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$M_2(CO)_6$(ligand) Complexes

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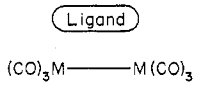
We present a systematic molecular orbital study of the electronic structure of complexes containing the $M_2(CO)_6$ binuclear transition-metal fragment bonded to a variety of ligands. These include acetylene, two carbonyls, C_4R_4 (the ferroles), C_6R_6 (flyover bridges), cyclobutadiene, dienes, azulene, cyclooctatetraene, pentalene, tetramethyleneethane, cycloheptatrienyl, hexatrienes, and other π-electron systems. The orientational preferences of these ligands are analyzed in detail. Some inferences are drawn on their reactivity, as well as the possible stability of some as yet unsynthesized complexes.

Dimers with the formula $M_2(CO)_6$(ligand), shown schematically in **1**, frequently crop up in transition-metal chemistry.



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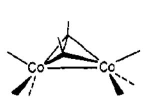
The ligands of primary interest are unsaturated organic molecules, ranging from acetylene to azulene. The number and variety of such complexes are remarkable. Several structural classes are discernible, each exemplified below by a single structure.[1] There are complexes with simple ligands such as acetylenes[2,3] (**2**), ferrole complexes of type **3**,[4,5] "flyover" bridges such as **4**,[6] and "picnic-table" compounds of type **5**.[7] This list does injustice to the beauty and complexity of the full range of compounds in which the $M_2(CO)_6$ unit appears. Other complexes, and some discussion of bonding and structural trends, are given in several recent review articles.[8,9]



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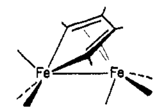

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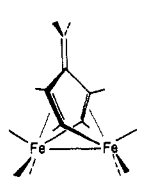

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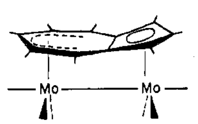

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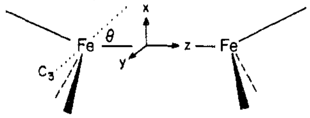
One feature common to all these molecules is the metal–metal-bonded $M_2(CO)_6$ unit. A study of the orbitals and bonding capabilities of such $M_2(CO)_6$ fragments should aid in understanding the structures and, perhaps, the chemistry of these molecules. This approach is a natural extension of earlier work on metal carbonyl fragments[10] and MCp_2 fragments.[11] We begin with a development of the valence orbitals of $Fe_2(CO)_6$, Fe being chosen as a typical transition metal, followed by a brief look at other related fragments, and then a discussion of bonding patterns with various ligands.

All calculations are of the extended Hückel type, and the parameters used are discussed in Appendix I. The reader should be aware that the extended Hückel procedure has well-known deficiencies. The conclusions drawn in this paper should be viewed as being only indicative of bonding trends and not as definitive statements of fact.

Orbitals of $M_2(CO)_6$

A typical geometry of the $Fe_2(CO)_6$ fragment is shown in **6**. It is perhaps most readily considered as arising from the combination of two $Fe(CO)_3$ fragments. In these calculations a local C_3 axis is retained for each $Fe(CO)_3$ unit, with a C–Fe–C angle of 95°, Fe–C 1.74 Å, and C–O 1.13 Å. With these held constant, and the additional constraint of C_{2v} symmetry, the $Fe_2(CO)_6$ fragment has only two degrees of freedom: the metal–metal distance R and the angle of tilt θ, defined as the angle between the local C_3 axis and the metal–metal bond.



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The orbitals of $Fe_2(CO)_6$ can be built up by interacting the orbitals of the two $Fe(CO)_3$ fragments. Figure 1 shows the resulting orbitals when the $Fe(CO)_3$ fragments[10] are brought together in D_{3h} symmetry ($\theta = 0°$). Of the six metal-type orbitals of $Fe(CO)_3$ the lower three (heavily involved in Fe–CO back-bonding) hardly interact at all, and in $Fe_2(CO)_6$ they form a low-lying nest of six orbitals. However, the upper three orbitals of $Fe(CO)_3$ interact strongly to form six "valence" orbitals of the $Fe_2(CO)_6$ fragment. Only five of them are available for bonding with ligands, as the highest (a_2'', σ^*) is too strongly antibonding to be used.

To make the $Fe_2(CO)_6$ fragment resemble the "sawhorse" geometry that is found in many of the crystal structures, θ must be increased from 0° to nearly 60°. (A sawhorse with a perfectly linear spine, O–C–Fe–Fe–C–O, has θ equal to 58.357° when the CO–Fe–CO angle is 95°.) This lowers the

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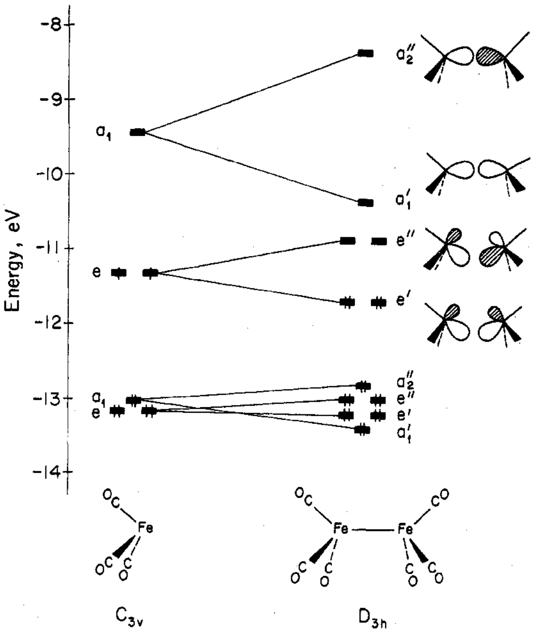


Figure 1. The orbitals of $Fe_2(CO)_8$ built up from those of two $Fe(CO)_3$ fragments. Fe–Fe is 2.5 Å. Only one component of every pair of degenerate levels is shown at right.

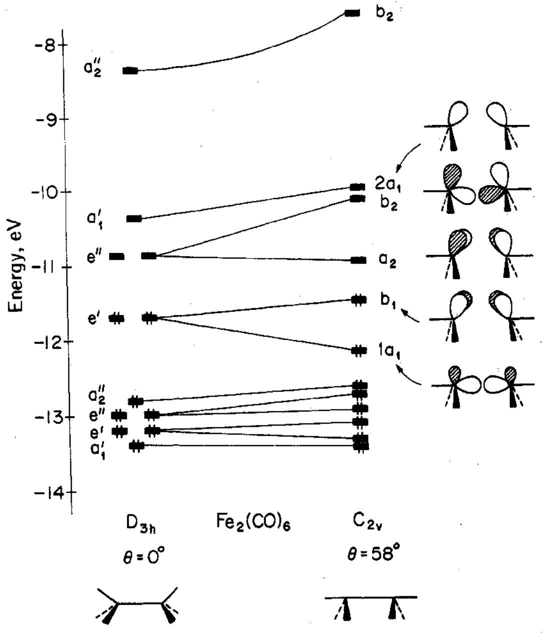
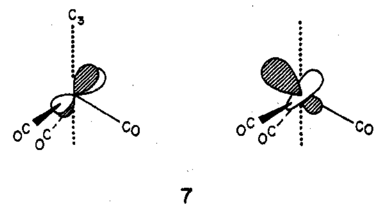


Figure 2. Evolution of $Fe_2(CO)_6$ orbitals as θ is increased.

symmetry from D_{3h} to C_{2v} and the degenerate levels split, as shown in Figure 2. The resultant orbitals are labeled according to their C_{2v} symmetry characteristics.

The details of the orbital ordering may be understood from the specific shape and hybridization of the $Fe(CO)_3$ fragment orbitals. The upper e level of $Fe(CO)_3$ is not only hybridized away from the carbonyls but is also "tilted", as shown in **7**.



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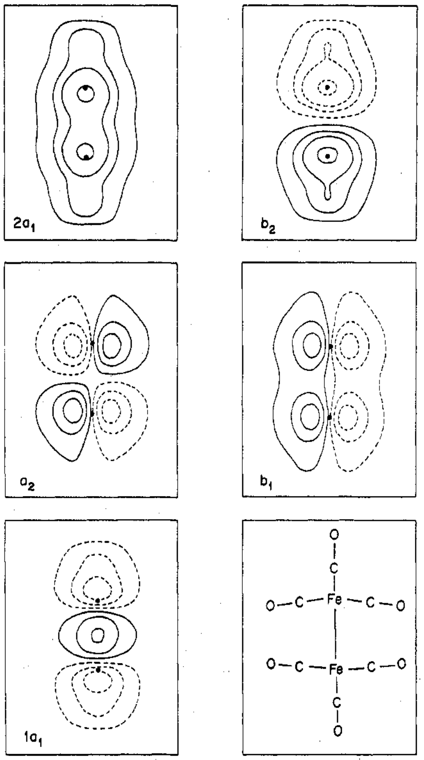
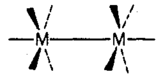


Figure 3. Contour maps of the five valence orbitals of an $Fe_2(CO)_6$ fragment. Each plot is in a plane parallel to the yz plane (see coordinate system in **6**) and 1 Å above the iron atoms. Fe–Fe = 2.5 Å, θ = 58°. The contour levels of ψ are 0.01, 0.03, 0.05 and 0.10 in atomic units, with negative values in dashed lines. The picture at lower right shows the projection of the sawhorse on this plane, while the five contour diagrams indicate the projected positions of the iron atoms by dark dots.

Partly because of this tilting, the $1a_1$ orbital (derived from the e' in D_{3h}) is stabilized as the symmetry is lowered, because the larger lobes of the $Fe(CO)_3$ hybrids point more toward each other. The other component of e', b_1, is *de*stabilized because the lobes are pulled away from each other. Similar effects operate in the split e'' level except the trends reverse. b_2 is destabilized and a_2 is changed little.

The general appearance of the valence orbitals is indicated schematically in Figure 2. Actual contour maps of ψ for the five valence orbitals are given in Figure 3. Note the general pattern of no nodes in $2a_1$, one each in b_1 and b_2, and two in a_2. Also of special importance is the shape of the $1a_1$ orbital. It has two nodes, which in this geometry extend vertically upward from the iron atoms. These nodes figure crucially in interactions with ligands. The $1a_1$ orbital will become the Fe–Fe σ bond in $Fe_2(CO)_8^{2-}$ and the bent metal-metal bond in such complexes as $Co_2(CO)_6$(acetylene) and $Fe_2(CO)_6$(azomethane).[9b]

There is another way to obtain qualitatively the valence orbitals of a sawhorse $M_2(CO)_6$. This is to realize that the fragment may be formally derived by removing four carbonyl groups from an electron-precise bioctahedral $M_2(CO)_{10}$ structure, **8**. The fragment left behind, **9**, will retain the six



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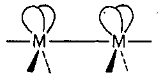

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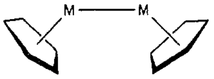
low-lying orbitals associated with the two octahedral centers and in addition will be characterized by four localized orbitals pointing toward the missing carbonyls. These four orbitals transform as $A_1 + B_1 + B_2 + A_2$ in C_{2v} and, when the proper symmetry-adapted linear combinations are taken, will yield just the $2a_1$, b_1, b_2, and a_2 orbitals of Figures 2 and 3. The other a_1 orbital in the valence set is derived from the metal–metal σ bond of $M_2(CO)_{10}$.

The orbitals of $Fe_2(CO)_6$ fall into a pattern: a very high-lying b_2 orbital, essentially unavailable for any ligand, five "valence" orbitals, and six low-lying orbitals. These lower six may be of some importance in determining structural details since they are not sufficiently low-lying as to be unaffected by incoming ligands. However, they are so heavily involved in back-bonding to the carbonyls that their overlap with incoming ligand orbitals is poor. We have found it possible to neglect these low-lying orbitals except in some specific instances.

The focus of this study is on the five valence orbitals of $M_2(CO)_6$ fragments and their interactions with ligand orbitals. The energy pattern in these five is important. The lower two are $1a_1$, b_1, both metal–metal bonding ("σ" and "π", respectively). The remaining three, $2a_1$, b_2, and a_2, are appreciably higher in energy because of the metal–metal antibonding nature of the a_2, b_2 orbitals and the large sp character of the $2a_1$ orbital. The similarity of these orbitals to the orbitals of acetylene should be noted: $2a_1$ and b_1 resemble C≡C π bonds, a_2 and b_2 resemble C≡C π^* bonds, and $1a_1$ resembles the C≡C σ bond. This correspondence is not surprising, for it follows from the analogy between the orbitals of CH and $Co(CO)_3$,[10,13] which in turn leads to a similarity of acetylene with $Co_2(CO)_6$.

With other $M_2(CO)_6$ fragments the basic pattern prevails, while the orbital energies and absolute orderings do fluctuate somewhat. A similar level pattern is found for the isolobal[10b] M_2Cp_2 fragment **10**, which we include in our study as well.



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When one or more carbonyls in $M_2(CO)_6$ are replaced by ligands that differ significantly in σ or π donor or acceptor capability from CO, then more significant changes in the level pattern ensue. These are discussed in Appendix II, where Figure 17 shows the effect of metal and the isolobal MCp replacement as well.

The final prelude to a consideration of specific complexes is the business of electron counting. Since there are six low-lying orbitals below the five valence orbitals of Figures 2 and 3, a neutral $Fe_2(CO)_6$ fragment with its 16 d electrons would place 4 electrons in the valence band, a $Mo_2(CO)_6$ 0, a $Mn_2(CO)_6$ 2, a $Co_2(CO)_6$ 6, and a Ni_2Cp_2 similarly 6. It does not make sense to in fact put them into these orbitals, for as soon as a ligand approaches the $M_2(CO)_6$ fragment it will perturb strongly that standard level pattern. Nevertheless, it is clear from the outset that an $Mo_2(CO)_6$ will seek out a ten-electron donor to interact with its five empty valence orbitals, an $Fe_2(CO)_6$ will prefer a six-electron ligand for its three empty orbitals, etc.

Bonding with Small Molecules

This section begins the analyses of $M_2(CO)_6$–ligand interactions for the common case of acetylene and carbon monoxide as ligands. There are many other small molecules that might have been included, for instance, such well-known bridging species as NO, NR_2, SR, and RNC, but we think that the essential bonding features will be revealed by those ligands considered. The reader is referred to an excellent theoretical paper by Teo, Hall, Fenske, and Dahl[9b] for a parallel analysis of some of these small-ligand bridging species.

Acetylenes. The prototype acetylene complex is $Co_2(CO)_6(HCCH)$, illustrated in structure **2**. We know from the isolobal analogy that this should be a stable molecule with localized single bonds, a mixed organic–inorganic analogue of tetrahedrane.[12a,b] Let us see how these expectations are achieved from the starting point of a fragment analysis.

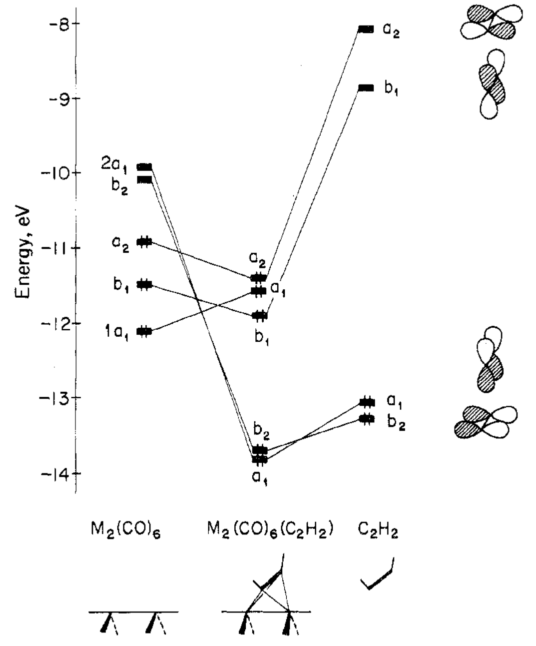
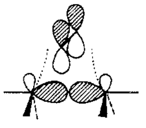


Figure 4. Orbital interaction diagram for $M_2(CO)_6$(acetylene). The calculation was done for M = Fe, but applies equally well to the case M = Co, for which the orbital occupation indicated is appropriate.

Figure 4 gives the interaction diagram for bonding an acetylene to an $M_2(CO)_6$ fragment. In the orientation shown, the acetylene provides two donor orbitals, its π orbitals, of a_1 and b_2 symmetry, and two acceptor orbitals, π^*, of a_2 and b_1 symmetry. The acetylene donor orbitals form bonds with the sawhorse b_2 and $2a_1$ orbitals, and the acetylene acceptor orbitals stabilize the sawhorse b_1, a_2. The sawhorse $1a_1$ orbital is destabilized by the acetylene a_1 donor. In the cobalt sawhorse there are six electrons in the valence orbitals; these combine with the four acetylene π electrons to fill the five lower orbitals.

A "linear spine", θ as defined in **6** equal to 58.3°, for the $M_2(CO)_6$ unit was assumed in the figure. In this geometry there is considerable repulsion between the filled $1a_1$ orbital of $M_2(CO)_6$ and the filled a_1 acetylene donor orbital, as indicated in **11**. To help relieve this repulsion the $M_2(CO)_6$ fragment can tilt to decrease θ, **12**. This motion is stabilizing as a whole because it also relieves considerable carbonyl–carbonyl steric repulsion, a consequence of the fairly close M–M distance (~2.47 Å) demanded by the small acetylene orbitals. The $1a_1$ orbital becomes essentially sawhorse–acetylene nonbonding and forms the "bent metal–metal bond".[9b]



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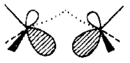

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The $Co_2(CO)_6$(acetylene) system is quite stable, and complexes have been formed with many acetylenes.[13] The $Fe_2(CO)_6$(acetylene) system[2c] has two fewer electrons and a considerably closer metal–metal distance (2.316 Å) than the cobalt system (2.47 Å).[2a,b,e] Just from looking at the level scheme for $Co_2(CO)_6$(acetylene) at Co–Co 2.47 Å (Figure 4), it is not clear which of the three higher lying occupied orbitals

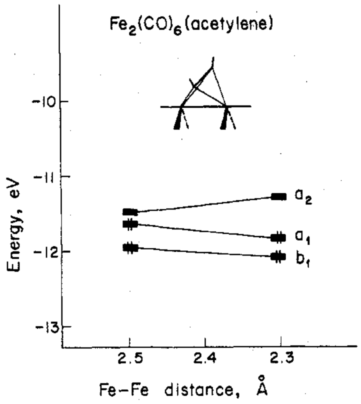
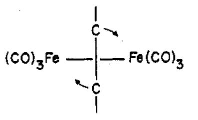


Figure 5. Effect of decreasing Fe–Fe distance on important $Fe(CO)_6(C_2H_2)$ levels.

is to be vacated in the iron dimer. However, it is only the a_2 orbital which is metal–metal antibonding among these three, and Figure 5 shows that, as expected, it rises in energy with decreasing M–M separation. In $Fe_2(CO)_6$(acetylene) this a_2 MO is empty, becoming the lowest unfilled molecular orbital (LUMO) of the complex, and a low-lying one at that. The color of the complex (green) suggests a low-lying empty orbital. Cotton and co-workers[2c] point out that the short metal–metal distance and scarcity of electrons imply an iron–iron double bond. In our scheme the double bond is made up of the $1a_1$ and b_1 orbitals. In the cobalt complex the Fe–Fe antibonding counterpart of the b_1 orbital, the a_2 orbital, is also filled, and only a formal single bond remains.

This low-lying empty a_2 orbital has several consequences. One possibility is a second-order Jahn–Teller distortion[14] of $a_2 \times a_1 = A_2$ symmetry. A conceivable distortion of A_2 symmetry is shown in **13**, corresponding to rotating the acetylene relative to the $Fe_2(CO)_6$ fragment. Calculations along this distortion give a minimum at roughly 20° twisted from perpendicular. A calculation by Anderson,[9c] who also has analyzed these Co and Fe acetylene complexes, gives a twist angle of 30°.



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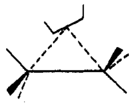

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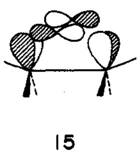
The observed $Fe_2(CO)_6$(acetylene) structure shows some twisting, 4–5°, but the magnitude is much smaller than that calculated. In fact, it is not much greater than the 2–3° twist found in the three cobalt complexes. But the molecule is actually more cunning than this, for it does perform a distortion, a rotation of one $Fe(CO)_3$ unit to give **14**.

While this distortion was not anticipated by us, it clearly relieves the situation of LUMO close to HOMO which favors distortion. The "a_2" LUMO of **14**[15] is raised in energy by the $Fe(CO)_3$ twist. This in turn is a consequence of the nature of the $Fe_2(CO)_6$ fragment a_2, and deeper still from the "tilting" of the $Fe(CO)_3$ orbitals from which it is descended. Consider, in fact, the shape of the a_2 orbital in the sawhorse and $Fe(CO)_3$ rotated conformations, **15** and **16**. Note that in **16** the tilting of the $Fe(CO)_3$ makes for a poorer overlap with the acetylene, which in turn leads to a higher energy for this orbital. This is fine for $Fe_2(CO)_6$(acetylene), but in the corresponding Co complex where the a_2 orbital is filled this destabilization must be avoided and the sawhorse geometry restored. If further $Fe_2(CO)_6$(acetylene) structures are studied, we anticipate a variable range of twisting of the Fe–Fe axis relative to the acetylene, coupled with the rotation of one $Fe(CO)_3$ unit noted above.



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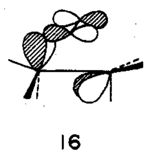

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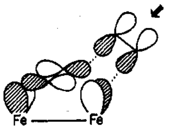
Another consequence of the empty a_2 orbital in $Fe_2(CO)_6$(acetylene) is chemical reactivity. Iron carbonyl complexes react with acetylenes to give a wide array of compounds,[13] including the ferrole and flyover bridges noted at the outset. One possible mechanism for coupling two acetylenes by iron carbonyls would involve initial formation of a $Fe_2(CO)_6$(acetylene) complex, followed by attack by another acetylene molecule.[13] If the LUMO of the initial $Fe_2(CO)_6$(acetylene) is the a_2 orbital, the donor orbital of an attacking acetylene has an ideal orbital with which to bond (**17**), forming, concertedly, a Fe–C bond and a C–C bond.



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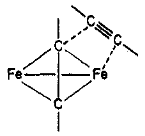
Calculations do show this. "Side-on" attack, **18**, where the entering acetylene π orbital can utilize the empty a_2, is indicated to be considerably more favorable than "straight-on" attack, **19**, where the π orbital hits a node in the a_2. Bulky substituents on the acetylene should help prevent such attack, and the iron complex[2c] may owe its very existence to the *t*-Bu groups on the acetylene. We note that this mechanism definitely does *not* explain the formation of the ferrole studied in ref 4f. However, $Rh_2(PF_3)_8$ couples acetylenes to give rhodicycles,[16a] possibly via an intermediate $Rh_2(PF_3)_5$(acetylene)[16b] which, like $Fe_2(CO)_6$(acetylene), has an empty orbital of pseudo-a_2 symmetry.



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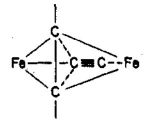

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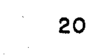
Carbonyls. We turn next to the interaction of an $M_2(CO)_6$ fragment with two or four carbonyls.[17] Four carbonyls return us to $Mn_2(CO)_{10}$, reversing the reasoning used above in the construction of the $M_2(CO)_6$ orbitals. Two carbonyls are more interesting, taking us to the structures of the isoelectronic $Co_2(CO)_8$ and $Fe_2(CO)_8^{2-}$. The solid-state structures of these molecules are shown below.[18a,b] In solution there is evidence that $Co_2(CO)_8$ exists in three isomeric forms, two of which are of type **20** and **21**, all close to each other in energy.[19]



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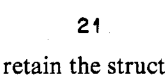

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Substituted derivatives generally retain the structural type set by the octacarbonyl, but there are some exceptions.[20] Our hope was to gain some insight from the $M_2(CO)_6$ + 2CO partitioning into the factors influencing a carbonyl group to bridge, but from the outset our expectations were tempered by the knowledge that it might prove impossible to track down what must by a small energy differential.

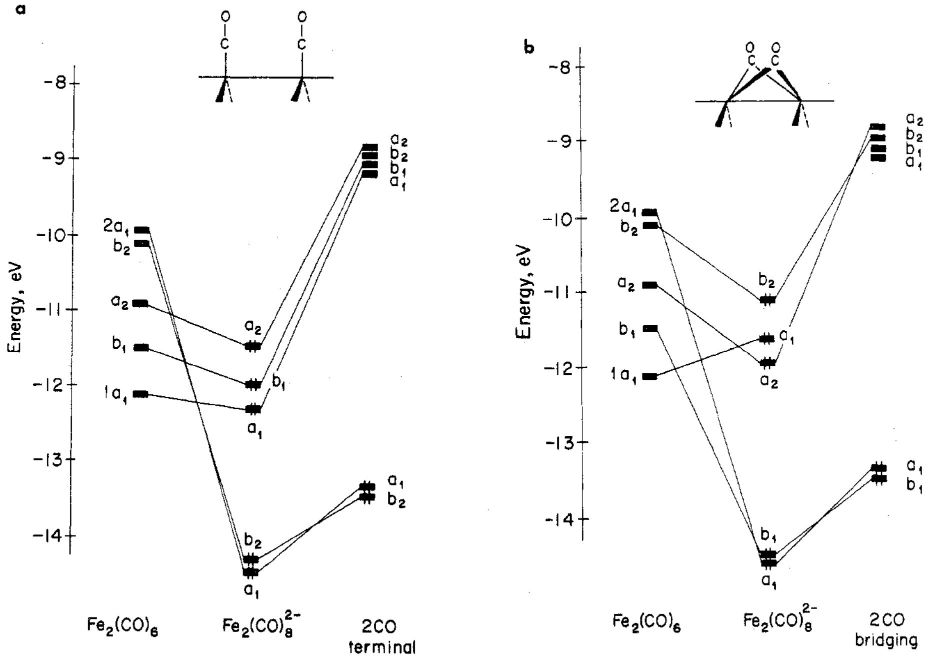

Figure 6. (a, left) Orbital interactions for terminal approach of two carbonyl ligands. The symmetry is only C_{2v}. If the angles were adjusted to give D_{3h} symmetry, a_2 and b_1 merge with Fe "lone pair" orbitals (not shown) to form e″ and e′ levels. (b, right) Orbital interactions for two carbonyls approaching in a bridging geometry. The electron occupation of the $Fe_2(CO)_6$ fragment is not indicated, but in the middle of each figure the electron occupation is that appropriate to $Fe_2(CO)_8{}^{2-}$ or $Co_2(CO)_8$.

Consider two carbonyls approaching the $M_2(CO)_6$ fragment. They can bridge, as in **20**, or seek out nonbridging terminal positions, as in **21**. For the fixed sawhorse $M_2(CO)_6$ geometry only minor angular distortions and the electronically trivial rotation from D_{3h} to D_{3d} are required to bring both approaching geometries into the solid-state structures of $Co_2(CO)_8$ and $Fe_2(CO)_8{}^{2-}$. Interaction diagrams for the two approaches are shown in Figure 6.

The interaction diagram for the terminal complex is in Figure 6a. Note the similarity to the acetylene complex: the two donor orbitals are a_1, b_2 symmetry, and there are acceptor orbitals of a_2, b_1 symmetry to stabilize $M_2(CO)_6$ orbitals. This differs from the acetylene example in the $1a_1$ orbital, however. Here the $1a_1$ orbital is unaffected by the a_1 donor orbital since the carbonyls sit on a node in the $1a_1$ orbital (see Figure 3). In fact, $1a_1$ is *stabilized* by an a_1 combination of CO π^* orbitals, **22**, which has no analogue in the acetylene case. The resulting orbital is seen to be the M–M σ bond.

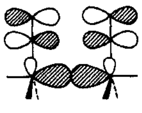

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Figure 6b gives the interaction diagram for the bridged complex **20**. This complex structurally resembles the acetylene complex, but it differs from the point of view of interactions. Here the donor orbitals are a_1, b_1 (instead of b_2), and acceptor orbitals of all symmetries are again provided. The presence of the b_1 donor combination makes the sawhorse b_1 unavailable for occupation, but the good b_2 acceptor forms a low-lying bonding orbital with the sawhorse b_2. This time, just like in the acetylene complex, $1a_1$ becomes the bent M–M bond.

The difference between the two interaction diagrams is mostly in the b_2 vs. b_1 donor combination and is schematically reproduced in Figure 7. It is tempting to claim that Figure 7a represents the more favorable interaction, corresponding in a sense to an "allowed" reaction. Indeed, if the interactions are similar (i.e., overlap and resonance integrals are comparable), then that shown in Figure 7a will be favored. However, if the interactions (especially b_2–b_2) emphasized in Figure 7b are stronger than those shown in Figure 7a, the former can become the favored case. Our calculations are ambiguous, giving nearly equal energies for the bridged and terminal geometries. Perhaps it is just as well that this somewhat unsatisfying result is obtained, for it reflects the delicate balance in which the real molecules find themselves.

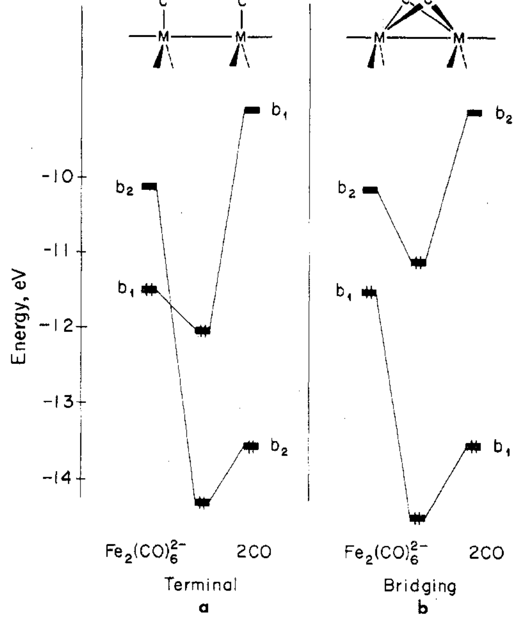
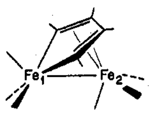


Figure 7. (a, left) b_1 and b_2 interactions for terminal carbonyls in $Fe_2(CO)_8{}^{2-}$. (b, right) Same for bridging carbonyls.

Figure 7 does explain the effect of substitution on the bridging–terminal equilibrium in dicobalt carbonyls. Replacing the carbonyls at the ends of the sawhorse by phosphines, presumably better σ donors, results in destabilization of the sawhorse b_2 orbital (see Appendix II). Such a perturbation adversely affects the bridging structure, Figure 7b, where the filled b$_2$ orbital contains a large sawhorse contribution. The terminal structure, Figure 7a, is less affected since the filled b$_2$ orbital has only a small sawhorse component. Thus, good σ donors at the ends of the sawhorse should diminish the tendency to bridge.

Ferroles, Flyover Bridges, and Other Medium-Sized Ligands

The remarkable ferrole structure **23**, formed by the reaction of iron carbonyls with acetylenes, as well as by other routes, is by now a rather common structural type, with many more examples known than those of which crystal structures are available.[4,5,8] The flyover structure **24**, although less frequently encountered,[6] is an interesting contrast to **23**. The questions that interest us here are those of structural choice made by the molecules. Why does a C$_4$R$_4$ ligand adopt the ferrole coordination mode **23** instead of other possible structures, such as the flyover **25**, the cyclobutadiene bridge **26**, or the inverse sandwich **27**? Likewise, why does C$_6$R$_6$ take on the flyover coordination mode **24** instead of such alternative structures as the ferrole analogue **28** or the fulvene complex **29**?



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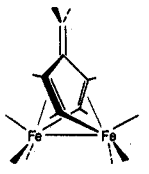

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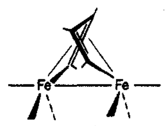

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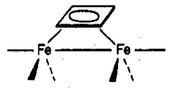

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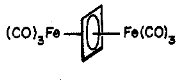

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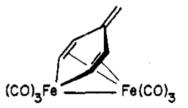

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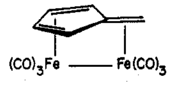

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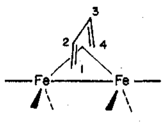
Ferroles. A starting point for an analysis of some of these possibilities is a hypothetical Fe$_2$(CO)$_6$(C$_4$H$_4$) structure of C_{2v} symmetry, **30**.[21] The butadienyl fragment carries four π-type orbitals and two radical or lone-pair lobes. The interaction diagram for this geometry is shown in Figure 8. Irrespective of whether the fragments are taken as butadienyl dianion and Fe$_2$(CO)$_6$$^{2+}$ or neutral C$_4$H$_4$ and Fe$_2$(CO)$_6$, the net result is that ten electrons enter this bonding scheme. Four of them are accommodated in bonding orbitals, but just as in the acetylene case the 1a$_1$ sawhorse orbital is destabilized, now by the strong a$_1$ σ-donor lobe combination of the C$_4$H$_4$ unit. Furthermore, there are two low-lying empty orbitals, a$_2$ and b$_2$, derived largely from the π* orbitals of the butadienyl unit.



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The frontier orbitals of the symmetrical structure predispose it to two distortions, which are derivable from either a second-order Jahn–Teller argument[14] or the equivalent analysis of the effect of lowered symmetry on orbital interactions. The highest occupied and low-lying unoccupied orbitals are shown below.

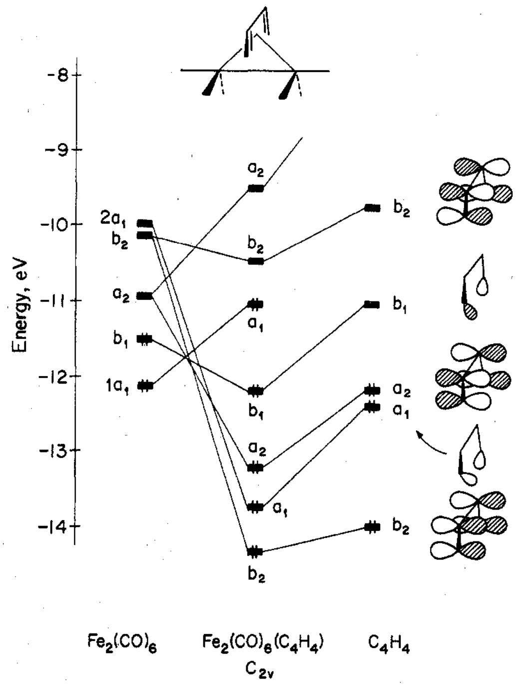
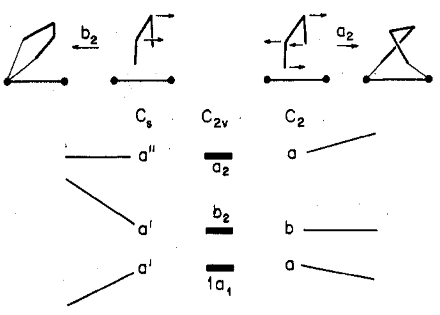
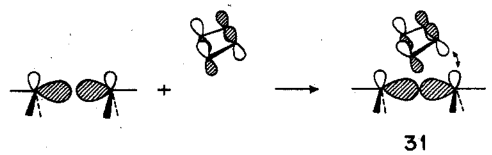


Figure 8. Orbital scheme for a hypothetical C_{2v} geometry of a ferrole complex. Fe–Fe = 2.5 Å, θ = 58°. The top diene π orbital is omitted.



Consider first the motion of b$_2$ symmetry, a bending over toward the ferrole geometry. (Perhaps we should call these "fallover bridges".) The symmetry is reduced to C_s. The 1a$_1$ and b$_2$ orbitals, now allowed to mix, do so. The 1a$_1$ is considerably stabilized, picking up π bonding with C$_1$ and C$_4$ of the butadienyl, as shown in **31**. Simultaneously, C$_2$ and C$_3$ bond to the other iron atom, Fe$_2$. In the idealized geometries used for the calculations, the distortion is stabilizing by ~1 eV, most of the preference due to this trend operating in the 1a$_1$ orbital. Note that interaction **31** implies considerable occupation of the lowest π* orbital of the C$_4$H$_4$ unit, which helps explain the "bond leveling" trends in the C–C bond lengths.[22a] Any perturbation of the C$_4$H$_4$ ligand which reduces the accepting ability of the lowest π*, such as successively replacing H by OH and O$^-$, should diminish the driving force for this distortion. This probably accounts for the rapid racemization of Fe$_2$(CO)$_6$(C$_6$H$_8$O$_2$) in alkaline solution.[21]



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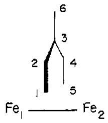
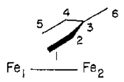
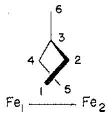
Alternatively, an a$_2$ distortion reduces the symmetry to C_2,

Table I. Overlap Population in a Hypothetical Symmetrical $Fe_2(CO)_6(C_6H_6)$ Complex and Its C_s and C_2 Distortions

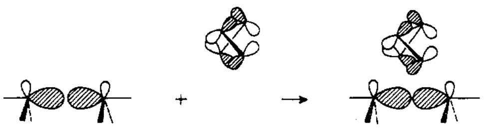






	Distance, A	population		Distance, A	Overlap population		Distance, A	Overlap population
Fe_1-C_1	2.02	0.3276	Fe_1-C_1	2.02	0.4007	Fe_1-C_1	2.02	0.4060
Fe_1-C_2	2.99	−0.0152	Fe_2-C_1	2.02	0.1695	Fe_1-C_3	3.13	−0.0281
Fe_1-C_3	3.37	−0.0180	Fe_2-C_2	2.11	0.0816	Fe_1-C_8	4.46	0.0003
Fe_1-C_6	4.71	−0.0003	Fe_2-C_3	2.15	−0.0154	Fe_1-C_5	2.02	0.2168
			Fe_2-C_6	3.31	−0.0281	Fe_1-C_4	2.59	0.0867

modeling a path to the flyover structures. This deformation allows the $1a_1$ and a_2 orbitals to mix, as shown in **32**. It is



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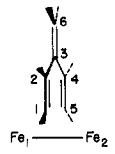
also stabilizing, but less so than the motion which carries the system to C_s symmetry. It appears that another relatively high-lying and occupied a_2 level (see Figure 8) partially negates the stabilizing effect of the a_2 π^* orbital.

If two further electrons are added to the system, the tendency to fall over is suppressed, while in principle that to twist remains. There appears to be some evidence for this in a structure of an $Fe_2(CO)_6$(dithiolato) complex.[22b]

Still other bonding possibilities are the cyclobutadiene complexes **26** and **27**. However, cyclobutadiene is only a four-electron donor while the $Fe_2(CO)_6$ fragment would ideally prefer a six-electron ligand. This is not an insurmountable difficulty for a "bridging" cyclobutadiene, **26** (discussed later), but for an inverse sandwich complex **27** it would result in a half-filled degenerate level.[23] Ferroles are sometimes prepared from cyclobutadiene–iron tricarbonyl complexes, and species such as **26** seem attractive intermediates for these processes. We will return later to this problem, as well as to the rotation of one $Fe(CO)_3$ group and the concomitant semibridging character of one carbonyl group, both features characteristic of the ferrole type.

Flyover Bridges. The system with C_6H_6 behaves exactly the opposite to a C_4H_4 ligand. We begin again with the C_{2v} symmetrical structure **33**, an interaction diagram for which



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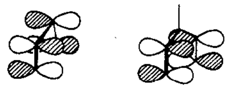
is shown in Figure 9. The ring-opened fulvene carries the two radical lobes and six π orbitals. These are essentially identical with those of 2-vinylbutadiene and are well-known.[24] Figure 9 again reveals a high-lying filled a_1 and low-lying empty a_2 and b_2 orbitals. However, the order of these unfilled orbitals is inverted relative to the C_4H_4 case. The reason for this is to be found in the position of the a_2 in the two hydrocarbon fragments. These fragment orbitals are shown in **34**. They



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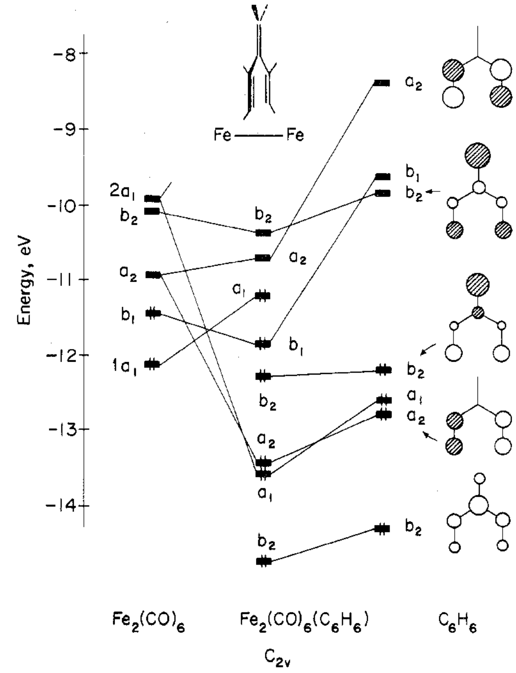
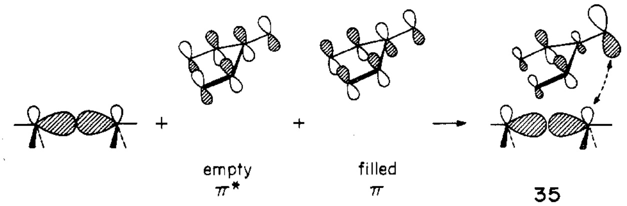


Figure 9. Orbital scheme for a hypothetical C_{2v} flyover geometry. The C_6H_6 n orbitals are not illustrated, nor is the highest π orbital.

are both antibonding in the double bond regions, but the C_6H_6 fragment is spared an additional antibonding interaction between the inner carbons.

Next one considers the distortions reducing the C_{2v} symmetry of **33** to C_s (a hypothetical ferrole structure) and C_2 (the observed flyover geometry). The argument is similar to that given above for C_4H_4, but the trends are reversed. Among the empty orbitals b_2 is now above a_2. The C_s distortion yields little stabilization, and in fact is calculated to be energetically unfavorable. The empty b_2 which mixes into the $1a_1$ does enhance Fe–C bonding at C_1, C_2, C_4, and C_5, but there is now a filled b_2 π orbital which intrudes, largely negating the bonding at C_1, C_5 and causing antibonding between C_3 and Fe_2, and C_6 and Fe_2 (**35**). The calculated overlap populations



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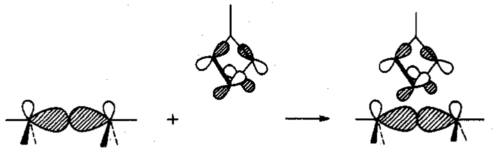
in Table I support this interpretation. The large antibonding between C_6 and Fe_2 suggests that the bridge is kept from falling over because the "tower" holds it up. This is a simple consequence of the electron count. The C_6H_6 unit is already a six-electron donor (two π bonds plus two Fe–C σ bonds) *without* the interaction of the C_3–C_6 π bond, and forcing the third π bond to interact with the $Fe_2(CO)_6$ fragment is guaranteed to be unfavorable.

The alternative distortion to C_2 symmetry allows mixing of the a_2 π^* orbital into the $1a_1$ orbital, **36**, resulting in splendid C–Fe bond formation between Fe_1 and C_1, C_4 and Fe_2 and C_2, C_5 (**36**), leaving the offending C_3–C_6 π bond alone. There is little occupation of any orbital which is C_3–C_6 antibonding, and the bond is of normal double-bond length. However, C_1–C_2 and C_4–C_5 are longer than ordinary double bonds and indicate strong participation in the bonding to the $Fe_2(CO)_6$ unit. Here the a_2 distortion corresponds to the observed structure; the five-carbon chain allows more freedom for the a_2 distortion than the four-carbon chain, and the filled a_2 π orbital is low enough in C_6H_6 that it does not destabilize the a_2 distortion. The complex, with C_2 symmetry, should exist in enantiomeric forms, and it may prove possible to interconvert them via a transition state resembling **33**. Such racemization should again be enhanced if a hydrogen from C_1 or C_2 (but not C_6) is replaced by a donating group, such as O^-.



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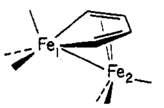
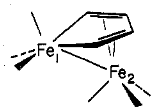
A fulvene complex of type **29** does not appear to be a promising structure. The fulvene π orbitals[24] do not contain a properly aligned acceptor orbital of pseudo-a_2 symmetry, and consequently the HOMO of a calculated model lies at very high energy. Interestingly, a complex of the composition $Fe_2(CO)_6$(fulvene) exists, but the $Fe_2(CO)_6$ fragment is $Fe(CO)_2$–$Fe(CO)_4$.[25]

Ferroles Again. We now return to one of the points which was bypassed in our initial discussion, namely that in most ferrole complexes the $Fe_2(CO)_6$ moiety does not assume a sawhorse geometry, **37a**, but instead rotates the $Fe(CO)_3$ group π bonded to the carbon atoms by 60°, as indicated in **37b**. The unique carbonyl of that group is then placed in a partially bridging position, its carbon typically 2.4–2.5 Å from the other iron atom.[4] It is tempting to attempt a rationalization of this interesting structural detail, but first the following facts should be noted. (1) The nonsawhorse geometry and semibridging carbonyl are not universal. The sawhorse geometry occurs in one substituted ferrole[4d] and in two $Os_2(CO)_6$ complexes of analogous structure.[4b,j] (2) ^{13}C NMR studies of the ferroles indicate a low barrier for scrambling the carbonyl groups on Fe_2. They are not frozen out at −125 °C.[4i,26] (3) If Fe_2 of the ferrole structure is thought of as being π bonded to a butadiene, then the geometry observed in most complexes, **37b**, is consistent with the many known structures of $Fe(CO)_3$-(butadiene) complexes.



37a

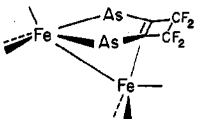


37b

Our calculations also indicate a delicate balance of forces behind this conformation choice. Direct Fe_2–ring overlaps appear to favor **37a**, but in **37b** we definitely note bonding interactions between Fe_1 and the unique carbonyl bonded to Fe_2. We calculate a slight preference of 0.2 eV for **37b**, but only a simple rotation of the $Fe(CO)_3$ group was explored.

Rotation of the $Fe(CO)_3$ group that is σ bonded to the carbons is considerably more difficult, facing a barrier of 0.7 eV in a model calculation. This is no surprise for the preferred geometry has optimal overlap of butadienyl and iron lobes, and this is ruined by the rotation.

Similar and yet different from the ferrole complexes are molecules of type **38**.[27] If one constructs an interaction diagram for this molecule beginning in a symmetrical C_{2v} structure analogous to **30**, one finds that as the bridge falls over an a_2 combination is stabilized. This orbital, a mixture of $Fe_2(CO)_6$ and the ethylene π^*, is shown in **39**. Its occupation weakens both Fe–Fe (2.9 Å) and the CC (1.5 Å) bonds. The orthodox fallover bridges in contrast populate a CC orbital which is bonding between the back carbons, shortening that bond to ~1.43 Å.



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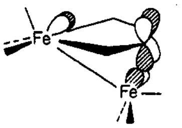

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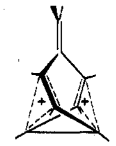
Before leaving the ferroles and flyover bridges, we should note where one comes to if one applies the isolobal analogy.[10,12] Since $Fe(CO)_3$ is like CH^+, the ferrole type is recognized as being similar to the pentagonal-pyramidal $C_6R_6^{2+}$[28] or the carboranes $C_4B_2R_6$.[29] Replacing only one $Fe(CO)_3$ by CH^+ gives $FeCp(CO)_3^+$. The analogue of the flyover structures is a $C_8R_8^{2+}$, a novel potentially nonclassical dication based on the heptafulvene geometry, **40**. We discuss its electronic structure in detail elsewhere.[30]



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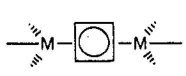
Cyclobutadiene. Complexes of $M_2(CO)_6$ with an intact bridging cyclobutadiene, **26**, have not been reported. A calculation on an assumed geometry, Figure 10, shows good interactions, but a relatively high-lying a_2 orbital, formed by a bonding interaction between a_2 of $M_2(CO)_6$ and the a_2 π^* orbital of cyclobutadiene. This orbital is high in energy because the a_2 π^* orbital of C_4H_4 is at higher energy than the corresponding acetylene π^* orbital. Otherwise, the interaction strongly resembles the acetylene system.

This a_2 orbital could be filled (corresponding to the complex $Co_2(CO)_6(C_4H_4)$) or empty ($Fe_2(CO)_6(C_4H_4)$). The geometry of the $Co_2(CO)_6(C_4H_4)$ complex, if ever made, will almost certainly be that assumed in Figure 10, **41**, in preference to **42**. In **42**, C_4H_4 presents no a_2 acceptor orbital, and the occupied a_2 will rise to the nonbonding $M_2(CO)_6$ level. The $Fe_2(CO)_6$ complex, if ever formed, should have little preference for orientation as in **41** or **42** since the a_2 orbital is empty. Second-order Jahn–Teller distortion (see $Fe_2(CO)_6$(acetylene)) might cause **41** to twist into **42** or an intermediate geometry, but a calculation suggests **41** to be slightly more stable, even for $Fe_2(CO)_6(C_4H_4)$. Very likely, again analogous to the acetylene complex, the iron complex with cyclobutadiene may rotate one of the $Fe(CO)_3$ groups from the sawhorse geometry.



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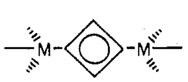

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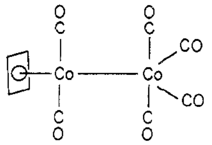
The complexes $Co_2(CO)_6$–(C_4Me_4) and –(C_4H_4) have been synthesized.[31] The parent compound has recently been shown to have the structure **43**.[31c] ^{13}C NMR studies show a rapid equilibration of the carbonyls down to very low tempera-



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tures,[31d] a process which could proceed through a bridged C_{2v} complex of type **41**. That isomer conceivably could be rendered more stable by lowering the energy of the π^* a_2 orbital, perhaps by substituting CF_3 for the methyl groups.

Similarly, the $Fe_2(CO)_6(C_4Me_4)$ complex is known.[32] Since the synthesis involves transfer of a cyclobutadiene entity from $(C_4Me_4PdBr_2)_2$ and opening the ring is forbidden if C_s symmetry is retained, there is a chance that the cyclobutadiene ring is intact and the bridging complex has been formed. However, the structure is assumed to be a ferrole.

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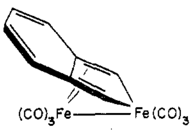

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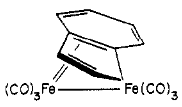

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This returns us to a point raised earlier, namely that ferroles are sometimes prepared from cyclobutadiene–iron tricarbonyl starting points.[33,34,35] A conceivable intermediate in this process could be $Fe_2(CO)_6$(cyclobutadiene) complex **44**. Yet the reaction interconverting **44** and **45** is a symmetry-forbidden process, as can be readily checked by a correlation diagram relating these species. Pettit and co-workers found that **46** and **47**, formed from the reaction of benzocyclobutadieneiron tricarbonyl with $Fe_3(CO)_{12}$, do not interconvert at 120°.[34] We think this supports the notion that the transformation **44** ⇄ **45** is difficult, for the intermediacy of a $Fe_2(CO)_6$(benzocyclobutadiene) would have allowed the interconversion of **46** and **47**.

How then do the reactions of $C_4R_4Fe(CO)_3$ with iron carbonyls proceed? At this point we do not have a good mechanism to suggest. We do plan to study potential-energy surfaces for the interaction of iron carbonyl fragments such as $Fe(CO)_3$ or $Fe(CO)_4$ with $(C_4H_4)Fe(CO)_3$.

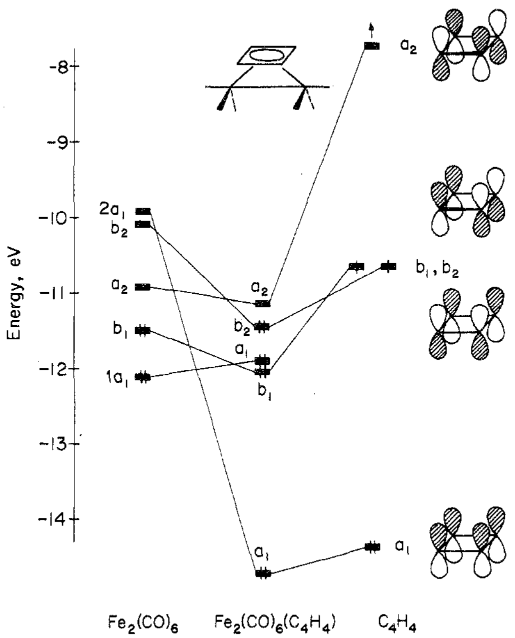


Figure 10. Interaction diagram for $Fe_2(CO)_6$(cyclobutadiene).

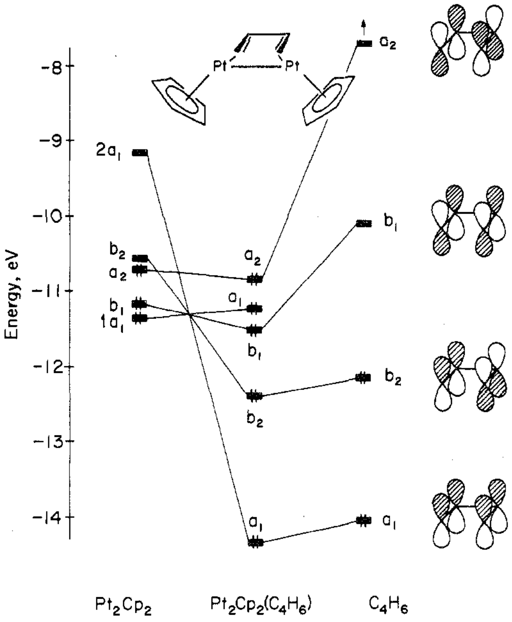
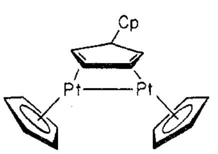


Figure 11. Interaction diagram for Pt_2Cp_2(butadiene). While the actual symmetry is C_s the orbitals are labeled with respect to the approximate C_{2v} pseudosymmetry.



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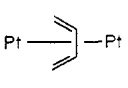

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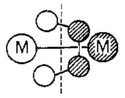
Dienes. The diene complex whose structure is known,[36,37] **48**, contains the Pt_2Cp_2 group, isolobal with $Co_2(CO)_6$. It is interesting that the geometry of **49** is preferred to **50**, which is also what our calculations give. Figure 11 shows an interaction diagram for **49**. The source of its preference to **50** lies largely in the nature of the donor orbitals. In **49** the butadiene donates by orbitals of (pseudo) a_1 and b_2 symmetry, with a_2 and b_1 acceptors; in **50** a_1 and b_1 donate with a_2 and b_2 acceptors. The discussion of the terminal *vs.* bridging carbonyls applies here. **50** might be favored if the bonding interactions (especially b_2–b_2) are stronger than in **49**, but exactly the opposite prevails. The b_2–b_2 overlap in **49** is ~0.19 and in **50** is only ~0.10 Å, mostly because in **50** the b_2 acceptor orbital of butadiene is tightly held in the nodal region of the b_2 orbital of fragment **51**, but in **49** the b_2 orbital (donor) is in the maximum-density region of $1b_2$ fragment orbital **52**. This complex, making the $M_2(CO)_6$–acetylene connection, is the analogue of a Diels–Alder adduct of acetylene with butadiene.



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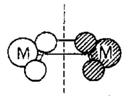

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Large Molecules as Ligands

Some of the most fascinating structures of the sawhorse type are those with ligand molecules that are large, unsaturated organic rings. Here we look briefly at the bonding between

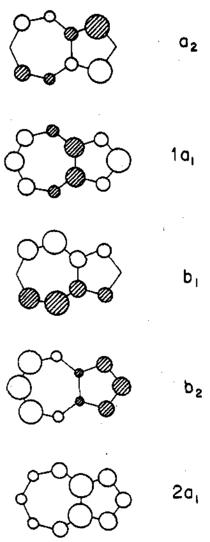
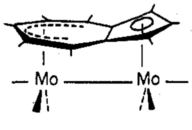


Figure 12. Diagrammatic representations of the occupied π orbitals of azulene. Each is labeled according to the sawhorse $M_2(CO)_6$ level with which its interaction is best.

such rings and sawhorse fragments for a few of the representative systems.

Ten-Electron Donors: Azulene. $Mo_2(CO)_6$ forms a complex with azulenes,[7a] **53**. As a ten-electron donor, the azulene molecule will only be likely to bond to a sawhorse fragment with five empty valence orbitals, such as $Mo_2(CO)_6$, if there is a good match between sawhorse valence orbitals and azulene donor orbitals. Such a correspondence is indeed present, as can be seen from Figure 12, which shows the five occupied π orbitals of azulene.[24] Note how beautifully these orbitals match the nodal properties of the five orbitals of $M_2(CO)_6$, as illustrated in Figure 3.



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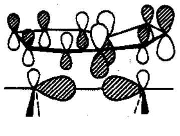

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In the isolated $Mo_2(CO)_6$ fragment there is very little metal–metal bonding, for the $1a_1$ orbital is unfilled. In the azulene complex some metal–metal bonding is restored, due to the partial occupation of this orbital as a consequence of donation from the second-highest occupied MO of azulene. The metal–metal bond should be quite weak. It is in fact quite long, typically ~3.25 Å.[7a]

In the $Mo_2(CO)_6$(azulene) complex there is a bonding interaction between the sawhorse $1a_1$ orbital and the ligand donor orbital (contrast the acetylene example), **54**, since the sawhorse $1a_1$ is nominally empty and there is no filled-orbital–filled-orbital repulsion. This is probably the major factor in causing the apparent "droop" of the sawhorse fragment and the nonplanarity of the azulene.[7a] The structure suggests, and calculations support, an attractive interaction between the central carbons of the azulene and the Mo–Mo bond.

In an interesting ^{13}C NMR study, Cotton, Hunter, and Lahuerta[38] showed that there is local scrambling of the three carbonyls on each Mo, but at quite different rates: resonances for one set coalesce below −112° and those of the other below −30 °C. We have studied a simple in-place rotation of either $Mo(CO)_3$ set, with no other geometrical relaxation involved.[39] The barrier so calculated for equivalencing the carbonyls around Mo_1 (under the seven-membered ring) is 23 kcal/mol and around Mo_2 (under the five-membered ring) it is 20 kcal/mol. Given the geometrical assumptions made, it is not surprising that both barriers are too large. Rotation about Mo_2 is easier. There is new experimental evidence that this is correct.[40]

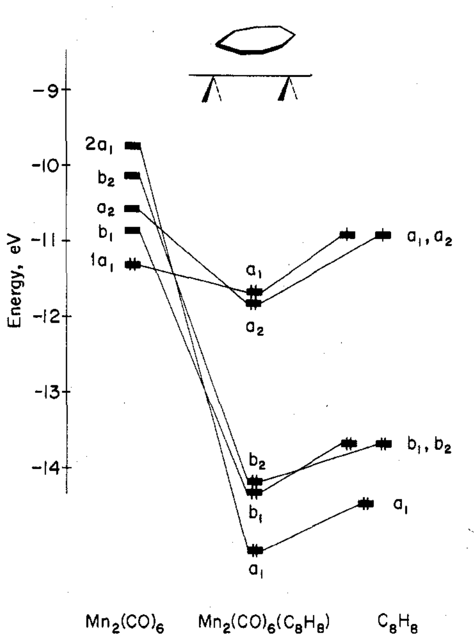
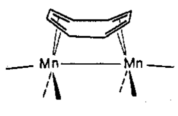


Figure 13. The occupied valence orbitals of $Mn_2(CO)_6(C_8H_8)$, built from $Mn_2(CO)_6$ and the π orbitals of planar cyclooctatetraene. Mn–Mn = 3.0 Å, θ = 55°.

The reason for easier rotation around Mo is not simple. Rotating either $M(CO)_3$ unit results in loss of some bonding with the organic ligand. From an analysis of our wave functions it appears that the difference may be traced to two of the six low-lying metal orbitals. These are involved in slight antibonding interactions with the organic donors. When an unsymmetrical donor ligand is attached, the $M(CO)_3$ unit under the end of stronger donation is repelled most and should have a greater tendency to rotate.

A point that is obvious, but perhaps should be mentioned explicitly, is that there would be a significant loss of bonding were the orientation of the azulene relative to the $Mo_2(CO)_6$ moiety not that indicated in **53**, but instead rotated by 90°. The bonding interactions would be smaller, but more importantly only a parallel alignment of the long axes of $Mo_2(CO)_6$, and the azulene allows the symmetries of the orbitals shown in **54** to match. They both have two nodal surfaces perpendicular to the long axes. Other ten-electron donors, specifically naphthalene and fulvalene,[41] possess orbitals of the right symmetry to form an $Mo_2(CO)_6$ complex.

Eight-Electron Donors: Cyclooctatetraene. The C_8 ring forms sawhorse complexes with $Mn_2(CO)_6$, $Fe_2(CO)_6$, and $Ru_2(CO)_6$. The Fe and Ru complexes, to be discussed below, only want six electrons from the C_8H_8 molecule and bend the ring so as to isolate a double bond and leave a hexatriene unit to interact with the sawhorse. $Mn_2(CO)_6$ wants all eight electrons and the structure,[7c] **55**, shows the C_8H_8 to be truly *octahapto* to the sawhorse, although the ring is still nonplanar. Treating the C_8H_8 ring as planar and using its well-known Hückel π orbitals,[24] the interaction diagram (Figure 13) is obvious.



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There are two points of some interest. First, again there is strong bonding between the $1a_1$ sawhorse orbital and an a_1 orbital of C_8H_8, suggesting that again the sawhorse should droop and the central carbons be pulled toward the metal–

metal bond, and the structure shows this. Of course, a localized butadiene complexed to a single metal center would distort in a similar way.

The second point concerns the ever-present a_2 bonding orbital. The stabilization offered by it is similar to that in $Co_2(CO)_6$(acetylene) and -(cyclobutadiene), as discussed above. It is essentially a "δ bond" (**56**) which would normally be broken if the ligand and sawhorse were forced to rotate relative to each other (**57**). This is why the cobalt–cyclobutadiene complex should prefer **41**. However, in cyclooctatetraene, the a_2 orbital is degenerate with an a_1 orbital. This degeneracy allows the C_8H_8 molecule to present orbitals of quasi-a_1 and a_2 symmetry, no matter how the C_8H_8 ring is aligned. Hence, there should be little preference for orientation **58** over **59**, and it is found that all eight ring hydrogens are equivalent on the NMR time scale at room temperature.[42] This could be interpreted as proceeding by rapid rotation of the C_8H_8 and $Mn_2(CO)_6$ fragments.

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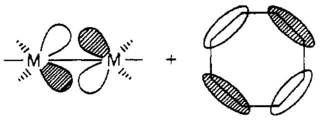

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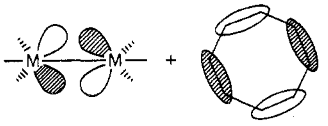

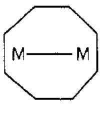

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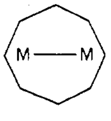

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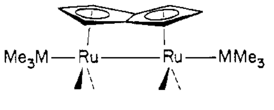
Cyclooctatetraene complexes with $((CO)_2(MMe_3)Ru)_2$, M = Si and Ge, are known.[43] Structures analogous to those of $(C_8H_8)Fe_2(CO)_5$[44] are suggested[43] (COT ring bent away from the metal atoms), but perhaps the $Mn_2(CO)_6$(cyclooctatetraene) structure also might serve as a model.

Pentalene. Complexes of the type $Ru_2(CO)_4(MMe_3)_2$, M = Ge and Si, form pentalene complexes,[7b,43] **60**. The π orbitals of pentalene[24] are diagrammed in Figure 14, and the interaction diagram is as expected. The M_2L_6 fragment is perturbed by the presence of two $GeMe_3$ groups. The consequences of this on the sawhorse level scheme are traced in Appendix II. The figure shows that classification of pentalene as an eight-electron ligand is to some extent a formality. The same orbitals are occupied as would be in a complex of a ten-electron donor with $M_2(CO)_6$, M being a d^6 metal.



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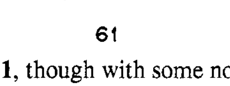
Six-Electron Donors: Tetramethyleneethane. Two crystal structures are known,[7d] and the bonding type appears in several other molecules.[45] The ligand could have been conceivably attached in two ways, **61** or **62**. The geometry observed is close to **61**, though with some nonplanarity of the C_6R_8 organic ligand.[7d] Interaction diagrams for both geometrical extremes are drawn in Figure 15. In **61** the ligand presents a low-lying filled b_2 orbital and a high-lying, nominally empty b_1 orbital. In **62** the low-lying orbital is b_1 and the high b_2. Recalling the bridging- vs. terminal-carbonyl case, **61** ought to be favored on this basis alone. **62** might be favored if the interactions were stronger, but—as in the butadiene case, and for the same reason—the interactions are weaker. The preference for **61** is 1.7 eV.



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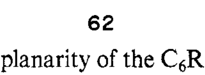

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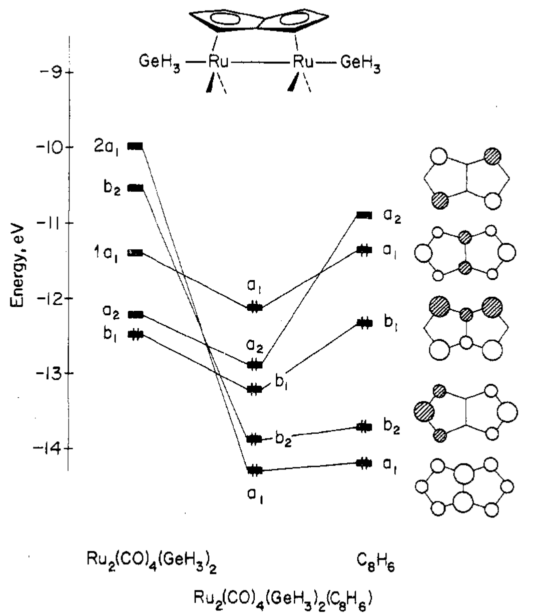
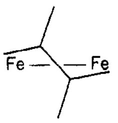


Figure 14. Orbital interaction diagram for $Ru_2(CO)_4(GeH_3)_2$-(pentalene). The lower six π orbitals of pentalene are shown.

Even less likely than **62** is the intermediate geometry **63**.



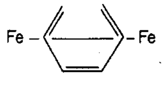
63

In **63** the a_2–a_2 δ bond has been broken (it forms nicely in both **61** and **62**, but a_2–a_2 overlap is nil in **63**). **63** is 1.2 eV even less stable than **62**.

There are some interesting experimental results to consider here. NMR studies by Nakamura and Hagihari[45a] led them to suggest a rapid interconversion between **61** and **62**. Later studies, on a phenyl-substituted tetramethyleneethane, showed no interconversion of this type.[45c] The prediction made here is that **61** should be more stable and conversion to **62** suffers a large barrier. If **61** and **62** do interconvert for the C_6H_8 compound, we think the mechanism is not a simple rotation.

Cycloheptatrienyl. The complex $Ru_2(CO)_5(SiMe_3)(C_7H_7)$ has been prepared.[7e] This molecule is related to $Mn_2(CO)_6$-(C_8H_8). Since the π orbitals of C_7H_7 are very similar to C_8H_8, the bonding in the two complexes should be nearly identical. In particular this complex is fluctional, like the manganese complex. The reported crystal structure[7e] is of a closely related derivative. The syntheses of heterodimetallic $(C_7H_7)Fe$-$(CO)_3M(CO)_3$, M = Mn and Re, have been reported recently.[46]

Hexatrienes in Rings. $M_2(CO)_6$ complexes, M = Fe, Ru, and Os, with cycloheptatrienes and cyclooctatrienes have been extensively studied by Cotton and his co-workers[7f] and by others.[47] To begin our discussion of these fascinating and complicated molecules, let us first consider bonding a planar hexatriene molecule to the $Fe_2(CO)_6$ fragment. As usual, the ligand can choose between two geometries, **64** and **65**. The bonding scheme for **64** is given in Figure 16. For the planar hexatriene **64** is indicated slightly more stable than **65**, but



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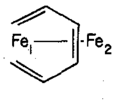
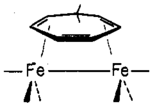


65

the preference is quite small. Experimentally, a planar hexatriene molecule is most closely approximated by cycloheptatriene, C_7H_8, and the structure,[48a] **66**, indeed resembles



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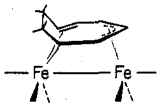
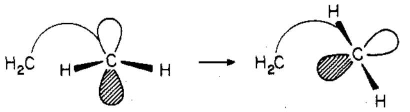


67

64, at least as far as the alignment of the Fe–Fe axis relative to the hexatriene.

In the complexes formed with eight-membered rings, for example in **67**,[48b] the geometry resembles **65** in that the "open face" of the hexatriene moiety is over an iron instead of between them. Further, the eight-membered rings are grossly nonplanar, due to the constraints in the ring system. The planar hexatriene model can be made to resemble the eight-membered ring system if a terminal CH_2 of the hexatriene is twisted so as to point its p orbital inward, **68**. A

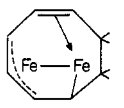


68

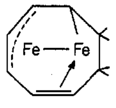
model makes it much more convincing that this is what happens in an eight-membered ring. Performing this distortion on the hexatriene in **64** results in *de*stabilization because the p orbital is being twisted away from the iron atom and toward the *xy* plane. The orbital which suffers most is the bonding combination of the $Fe_2(CO)_6$ a_2 and the hexatriene LUMO because the *xy* plane is a node in this orbital. Distorting **65** is stabilizing; now the p orbital is being twisted toward the iron atom and bonding is better. With a modestly twisted CH_2 group, **65** becomes favored over **64**. Further, Fe_1 in **65** wants to move toward the twisted CH_2, and this also is found in the structures.[7f]

The tentative suggestion being made here is that the ground-state geometry or steric constraints of the ligand may guide the coordination mode that is assumed. If the cyclic system can achieve a near-planar geometry for its hexatriene part, then it will tend toward **64**. If it must remain nonplanar, it will favor **65**.

One aspect of these molecules that has been studied[7f,47] is their fluctionality. The complexes with eight-membered rings show, at room temperature, a ^{13}C NMR spectrum consistent with a symmetric structure (C_s), but freeze out to a spectrum consistent with the nonsymmetric structure found in the crystal. This has been tracked down to a "twitching" process which interconverts enantiomers **69a,b**. More relevant to these

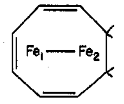


69a

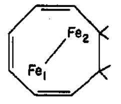


69b

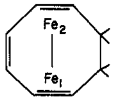
MO calculations is the finding that a "gliding" process, which would result in exchange of iron atoms (**70a–c**), does *not* occur on the NMR time scale. This is due to the familiar a_2 orbital: a vital feature of the sawhorse–hexatriene bond is the interaction of the hexatriene LUMO and sawhorse a_2 to form a filled bonding MO, and rotating the hexatriene through the



70a



70b



70c

waypoint **70b**, presumably necessary for "gliding", breaks the a_2–a_2 bond, requiring (calculated) nearly 2 eV. The bond forms again in **70c**. This is no longer the same situation as in $Mn_2(CO)_6(C_8H_8)$. The hexatriene unit has a pseudo-a_2 orbital which is *not* one of a degenerate pair, and so rotating from **70a** to **70b** results in a definite loss of overlap, exactly as in the tetramethyleneethane, cyclobutadiene, and acetylene complexes.

Incidentally, our calculation indicates that the $Fe(CO)_3$ group at Fe_2 in **65** should have a lower barrier to rotation about its axis than that at Fe_1. This is connected with the hexatriene HOMO being a better donor to Fe_2 and this lower barrier can be observed experimentally.[7f]

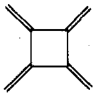
Molecules Not Yet Reported

In order for an organic ring system to form a reasonably good bond to an $M_2(CO)_6$ sawhorse, the following conditions must be satisfied. First, there must be the proper number of electrons. Counting the ligand and CO donor orbitals and the d electrons on the metal, that number is 34. Two more electrons (36) can be accommodated, but only if the metals are isolated, as there can no longer be a metal–metal bond. Second, there should be a good geometric match between the molecule and the sawhorse. If the organic portion is too small, maximum bonding between metal atoms and the organic molecule may require an uncomfortably close metal–metal distance. Third, there is a strong symmetry restriction in that the ligand must provide orbital combinations of appropriate symmetry. Specifically, six-electron donors usually have donor orbitals of a_1, b_1, and b_2 symmetry and must provide a low-lying empty orbital of a_2 symmetry. A noteworthy exception to this is the C_4H_4 entity of the ferrole system, which (in C_{2v}) has donors of b_2, a_2, and a_1 symmetry and is a good b_1 acceptor. Eight-electron donors have a_1, b_1, b_2, a_2 donors with an empty a_1 orbital, although there could be systems with a_1, b_1, b_2, a_1 donors and an a_2 acceptor. Ten-electron donors, of course, must have a_1, b_1, b_2, a_1, a_2 donors. Among the "small" and "medium-sized" molecules, four-electron donors have a_1, b_2 donor orbitals and b_1, a_2 acceptors (recall the exception of the bridging carbonyls).

With these restrictions in mind it is interesting to consider what organic entities, as yet unknown to bind as ligands to an $M_2(CO)_6$, might be likely candidates for synthesis.[49]

For ten-electron donors, naphthalene is an obvious molecule to try. Its donor orbitals are all of the proper symmetry for forming an $M_2(CO)_6$ complex, M = Cr and Mo.

Among eight-electron donors, the molecules **71–73** can be



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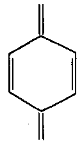

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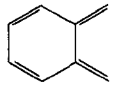
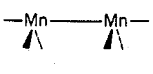


73

considered. Tetramethylenecyclobutane (**71**) has the appropriate donor orbitals of a_1, b_1, b_2, and a_2 symmetries, and should form a sawhorse-type complex **74** with $Mn_2(CO)_6$.



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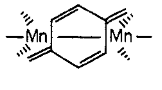

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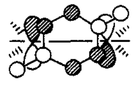

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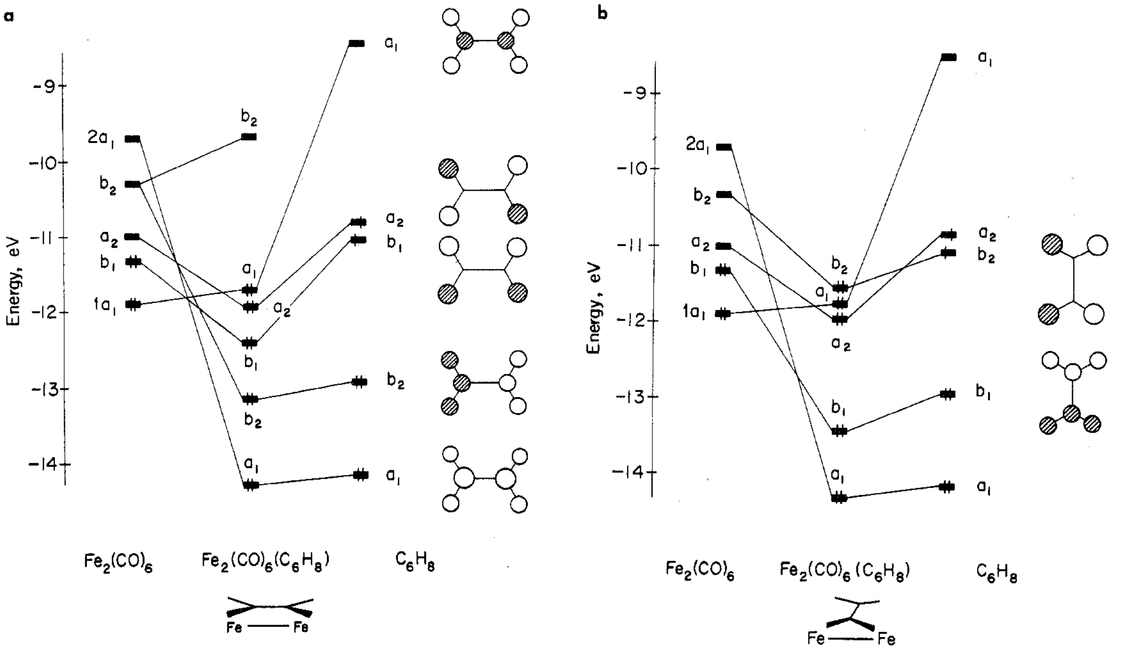


Figure 15. Interaction diagram for the π orbitals of tetramethyleneethane with $Fe_2(CO)_6$ in two possible orientations of C_{2v} symmetry: (a) (left) corresponds to **61** and is close to the observed structure; (b) (right) corresponds to **62**. Only two of the six ligand π orbitals are shown in the latter case.

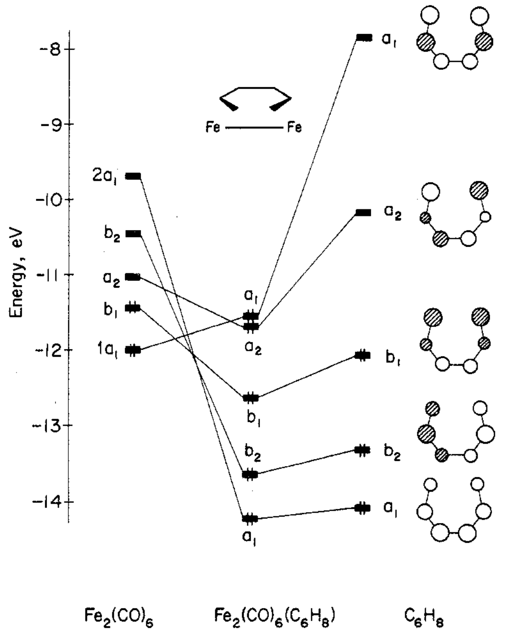


Figure 16. Interaction diagram for planar hexatriene with $Fe_2(CO)_6$. Fe–Fe = 2.8 Å, θ = 58°. The actual symmetry is only C_s, but the orbitals have near C_{2v} symmetry, and are so labeled.

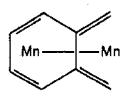
Table II. Extended Hückel Parameters

Orbital	H_{ii}, eV	Exponents[a]	
		ζ_1	ζ_2
H 1s	−13.6	1.3	
C 2s	−21.4	1.625	
2p	−11.4	1.625	
O 2s	−32.3	2.275	
2p	−14.8	2.275	
Ge 4s	−16.0	2.16	
4p	−9.0	1.85	
Fe 4s	−9.91	1.575	
4p	−5.07	0.975	
3d	−12.63	5.35 (0.5366)	1.8 (0.6678)
Fe 4s	−9.91	1.9	
4p	−5.07	1.9	
3d	−12.63	5.35 (0.5505)	2.0 (0.6260)
Mo 5s	−8.34	1.96	
5p	−5.24	1.90	
4d	−10.50	4.54 (0.6097)	1.90 (0.6097)
Mn 4s	−9.75	1.8	
4p	−5.89	1.8	
3d	−11.67	5.15 (0.5320)	1.90 (0.6490)
Ru 5s	−10.4	2.08	
5p	−6.87	2.04	
4d	−14.90	5.38 (0.5343)	2.30 (0.6368)
Co 4s	−9.21	2.0	
4p	−5.29	2.0	
3d	−13.18	5.55 (0.5680)	2.10 (0.6060)
Pt 6s	−9.077	2.554	
6p	−5.475	2.554	
5d	−12.59	6.013 (0.6334)	2.696 (0.5513)

[a] Two Slater exponents are listed for d functions. Each is followed in parentheses by its coefficient in the double-zeta expansion.

Molecule **72** is less likely to form complexes with eight-electron-accepting $M_2(CO)_6$ fragments: the a_2 orbital (empty) is at relatively high energy, and a C_{2v} complex with $Mn_2(CO)_6$ is not favorable. A complex of only C_2 symmetry, **75**, in which the HOMO of the ligand (**76**) interacts with the empty a_2 sawhorse orbital, is more likely.

Molecule **73**, *o*-quinodimethane, could conceivably form sawhorse complexes with $Mn_2(CO)_6$ (**77**); the orbitals are adequately arranged. Victor and Ben-Shoshan[45c] have synthesized some interesting complexes of this molecule with $Fe_2(CO)_6$, **78** and **79**. **78** involves no metal–metal interaction



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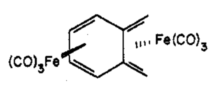

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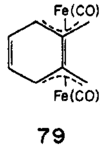

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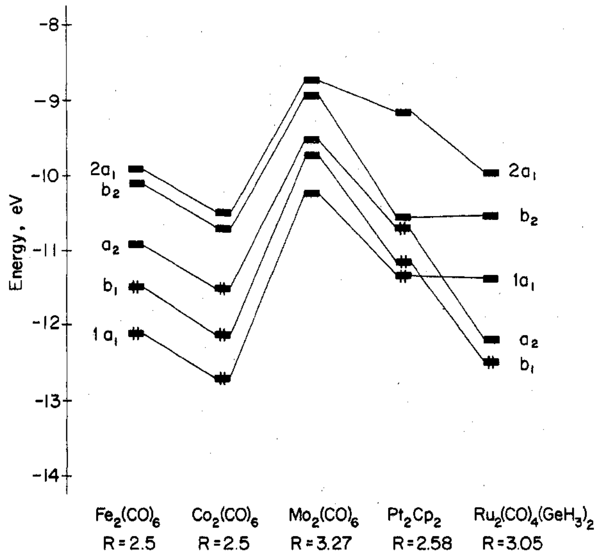

Figure 17. Valence levels for various sawhorses. The orbital occupations shown are those for neutral fragments. R is the M–M separation.

and **79** isolates a double bond and becomes a tetramethyleneethane complex with $Fe_2(CO)_6$.

Among six-electron-donor ligands the obvious one to consider is benzene. Bridging benzene complexes are known[50] but, since the a_2 orbital is at relatively high energy (a simple Hückel calculation puts the benzene a_2 orbital, one component of the empty e level, at β; the LUMO of hexatriene is at -0.45β), a benzene complex of this sort with $Fe_2(CO)_6$ is unlikely.

No doubt other molecules, not foreseen by us, will be created. While inorganic synthesis is hardly characterized by the systematic control and planning that typify organic synthesis, there appears to be no end to the variety of structural types that are made, by design or not.

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Appendix I

The parameters used in these extended Hückel[51] calculations (see Table II) were, for the most part, taken from earlier work.[52] Metal H_{ii} values for iron are taken from quadratic charge iteration on $Fe(CO)_5$.[53] Two sets of iron orbital exponents are listed in Table II. All numerical values quoted in the text and all figures, which refer to iron calculations, use the second parameter set.[52] Calculations using the first set[54] invariably gave qualitatively equivalent results. H_{ii} values for ruthenium are from charge iteration on $Ru(CO)_3Cl_3^-$;[53] the exponents are from the work of Basch and Gray,[55] as are the exponents for Mo and Pt. H_{ii} values for germanium are assumed, based upon the ionization potentials for Ge[56] and upon extrapolation from carbon values. Orbital exponents for Ge are also assumed, based on values by Clementi and Roetti.[57]

Appendix II

The $M_2(CO)_6$ valence levels for M = Fe, Co, and Mo, as well as Pt_2Cp_2, are shown in Figure 17. While there are some changes in the pattern, the overall similarity is clear.

Interesting things happen when one or more carbonyls are replaced by another ligand. The specific example included in Figure 17 is $Ru_2(CO)_4(GeH_3)_2$, hopefully a model for the fragment in the known pentalene complex.[7b] With the given germanium parameters GeH_3 is a much stronger σ donor than CO and, as such, destabilizes mainly the sawhorse $1a_1$, b_2, and $2a_1$ orbitals. (Recall that the sawhorse valence orbitals are derived from the upper three orbitals of $M(CO)_3$, which are M–CO σ antibonding. Also, the sawhorse b_1 and a_2 cannot be affected by the σ-donor strength of a substituent in the *xz* plane.) Exactly what this effect may have on the sawhorse–ligand interaction is uncertain.

Registry No. $Fe_2(CO)_6(C_2H_2)$, 60209-61-2; $Co_2(CO)_6(C_2H_2)$, 12264-05-0; $Fe_2(CO)_8^{2-}$, **20**, 58281-28-0; $Fe_2(CO)_8^{2-}$, **21**, 25463-33-6; $Fe_2(CO)_6(C_4H_4)$, **30**, 50277-83-3; $Fe_2(CO)_6(C_4H_4)$, **44**, 64425-28-1; $Fe_2(CO)_6(C_6H_6)$, 12088-77-6; $Pt_2Cp_2(C_4H_4)$, 64425-27-0; $Mn_2(CO)_6(C_8H_8)$, 49626-39-3; $Ru_2(CO)_4(GeH_3)_2(C_8H_6)$, 64425-26-9; $Fe_2(CO)_6(C_6H_8)$, **61**, 18662-05-0; $Fe_2(CO)_6(C_6H_8)$, **62**, 64425-25-8; $Fe_2(CO)_6(C_6H_8)$, **64**, 64425-24-7.

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(1) Throughout this paper we will generally refer to molecules whose structures have been established, usually by crystallographic procedures. No slight is intended to the more important synthetic work which led to these compounds in the first place. References to the syntheses may be found in the structural papers cited.

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