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M_2L_9 Complexes

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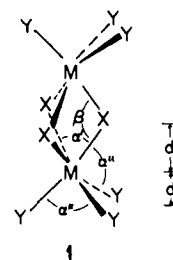
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Abstract: The electronic and geometrical structure of confacial bioctahedral complexes of the type $L_3MX_3ML_3$ is studied, for a variety of terminal ligands and hydride, halide, and carbonyl as representative bridging ligands. The factors which determine the dimer geometry in general and the metal-metal separation in particular are the geometrical preference of the L_3MX_3 monomer fragment, the symmetry-conditioned opportunities for interaction offered up by the orbitals of the bridging group (very different for H^- , Cl^- , or CO), and direct metal-metal bonding. There are cases in this class of triply bridged complexes where metal-metal bonding is determinative, but they are a minority. Several cases point up the fact that in bridged complexes neither a short metal-metal distance by itself nor electron counting conventions are a good guide to the presence or absence of substantial direct metal-metal interaction.

A convenient but not unique theoretical approach to bridged metal dimer (and cluster) complexes is to view the following three factors as determining the dimer molecular geometry and electronic structure: (1) the geometrical preference of the monomer fragment; (2) the symmetry-conditioned opportunity for interaction offered up by the orbitals of the bridging groups; (3) direct bonding or antibonding overlap of primarily metal-centered orbitals. The mix of these contributions is variable. In many cases, especially those in which compounds are compared which differ from each other only by one or two electrons, the last effect is important. This is clearly seen in the elegant body of work of Dahl and collaborators.¹ In other cases all three factors may enter, and direct metal-metal bonding may be relatively unimportant. In three previous papers we have implemented the protocol of analysis specified above, in a study of the superexchange problem in weakly coupled d^9 dimers,² in a detailed investigation of alternative geometries of M_2L_6 complexes,³ and in a discussion of triple-decker sandwiches.⁴ This contribution

deals with metal dimers bridged by three ligands, the M_2L_9 class of compounds. A number of these face-shared bioctahedra have been analyzed in terms of structural distortions and the 18-electron rule by Cotton and Ucko.⁵ We will expand on their important study using qualitative molecular orbital (MO) arguments and extended Hückel calculations.

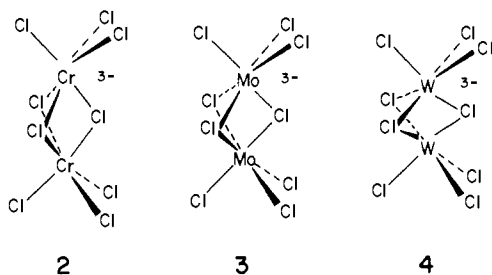
The method of Cotton and Ucko was based on the important insight that in bridged metal dimers a number of structural variables are interdependent. In complex **1** it takes one dis-



tance, M-M or M-X, plus one angle, M-X-M, M-M-X, or X-M-X, to fix the bridging region. The traditional emphasis in such structures has been on the metal-metal distance. The range of distances, however, is restricted by the limited flexibility of the bridge system. Cotton and Ucko chose to examine instead distortion that indicated elongation or contraction of the complex relative to an ideal bioctahedron.

The ideal structure has an angle, β , at the bridging group of 70.5° , angles between any two ligands on the same metal of 90° , and the metal equidistant between the planes of bridging and terminal ligands, $d' = d''$. Any real M_2L_9 complex will of course deviate from this ideal geometry, or approach it only accidentally. A complex in which a metal-metal bond exists would be expected to distort so that the metals are shifted toward one another: β would be less than 70.5° , α' greater than 90° , and d'/d'' less than 1. On the other hand, repulsions between the metals would cause elongation: β would be greater than 70.5° , α' less than 90° , and d'/d'' greater than 1.

The classic series to illustrate these distortions is the series of $M_2Cl_9^{3-}$ complexes of group 6, 2-4.⁵ In terms of valence



	2	3	4
M-M	3.12 Å	2.65	2.41
$\beta = \text{M-Cl-M}$	76°	65°	58°

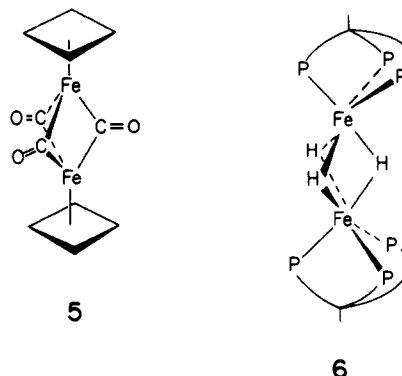
electrons these complexes are isoelectronic, d^3 , but the increase in size going from Cr to Mo to W allows more metal-metal interaction. In $\text{Cr}_2\text{Cl}_9^{3-}$ there are no d electrons paired in metal-metal bonds, and the complex is elongated from an ideal octahedron of $\beta = \text{M-X-M} = 70.5^\circ$. In $\text{Mo}_2\text{Cl}_9^{3-}$ two electrons are paired in a metal-metal bond and the complex is now slightly compressed from the ideal structure. In $\text{W}_2\text{Cl}_9^{3-}$ with all electrons paired in a metal-metal triple bond, $\beta = \text{W-Cl-W} = 58^\circ$, strongly compressed from the ideal 70.5° . In agreement metal-metal distances decrease sharply in going from Cr to W. In fact for dimetal nonahalide and closely related systems, metal-metal distances, the distortion parameters given above, and electron counting all lead to the same conclusions on metal-metal bonding.

Complications may arise, however, when different bridging groups are involved or when bridging and terminal ligands are not the same. In such cases distortions from an ideal geometry might be considerable in a corresponding monomer, to the extent that the regular octahedron may not be the best model.

Consider, for example, complexes which by electron counting have metal-metal triple bonds. $\text{W}_2\text{Cl}_9^{3-}$ (4) has a metal-metal distance of 2.41 Å and is strongly compressed, $\text{W-Cl-W} = 58^\circ$. Complex 5 with a very short iron-iron distance of 2.18 Å is only slightly compressed by the angular criterion, $\text{Fe-C-Fe} = 67^\circ$.⁶ However, the hydride bridged complex 6,⁷ although its Fe-bridge bonds are shorter than in 5, has a longer iron-iron distance, 2.33 Å, and is elongated, $\text{Fe-H-Fe} = 79^\circ$. We will consider the individual electronic structures and the geometries of octahedral monomers in seeking to explain such differences.

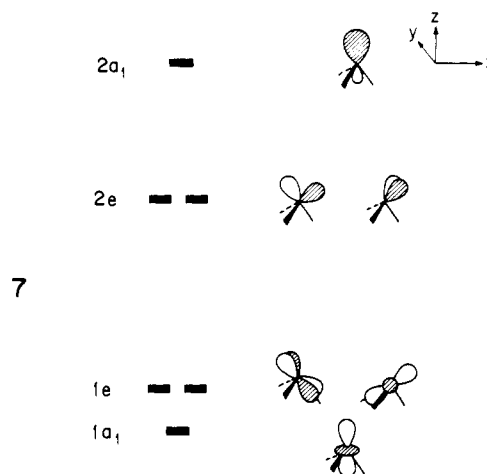
The Fragment Approach. M_2L_6

The electronic structure of the confacial bioctahedra can



be developed in a number of ways. One procedure, which focuses sharply on the bonding in the bridge region, is to construct the complex from two fragments—one composed of the three bridging ligands, the other of the two metals with their total of six terminal ligands. This second piece can in turn be assembled as a dimer of two conical ML_3 fragments. Other theoretical approaches have considered the interacting metal orbitals alone^{8,9} or the whole molecule.¹⁰

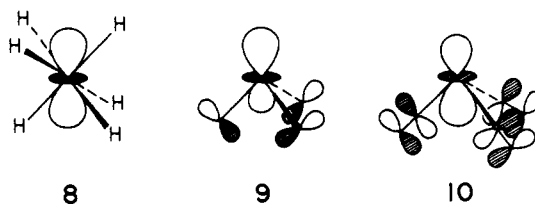
We have discussed previously the similarities and differences of the isolobal conical fragments ML_3 , MCp , and $M(\text{arene})$.^{12a} The basic ordering in energy and shape of the frontier orbitals of these fragments is shown in 7.



At relatively high energy there is an a_1 orbital, $2a_1$, composed of metal s, p and a variable contribution of z^2 , and a $2e$ set made up of a mixture of metal xz , yz and x, y . These orbitals are the equivalent of three hybrids pointing at the vacant corners of an octahedron. They are the orbitals which will undergo the greatest interaction with the bridging ligands.

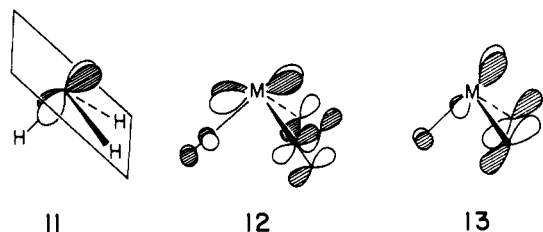
The lower set of orbitals would become the t_{2g} set of non-bonding levels in a pure octahedral complex. In a bioctahedron, however, they may be a major source of metal-metal interaction. In addition, although ligands interact much less with these lower orbitals, they are quite important in determining angular geometry. We will therefore discuss their nature in some detail.

The low-lying $1a_1$ is composed largely of metal z^2 . In an ideal octahedron with σ donating ligands alone, i.e., MH_6 , the orbital is 100% on the metal and completely nonbonding. The ligands all lie on the node of the z^2 orbital, 8. Of course inter-



actions with ligand π orbitals can affect the composition and energy of this orbital. π -donor ligands such as Cl will push this orbital up in energy. Small amounts of s and p will mix in to reduce the overlap with a $Cl_3 a_1$ orbital. The result will be a slight extension of the lobe protruding from the fragment, **9**. For CO, a model acceptor, the effect will be reversed. A decrease in energy and extension toward the ligands will characterize the $1a_1$ orbital in an $M(CO)_3$ fragment, **10**. In addition the electrons are more delocalized to the ligands in $M(CO)_3$. The metal character of $1a_1$ is 80% in $M(CO)_3$ and 95% in MCl_3 .

The lower 1e set of an ML_3 fragment would also be non-bonding as part of the t_{2g} set of an octahedral complex. In the conical fragment these orbitals are mostly xy and $x^2 - y^2$ with some xz or yz mixed in to provide a tilt, so that the ligands are on the node, as they were in the $1a_1$ orbital. With this tilt the lower e set presents a mixture of π and δ (mostly δ) character to a fragment approaching along the C_3 axis.¹² The degree of tilt, and thus of π or δ character, will depend on the nature of the π interactions with the terminal ligands. The tilt in an MH_3 octahedral fragment, 35.3° from the xy plane, will place the ligands exactly on the nodes of this orbital, **11**. If the ligands are π acceptors like CO, the π interactions will lessen the tilt and give the orbital more δ character, **12**. When the ligands



are π donors, the orbital will tilt more from the xy plane and a small amount of metal p will mix in to hybridize the orbital out from the metal, **13**. This increases the π -bonding abilities of the lower 1e set. The explanation of the orbital tilt, important in the subsequent argument, has been given elsewhere.^{12b}

The net effect of π interactions of terminal ligands is that in an ML_3 fragment with L as a σ donor the lower $1a_1$ and 1e sets will interact much more strongly with any probe approaching along the C_3 axis than will the corresponding orbitals with L as a π acceptor.

The π effects on $1a_1$ and 1e and their consequences on the interacting ability are illustrated in Figure 1, where ML_3 fragments are dimerized to $D_{3h} M_2L_6$, the next step in constructing the bioctahedron. The lower d orbitals are stabilized by the π acceptor CO and destabilized by the π donor Cl. The orbitals of M_2Cl_6 are more widely split, as expected, than those of $M_2(CO)_6$. There are cases where isolable M_2L_6 complexes can exist in an ethane-like structure. The electronic structure of molecules such as $Mo_2(NMe_2)_6$,^{13a} $W_2(NMe_2)_6$,^{13b} $Mo_2(CH_2Si(CH_3)_3)_6$,^{13c} $W_2(NEt_2)_4Cl_2$,^{13d} and related systems is straightforward. The metals are each d^3 and so the lower $1a_1'$ and $1e'$ sets of the M_2L_6 complex are filled to give a triple bond, one σ component and two π bonds with some δ character. We note here two points: (1) the metal-metal bonding orbitals are well defined in these complexes, and (2) there are no isolable complexes of this type with π -acceptor ligands. The reasons for the second statement are probably that π acceptors would decrease metal-metal interaction so that a stable dimer could not form and, perhaps more importantly, for CO complexes to be stable there must be filled d orbitals which can form π bonds with the CO π^* MOs. There is probably not enough back-bonding in a $d^3 M(CO)_3$ fragment. A more complete theoretical discussion of these ethane-like dimers, particularly with respect to barriers to internal rotation, is forthcoming.¹⁴

To proceed toward the construction of M_2L_9 we show a

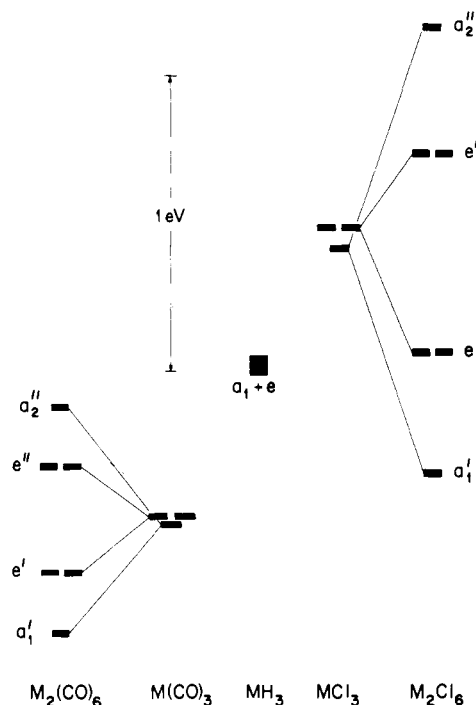


Figure 1. The lower d block orbitals of $M(CO)_3$, MH_3 , and MCl_3 in the middle are dimerized to $M_2(CO)_6$ and M_2Cl_6 fragments at left and right.

schematic diagram of the valence orbitals of a $D_{3h} M_2L_6$ fragment (Figure 2) and the specific behavior of these levels with MM separation for $Fe_2(CO)_6$ (Figure 3). The orbitals in Figure 2 are obviously grouped as symmetric and antisymmetric combinations with respect to the xy plane that bisects the MM axis. So they are in Figure 3. The increasing splitting with decreasing metal-metal separation is a clear sign of direct metal-metal interaction. The upper orbitals split more, because they are better directed for interaction. In fact one of the orbitals, the $\sigma^* 2a_2''$, is off the graph. The directional character of the upper orbitals is maintained in the dimer. It will lead to important interactions with bridging groups, which we now bring in.

Complexes Bridged by Three Hydrides

The simplest bridging ligand is, of course, hydride. There are a number of complexes known in which two metals are bridged by three hydrides: **14**,⁷ **15**,⁷ **16**,^{15a} **17**,¹⁶ and **18**.¹⁷ Structures with the hydrides located are available for **14** and **15**,⁷ and recently a neutron diffraction study of **16** has been completed.^{15b}

All these complexes except **15** are d^6 - d^6 and by normal electron counting conventions should have metal-metal triple bonds. However, the angle at H in **14** is large compared to a regular octahedron and **15** is even more elongated. The Ir-H-Ir angle in **16** is no less than 89.5° .^{15b} Although these complexes are not compressed, as one would expect if a metal-metal bond were present, the metal-metal distances are quite short: Fe-Fe = 2.33 Å in **14**, Co-Co = 2.37 Å in **15**, Ir-Ir = 2.46 Å in **16**.

Consider the orbitals of an H_3 bridging group. There are three such, an a_1' and e' set in D_{3h} , **19** and **20**. These orbitals, derived from atomic s orbitals and symmetric with respect to the xy plane, are concentrated on the bridging atoms which will be at the empty octahedral positions of M_2L_6 . They will thus interact most strongly with the upper a_1' and e' of such a fragment. An interaction diagram is shown in Figure 4 for the model system $Fe_2CO_6 + H_3$, with an electron count appropriate for $Fe_2(CO)_6H_3^+$.

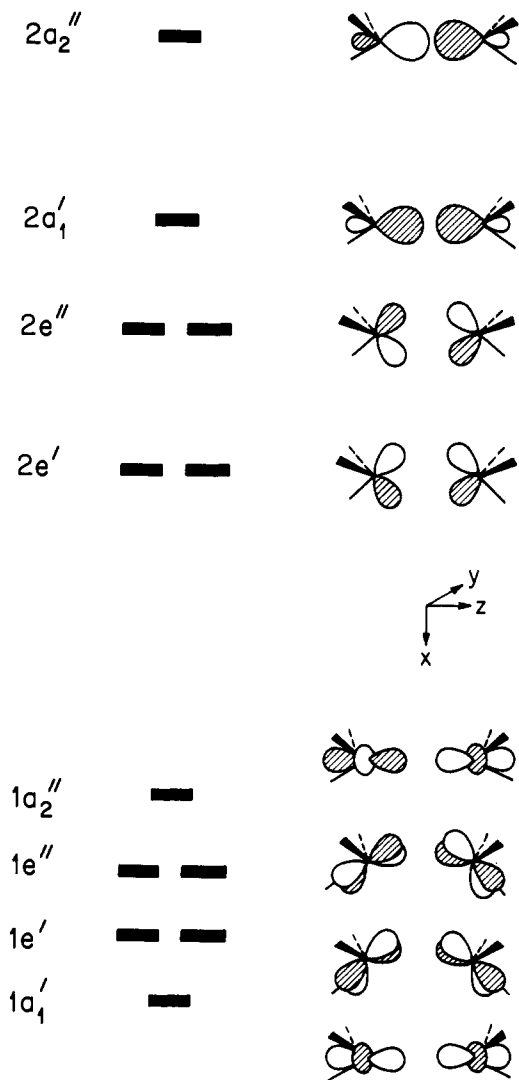


Figure 2. A schematic drawing of the valence orbitals of M_2L_6 .

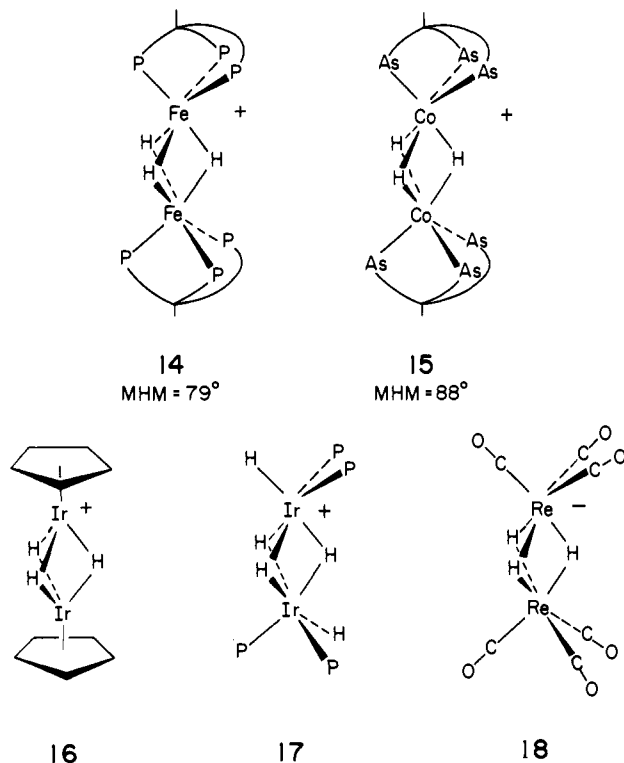
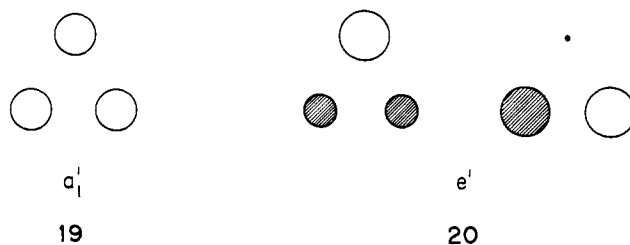
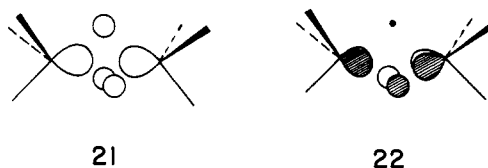


Figure 3. Variation in energy with metal-metal separation of the frontier orbitals of $Fe_2(CO)_6$.



The first question that arises is "Is there a metal-metal triple bond in the system?" The answer unfortunately must be "yes and no". The six orbitals derived from the lower set of each $M(CO)_3$ fragment remain bunched together, contributing all together essentially nothing to metal-metal bonding. They have become the " t_{2g} " sets of the two now completed octahedra. The only candidates for metal-metal bonding are the lower a_1' and e' orbitals. These are derived primarily from the hydride ligands, and their qualitative appearance is shown in **21** and **22**.



These orbitals are certainly metal-metal bonding, but they are also metal-bridging hydride bonding.^{2n,u,18} The ambiguity we encounter is nothing new, for it occurs in a molecule as simple as diborane.^{19a} The two molecular orbitals most involved in bridge bonding, $1b_{2u}$ and $3a_g$, are shown schematically in **23** and **24**. Both are B-B and B-H bonding. Descriptions corresponding to either extreme, boron-boron double bonding, **25**, or no bonding at all, **26**, have played their role in the fascinating history of the geometrical and electronic structure of the boron hydrides. Even quite good quantum mechanical calculations are not of much help, for the B-B

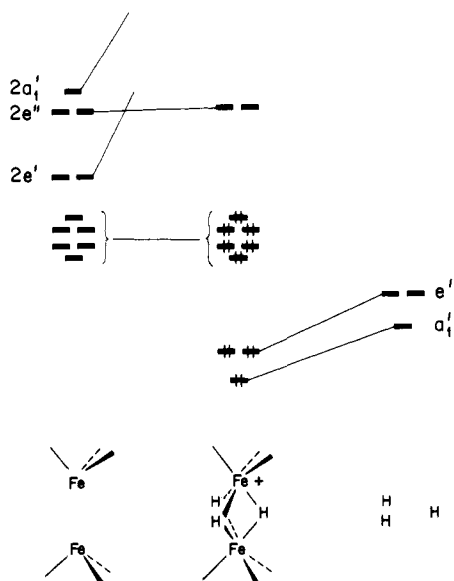
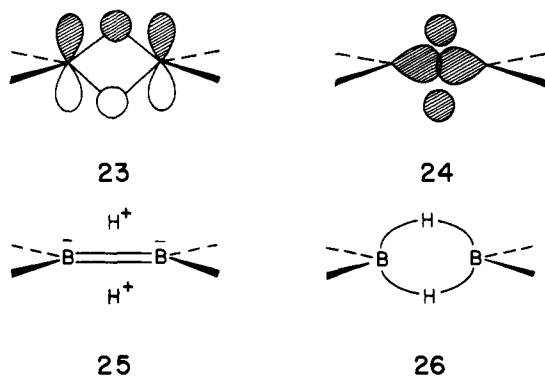


Figure 4. Interaction diagram for $(CO)_3FeH_3Fe(CO)_3$.



overlap population appears to be sensitive to basis set quality.¹⁹ Localization procedures yield a picture corresponding closer to **26**.

Our conclusion for both diborane and the $L_3FeH_3L_3^-$ transition metal dimer is that it is best not to argue over whether there is or is not metal-metal bonding in these molecules. The orbitals in question are delocalized and are used to bond a metal atom *both* to its metal partner and to the bridging group.

We now return to the basic question raised in the introduction: Why is **14** elongated? The $(\mu-CO)_3$ complex **5** has a shorter Fe-Fe distance and is compressed. Also, why is **15** still more elongated? The answers to these two questions reflect on the relative importance of the various factors which influence metal-metal bonding. The elongation of **14** can be traced to a monomer geometrical preference, and the additional increment of **15** over **14** to direct metal-metal interaction.

Consider a d^6 octahedral monomer, H_3ML_3 , **27**, in which



27

the three hydrides are allowed to distort in the same way that in a dimer would cause elongation or compression of the bioctahedron. If the lower ligands were all hydrides, the energy

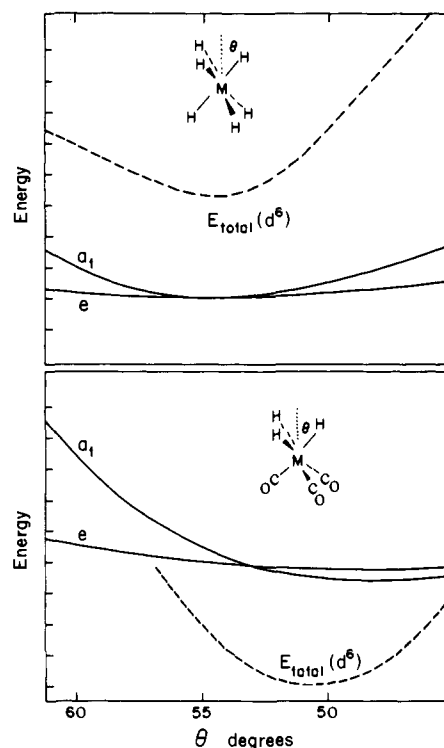


Figure 5. a_1 and e levels and total energies for two d^6 monomers as a function of the angle θ between the threefold axis and the M-H bonds. MH_6 at top, $M(CO)_3H_3$ at bottom. The energy scale markings are in 0.1 eV.

minimizes at $\theta = 54.75^\circ$, a regular octahedron. θ is the angle between the C_3 axis and an M-H bond. At that geometry there is minimal (repulsive) interaction between the hydrides and the metal a_1 or z^2 , as shown at top in Figure 5.

Now consider the interaction of H_3 with the $M(CO)_3$ fragment. Again it is favorable for the hydrides to minimize interaction with the lower a_1 by sitting on its node. But CO (and to some extent phosphine) is a π acceptor and, as described in the previous section, will interact to decrease the cone angle at the node. The H_3 face should close. This is exactly what happens. The energies of the a_1 and e orbitals of $H_3M(CO)_3$ are plotted at the bottom of Figure 5 along with the total energy of a d^6 complex. The H_3 face does close, in part following the node of the a_1 . The C_3 axis-M-H angle θ minimizes at 50° . If two monomers are superimposed to give a dimer, the angle at the bridge would be the complement of 2θ , 80° , close to the experimentally observed 79° in **14**.

We have proceeded to optimize the bridging angle in model systems for **14** and **15**. The results are shown in Table I.

When we tried to optimize the actual dimer geometry we obtained an unsatisfactory angle of 62° for $Fe_2(CO)_6H_3^+$, increasing to 91° in the system with two electrons more. The results are unfortunately sensitive to the parameters, especially the s and p exponents. For instance, with a different choice of s and p exponents, based on Burns' rules,²⁰ the corresponding optimum angles were 81 and 96° . In either semiempirical or ab initio calculations the s and p functions are the ones whose shape is most uncertain, and the reader should be aware of the limitations placed on the reliability of the calculations by the choice of s and p exponent. The two sets of s and p orbitals used by us differ in how contracted or diffuse they are. This has no effect on the monomer geometry, which is set largely by metal d-ligand overlaps. It does affect, in an understandable way, the dimer calculation. Contracting the s and p orbitals increases their overlap with d functions, in particular with d functions on the other metal. The too small MHM angle in $Fe_2(CO)_6H_3^+$ with contracted functions can be traced to an

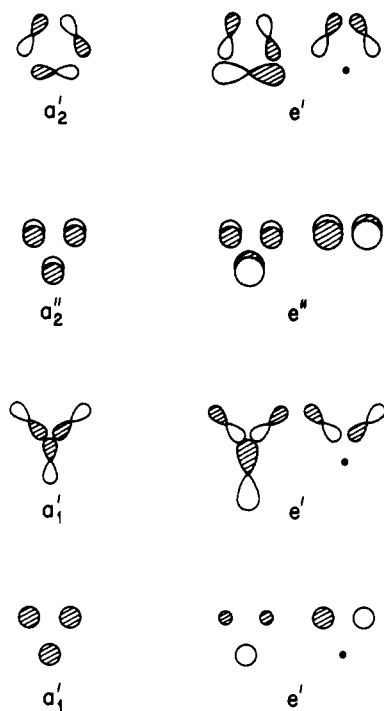


Figure 6. The 12 symmetry-adapted combinations formed from the orbitals of three bridging halides. The view is along the threefold axis, onto the plane containing the halides.

Table I. MHM Angles Calculated for H₃ Bridged Dimers

molecule	bridging angle, deg	
	superimposed monomers	expt (ref 7)
Fe ₂ (CO) ₆ H ₃ ⁺	80	79.4
Fe ₂ (CO) ₆ H ₃ ⁻	81	88.0

overemphasis of two-electron attractive interactions between the s- and the p-like 2a₁ on one center with the d-like 1a₁ on the other.

The elongation of Fe₂(CO)₆H₃⁻, a model for the known Co₂L₆H₃⁺, is given by the calculations, no matter which basis set is used. The complex is paramagnetic, the two extra electrons entering the low-lying e'' orbital in Figure 4. By symmetry the e'' does not interact with the bridging hydrides. It is an orbital pair that is unchanged from Fe₂(CO)₆, antibonding between the metals. The resulting metal-metal repulsion causes an increase in the elongation of the complex. That this is *not* a result of ligand distribution in the monomer is obvious from Table I. The extra electron causes almost no change in monomer geometry.

Complexes Bridged by π Donors

The triply bridged dimers greatest in number are those with π-donating bridging groups such as halide, OR⁻, SR⁻, etc. These should be divided into two groups, those which also have π-donating terminal ligands and those which have terminal π acceptors. The first group, with terminal donors, may have a variety of electronic configurations. Examples are Ti₂Cl₉⁻, d⁰-d⁰,²¹ Ti₂Cl₉³⁻, d¹-d¹,²² Nb₂Cl₉³⁻²³ and Nb₂Br₆(μ-SC₄H₈)₃,^{9a} d²-d²; **2**, **3**, **4**,²⁴ and the extended ReCl₄ structure,²⁵ d³-d³; W₂Br₉²⁻, d³-d⁴,^{9b} Mn₂Cl₉⁵⁻, d⁵-d⁵,²⁶ Rh₂Cl₉³⁻, d⁶-d⁶,^{5,27} I₂O₉^{4-28a} and Ti₂Cl₉³⁻, d¹⁰-d¹⁰,^{28b,c} Sb₂Br₉³⁻, "d¹²-d¹²",²⁹ among others.³⁰ On the other hand, dimers with terminal π acceptors, particularly CO, are almost invariably d⁶ with the lower three octahedral d orbitals on each metal filled. The necessity for π bonding between the metal

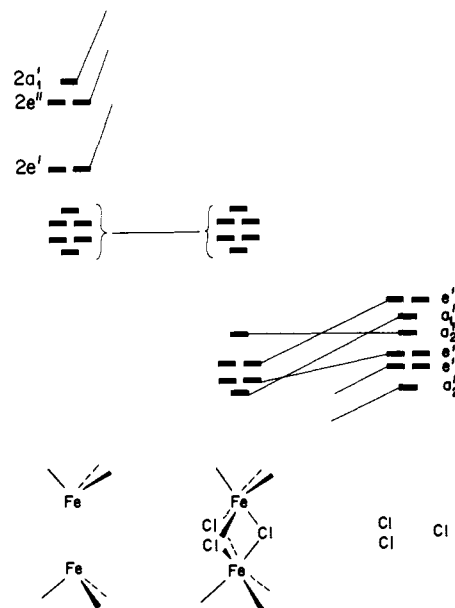
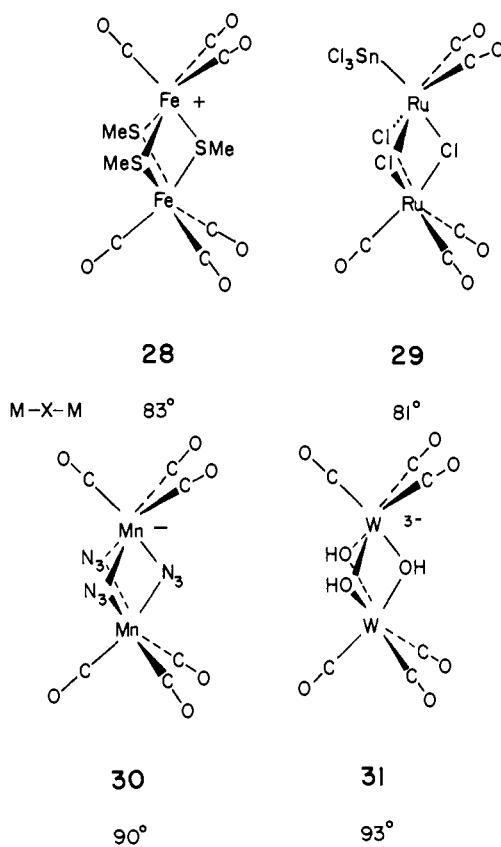


Figure 7. Interaction diagram for (CO)₃FeCl₃Fe(CO)₃.

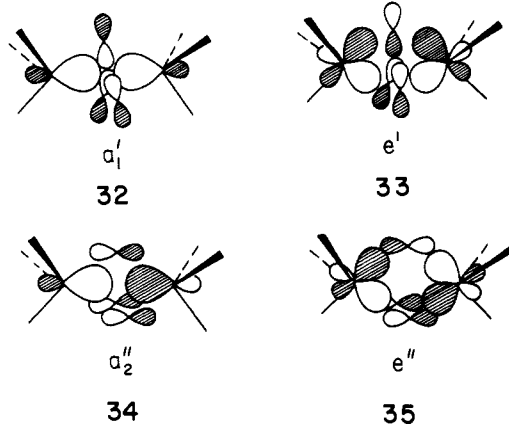
and the CO π* orbitals presumably requires the d levels to be filled. These complexes have 18 electrons per metal without metal-metal interaction and are all elongated from the ideal bioctahedron. Examples are **28**,³¹ **29**,³² **30**,³³ and **31**.³⁴ Other



structures of this type are Re₂(CO)₆X₃³⁵ and Mo₂(CO)₆(HNPPH₃)₃.^{36,37}

The orbitals of an X₃ fragment, in which p orbitals are important, will be more complicated than H₃. There are now 12 rather than 3 orbitals. These are shown in generalized form in Figure 6. For Cl₃³⁻ they are all filled and, because the s-type orbitals are at low energy, the p-type orbitals will be most important in interactions with M₂L₆.

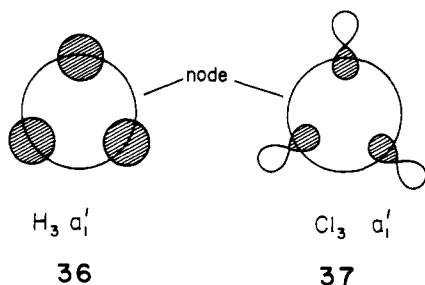
Figure 7 is an interaction diagram for the X_3^{3-} π donor fragment with M_2CO_6 . The diagram would be quite similar for M_2Cl_6 . The biggest difference between Cl_3 and H_3 is that Cl_3 has p-orbital combinations antisymmetric to the plane of the atoms, a_2'' and e'' . As Figure 7 shows, there are now bridge donor orbitals of proper symmetry to match each acceptor orbital on $Fe_2CO_6^{4+}$. If the lower d levels are filled, there is little opportunity for metal-metal bonding in these complexes. In terms of the contribution of bridge bonds to metal-metal bonding this means that, for every filled M-L-M bond orbital



symmetric between the metals, a_1' , **32**, or e' , **33**, there is an antisymmetric counterpart a_2'' , **34**, or e'' , **35**.

Consider now the behavior of the lower d levels as the complex is elongated or compressed, in analogy to the $M_2(CO)_6(\mu-H)_3$ system. For $M_2(CO)_6(\mu-X)_3$ we are interested in the general trend of these six orbitals with a given distortion. The behavior of individual levels will be important to complexes such as **2**, **3**, and **4** where the d band is only partially filled. Since the interaction of an X_3 bridging fragment with M_2L_6 is similar for $L = CO$ or Cl we will discuss only the former in detail.

The interaction of the $M_2(CO)_6$ d levels with a Cl_3^{3-} fragment as a function of M-Cl-M angle is shown in Figure 8. This is a plot of the energy levels of $M_2(CO)_6(\mu-X)_3$ minus those of $M_2(CO)_6$. The a_1' orbital has a minimum at an M-Cl-M angle of $\sim 60^\circ$. This is because the antibonding interaction is least when the maximum density of the X_3 fragment a_1' orbital is on the node of the M_2CO_6 lower a_1' (z^2). This minimum interaction occurs at a more compressed geometry (larger C_3 axis-M-X angle) for Cl than H bridging. The reason is simple. While the density in an H_3 fragment a_1' is in s-type orbitals largely at the atomic nuclei, the density in a Cl_3^{3-} a_1' orbital is in p-type orbitals with maximum density away from the nucleus and closer to the center of the fragment. Thus in placing maximum density of the bridge fragment orbital on



the node the H_3 group will be closer together, **36**, than will the Cl_3 group, **37**.

The a_2'' and e'' orbitals of $M_2(CO)_6$ were unaffected by the H_3^{3-} bridge, but in Cl_3^{3-} there are donor orbitals of the proper symmetry to interact. In both cases this interaction decreases sharply as the complex elongates. As was the case with the a_1 ,

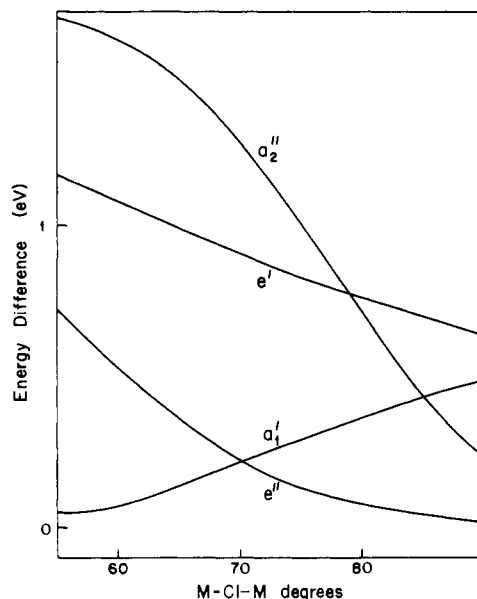
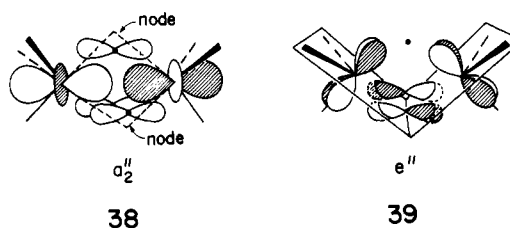


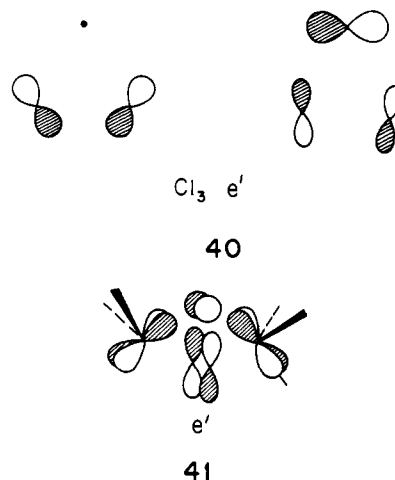
Figure 8. Difference in energy between some energy levels of $(CO)_3MCl_3M(CO)_3$ and $(CO)_3MM(CO)_3$ as a function of M-Cl-M angle.

the bridge fragment orbitals are approaching a node in the appropriate $M_2(CO)_6$ orbital, so that even though the two orbitals are of the same symmetry type overlap is poor. The situation for the a_2'' orbital is shown in **38** and for a member of the e'' set in **39**. Because the p-orbital density is not con-



centrated at the nucleus, the geometry which minimizes their interaction with the $Fe_2(CO)_6$ fragment does not have the bridging atoms themselves on the nodes but is elongated.

The e' orbitals show a large interaction, but less change with distortion than the other orbitals. The Cl_3^{3-} e' orbitals which interact most with the M_2L_6 fragment are the ones composed of peripheral p orbitals, **40**. Their density is concentrated *between* the bridging atoms, as is the lower e' of M_2L_6 . Thus the overlap is large, **41**, although the overlap of the fragments



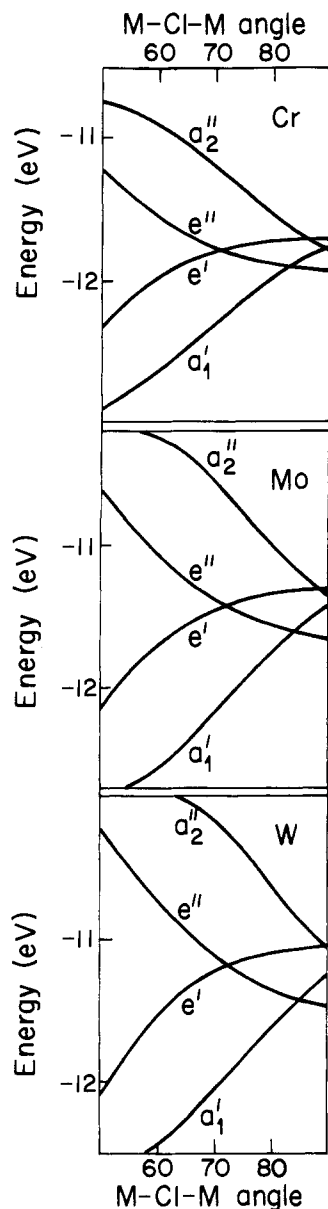
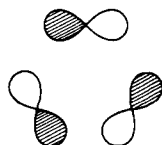


Figure 9. The energy levels of $M_2Cl_9^{3-}$. M = Cr (top), Mo (middle), W (bottom), as a function of M-Cl-M angle.

combined will drop as the complex is elongated, and M-Cl increases. There is no special interaction of the Cl_3^{3-} orbital with the nodes of the M_2L_6 orbital, so the change is less than for the cases given above.

The combined effect of filling all the orbitals shown in Figure 8 would be a tendency to elongate the dimer, even compared to the complex with bridging hydrides. The d orbitals in the $M(CO)_3Cl_3$ monomer show similar behavior to those in $M(CO)_3H_3$. Yet the observed elongation in the dimers is similar to that in $M_2(CO)_6(\mu-H)_3$: 81° in $Ru_2(CO)_5SnCl_3(\mu-Cl)_3$ and 83° in $Fe_2(CO)_6(\mu-SMe)_3^+$. [We compute 74° for the superimposed monomers and 83° for the model dimer $Fe_2(CO)_6Cl_3^+$.] Also the calculated $M(CO)_3Cl_3$ monomer has a more open X_3 face. The reason for this is that



42

Table II. σ and π d Orbital Overlaps at 2.87 Å

	$\langle z^2 z^2 \rangle$ σ	$\langle xz xz \rangle$ π
Cr-Cr	0.0534	-0.0352
Mo-Mo	0.0757	-0.0594
W-W	0.0854	-0.0747

the d levels here are not the only thing that matters. Steric interactions of the chlorines can be a factor. This is best illustrated by the behavior of the mainly chlorine a_2 orbital in $M(CO)_3Cl_3$, **42**. This orbital, which cannot interact with the metal atom by symmetry, is Cl-Cl antibonding. In our calculations it rises rapidly as the Cl_3 face is closed or the dimer is elongated. The role of ligand-ligand interactions in the bridge in determining geometrical aspects of dimer structures has been stressed by Ross and Stucky.³⁸

As we have said, complexes of the type $M_2(CO)_6(\mu-X)_3$ are almost always d^6 , with the lower six d levels filled. In complexes with terminal π donors, however, these lower levels may be only partially filled. In these complexes it is necessary to consider the specific order of the d levels.

We will take as our models $Cr_2Cl_9^{3-}$ (**2**), $Mo_2Cl_9^{3-}$ (**3**), and $W_2Cl_9^{3-}$ (**4**), which have been the object of previous theoretical studies.⁸⁻¹¹ An MCl_3 dimer will behave much as the $M(CO)_3$ dimer of Figure 3 does. As the metal-metal distance decreases, the lower d orbitals will split into a lower set of M-M bonding orbitals, a_1' (σ) and e' (π), and a higher set antibonding between the metals, a_2'' (σ^*) and e'' (π^*). Superimposed on this splitting will be the interactions of Figure 8. At short distances between metals the metal-metal interaction will dominate. However, in elongated complexes with large metal-metal distances and small direct splittings the metal-bridge interactions will become more important. Examine the interactions of Cl_3 and $M_2(CO)_6$ in Figure 8. In an elongated geometry, $M-Cl-M \sim 90^\circ$, the a_2'' and e'' (σ^* and π^*) orbitals interact very little for reasons we have just described. The a_1' and e' (σ and π) orbitals, on the other hand, interact more strongly and are pushed up. If the direct splitting is small, then the a_1' and e' orbitals may actually cross the a_2'' and e'' to become the highest levels in the d band.

The actual behavior of these orbitals for **2**, **3**, and **4** is shown in Figure 9. There are indeed orbital crossings for e' and e'' near $M-Cl-M = 70^\circ$ and for a_1' and a_2'' at $M-Cl-M \geq 90^\circ$. In order to form a diamagnetic complex with a metal-metal triple bond (a_1' and e' occupied) the complex must be compressed so that e' and e'' splitting is enough to overcome the repulsions of pairing electrons in the lower orbitals. The compression is in turn resisted by nonbonded interactions of terminal and bridging chlorines. For the compression to be favored the metal-metal interaction (as expressed in the downward slopes of the bonding orbitals) must be great enough to overcome the chlorine-chlorine repulsions.

The metal-metal interaction is, of course, dependent on the overlaps of d orbitals on one metal for their counterpart on the other. These are given for Cr, Mo, and W at an intermediate distance in Table II. As we go from Cr to Mo to W, the metal orbital overlap becomes greater. In $Cr_2Cl_9^{3-}$ (**2**), the interaction is not sufficient to compress the complex even enough to pair electrons in the a_1' metal-metal σ bond. In $W_2Cl_9^{3-}$ (**4**) the much larger interaction is sufficient to compress the complex and form a W-W triple bond. In $Mo_2Cl_9^{3-}$ (**3**) there is compression. The a_1' and a_2'' levels split enough to allow a σ bond to form. However, because of the greater interaction of e' than e'' with the bridging chlorines, the substantial π interaction directly between metals in $Mo_2Cl_9^{3-}$ results not in a greater splitting but in a smaller one. The e' and e'' levels are close and all occupied by one electron. These conclusions are identical with those of Korol'kov and co-workers.^{10a,b}

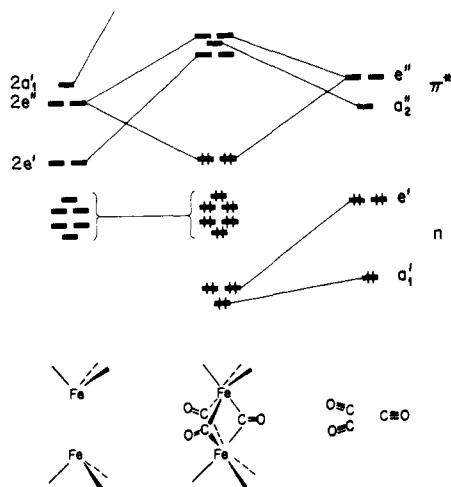
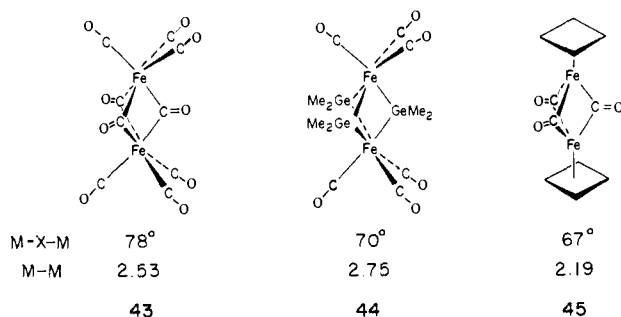


Figure 10. Interaction diagram for $Fe_2(CO)_9$ constructed from $Fe_2(CO)_6$ and three bridging carbonyls.

In a thorough recent study, Natkaniec^{10c} has applied a variety of computational techniques to the M_2Cl_9 dimers. Especially in his angular overlap model calculations one can see the same type of construction as that used by us, with similar results.

Complexes Bridged by π Acceptors

In addition to halide bridged complexes there are a number of bioctahedra bridged by three π acceptors. These π acceptors are two-electron donors which have vacant p orbitals available to accept metal electrons: CO, GeR_2 , etc. The best known example of such a complex is $Fe_2(CO)_9$ ³⁹ (**43**), with eight d electrons per metal and isoelectronic with $Fe_2(CO)_6(\mu-GeMe_2)_3$ ⁴⁰ (**44**). Complexes **43** and **44** have 17 electrons per metal and have been assigned iron-iron single bonds. Complex **45** has four electrons less and has been assigned a metal-metal



triple bond.⁶ The gross electronic structure of such complexes has been described briefly by us,⁴ and we elaborate on that here.

The CO bridging ligand has π^* acceptor orbitals which dominate its behavior. The $(CO)_3$ fragment can be viewed as having the same orbitals as Cl_3 (Figure 6) except that all peripheral and out-of-plane p orbital combinations will now be acceptors, *not donors*. An a_1' , **46**, and e' , **47**, set of σ donors will arise from the CO lone pairs which are approximate sp hybrids. The primary acceptor orbitals will be e' (peripheral), a_2'' , and e'' (Figure 6). The general electronic structure shown in Figure

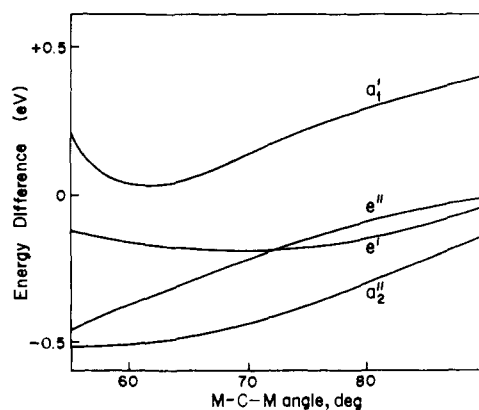
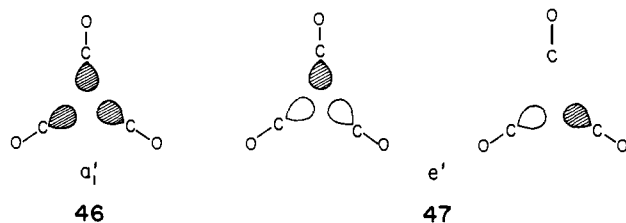


Figure 11. Difference in energy between some energy levels of $(CO)_3M(CO)_3M(CO)_3$ and those of $(CO)_3MM(CO)_3$ as a function of bridging M-C-M angle.

10 resembles that of the $(\mu-H)_3$ complex (Figure 4) in many ways. Only the upper a_1' and e' orbitals of $M_2(CO)_6$ are pushed up by the donor orbitals of $(CO)_3$. The upper e'' orbital remains at low energy and is even depressed, compared to the hydride bridged complexes, by interaction with the $(CO)_3$ e'' π^* orbital. In **43** and **44** this orbital is filled and antibonding between the metals. In **45** this orbital is empty, the metals are d^6 . Electron counting as in **14** suggests an Fe-Fe triple bond, but the same quandary arises about the nature of the bridge region orbitals as we discussed earlier. There are, however, differences in geometry. **45** has a shorter Fe-Fe distance (2.19 Å) than **14** (2.33 Å) in spite of the longer Fe-bridge bonds. The Fe-bridge-Fe angle is thus compressed in **45** relative to the hydride complex, 67° vs. 78°.

Since $(cyclobutadiene)_2Fe$ is isolobal¹² with $Fe_2(CO)_6$, let us look at the effect of bridging $(CO)_3$ on the lower orbitals of the dimer (Figure 11). Note that the a_1' behaves much as it does with $(\mu-H)_3$ and $(\mu-Cl)_3$. The interaction (overlap) will minimize at a value between the other two because the donor orbitals of CO are near sp hybrids, whereas the H_3 orbital is pure s and the Cl_3 orbital is almost all p.

At first glance the effect of the $(\mu-CO)_3$ group on the other orbitals is quite different than that of $(\mu-Cl)_3$. These orbitals all drop (not rise) in energy as the complex is compressed. The interactions are in fact exactly the same for CO and Cl, but the bridge fragment orbitals in CO are acceptors which stabilize, not donors which destabilize, as in Cl. The reason for the behavior of the a_2'' and e'' metal orbitals on distortion is now obvious. It is a mirror image of the Cl interactions.

The behavior of the e' orbital is more complex because there are two bridge orbitals of e' symmetry, a σ donor and an acceptor of the peripheral p type. The σ donor, localized near the bridge atom positions, interacts mostly with the upper e' of $M_2(CO)_6$. The e' CO π^* acceptor orbital concentrated between the bridging atoms is ideally situated to interact with the lower e' orbital of $M_2(CO)_6$. It is the acceptor orbital which dominates and the e' of $M_2(CO)_6$ which is stabilized.

The behavior of the orbital interactions in Figure 11 suggests that a CO bridged dimer would compress relative to one bridged by H or Cl. Similarly in a model monomer with three COs in a bridging geometry, **48**, the face with the "bridge-

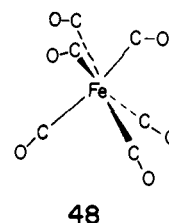


Table III. M-C-M Angles (deg) Calculated for (CO)₃ Bridged Dimers

molecule	d electrons per metal		superimposed monomers	calcd dimer
	metal	expt		
Fe ₂ (CO) ₉ ⁴⁺	6		62	55
(cyclobutadiene) ₂ Fe ₂ (CO) ₃	6	67		
Fe ₂ (CO) ₉	8	78	64	79.5

Table IV. Charge Iteration Parameters for Molybdenum^a

parameter	orbital		
	5s	5p	4d
A	0.50	0.45	0.74
B	6.78	5.78	9.40
C	6.82	3.94	8.37

^a Calculated from data in ref 50.

type" ligands should open. This is exactly what is observed (Table III). Two Fe(CO)₆²⁺ monomers with three COs in a bridging geometry, **48**, if superimposed would have an Fe-C-Fe angle of 62°, compressed and less than the experimental 67° in **45**. The conclusion for **45** is essentially the same as for the hydrides: there is little evidence for an important *geometry-determining* attraction between the irons.

If we now look at Fe₂(CO)₉, we find that four electrons have been added to the e'' orbitals. These are antibonding between the metals and the complex is elongated. This change in geometry (*elongation*) is not found in the monomer (Table III), so it can be considered to arise from direct metal-metal interaction. In the case at hand we consider that interaction to be *repulsive*, not attractive, as one might have been led to think from electron-counting considerations and the postulate of a metal-metal single bond in this common and important iron carbonyl.

The general question whether metal-metal bonding is present or absent in these systems is bothersome enough so that we will try to discuss it in another way. Though we refrained from characterizing delocalized molecular orbitals as being metal or bridge type before, let us try to make that precarious assignment qualitatively for the various dimers.

When two orbitals of different energy (electronegativity) interact, the lower resulting orbital always has more of the character of the lower of the original orbitals, increasingly so the greater the energy difference between the original orbitals. Donor orbitals for bridging H, CO, or Cl are usually quite low in energy compared to the acceptor orbitals on Fe₂(CO)₆, Figures 4, 7, and 10. Therefore the resulting bridge bonds in M₂(CO)₆X₃ (and bridge antibonds also for X = Cl) are mostly on the bridging group with slight metal character. Now consider Fe₂(CO)₉ (Figure 10). The donor orbital is now on the Fe₂(CO)₆ fragment, so the resulting bridge e'' orbitals will have more metal character than the e' orbitals arising from the (CO)₃ e' donor.

In M₂(CO)₆X₃ we drew filled bridge orbitals **32-35**, all arising from bridge fragment donors and therefore largely localized on the bridge. These bonding and antibonding orbitals balanced both in number and approximate strength. In Fe₂(CO)₆(μ-H)₃⁺ only **32** and **33** were filled, which by electron counting would give an Fe-Fe "triple bond". In Fe₂(CO)₉ three orbitals, Fe-Fe bonding but arising from ligand donors, are filled, **32** and **33** (**33** is one member of a degenerate pair). Two orbitals antibonding between irons, **35** and its partner, are also filled, but these are localized mainly on the Fe₂(CO)₆ fragment. If one simply counts up the three filled bonding and two filled antibonding orbitals, one comes to a single Fe-Fe bond. However, whereas with the (μ-Cl)₃ complexes the

Table V. Extended Hückel Parameters

orbital	H _{ii} eV	exponents ^a	
		ζ ₁	ζ ₂
H 1s	-13.6	1.3	
C 2s	-21.4	1.625	
C 2p	-11.4	1.625	
O 2s	-32.3	2.275	
O 2p	-14.8	2.275	
Cl 3s	-27.5	2.356	
Cl 3p	-15.4	2.04	
Fe 4s	-9.10	1.9	
Fe 4p	-5.32	1.9	
Fe 3d	-12.6	5.35 (0.5505)	2.00 (0.6260)
Cr 4s	-9.66	1.7	
Cr 4p	-6.36	1.7	
Cr 3d	-12.3	4.95 (0.505 79)	1.80 (0.674 72)
Mo 5s	-9.66	1.96	
Mo 5p	-6.36	1.90	
Mo 4d	-12.3	4.54 (0.589 88)	1.90 (0.589 88)
W 6s	-9.66	2.34	
W 6p	-6.36	2.31	
W 5d	-12.3	4.98 (0.668 27)	2.07 (0.542 22)

^a Two Slater exponents are listed for the d functions. Each is followed in parentheses by the coefficient in the double ζ expansion.

bonding and antibonding orbitals were of approximately equal metal-metal bonding strength, in Fe₂(CO)₉ the two e'' antibonding orbitals clearly have more metal character than their bonding counterparts.

We have presented a general analysis of the role of monomer geometrical preferences, through-bond coupling by bridging ligands, and metal-metal interaction in confacial bioctahedral complexes. Hydride, chloride, and carbonyl were studied as representative bridges. While we have restricted ourselves to three identical bridging groups,⁴¹ the general conclusions are clear. Direct metal-metal bonding plays a role in determining the geometry of only a minority of these complexes—other factors such as the monomer distortions and the symmetry-conditioned interaction opportunities offered up by the orbitals of the bridging ligand are often more important. Cautions concerning simplistic conclusions about metal-metal bonding in these and related molecules have been stated in the literature previously.^{1,5,18b,42-44} A delocalized bonding picture is the appropriate one for all of the confacial bioctahedra.

Acknowledgment. We are grateful to J. Jorgensen for the expert drawings, and to the National Science Foundation for its support of this research through Grant CHE 7606099.

Appendix

All the calculations were of the extended Hückel type.⁴⁵ Parameters used for carbon, oxygen, and hydrogen were the same as in previous work. The exponents for the 3s and 3p orbitals of chlorine were taken from the work of Clementi and Roetti.⁴⁶ The exponents for the 4s and 4p orbitals of iron and chromium and all iron orbital H_{ii}'s were taken from our previous work.³ The double ζ 3d orbital exponents for iron and chromium were those determined by Richardson et al.⁴⁷ All orbital exponents for molybdenum and tungsten were taken from the work of Basch and Gray.⁴⁸ For the calculations on M₂X₉ trianions the metal H_{ii}'s were assumed equal for Cr, Mo, and W. They were determined by charge iteration on MoCl₆²⁻ assuming a quadratic dependence of metal H_{ii}'s on charge⁴⁹ while keeping the chlorine 3s and 3p orbital H_{ii}'s constant at -27.5 and -15.4 eV, respectively. The iteration parameters for molybdenum were taken from Baranovskii and Nikol'skii⁵⁰ and are listed in Table IV. The final parameters for all calculations are listed in Table V.

References and Notes

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