Thus the results can be applied with confidence to clusters of other metals. This agrees with the experimental facts which indicate that in general clusters of different metals obey the same electron counting rules. The exceptions are clusters of palladium, platinum, and the group 1B metals which characteristically form electron-deficient compounds. For such metals it is known that the p orbitals are higher in energy with respect to the s and d orbitals than is the case for the earlier transition metals. This means that the Rh parameters are not suitable for predictions of stoichiometries of cluster compounds of these particular metals.

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## Proton Magnetic Resonance Properties of the Tetranuclear Clusters $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ , Analogues of the 4-Fe Sites of Reduced Ferredoxins

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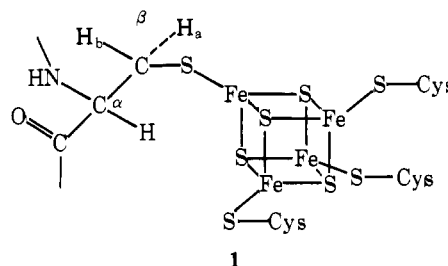
**Abstract:** The recent synthesis of the reduced tetranuclear clusters  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$  has permitted a detailed examination of structural and electronic properties, demonstrating that these trianions are analogues of the 4-Fe sites of reduced ferredoxin proteins ( $\text{Fd}_{\text{red}}$ ). Reported here are 100-MHz FT  $^1\text{H}$  magnetic resonance spectra of the series  $\text{R} = \text{CH}_2\text{Ph}$ ,  $\text{Ph}$ ,  $o\text{-C}_6\text{H}_4\text{CH}_3$ ,  $m\text{-C}_6\text{H}_4\text{CH}_3$ ,  $p\text{-C}_6\text{H}_4\text{CH}_3$  in  $\text{CD}_3\text{CN}$  solution over the temperature range of ca.  $-40$  to  $70$   $^\circ\text{C}$ . Also included are  $^1\text{H}$  NMR data not reported previously for the corresponding  $\text{Fd}_{\text{ox}}$  analogues  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ . Trianions exhibit rather well-resolved spectra with large isotropic shifts. The temperature dependencies of methylene proton isotropic shifts and solution susceptibilities of  $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{3-}$  parallel each other, indicating dominant contact interactions. Further evidence that isotropic shifts are principally contact in origin is obtained from the signs and temperature dependencies of shifts of  $\text{R} = \text{Ph}$  and tolyl complexes. In all cases the contact interactions appear to arise from ligand  $\rightarrow$  Fe(core) antiparallel spin transfer. The same properties follow from the  $^1\text{H}$  NMR spectra of the  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  series, whose smaller isotropic shifts at ambient temperature are primarily due to smaller magnetic susceptibilities rather than large differences in contact interaction constants. All results support previous proposals that signal multiplicities and chemical shift ranges for the  $\beta\text{-H}$  protons of cysteinate residues bound to Fe in  $\text{Fd}_{\text{ox,red}}$  proteins arise from angularly dependent contact interactions within rigid protein structure. The analogue  $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{3-}$  does not exhibit the positive and negative temperature coefficients of shifts observed in all  $\text{Fd}_{\text{red}}$  spectra, suggesting that the protein structure freezes an unsymmetrical electron distribution in the  $\text{Fe}_4\text{S}_4$  unit for a time long on the  $^1\text{H}$  NMR time scale.

### Introduction

NMR spectroscopy has proven to be a valuable component of the armamentarium of physicochemical techniques which have been applied to an elucidation of the properties of the redox sites of ferredoxin (Fd) proteins.<sup>1-3</sup> Spectroscopic studies in this field were pioneered by Phillips and co-workers, and include  $^1\text{H}$  spectral examinations of  $\text{Fd}_{\text{ox}}$  and  $\text{Fd}_{\text{red}}$  proteins having 2-Fe<sup>4-7</sup> ( $[\text{Fe}_2\text{S}_2(\text{S-Cys})_4]$ ) and one<sup>8-11</sup> and two<sup>12-16</sup> 4-Fe ( $[\text{Fe}_4\text{S}_4(\text{S-Cys})_4]$ ) sites per molecule. In addition  $^{13}\text{C}$  NMR studies of proteins of the last type have been reported.<sup>17,18</sup> Much of the work executed in the 1970-1973 period has been reviewed.<sup>14,15</sup>

Among the protein site properties which have been usefully probed by NMR spectroscopy are the nature of magnetic coupling within  $\text{Fe}_2\text{S}_2$  and  $\text{Fe}_4\text{S}_4$  core substructural units of the sites, electron distribution in these cores, similarities and differences in molecular environments of cysteinate and aromatic residues in related proteins, and redox potentials.<sup>18</sup> Such information is often accessible from NMR observations because 2-Fe and 4-Fe sites in all protein oxidation states obtainable in vitro are paramagnetic. This property generates

sizeable isotropic components (contact, dipolar) to the total chemical shifts of  $\alpha$  and  $\beta$  protons of cysteinate residues directly bonded to iron atoms, as for the cubane-type 4-Fe sites 1 established in several proteins by x-ray crystallography.<sup>19</sup>



The sign and magnitudes of the isotropic interactions are such as usually to shift  $\alpha$  and  $\beta$  resonances downfield of the complex absorption pattern at ca. 0-10 ppm arising from nonexchangeable protons of the polypeptide chain, thereby permitting their observation in a region uncomplicated by other signals.