

- (1971); G. Zakrzewski and E. C. Lingefelter, *Inorg. Chim. Acta*, **4**, 251 (1970).
 (24) M. Di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B*, **24**, 1269 (1968); S. J. Rettig and J. Trotter, *Can. J. Chem.*, **51**, 1303 (1973); S. Richards, B. Pederson, J. V. Silvertone, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).
 (25) S. M. Peng and V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8500 (1976).
 (26) P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 129 (1971), and references cited therein.

- (27) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).
 (28) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4452 (1974).
 (29) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 5097 (1973).
 (30) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *J. Am. Chem. Soc.*, **96**, 5661 (1974).
 (31) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).
 (32) D. G. Brown, *Prog. Inorg. Chem.* **18** (1973).

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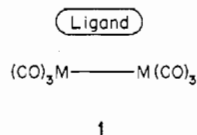
$M_2(CO)_6(\text{ligand})$ Complexes

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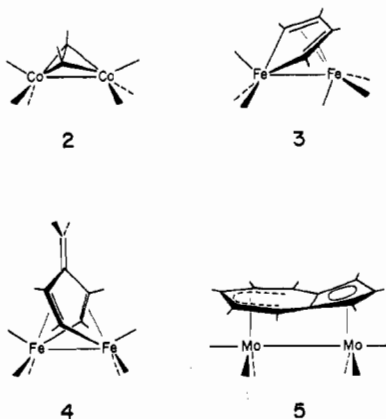
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We present a systematic molecular orbital study of the electronic structure of complexes containing the $M_2(CO)_6$ binuclear transition-metal fragment bonded to a variety of ligands. These include acetylene, two carbonyls, C_4R_4 (the ferroles), C_6R_6 (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 $M_2(CO)_6(\text{ligand})$, shown schematically in **1**, frequently crop up in transition-metal chemistry.



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}

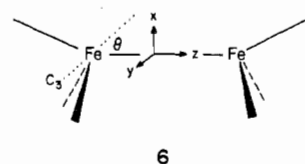
One feature common to all these molecules is the metal-metal-bonded $M_2(CO)_6$ unit. A study of the orbitals and bonding capabilities of such $M_2(CO)_6$ fragments should aid in understanding the structures and, perhaps, the chemistry of these molecules. This approach is a natural extension of earlier work on metal carbonyl fragments¹⁰ 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.

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 $Fe(CO)_3$ fragments¹⁰ are brought together in D_{3h} symmetry ($\theta = 0^\circ$). 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

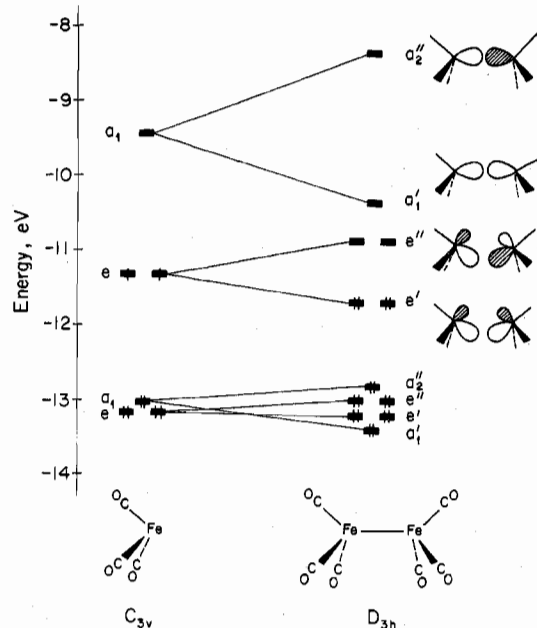


Figure 1. The orbitals of $Fe_2(CO)_8$ built up from those of two $Fe(CO)_3$ fragments. Fe-Fe is 2.5 Å. Only one component of every pair of degenerate levels is shown at right.

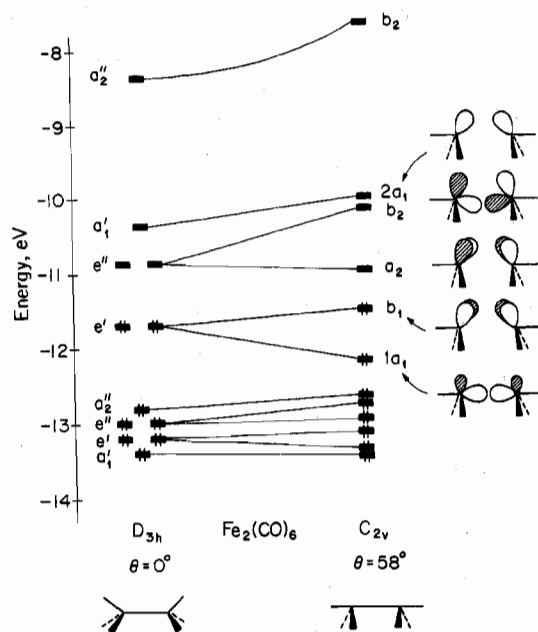
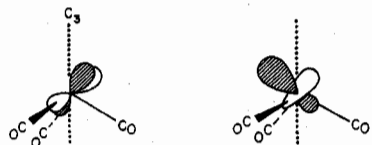


Figure 2. Evolution of $Fe_2(CO)_6$ orbitals as θ is increased.

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.



7

Partly because of this tilting, the $1a_1$ orbital (derived from the

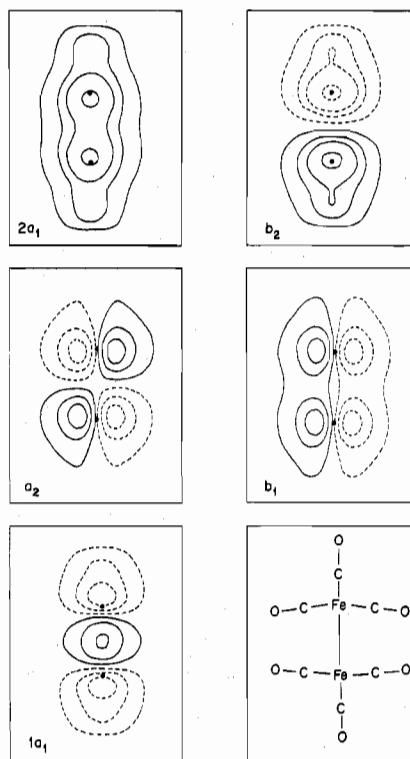
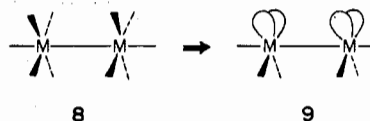


Figure 3. Contour maps of the five valence orbitals of an $Fe_2(CO)_6$ fragment. Each plot is in a plane parallel to the yz plane (see coordinate system in 6) and 1 Å above the iron atoms. Fe-Fe = 2.5 Å, $\theta = 58^\circ$. The contour levels of ψ are 0.01, 0.03, 0.05 and 0.10 in atomic units, with 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.

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 destabilized 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 $Co_2(CO)_6(\text{acetylene})$ and $Fe_2(CO)_6(\text{azomethane})$.^{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



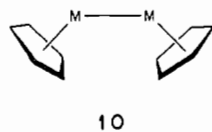
low-lying orbitals associated with the two octahedral centers and in addition will be characterized by four localized orbitals pointing toward the missing carbonyls. These four orbitals transform as $A_1 + B_1 + B_2 + A_2$ in C_{2v} and, when the proper symmetry-adapted linear combinations are taken, 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 $C\equiv C$ π bonds, a_2 and b_2 resemble $C\equiv C$ π^* bonds, and $1a_1$ resembles the $C\equiv C$ 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.



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

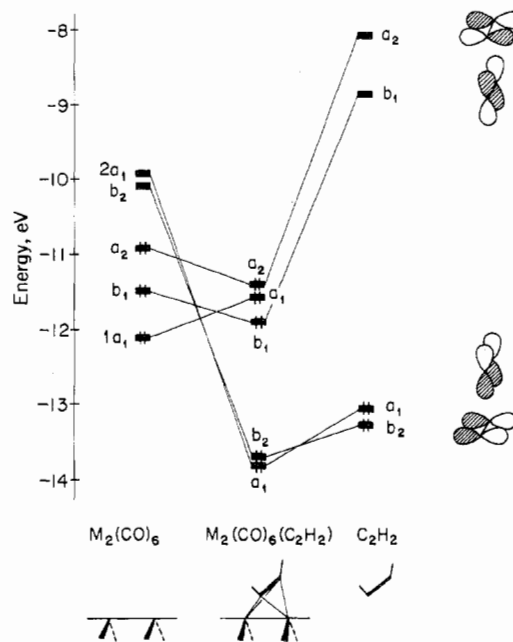
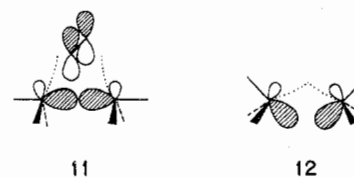


Figure 4. Orbital interaction diagram for $M_2(CO)_6$ (acetylene). The calculation was done for $M = Fe$, but applies equally well to the case $M = Co$, for which the orbital occupation indicated is appropriate.

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 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}

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

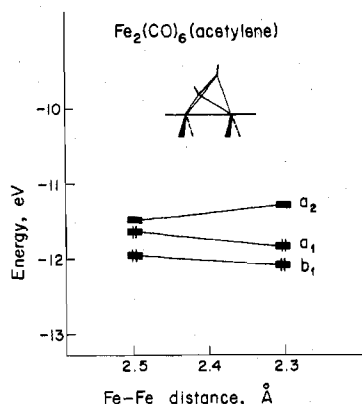
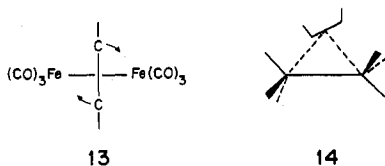


Figure 5. Effect of decreasing Fe-Fe distance on important Fe(CO)₃(C₂H₂) levels.

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 Fe₂(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 1*a*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.

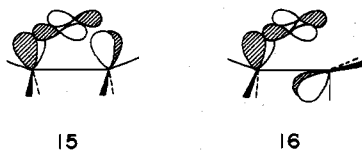
This low-lying empty *a*₂ orbital has several consequences. One possibility is a second-order Jahn-Teller distortion¹⁴ of *a*₂ × *a*₁ = A₂ symmetry. A conceivable distortion of A₂ symmetry is shown in 13, corresponding to rotating the



acetylene relative to the Fe₂(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°.

The observed Fe₂(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.

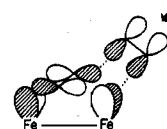
While this distortion was not anticipated by us, it clearly relieves the situation of LUMO close to HOMO which favors distortion. The “*a*₂” LUMO of 14¹⁵ is raised in energy by the Fe(CO)₃ twist. This in turn is a consequence of the nature of the Fe₂(CO)₆ fragment *a*₂, and deeper still from the “tilting” 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,

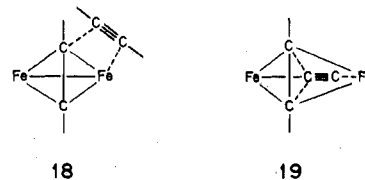
which in turn leads to a higher energy for this orbital. This is fine for Fe₂(CO)₆(acetylene), but in the corresponding Co complex where the *a*₂ orbital is filled this destabilization must be avoided and the sawhorse geometry restored. If further Fe₂(CO)₆(acetylene) structures are studied, we anticipate 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:

Another consequence of the empty *a*₂ orbital in Fe₂(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 Fe₂(CO)₆(acetylene) complex, followed by attack by another acetylene molecule.¹³ If the LUMO of the initial Fe₂(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.



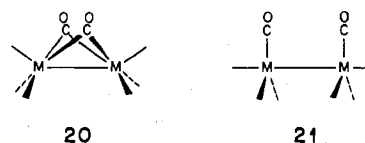
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Calculations do show this. “Side-on” attack, 18, where the



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, Rh₂(PF₃)₈ couples acetylenes to give rhodicyles,^{16a} possibly via an intermediate Rh₂(PF₃)₅(acetylene)^{16b} which, like Fe₂(CO)₆(acetylene), has an empty orbital of pseudo-*a*₂ symmetry.

Carbonyls. We turn next to the interaction of an M₂(CO)₆ fragment with two or four carbonyls.¹⁷ Four carbonyls return us to Mn₂(CO)₁₀, reversing the reasoning used above in the construction of the M₂(CO)₆ orbitals. Two carbonyls are more interesting, taking us to the structures of the isoelectronic Co₂(CO)₈ and Fe₂(CO)₈²⁻. The solid-state structures of these molecules are shown below.^{18a,b} In solution there is evidence that Co₂(CO)₈ exists in three isomeric forms, two of which are of type 20 and 21, all close to each other in energy.¹⁹



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 M₂(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.

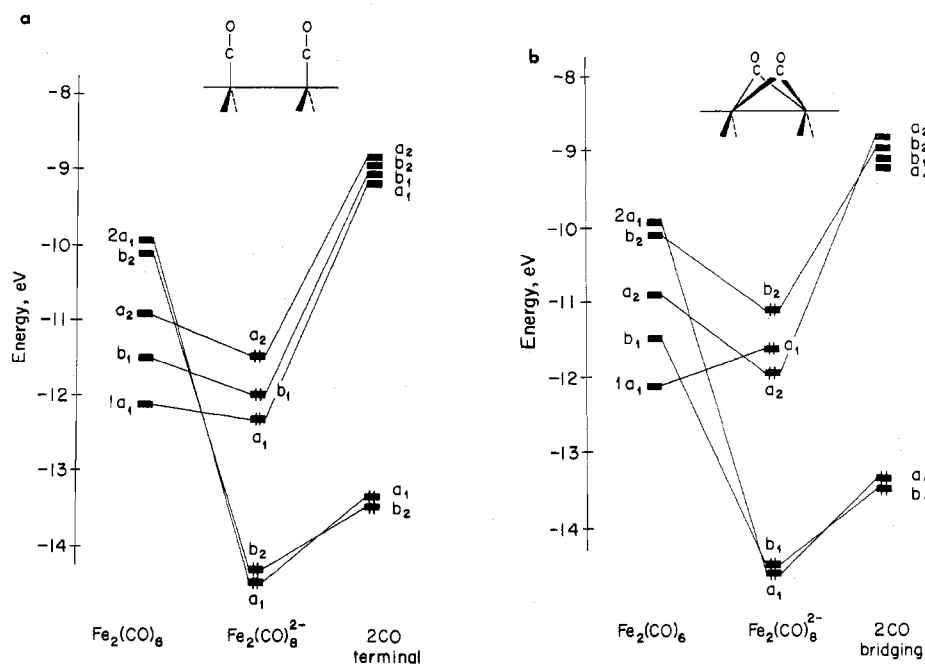
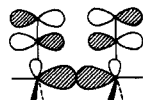


Figure 6. (a, left) Orbital interactions for terminal approach of two carbonyl ligands. The symmetry is only C_{2v} . If the angles were adjusted to give D_{3h} symmetry, a_2 and b_1 merge with Fe "lone pair" orbitals (not shown) to form e'' and e' levels. (b, right) Orbital interactions for two carbonyls 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



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resulting orbital is seen to be the M-M σ bond.

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 com-

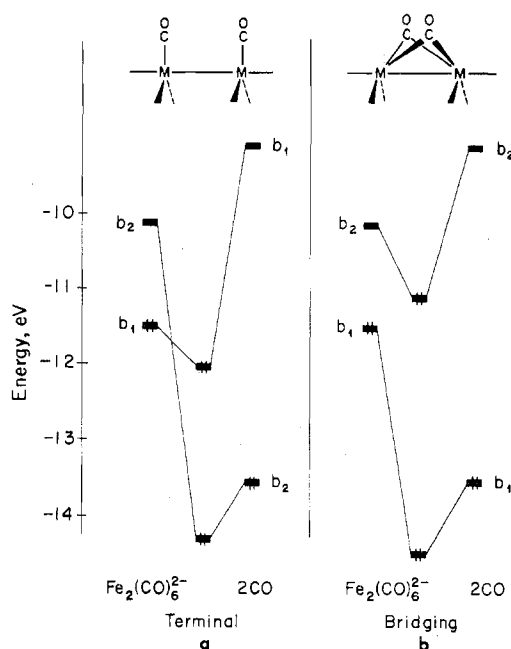


Figure 7. (a, left) b_1 and b_2 interactions for terminal carbonyls in $Fe_2(CO)_8^{2-}$. (b, right) Same for bridging carbonyls.

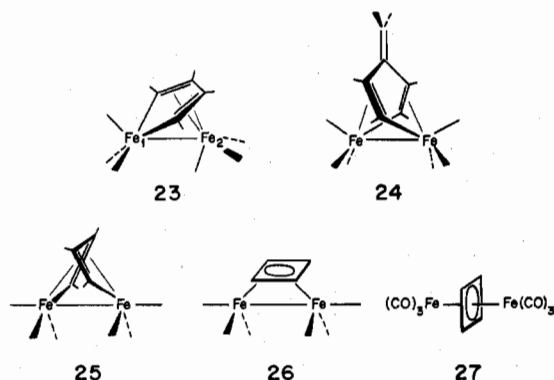
parable), then that shown in Figure 7a will be favored. However, if the interactions (especially b_2 - b_2) emphasized in Figure 7b are stronger than those shown in Figure 7a, the former can become the favored case. Our calculations are ambiguous, giving nearly equal energies for the bridged and terminal 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 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 per-

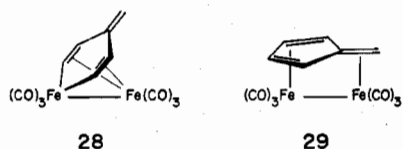
turbation adversely affects the bridging structure, Figure 7b, where the filled b₂ orbital contains a large sawhorse contribution. The terminal structure, Figure 7a, is less affected since the filled b₂ orbital has only a small sawhorse component. Thus, good σ donors at the ends of the sawhorse should diminish the tendency to bridge.

Ferroles, Flyover Bridges, and Other Medium-Sized Ligands

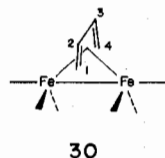
The remarkable ferrole structure **23**, formed by the reaction



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 C₄R₄ 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 C₆R₆ take on the flyover coordination mode **24** instead of such alternative structures as the ferrole analogue **28** or the fulvene complex **29**?



Ferroles. A starting point for an analysis of some of these possibilities is a hypothetical Fe₂(CO)₆(C₄H₄) 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 Fe₂(CO)₆²⁺ or neutral C₄H₄ and Fe₂(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 1a₁ sawhorse orbital is destabilized, now by the strong a₁ σ-donor lobe combination of the C₄H₄ unit. Furthermore, there are two low-lying empty orbitals, a₂ and b₂, derived largely from the π* orbitals of the butadienyl unit.

The frontier orbitals of the symmetrical structure predispose it to two distortions, which are derivable from either a second-order Jahn–Teller argument¹⁴ or the equivalent analysis

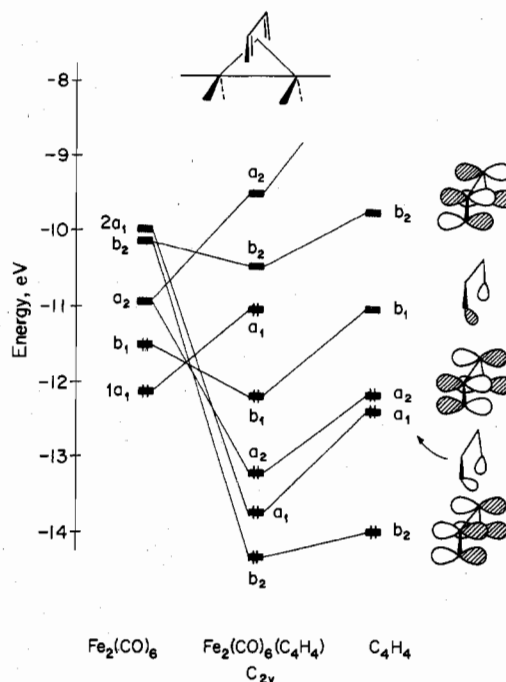
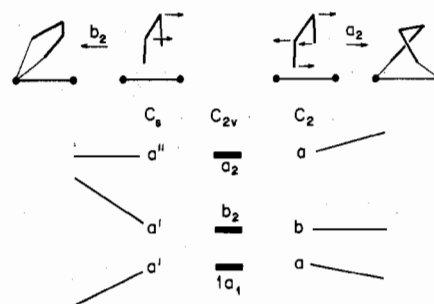
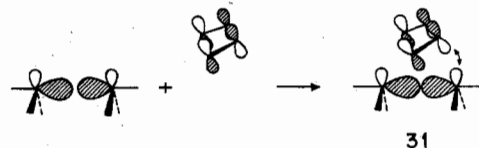


Figure 8. Orbital scheme for a hypothetical C_{2v} geometry of a ferrole complex. Fe–Fe = 2.5 Å, θ = 58°. The top diene π orbital is omitted.

of the effect of lowered symmetry on orbital interactions. The highest occupied and low-lying unoccupied orbitals are shown below.



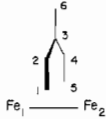
Consider first the motion of b₂ symmetry, a bending over toward the ferrole geometry. (Perhaps we should call these “fall-over bridges”.) The symmetry is reduced to C_s. The 1a₁ and b₂ orbitals, now allowed to mix, do so. The 1a₁ is considerably stabilized, picking up π bonding with C₁ and C₄ of the butadienyl, as shown in **31**. Simultaneously, C₂ and C₃



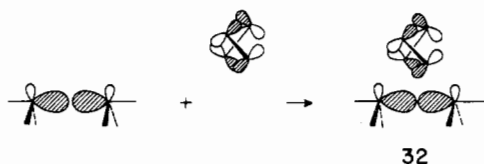
bond to the other iron atom, Fe₂. In the idealized geometries used for the calculations, the distortion is stabilizing by ~1 eV, most of the preference due to this trend operating in the 1a₁ orbital. Note that interaction **31** implies considerable occupation of the lowest π* orbital of the C₄H₄ unit, which helps explain the “bond leveling” trends in the C–C bond lengths.^{22a} Any perturbation of the C₄H₄ 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 Fe₂(CO)₆(C₆H₈O₂) in alkaline solution.²¹

Alternatively, an a₂ distortion reduces the symmetry to C₂,

Table I. Overlap Population in a Hypothetical Symmetrical $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_6)$ Complex and Its C_3 and C_2 Distortions

| | Distance, A | Overlap population | | Distance, A | Overlap population | | Distance, A | Overlap population | |
|---|--------------------------|--------------------|---------|--------------------------|--------------------|---------|--------------------------|--------------------|---------|
|  | $\text{Fe}_1\text{-C}_1$ | 2.02 | 0.3276 | $\text{Fe}_1\text{-C}_1$ | 2.02 | 0.4007 | $\text{Fe}_1\text{-C}_1$ | 2.02 | 0.4060 |
| | $\text{Fe}_1\text{-C}_2$ | 2.99 | -0.0152 | $\text{Fe}_2\text{-C}_1$ | 2.02 | 0.1695 | $\text{Fe}_1\text{-C}_3$ | 3.13 | -0.0281 |
| | $\text{Fe}_1\text{-C}_3$ | 3.37 | -0.0180 | $\text{Fe}_2\text{-C}_2$ | 2.11 | 0.0816 | $\text{Fe}_1\text{-C}_4$ | 4.46 | 0.0003 |
| | $\text{Fe}_1\text{-C}_6$ | 4.71 | -0.0003 | $\text{Fe}_2\text{-C}_3$ | 2.15 | -0.0154 | $\text{Fe}_1\text{-C}_5$ | 2.02 | 0.2168 |
| | | | | $\text{Fe}_2\text{-C}_4$ | 3.31 | -0.0281 | $\text{Fe}_1\text{-C}_6$ | 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

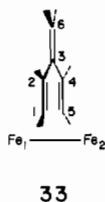


also stabilizing, but less so than the motion which carries the system to C_3 symmetry. It appears that another relatively high-lying and occupied a_2 level (see Figure 8) partially negates the stabilizing effect of the $a_2 \pi^*$ orbital.

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 $\text{Fe}_2(\text{CO})_6$ (dithiolato) complex.^{22b}

Still other bonding possibilities are the cyclobutadiene complexes **26** and **27**. However, cyclobutadiene is only a four-electron donor while the $\text{Fe}_2(\text{CO})_6$ 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 $\text{Fe}(\text{CO})_3$ 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



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

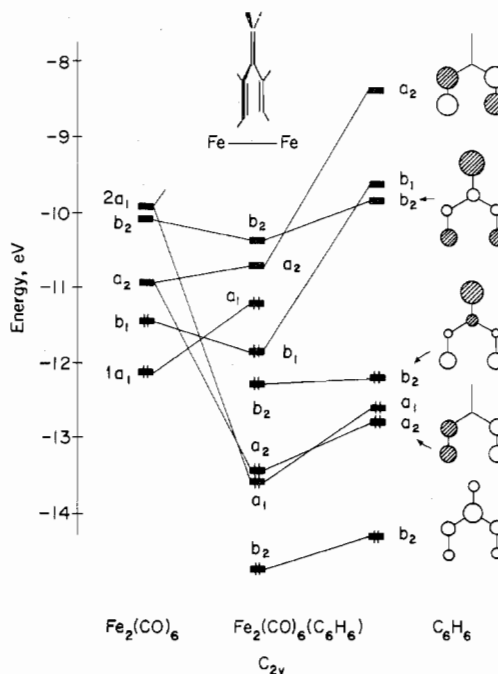
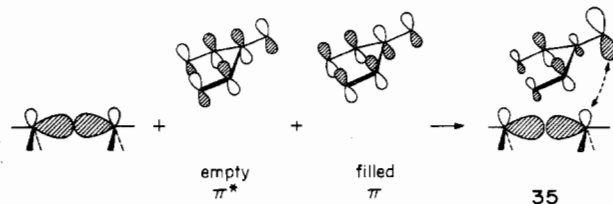


Figure 9. Orbital scheme for a hypothetical C_{2v} flyover geometry. The C_6H_6 n orbitals are not illustrated, nor is the highest π orbital.

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

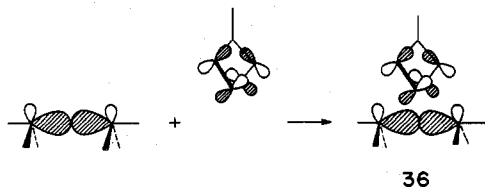
Next one considers the distortions reducing the C_{2v} symmetry of **33** to C_3 (a hypothetical ferrole structure) and C_2 (the observed flyover geometry). The argument is similar to that given above for C_4H_4 , but the trends are reversed. Among the empty orbitals b_2 is now above a_2 . The C_3 distortion 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 $b_2 \pi$ 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



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 C₃-C₆ π bond, and forcing the third π bond to interact with the Fe₂(CO)₆ fragment is guaranteed to be unfavorable.

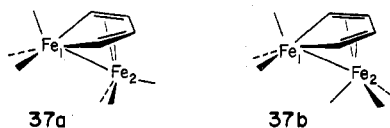
The alternative distortion to C₂ symmetry allows mixing of the a₂ π^* orbital into the 1a₁ orbital, **36**, resulting in splendid C-Fe bond formation between Fe₁ and C₁, C₄ and Fe₂ and C₂, C₅ (**36**), leaving the offending C₃-C₆ π bond alone. There



is little occupation of any orbital which is C₃-C₆ antibonding, and the bond is of normal double-bond length. However, C₁-C₂ and C₄-C₅ are longer than ordinary double bonds and indicate strong participation in the bonding to the Fe₂(CO)₆ unit. Here the a₂ distortion corresponds to the observed structure; the five-carbon chain allows more freedom for the a₂ distortion than the four-carbon chain, and the filled a₂ π orbital is low enough in C₆H₆ that it does not destabilize the a₂ distortion. The complex, with C₂ 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 C₁ or C₂ (but not C₆) is replaced by a donating group, such as O⁻.

A fulvene complex of type **29** does not appear to be a promising structure. The fulvene π orbitals²⁴ do not contain a properly aligned acceptor orbital of pseudo-a₂ symmetry, and consequently the HOMO of a calculated model lies at very high energy. Interestingly, a complex of the composition Fe₂(CO)₆(fulvene) exists, but the Fe₂(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 Fe₂(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 Os₂(CO)₆ complexes of analogous structure.^{4bj} (2) ¹³C NMR studies of the ferroles indicate a low barrier for scrambling the carbonyl groups on Fe₂. They are not frozen out at -125 °C.^{4i,26} (3) If Fe₂ 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.

Our calculations also indicate a delicate balance of forces behind this conformation choice. Direct Fe₂-ring overlaps appear to favor **37a**, but in **37b** we definitely note bonding interactions between Fe₁ and the unique carbonyl bonded to Fe₂. 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

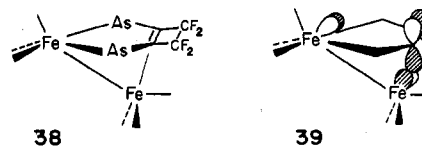


diagram for this molecule beginning in a symmetrical C_{2v} structure analogous to **30**, one finds that as the bridge falls over an a₂ combination is stabilized. This orbital, a mixture of Fe₂(CO)₆ and the ethylene π^* , is shown in **39**. Its occupation weakens both Fe-Fe (2.9 Å) and the CC (1.5 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.

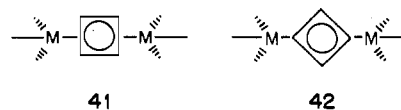
Before leaving the ferroles and flyover bridges, we should note where one comes to if one applies the isolobal analogy.^{10,12} Since Fe(CO)₃ is like CH⁺, the ferrole type is recognized as being similar to the pentagonal-pyramidal C₆R₆²⁺²⁸ or the carboranes C₄B₂R₆.²⁹ Replacing only one Fe(CO)₃ by CH⁺ gives FeCp(CO)₃⁺. The analogue of the flyover structures is a C₈R₈²⁺, a novel potentially nonclassical dication based on the heptafulvene geometry, **40**. We discuss its electronic



structure in detail elsewhere.³⁰

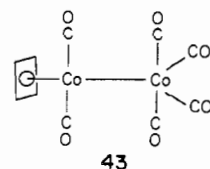
Cyclobutadiene. Complexes of M₂(CO)₆ with an intact bridging cyclobutadiene, **26**, have not been reported. A calculation on an assumed geometry, Figure 10, shows good interactions, but a relatively high-lying a₂ orbital, formed by a bonding interaction between a₂ of M₂(CO)₆ and the a₂ π^* orbital of cyclobutadiene. This orbital is high in energy because the a₂ π^* orbital of C₄H₄ is at higher energy than the corresponding acetylene π^* orbital. Otherwise, the interaction strongly resembles the acetylene system.

This a₂ orbital could be filled (corresponding to the complex Co₂(CO)₆(C₄H₄) or empty (Fe₂(CO)₆(C₄H₄)). The geometry of the Co₂(CO)₆(C₄H₄) complex, if ever made, will almost certainly be that assumed in Figure 10, **41**, in preference to



42. In **42**, C₄H₄ presents no a₂ acceptor orbital, and the occupied a₂ will rise to the nonbonding M₂(CO)₆ level. The Fe₂(CO)₆ complex, if ever formed, should have little preference for orientation as in **41** or **42** since the a₂ orbital is empty. Second-order Jahn-Teller distortion (see Fe₂(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 Fe₂(CO)₆(C₄H₄). 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.

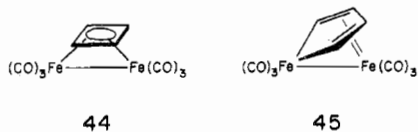
The complexes Co₂(CO)₆-(C₄Me₄) and -(C₄H₄) have been synthesized.³¹ The parent compound has recently been shown to have the structure **43**.^{31c} ¹³C NMR studies show a rapid equilibration of the carbonyls down to very low tempera-



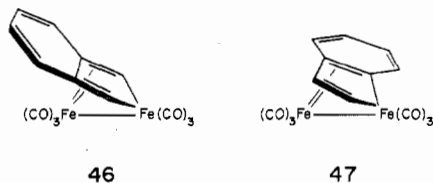
tures,^{31d} a process which could proceed through a bridged C_{2v} complex of type **41**. That isomer conceivably could be rendered more stable by lowering the energy of the π^* a_2 orbital, perhaps by substituting CF_3 for the methyl groups.

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.

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 $Fe_2(CO)_6(\text{cyclobutadiene})$ complex **44**. Yet the



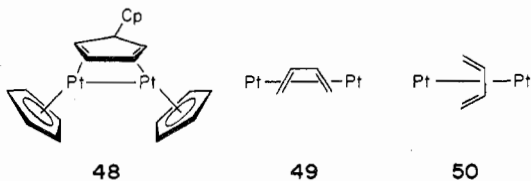
reaction interconverting **44** and **45** is a symmetry-forbidden process, as can be readily checked by a correlation diagram relating these species. Pettit and co-workers found that **46** and **47**, formed from the reaction of benzocyclobutadieneiron



tricarbonyl with $Fe_3(CO)_{12}$, do not interconvert at 120° .³⁴ We think this supports the notion that the transformation $44 \rightleftharpoons 45$ is difficult, for the intermediacy of a $Fe_2(CO)_6(\text{benzocyclobutadiene})$ 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 $(C_4H_4)Fe(CO)_3$.

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 ac-

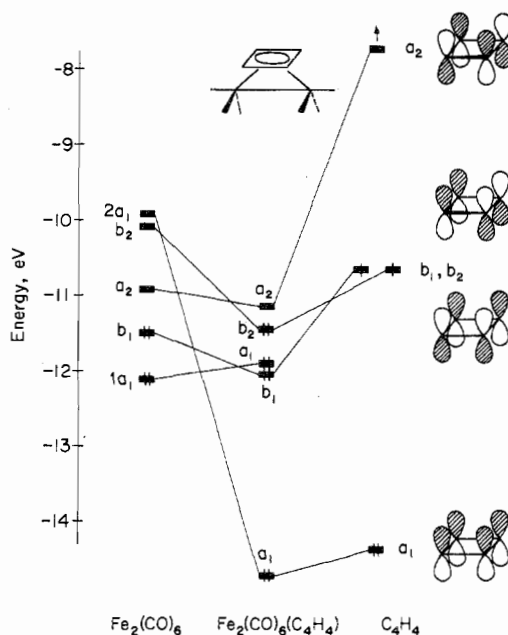


Figure 10. Interaction diagram for $Fe_2(CO)_6(\text{cyclobutadiene})$.

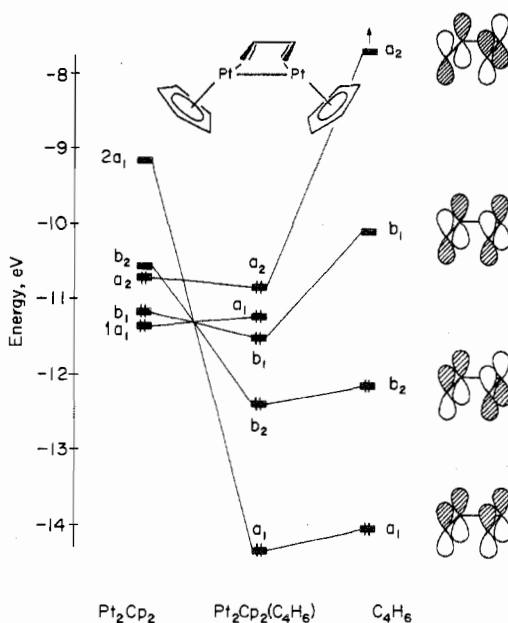


Figure 11. Interaction diagram for $Pt_2Cp_2(\text{butadiene})$. While the actual symmetry is C_s , the orbitals are labeled with respect to the approximate C_{2v} pseudosymmetry.

ceptor 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.

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

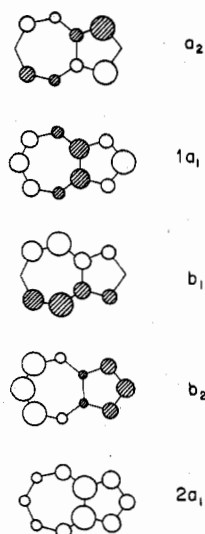
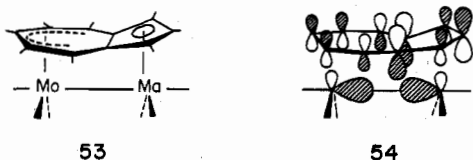


Figure 12. Diagrammatic representations of the occupied π orbitals of azulene. Each is labeled according to the sawhorse M₂(CO)₆ level with which its interaction is best.

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

Ten-Electron Donors: Azulene. Mo₂(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 Mo₂(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 M₂(CO)₆, as illustrated in Figure 3.

In the isolated Mo₂(CO)₆ fragment there is very little metal-metal bonding, for the 1a₁ 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 Mo₂(CO)₆(azulene) complex there is a bonding interaction between the sawhorse 1a₁ orbital and the ligand donor orbital (contrast the acetylene example), **54**, since the sawhorse 1a₁ 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 ¹³C NMR study, Cotton, Hunter, and Lahuerta³⁸ 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 Mo₁ (under the seven-membered ring) is 23 kcal/mol and around Mo₂ (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

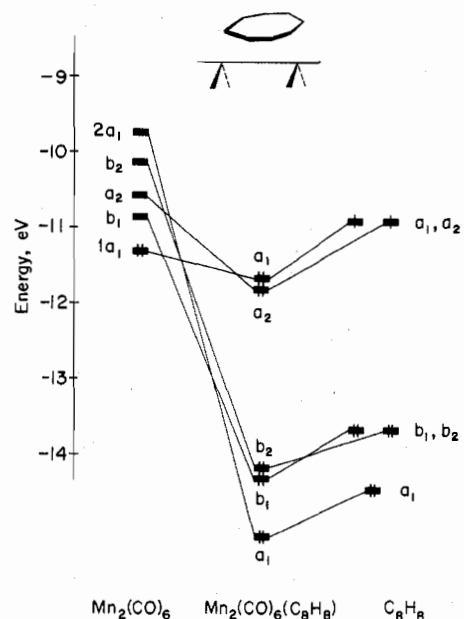


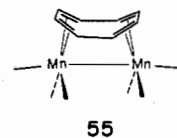
Figure 13. The occupied valence orbitals of Mn₂(CO)₆(C₈H₈), built from Mn₂(CO)₆ and the π orbitals of planar cyclooctatetraene. Mn-Mn = 3.0 Å, $\theta = 55^\circ$.

Mo₂ is easier. There is new experimental evidence that this is correct.⁴⁰

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 Mo₂(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 Mo₂(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 Mo₂(CO)₆ complex.

Eight-Electron Donors: Cyclooctatetraene. The C₈ ring forms sawhorse complexes with Mn₂(CO)₆, Fe₂(CO)₆, and Ru₂(CO)₆. The Fe and Ru complexes, to be discussed below, only want six electrons from the C₈H₈ molecule and bend the ring so as to isolate a double bond and leave a hexatriene unit to interact with the sawhorse. Mn₂(CO)₆ wants all eight electrons and the structure,^{7c} **55**, shows the C₈H₈ to be truly

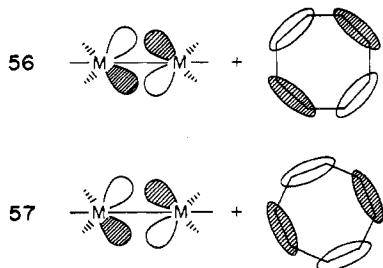


octahapto to the sawhorse, although the ring is still nonplanar. Treating the C₈H₈ ring as planar and using its well-known Hückel π orbitals,²⁴ the interaction diagram (Figure 13) is obvious.

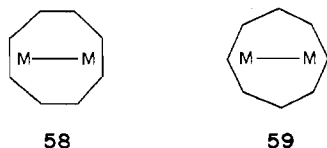
There are two points of some interest. First, again there is strong bonding between the 1a₁ sawhorse orbital and an a₁ orbital of C₈H₈, suggesting that again the sawhorse should droop and the central carbons be pulled toward the metal-

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 $\text{Co}_2(\text{CO})_6$ (acetylene) and $-(\text{cyclobutadiene})$, as discussed above. It is essentially a " δ bond" (56) which would normally



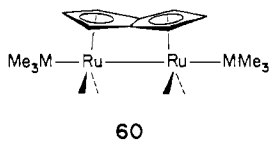
be broken if the ligand and sawhorse were forced to rotate relative to each other (57). This is why the cobalt-cyclobutadiene complex should prefer 41. However, in cyclooctatetraene, the a_2 orbital is degenerate with an a_1 orbital. This degeneracy allows the C_8H_8 molecule to present orbitals of quasi- 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 hy-



drogens 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 $\text{Mn}_2(\text{CO})_6$ fragments.

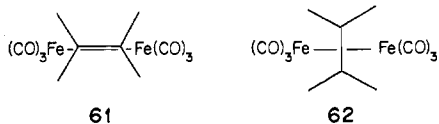
Cyclooctatetraene complexes with $((\text{CO})_2(\text{MMe}_3)\text{Ru})_2$, $\text{M} = \text{Si}$ and Ge , are known.⁴³ Structures analogous to those of $(\text{C}_8\text{H}_8)\text{Fe}_2(\text{CO})_5$ ⁴⁴ are suggested⁴³ (COT ring bent away from the metal atoms), but perhaps the $\text{Mn}_2(\text{CO})_6$ (cyclooctatetraene) structure also might serve as a model.

Pentalene. Complexes of the type $\text{Ru}_2(\text{CO})_4(\text{MMe}_3)_2$, $\text{M} = \text{Ge}$ and Si , form pentalene complexes,^{7b,43} 60. The π



orbitals of pentalene²⁴ 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 $\text{M}_2(\text{CO})_6$, M being a d^6 metal.

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

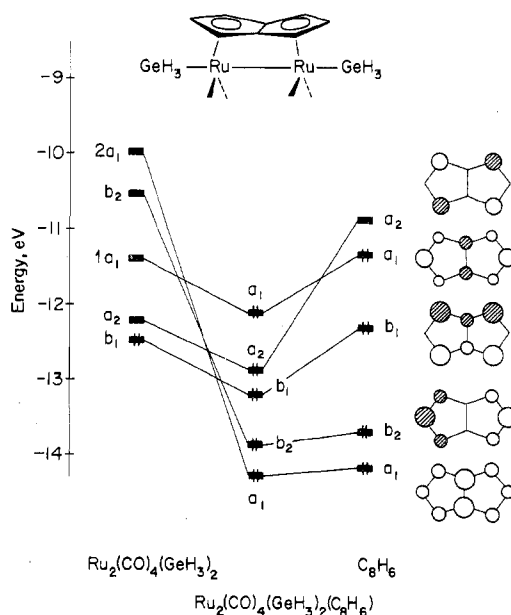
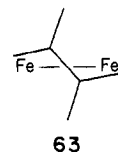


Figure 14. Orbital interaction diagram for $\text{Ru}_2(\text{CO})_4(\text{GeH}_3)_2$ (pentalene). The lower six π orbitals of pentalene are shown.

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.

Even less likely than 62 is the intermediate geometry 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.

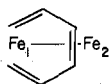
There are some interesting experimental results to consider here. NMR studies by Nakamura and Hagihari^{45a} led them to suggest a rapid interconversion between 61 and 62. Later studies, on a phenyl-substituted tetramethyleneethane, showed no interconversion of this type.^{45c} The prediction made here 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 $\text{Ru}_2(\text{CO})_5(\text{SiMe}_3)(\text{C}_7\text{H}_7)$ has been prepared.^{7c} This molecule is related to $\text{Mn}_2(\text{CO})_6(\text{C}_8\text{H}_8)$. 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 fluxional, like the manganese complex. The reported crystal structure^{7e} is of a closely related derivative. The syntheses of heterodimetallic $(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3\text{M}(\text{CO})_3$, $\text{M} = \text{Mn}$ and Re , have been reported recently.⁴⁶

Hexatrienes in Rings. $\text{M}_2(\text{CO})_6$ complexes, $\text{M} = \text{Fe}$, 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 $\text{Fe}_2(\text{CO})_6$ 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



64

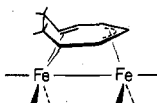


65

the preference is quite small. Experimentally, a planar hexatriene molecule is most closely approximated by cycloheptatriene, C₇H₈, and the structure, ^{48a} **66**, indeed resembles



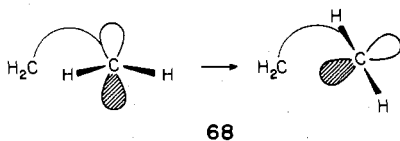
66



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 CH₂ of the hexatriene is twisted so as to point its p orbital inward, **68**. A

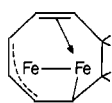


68

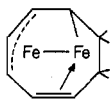
model makes it much more convincing that this is what happens in an eight-membered ring. Performing this distortion on the hexatriene in **64** results in *destabilization* because the p orbital is being twisted away from the iron atom and toward the xy plane. The orbital which suffers most is the bonding combination of the Fe₂(CO)₆ a₂ 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 CH₂ group, **65** becomes favored over **64**. Further, Fe₁ in **65** wants to move toward the twisted CH₂, 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 fluctuallity. The complexes with eight-membered rings show, at room temperature, a ¹³C 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

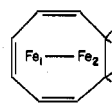


69a

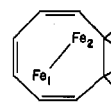


69b

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 a₂ orbital: a vital feature of the sawhorse-hexatriene bond is the interaction of the hexatriene LUMO and sawhorse a₂ to form a filled bonding MO, and rotating the hexatriene through the



70a



70b



70c

waypoint **70b**, presumably necessary for "gliding", breaks the a₂-a₂ bond, requiring (calculated) nearly 2 eV. The bond forms again in **70c**. This is no longer the same situation as in Mn₂(CO)₆(C₈H₈). The hexatriene unit has a pseudo-a₂ 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 tetramethylethane, cyclobutadiene, and acetylene complexes.

Incidentally, our calculation indicates that the Fe(CO)₃ group at Fe₂ in **65** should have a lower barrier to rotation about its axis than that at Fe₁. This is connected with the hexatriene HOMO being a better donor to Fe₂ and this lower barrier can be observed experimentally.^{7f}

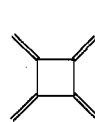
Molecules Not Yet Reported

In order for an organic ring system to form a reasonably good bond to an M₂(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 a₁, b₁, and b₂ symmetry and must provide a low-lying empty orbital of a₂ symmetry. A noteworthy exception to this is the C₄H₄ entity of the ferrole system, which (in C_{2v}) has donors of b₂, a₂, and a₁ symmetry and is a good b₁ acceptor. Eight-electron donors have a₁, b₁, b₂, a₂ donors with an empty a₁ orbital, although there could be systems with a₁, b₁, b₂, a₁ donors and an a₂ acceptor. Ten-electron donors, of course, must have a₁, b₁, b₂, a₁, a₂ donors. Among the "small" and "medium-sized" molecules, four-electron donors have a₁, b₂ donor orbitals and b₁, a₂ acceptors (recall the exception of the bridging carbonyls).

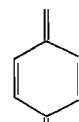
With these restrictions in mind it is interesting to consider what organic entities, as yet unknown to bind as ligands to an M₂(CO)₆, might be likely candidates for synthesis.⁴⁹

For ten-electron donors, naphthalene is an obvious molecule to try. Its donor orbitals are all of the proper symmetry for forming an M₂(CO)₆ complex, M = Cr and Mo.

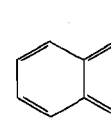
Among eight-electron donors, the molecules **71-73** can be



71

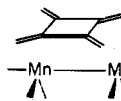


72

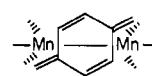


73

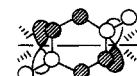
considered. Tetramethylenecyclobutane (**71**) has the appropriate donor orbitals of a₁, b₁, b₂, and a₂ symmetries, and should form a sawhorse-type complex **74** with Mn₂(CO)₆.



74



75



76

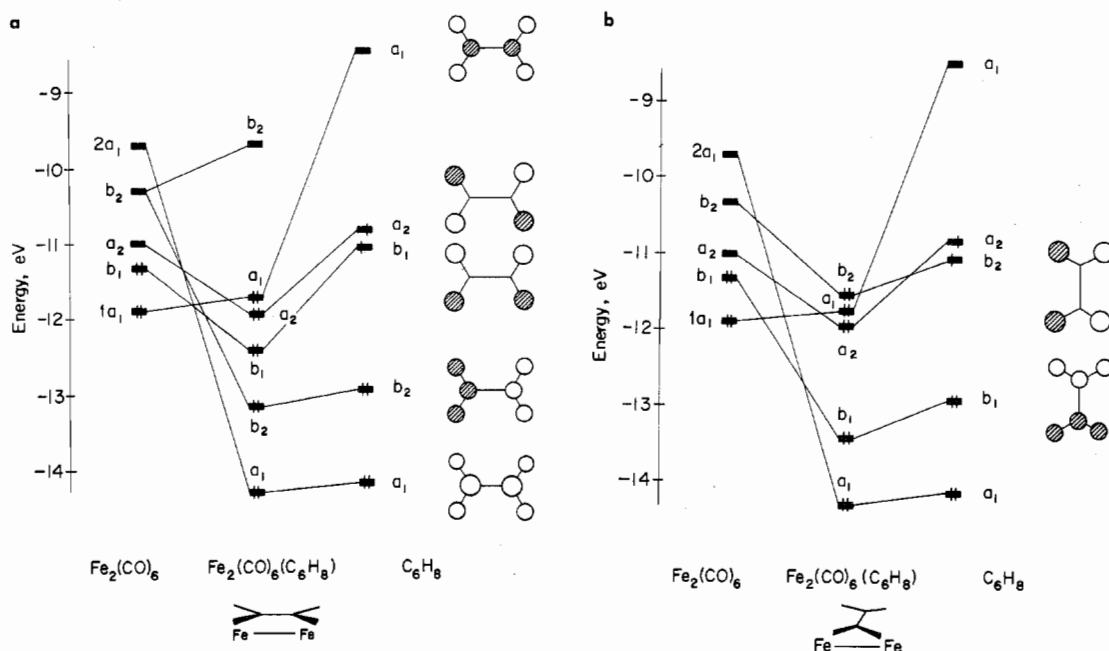


Figure 15. Interaction diagram for the π orbitals of tetramethylethane with $\text{Fe}_2(\text{CO})_6$ in two possible orientations of C_{2v} symmetry: (a) (left) corresponds to **61** and is close to the observed structure; (b) (right) corresponds to **62**. Only two of the six ligand π orbitals are shown in the latter case.

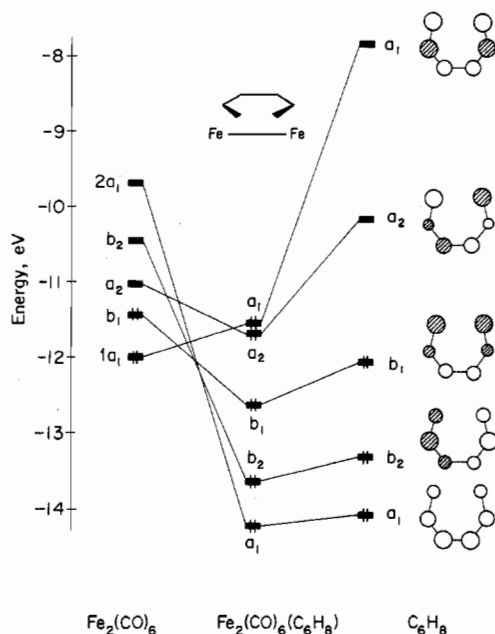
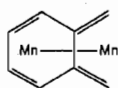


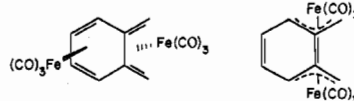
Figure 16. Interaction diagram for planar hexatriene with $\text{Fe}_2(\text{CO})_6$. $\text{Fe}-\text{Fe} = 2.8 \text{ \AA}$, $\theta = 58^\circ$. The actual symmetry is only C_s , but the orbitals have near C_{2v} symmetry, and are so labeled.

Molecule **72** is less likely to form complexes with eight-electron-accepting $\text{M}_2(\text{CO})_6$ fragments: the a_2 orbital (empty) is at relatively high energy, and a C_{2v} complex with $\text{Mn}_2(\text{CO})_6$ 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 $\text{Mn}_2(\text{CO})_6$ (**77**); the orbitals are



77



78

79

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 | |
| C 2p | -11.4 | 1.625 | |
| O 2s | -32.3 | 2.275 | |
| O 2p | -14.8 | 2.275 | |
| Ge 4s | -16.0 | 2.16 | |
| Ge 4p | -9.0 | 1.85 | |
| Fe 4s | -9.91 | 1.575 | |
| Fe 4p | -5.07 | 0.975 | |
| Fe 3d | -12.63 | 5.35 (0.5366) | 1.8 (0.6678) |
| Fe 4s | -9.91 | 1.9 | |
| Fe 4p | -5.07 | 1.9 | |
| Fe 3d | -12.63 | 5.35 (0.5505) | 2.0 (0.6260) |
| Mo 5s | -8.34 | 1.96 | |
| Mo 5p | -5.24 | 1.90 | |
| Mo 4d | -10.50 | 4.54 (0.6097) | 1.90 (0.6097) |
| Mn 4s | -9.75 | 1.8 | |
| Mn 4p | -5.89 | 1.8 | |
| Mn 3d | -11.67 | 5.15 (0.5320) | 1.90 (0.6490) |
| Ru 5s | -10.4 | 2.08 | |
| Ru 5p | -6.87 | 2.04 | |
| Ru 4d | -14.90 | 5.38 (0.5343) | 2.30 (0.6368) |
| Co 4s | -9.21 | 2.0 | |
| Co 4p | -5.29 | 2.0 | |
| Co 3d | -13.18 | 5.55 (0.5680) | 2.10 (0.6060) |
| Pt 6s | -9.077 | 2.554 | |
| Pt 6p | -5.475 | 2.554 | |
| Pt 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.

adequately arranged. Victor and Ben-Shoshan^{45e} have synthesized some interesting complexes of this molecule with $\text{Fe}_2(\text{CO})_6$, **78** and **79**. **78** involves no metal-metal interaction

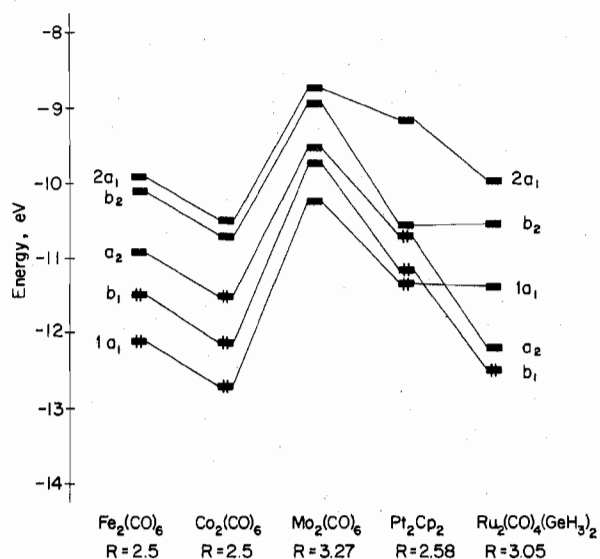


Figure 17. Valence levels for various sawhorses. The orbital occupations shown are those for neutral fragments. R is the M–M separation.

and **79** isolates a double bond and becomes a tetramethylenethane complex with Fe₂(CO)₆.

Among six-electron-donor ligands the obvious one to consider is benzene. Bridging benzene complexes are known⁵⁰ but, since the a₂ orbital is at relatively high energy (a simple Hückel calculation puts the benzene a₂ 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 Fe₂(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.

Acknowledgment. We are grateful to the members of our research group, and especially R. H. Summerville, for their interest and discussion. Part of the stimulus for our work came from the research of S. Sarel, R. Victor, and R. Ben-Shoshan. We are grateful to them and to R. Pettit, F. A. Cotton, J. C. Smart, and A. B. Anderson for communicating results prior to publication. We also wish to thank E. Kronman for the typing and J. Jorgensen for the drawings. Our research was supported by the National Science Foundation through Grant CHE-7606099, as well as through the Materials Science Center at Cornell University.

Appendix I

The parameters used in these extended Hückel⁵¹ 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 set⁵⁴ invariably gave qualitatively equivalent results. H_{ii} values for ruthenium are from charge iteration on Ru(CO)₃Cl₃⁻; 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 Ge⁵⁶ and upon extrapolation from carbon values. Orbital exponents for Ge are also assumed, based on values by Clementi and Roetti.⁵⁷

Appendix II

The M₂(CO)₆ valence levels for M = Fe, Co, and Mo, as

well as Pt₂Cp₂, 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 Ru₂(CO)₄(GeH₃)₂, hopefully a model for the fragment in the known pentalene complex.^{7b} With the given germanium parameters GeH₃ is a much stronger σ donor than CO and, as such, destabilizes mainly the sawhorse 1a₁, b₂, and 2a₁ 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 b₁ and a₂ 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. Fe₂(CO)₆(C₂H₂), 60209-61-2; Co₂(CO)₆(C₂H₂), 12264-05-0; Fe₂(CO)₈²⁻, **20**, 58281-28-0; Fe₂(CO)₈²⁻, **21**, 25463-33-6; Fe₂(CO)₆(C₄H₄), **30**, 50277-83-3; Fe₂(CO)₆(C₄H₄), **44**, 64425-28-1; Fe₂(CO)₆(C₆H₆), 12088-77-6; Pt₂Cp₂(C₄H₄), 64425-27-0; Mn₂(CO)₆(C₈H₈), 49626-39-3; Ru₂(CO)₄(GeH₃)₂(C₈H₈), 64425-26-9; Fe₂(CO)₆(C₆H₈), **61**, 18662-05-0; Fe₂(CO)₆(C₆H₈), **62**, 64425-25-8; Fe₂(CO)₆(C₆H₈), **64**, 64425-24-7.

References and Notes

- 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.
- (a) Co₂(CO)₆(PhCCPh): W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959). (b) [Co₂(CO)₅PPh₂CCF₃]₂: N. K. Hota, H. A. Patel, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Organomet. Chem.*, **32**, C55 (1971). (c) M₂(CO)₆(*t*-BuCC-*t*-Bu), M = Fe and Co: F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 1774 (1976). (d) Fe₂(CO)₆(azomethane): R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **8**, 2709 (1969). (e) Co₂(CO)₆(C₆F₆): N. A. Bailey and R. Mason, *J. Chem. Soc. A*, 1293 (1968). (f) A related M₂L₆ structure with L = phosphine is that of Rh₂(PF₃)₄(PPh₃)₂(PhCCPh): M. A. Bennett, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Inorg. Chem.*, **15**, 97 (1976).
- Related structures incorporating the isolobal MCP unit are the following: (a) Ni₂Cp₂(PhCCPh): O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968); (b) Pd₂(Ph₂Cp)₂(PhCCPh): E. Ban, P.-T. Cheng, T. Jack, S. C. Nyburg, and J. Powell, *J. Chem. Soc., Chem. Commun.*, 368 (1973); (c) Ni₂Cp₂(HCCH): Y. Wang and P. Coppens, *Inorg. Chem.*, **15**, 1123 (1976).
- (a) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961); (b) R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc., London*, 380 (1963); (c) Y. Degrève, J. Meunier-Piret, M. Van Meerssche, and P. Piret, *Acta Crystallogr.*, **23**, 119 (1967); (d) J. E. Jeffreys and C. M. Willis, *J. Chem. Soc., Dalton Trans.*, 2169 (1972); (e) M. J. Bennett, W. A. G. Graham, R. A. Smith, and R. P. Stewart, Jr., *J. Am. Chem. Soc.*, **95**, 1684 (1973); (f) H. B. Chin and R. Bau, *ibid.*, **95**, 5068 (1973); (g) P. E. Riley and R. E. Davis, *Acta Crystallogr., Sect. B*, **31**, 2928 (1975); (h) G. Dettlaf and E. Weiss, *J. Organomet. Chem.*, **108**, 213 (1976); (i) L. J. Todd, J. P. Hickey, J. R. Wilkinson, J. C. Huffman, and K. Folling, *ibid.*, **112**, 167 (1976); (j) P. J. Harris, J. A. K. Howard, S. A. R. Knox, R. P. Phillips, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 377 (1976); (k) M. G. Reisner, Dissertation, Technion, Haifa, Israel, 1975; (l) S. R. Prince, *Cryst. Struct. Commun.*, **5**, 451 (1976).
- For related structures see the following: (a) L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 7292 (1969); (b) E. F. Epstein and L. F. Dahl, *ibid.*, **92**, 493, 502 (1970); (c) J. L. Davidson, R. Herak, L. Manojlovic-Muir, K. W. Muir, and D. W. A. Sharp, *J. Chem. Soc., Chem. Commun.*, 865 (1973).
- (a) P. Piret, J. Meunier-Piret, M. Van Meerssche, and G. S. D. King, *Acta Crystallogr.*, **19**, 78 (1965); (b) J. Piron, P. Piret, J. Meunier-Piret, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, **78**, 121 (1969); (c) F. A. Cotton, D. L. Hunter, and J. M. Troup, *Inorg. Chem.*, **15**, 63 (1976); (d) R. S. Dickson, B. M. Gatehouse, and S. H. Johnson, *Acta Crystallogr., Sect. B*, **33**, 319 (1977).
- Many ligands can sit atop an M₂(CO)₆ fragment: (a) Azulenes: M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968); M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967); J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967); A. W. Schlüter and R. A. Jacobson, *Inorg. Chim. Acta*, **2**, 241 (1968). (b) Pentalene: A. Brookes, J. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 587 (1973). (c) Cyclooctatetraene: M. R. Churchill, F. J. Rotella, R. B. King, and M. N. Ackermann, *J. Organomet. Chem.*, **99**, C15 (1975). (d) Tetramethylenethane: J. A. S. Howell, J. Lewis, T. W. Matheson, and D. R. Russell, *ibid.*, **99**, C55 (1975). (e) Tropylum: J. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 59 (1975); A. Brookes, J. Howard, S. A. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 727 (1973). (f) Cyclic

- trienes, specifically cycloheptatriene: F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Am. Chem. Soc.*, **93**, 5069 (1971). Cyclooctatrienes: F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968); **91**, 843 (1969); F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973); J. Takats, *ibid.*, **90**, 211 (1975); F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, **97**, 5739 (1975). The $Ru_2(CO)_6$ (cyclooctatetraene) structure of F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968), is really in this category since one of the COT double bonds is not coordinated to the metal. (g) Dienes, primarily with M_2Cp_2 : K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971).
- (8) (a) A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, and V. S. Kaganovich, *J. Organomet. Chem.*, **47**, 1 (1973); (b) G. Deganello, P. Uguagliati, L. Calligaro, P. L. Sandrini, and F. Zingales, *Inorg. Chim. Acta*, **13**, 247 (1975).
- (9) For some other theoretical studies on $M_2(CO)_6$ (ligand) systems see the following: (a) D. A. Brown, *J. Inorg. Nucl. Chem.*, **11**, 9 (1959); D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960); (b) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975); (c) A. B. Anderson, *ibid.*, **15**, 2598 (1976).
- (10) (a) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); (b) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *ibid.*, **15**, 1148 (1976).
- (11) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).
- (12) (a) K. Wade, *Chem. Commun.*, 792 (1971); *Inorg. Nucl. Chem. Lett.*, **8**, 559, 563 (1972); *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) D. M. P. Mingos, *Nature (London)*, *Phys. Sci.*, **236**, 99 (1972); (c) J. Halpern, *Adv. Chem. Ser.*, No. **70**, 1 (1968); (d) A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 5633 (1969), and references therein.
- (13) W. Hübel in "Organic Synthesis via Metal Carbonyls", I. Wender and P. Pino, Ed., Wiley-Interscience, New York, N.Y., 1968, p. 273.
- (14) (a) D. H. W. DenBoer, P. D. DenBoer, and H. C. Longuet-Higgins, *Mol. Phys.*, **5**, 387 (1962); B. J. Nicholson and H. C. Longuet-Higgins, *ibid.*, **9**, 461 (1965); (b) R. F. W. Bader, *ibid.*, **3**, 137 (1960); *Can. J. Chem.*, **40**, 1164 (1962); (c) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); L. S. Bartell and R. M. Gavin, Jr., *J. Chem. Phys.*, **48**, 2466 (1968); (d) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); L. Salem and J. S. Wright, *J. Am. Chem. Soc.*, **91**, 5947 (1969); L. Salem, *Chem. Br.*, **5**, 449 (1969); (e) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252 (1969); R. G. Pearson, *ibid.*, **91**, 4947 (1969).
- (15) The actual symmetry in **14** is C_2 , but the pseudosymmetry of the orbitals is still near C_{2v} .
- (16) (a) M. A. Bennett, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, **15**, 107 (1976); (b) M. A. Bennett, R. N. Johnson, and T. W. Turney, *ibid.*, **15**, 111 (1976).
- (17) The case of three carbonyls, directed toward $Fe_2(CO)_9$, is discussed by J. W. Lauher, M. Elian, R. H. Summerville, and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976).
- (18) (a) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964); (b) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, **96**, 5285 (1974).
- (19) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); *Helv. Chim. Acta*, **47**, 1064 (1964); *J. Organomet. Chem.*, **7**, 151 (1967); G. Bor, *Spectrochim. Acta*, **19**, 2065 (1963); G. Bor, U. K. Dietler, and K. Noack, *J. Chem. Soc., Chem. Commun.*, 914 (1976); G. Bor and K. Noack, *J. Organomet. Chem.*, **64**, 367 (1974), and references therein; R. L. Sweany and T. L. Brown, *Inorg. Chem.*, **16**, 415 (1977).
- (20) $Co_2(PBu_3)_2(CO)_6$ takes on the D_{3d} structure: J. A. Ibers, *J. Organomet. Chem.*, **14**, 423 (1968); R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968). Other $Co_2(CO)_6P_2$ structures without bridging carbonyls are known: L. S. Chia and W. R. Cullen, *Inorg. Chem.*, **14**, 485 (1975); A. S. Foust, Ph.D. Dissertation, University of Wisconsin, 1970; J. A. M. Case, Ph.D. Dissertation, University of Wisconsin, 1967.
- (21) Such a geometry has been suggested as a transition state in the racemization of $Fe_2(CO)_6(C_{10}H_{16}O_2)$: R. Case, E. R. H. Jones, N. V. Schwarz, and M. C. Whiting, *Proc. Chem. Soc., London*, 256 (1962). See also M. Rosenblum, B. North, D. Wells, and W. P. Giering, *J. Am. Chem. Soc.*, **94**, 1239 (1972).
- (22) (a) See the structural data in ref 4 and 5 and the discussion on p 6 of ref 8a. (b) H. P. Weber and R. F. Bryan, *J. Chem. Soc. A*, 182 (1967).
- (23) J. W. Lauher, M. Elian, R. H. Summerville, and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976).
- (24) C. A. Coulson and A. Streitwieser, "Dictionary of π -Electron Calculations", W. H. Freeman, San Francisco, Calif., 1965; E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals", Springer-Verlag, West Berlin, 1966.
- (25) J. Meunier-Piret, P. Piret, and M. Van Meersehe, *Acta Crystallogr.*, **19**, 85 (1965).
- (26) S. Aime, L. Milone, and E. Sappa, *J. Chem. Soc., Dalton Trans.*, 838 (1976).
- (27) F. W. B. Einstein and J. Trotter, *J. Chem. Soc. A*, 824 (1967).
- (28) H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **95**, 7315 (1973); *Tetrahedron Lett.*, 1665, 3747 (1973); 4351 (1974).
- (29) P. Binger, *Tetrahedron Lett.*, 2675 (1966); T. P. Onak and G. T. F. Wong, *J. Am. Chem. Soc.*, **92**, 5226 (1970); V. R. Miller and R. N. Grimes, *Inorg. Chem.*, **11**, 862 (1972).
- (30) R. Hoffmann, D. L. Thorn, A. Devaquet, and A. Sevin, to be published.
- (31) (a) R. Bruce and P. M. Maitlis, *Can. J. Chem.*, **45**, 2017 (1967); (b) R. G. Amiet and R. Pettit, *J. Am. Chem. Soc.*, **90**, 1059 (1968); (c) P. E. Riley and R. E. Davis, private communication; (d) R. Pettit, private communication.
- (32) R. Bruce, K. Moseley, and P. M. Maitlis, *Can. J. Chem.*, **45**, 2011 (1967).
- (33) R. Victor and R. Ben-Shoshan, *J. Chem. Soc., Chem. Commun.*, 93 (1974).
- (34) R. E. Davis, B. L. Barnett, R. G. Amiet, W. Merk, J. S. McKennis, and R. Pettit, *J. Am. Chem. Soc.*, **96**, 7108 (1974). For another example of noninterconverting isomers see P. Hübener and E. Weiss, *J. Organomet. Chem.*, **129**, 105 (1977).
- (35) Many other ferrole structures result from acetylenic precursors, and cyclobutadiene complexes might seem likely intermediates. See W. Reppe and H. Vetter, *Justus Liebigs Ann. Chem.*, **582**, 133 (1953); I. Wender, R. A. Friedel, R. Markby, and H. W. Sternberg, *J. Am. Chem. Soc.*, **77**, 4946 (1955); R. Clarkson, E. R. H. Jones, P. C. Wailes, and M. C. Whiting, *ibid.*, **78**, 6206 (1956); W. Hübel, E. H. Braye, A. Claus, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); W. Hübel and E. H. Braye, *ibid.*, **10**, 250 (1959); G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959); R. B. King and A. Efraty, *ibid.*, **92**, 6071 (1970); **94**, 3021 (1972); R. B. King and I. Haiduc, *ibid.*, **94**, 4044 (1972). These are but a small sample of many relevant references. See also the reviews by P. M. Maitlis, *Adv. Organomet. Chem.*, **4**, 95 (1966), and F. L. Bowden and A. B. P. Lever, *Organomet. Chem. Rev., Sect. A*, **3**, 227 (1968).
- (36) K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971). The compound was prepared by E. O. Fischer and H. Schuster-Woldan, *Chem. Ber.*, **100**, 705 (1967).
- (37) (a) Ni_2Cp_2 (cyclopentadiene) has been reported by E. O. Fischer, P. Meyer, C. G. Kreiter, and J. Müller, *Chem. Ber.*, **105**, 3014 (1972). (b) A butadiene complex whose crystal structure has to our knowledge not been determined is $Co_2(CO)_6(C_4F_6)$: R. L. Hunt, D. M. Roundhill, and G. Wilkinson, *J. Chem. Soc. A*, 982 (1967).
- (38) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Organomet. Chem.*, **87**, C42 (1975).
- (39) The calculations on this problem were originally performed by R. H. Summerville in our group.
- (40) F. A. Cotton, personal communication; F. A. Cotton, P. Lahuerta, and B. R. Stults, *Inorg. Chem.*, **15**, 1866 (1976); F. A. Cotton and B. E. Hanson, *ibid.*, **15**, 2806 (1976).
- (41) The fulvalene complex has been made: J. C. Smart, University of California at Berkeley, personal communication.
- (42) R. B. King and M. N. Ackermann, *Inorg. Chem.*, **13**, 637 (1974).
- (43) S. A. R. Knox and F. G. A. Stone, *Acc. Chem. Res.*, **7**, 321 (1974).
- (44) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).
- (45) (a) A. Nakamura and N. Hagihari, *J. Organomet. Chem.*, **3**, 480 (1965); (b) R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 247 (1968); (c) S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc. A*, 2248 (1968); (d) R. A. Bauer, E. O. Fischer, and C. G. Kreiter, *J. Organomet. Chem.*, **24**, 737 (1970); (e) R. Victor and R. Ben-Shoshan, *ibid.*, **80**, C1 (1974); (f) R. B. King and C. A. Harmon, *ibid.*, **86**, 239 (1975); (g) D. F. Hunt and J. W. Russell, *ibid.*, **104**, 373 (1976); (h) for a rather different structure which may be an intermediate in the formation of one of these complexes see B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **33**, 175 (1977).
- (46) M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. LiShingMan, and J. Takats, *J. Am. Chem. Soc.*, **98**, 4810 (1976).
- (47) (a) G. Deganello, *J. Organomet. Chem.*, **59**, 329 (1973); (b) R. Goddard, A. P. Humphries, S. A. R. Knox, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 508 (1975); (c) J. Takats, *J. Organomet. Chem.*, **90**, 211 (1975); (d) G. Deganello and L. K. K. LiShingMan, *ibid.*, **132**, 265 (1977).
- (48) (a) Cotton, DeBoer, and Marks in ref 7f. (b) Cotton and Edwards in ref 7f.
- (49) The π orbitals of many polycyclic hydrocarbons are available in ref 24.
- (50) G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Porri, and G. Vitulli, *J. Am. Chem. Soc.*, **92**, 289 (1970).
- (51) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
- (52) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).
- (53) R. H. Summerville, personal communication.
- (54) (a) s, p exponents are from G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964); (b) d exponents are from J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
- (55) H. Basch and H. B. Gray, *Theor. Chim. Acta*, **4**, 367 (1966).
- (56) C. E. Moore, *Natl. Bur. Stand. (U.S.), Circ.*, **467**, 135 (1952).
- (57) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 179 (1974).