

Conformational Preferences and Rotational Barriers in Polyene-ML₃ Transition Metal Complexes

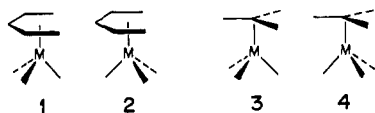
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Abstract: Conformational preferences, the magnitudes of rotational barriers, and their physical origin are analyzed for a series of cyclic and acyclic polyene-ML₃ transition metal complexes. The cases which are described in detail are the barriers in trimethylenemethane, benzene, and pentadienyl-M(CO)₃ compounds. The treatment is then extended to other polyene systems and comparisons are made with the available experimental information. The barriers in these molecules span a range from large (≥ 20 kcal/mol) in octahedral molecules and trimethylenemethane complexes, through intermediate values (5–15 kcal/mol) in butadiene, pentadienyl, and hexatriene-M(CO)₃, to tiny barriers in cyclopentadienyl and benzene complexes. The methodology used to analyze these barriers is based upon a reconstitution of the orbitals of the molecule from the valence orbitals of the polyene and ML₃ fragments. The symmetry of the fragment rotors plays a crucial role in setting the size of the barrier. However, the substantial threefold barrier component is set not so much by interligand repulsions as it is by intrinsic overlap differences between the fragment orbitals in the various conformations. The same controlling factor differentiates between octahedral and trigonal prismatic Cr(CO)₆. The more a polyene-M(CO)₃ complex resembles an octahedron the greater will be the barrier to internal rotation in that molecule. Using benzenechromium tricarbonyl as a model it is shown how perturbations within the π framework dictate the magnitude of the barrier and conformational preferences. Substantial barriers may be expected when the substitution pattern reinforces local octahedral symmetry. Variations within the ML₃ framework by changing the ligand from a π acceptor to a π donor and altering the L-M-L angle are also described.

A delineation of the magnitudes and physical basis of rotational barriers in organic molecules has been of some concern to chemists since the beginnings of modern structural chemistry. It is a subject which has been shared by theoreticians and experimentalists alike.¹ There is a growing body of experimental data, gathered mainly by NMR methods, on rotational barriers of organometallic compounds,² as well as on conformational preferences as obtained by diffraction methods. Although there are many studies of the bonding and reactivity in polyene organometallic complexes³ in general, relatively few have probed the barrier problem.⁴

The present work is directed at obtaining an understanding of the barriers to internal rotation in cyclic and acyclic polyenes bonded to an ML₃ transition metal fragment. Typical of the questions that we are interested in is what factors are important in determining the preference of **1** over **2** in pentadienyl, or **3** over **4** in trimethylenemethane complexes. The x-ray results

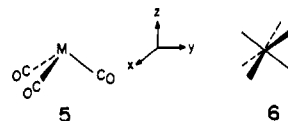


for compounds analogous to these have indeed shown that **1** and **3** are the most stable conformers^{5,6} and NMR measurements have indicated appreciable barriers for each system.^{3a,7,8} On the other hand, the barrier of rotation in benzenechromium tricarbonyl has been shown to be very small.⁹ The range of internal rotation barriers in organometallic compounds containing the threefold ML₃ rotor appears to be larger than in organic compounds.

A natural development of a unified theory of these conformational preferences is through a fragment molecular orbital approach. We shall begin our discussion by constructing the important valence orbitals of the ML₃ fragment and then interact these orbitals with those of a polyene in several possible conformations. Changes in the magnitude of the barriers will be examined in light of perturbations within the polyene or ML₃ fragments. The effect of geometrical relaxation upon rotation will also be briefly explored. Finally two ML₃ fragments are interacted with each other and the resultant barriers of rotation in these ethanelike molecules will be examined as

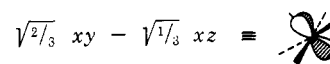
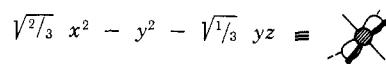
a function of the number of d electrons within the system. Our computations are of the extended Hückel type with details given in the Appendix.

The ML₃ Fragment. A detailed derivation of the molecular orbitals for a ML₃ fragment has been given elsewhere.¹⁰ We shall briefly note the salient features of the analysis. Consider an M(CO)₃ fragment in C_{3v} geometry, with C-M-C angles of 90°. Using the coordinate system given in **5** there is a set of

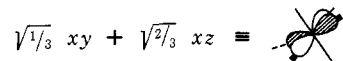
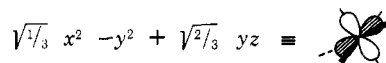


three low-lying orbitals, $a_1 + e$, comprised mainly of $z^2(1a_1)$, xy , and $x^2 - y^2(1e)$.¹¹ The π^* orbitals on the carbonyls interact in phase with these three. At somewhat higher energy there is an e set of largely xz and yz character ($2e$) which are antibonding to the σ levels of the ligands. Finally at still higher energy is a sp hybrid orbital ($2a_1$).

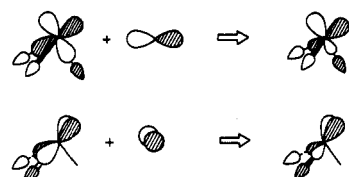
An important point is that there is mixing between xy and xz and between $x^2 - y^2$ and yz in the e sets. The $1a_1 + 1e$ and $2e$ levels are related in a transparent manner to the t_{2g} and e_g sets, respectively, of a normal octahedron. This is perhaps the best way to view the important intermixing between the $1e$ and $2e$ levels. Consider an octahedron lying on one of its threefold axes, as in **6**. The t_{2g} set is given by z^2 and



The e_g set is then

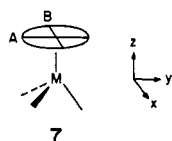


This has been known for some time;¹² the intermixing between the e sets, in other words, the tilting of the $x^2 - y^2$, xy , xz , and yz orbitals from their axes, follows from this transformation. Removing the top three ligands of the octahedron to obtain $M(\text{CO})_3$ causes only a relatively minor perturbation. The splitting between the $1a_1 + 1e$ and $2e$ sets is decreased since the bonding with π^* and the antibonding with the σ orbitals on CO is decreased. Furthermore, there is some mixing of the metal p character in the $2e$ set because of the reduced C_{3v} symmetry of $M(\text{CO})_3$. This lowers the σ antibonding still further, as shown below.



A side view in the yz plane of these levels is given in Figure 1. This figure clearly shows the tilting of the orbitals in the e sets, which is of vital importance to our discussion. Each orbital drawing contains in addition to the actual contours a little schematic representation which will be used in the subsequent discussion.

The reason the tilting in the e orbitals is important is that it provides an asymmetry to the ML_3 orbitals. Consider an ML_3 fragment with a mirror plane defined as in 7. The $1e$ and



$2e$ orbitals are not symmetric (or antisymmetric) with respect to the xz plane. This can be seen graphically by an examination in Figure 2 of a slice of the wave functions in the xy plane, 1 Å away from the metal. This is the approximate region of maximum bonding with an attached ligand. A cyclic or acyclic polyene generally has at least a single mirror plane A which can align itself with the yz mirror plane of the ML_3 fragment. The polyene may or may not possess another vertical mirror plane, B. If it does not carry that second mirror plane of symmetry, then a significant rotational barrier may result from a matching of the asymmetries of the ML_3 and polyene fragment orbitals. We shall now turn our attention to a detailed analysis of this problem.

Cyclic Polyene and Trimethylenemethane Complexes. The barrier of rotation in substituted trimethylenemethaneiron tricarbonyl complexes has been measured as 19–20 kcal/mol.^{8,13} Consider the interaction diagram given in Figure 3 for a planar trimethylenemethane (TMM) ligand where the geometry is that given by 3 (staggered). Figure 3 shows that the primary bonding interaction in the complex is that between $2e$ set on the $\text{Fe}(\text{CO})_3$ fragment and e'' on TMM. However, upon rotation about the iron–TMM axis by 60° into 4 (eclipsed) the interaction of these orbitals is decreased because the overlap between them decreases. This is shown below.

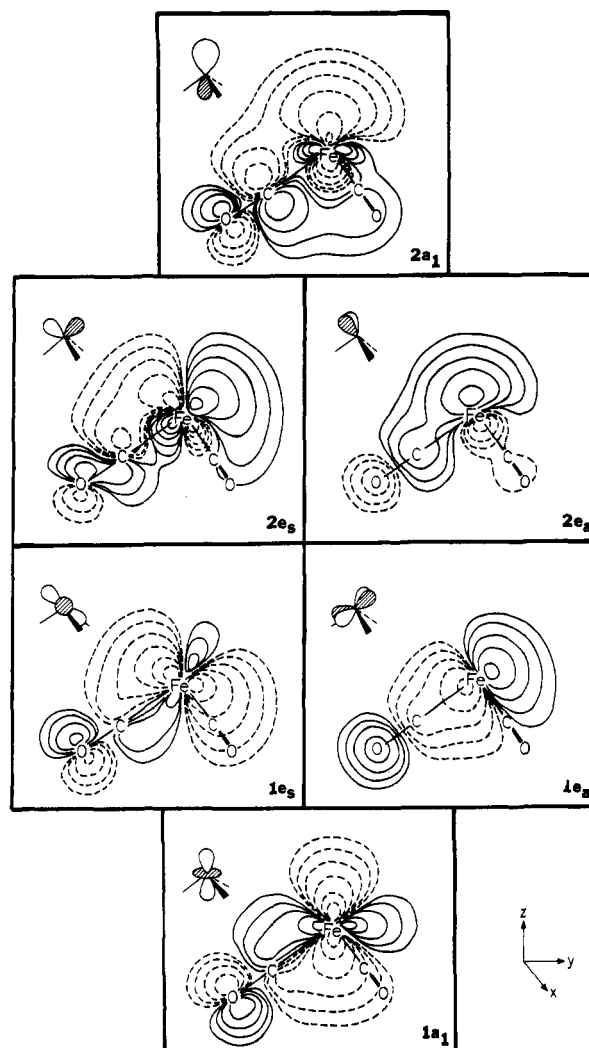
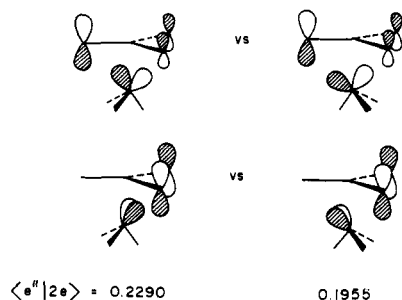


Figure 1. A plot of the valence orbitals in an $M(\text{CO})_3$ fragment in the yz plane. The values of the contours and computational details are given in the Appendix. The orbitals which possess a node in the yz plane were plotted in this plane 0.5 \AA in the x direction.

Therefore the energy of the HOMO in the molecule increases in the eclipsed form and this is the main, but, as we discuss next, not the only factor behind the barrier.

In the staggered geometry the overlap between the $1e$ set and e'' is almost zero (0.0116) since that portion of $1e$ pointing up toward TMM lies in the nodal region of e'' . However, upon rotation to the eclipsed geometry the overlap increases by an order of magnitude (0.1193). The interaction between $1e$ and e'' is a four-electron repulsive one—the greater the interaction, the less stable the structure. This is then another factor contributing to the overall preference for the staggered conformation.

Our extended Hückel calculations give a barrier of 20.8 kcal/mol using a planar TMM ligand and carbonyl–iron–carbonyl angles of 90° . Considering only the changes in the upper two filled e sets in Figure 3, the staggered geometry is more stable than the eclipsed by 33.2 kcal/mol. By completely deleting the interactions between $1e$ with TMM orbitals or from perturbation theoretical considerations, we estimate that approximately two-thirds of this difference is due to loss of overlap between $2e$ and e'' and one-third from the repulsions of $1e$. To reiterate, the rotational barrier in $\text{TMM-Fe}(\text{CO})_3$ is largely due to loss of overlap between the fragment orbitals which constitute the major source of bonding in the molecule and increased repulsions of the $1e$ levels. In a sense the repulsive portion can be regarded as originating from lone pairs on the

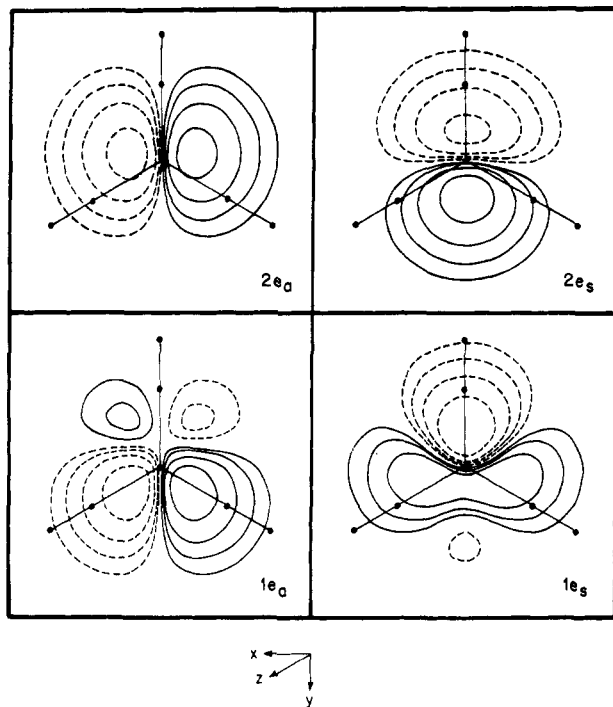
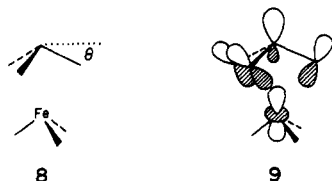


Figure 2. A plot of the 1e and 2e sets of an $M(\text{CO})_3$ fragment in the xy plane, 1.0 Å away from the metal in the z direction.

metal; minimizing their interactions with the rest of the molecule leads to the most stable conformation.

Structural studies on various TMM- $\text{Fe}(\text{CO})_3$ complexes have indicated that the TMM ligand is not planar.^{6,14} It is puckered in a manner which brings the terminal carbons somewhat closer to the iron and the central carbon away from it, as in **8**. Normally θ is in the range of 12° . There are two



reasons for this puckering motion. Firstly, as can be seen from Figure 3, there is a repulsive interaction between a_2'' on TMM and $1a_1$ (this is moderated somewhat by the intervention of $2a_1$). Increasing θ reorients a_2'' so that the methylene orbitals lie in the nodal region of z^2 . It also mixes s character into the central carbon of a_2'' from a higher, unoccupied orbital. This mixing occurs as shown in **9** in such a manner as to hybridize that π component on the central carbon away from the iron. The situation is completely analogous to that occurring in the pyramidal inversion of an AH_3 molecule.¹⁵ This factor does not alter the magnitude of the rotational barrier since the orbital is centrosymmetric.

The second factor which plays an important role in increasing θ is the mixing between e'' and e' on TMM. This mixing was not allowed by symmetry in the D_{3h} geometry but occurs in the nonplanar ligand. A detailed analysis shows that e' mixes into e'' so that the orbitals are not only directed more toward the corners of an octahedron and consequently overlap in the staggered conformation more effectively with the $2e$ set on $\text{Fe}(\text{CO})_3$, but they are also hybridized toward the iron. Bending the terminal hydrogens away from the iron also enhances this hybridization. In a sense the orbitals of TMM tilt to match the tilting in the e sets of $\text{Fe}(\text{CO})_3$. Therefore as θ increases, the mismatch of overlap between e'' and $2e$ and increasing repulsions from $1e$ in the eclipsed geometry create a

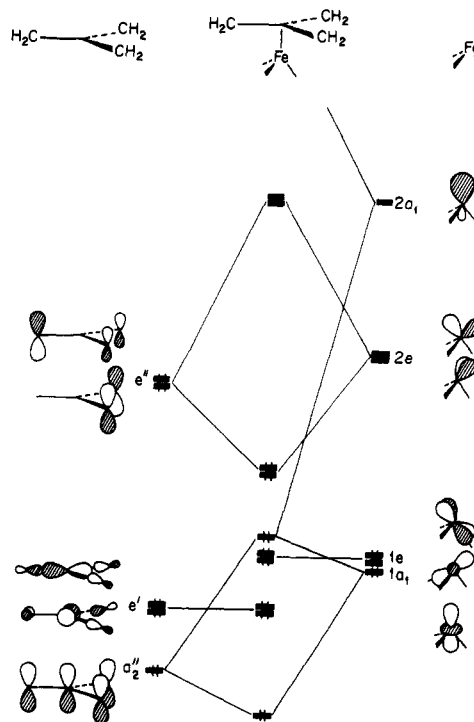
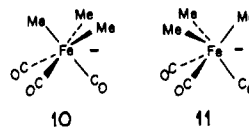


Figure 3. The orbital interaction diagram for a planar trimethylenemethane and iron tricarbonyl in the staggered geometry, **3**.

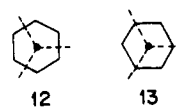
larger barrier. At the experimental geometry for TMM- $\text{Fe}(\text{CO})_3$,^{6a} ($\theta = 12^\circ$), we calculate a barrier of 23.6 kcal/mol.

An obvious extension of this analysis is to trimethyliron tricarbonyl anion in an octahedral, **10**, and trigonal prismatic, **11**, geometry.¹⁶ The lone pair orbitals of methyl groups form



an e and a_1 set. The energy and nodal properties are similar to those in trimethylenemethane. The only significant difference is that at the octahedral geometry with all C-Fe-C angles equal to 90° the overlap between the methyl e level and $2e$ is maximized. Likewise the repulsive interaction with $1e$ is maximized in **11**. Therefore, the barrier which we calculate (49.8 kcal/mol) is larger than that in TMM- $\text{Fe}(\text{CO})_3$. Nevertheless this analysis shows that the barrier in both types of compounds has a common origin. A discussion of the effect of varying the carbonyl-Fe-carbonyl angles and replacement of other ligands on iron on the barrier in TMM- FeL_3 will be postponed to a later section.

Benzenechromium tricarbonyl and its derivatives have been shown by electron diffraction⁹ and NMR¹⁷ methods to possess a very small rotational barrier. Our EHT calculations predict the staggered geometry, **12**, to be more stable than the eclipsed, **13**, in accord with x-ray¹⁸ and neutron diffraction¹⁹ results.



However, this difference is only 0.3 kcal/mol. There are also two $\eta^6\text{-C}_6\text{H}_6\text{RuL}_3$ complexes which have the eclipsed structure^{20a} and one which has the staggered,^{20b} again implying a low barrier.

The interaction diagram for the benzene and chromium

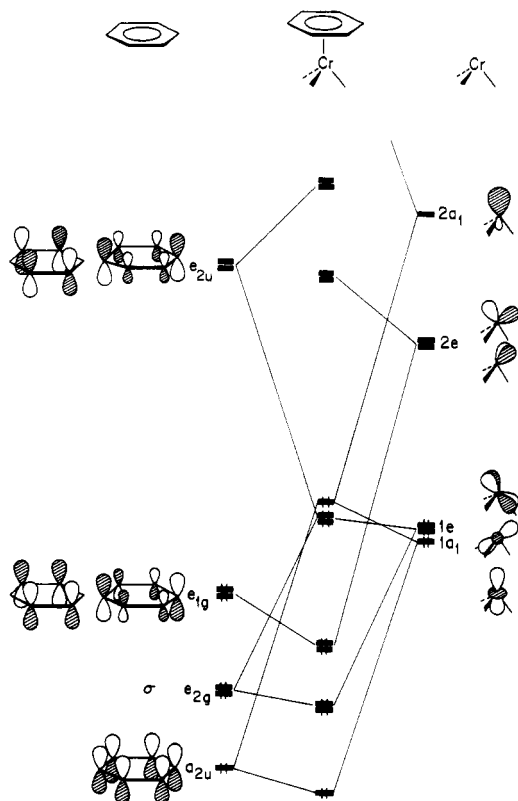
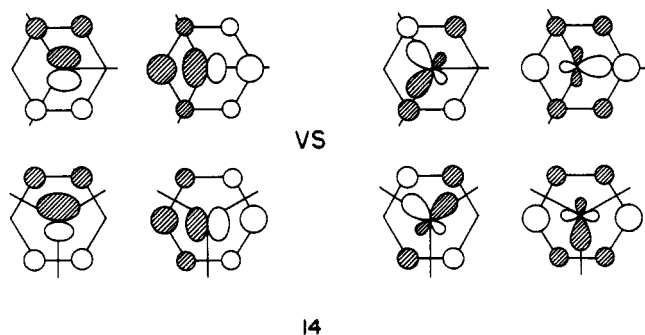


Figure 4. Interaction diagram for benzenechromium tricarbonyl.

tricarbonyl fragments in Figure 4 shows that the major interaction occurs between the $1e$, e_{2u} and $2e$, e_{1g} fragment orbitals. There is no difference in the overlap between the fragments, as may be seen from a view of these orbitals along the z axis shown below.



The π and π^* orbitals have mirror planes along the yz and xz axes; although the e sets of $\text{Cr}(\text{CO})_3$ are not left-right or top-bottom symmetric, their overlap with π and π^* must necessarily be the same in both conformations. Another factor which we may see from this fragment analysis is that because of the δ symmetry of e_{2u} , a small mixing between $1e$ and $2e$ occurs. It does so in a manner to build more $x^2 - y^2$ and xy into the $1e$, e_{2u} bonding combination. Likewise, more xz and yz character is mixed into the level derived from e_{1g} and $2e$. Therefore, the hybridization which went into making the ML_3 orbitals point toward the corners and edges of an octahedron is undone by the δ symmetry inherent in the e_{2u} orbitals of benzene. On symmetry grounds alone a sixfold barrier such as is present in this system would not be expected to be large.

There is a long-standing controversy about whether the C-C bonds are fixed into double and single bonds in benzenechromium tricarbonyl and related compounds.^{18,21} The most accurate structural study to date¹⁹ has shown that the C-C bonds

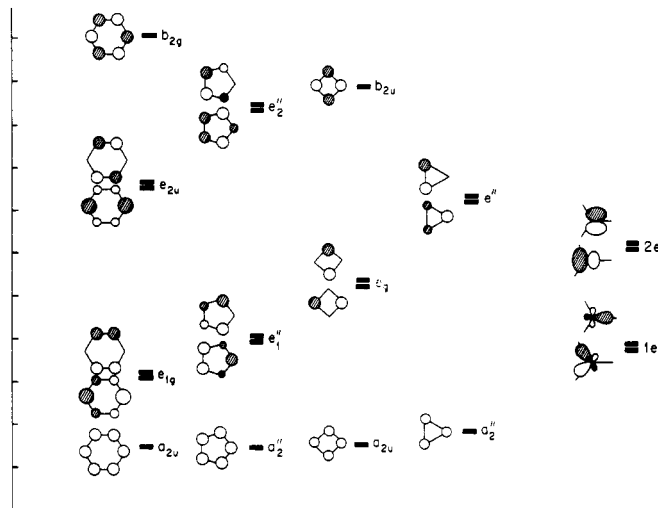
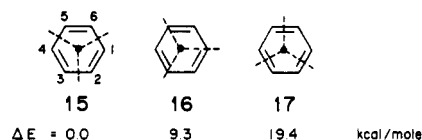


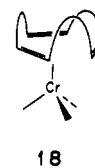
Figure 5. The energies and nodal properties of C_nH_n molecules relative to an $\text{M}(\text{CO})_3$ fragment. The units of the energy scale on the left are in electron volts.

eclipsing the chromium-carbonyl bonds are 0.018 (2) Å longer than those in the other set. Our extended Hückel results also indicate this trend in the overlap populations.

If the bonds in the benzene fragment were completely localized, then this could have a significant effect on the barrier of rotation. We can simulate localization of the π and π^* orbitals by deleting all z overlaps except those between carbons 1 and 2, 3 and 4, and 5 and 6. The relative energies for the three possible conformations now become quite large:

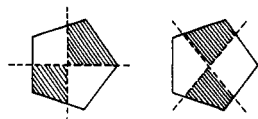


Large barriers, such as those implied by **16** or **17**, are inconsistent with what is known experimentally about the system. This is no surprise, since the double bonds are not much localized. However, a corollary of this discussion is that non-conjugated triene complexes such as **18** would be expected to possess a large barrier to rotation.

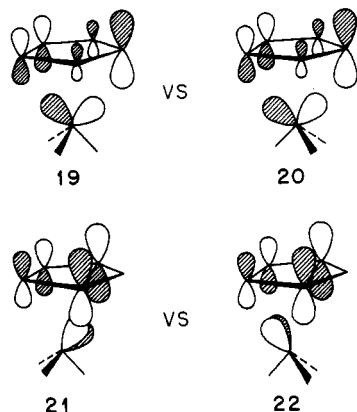


The other cyclic polyenes are essentially straightforward adaptations of our two previous case histories: trimethylenemethane- and benzene- ML_3 complexes. Figure 5 shows a graph of the energy of C_nH_n orbitals along with their nodal properties. The energy of the $\text{M}(\text{CO})_3$ orbitals, of course, varies somewhat (less than ± 1 eV) depending upon M. It is clear that cyclobutadiene (as well as η^8 -cyclooctatetraene) ML_3 complexes should have very low rotational barriers since there are two mirror planes in the polyene. Our calculation gives a barrier of 0.002 kcal/mol. Electron diffraction²² and microwave studies²³ have indicated that there is essentially free rotation around the polyene-iron bond in cyclobutadieneiron tricarbonyl. X-ray studies on various analogues have likewise shown a mixture of the two possible conformers.²⁴

The cyclopentadienyl fragment does not possess two perpendicular mirror planes; however, the e_2'' set has δ symmetry. Again the $1e$ and $2e$ levels will intermix, building more $x^2 - y^2$ into the $e_2'' + 1e$ interaction. The overlaps between the

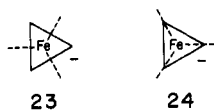


fragment orbitals in the two possible conformations, shown below, are not precisely identical for each component, as may be seen in **19**–**22**. For example, in **21** the overlap between $2e$ and e_1'' is 0.2812 while that in **22** is 0.2793. However, this

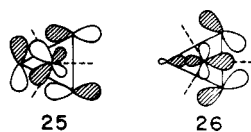


differential is precisely compensated by a larger overlap in **20** vs. that in **19**. The same relationship occurs in the e_2'' , $1e$ combination. Accordingly, we calculate a very small barrier of rotation for this complex, 0.002 kcal/mol. The available structures²⁵ show that the conformation in the solid is likely to be dictated by crystal packing forces; for example, cyclopentadienylmanganese tricarbonyl^{25a} has the conformation given by **20** while that of cyclopentadienyliron tricarbonyl cation^{25b} is given by **21**. We would also expect a very small rotational barrier in the η^7 -cycloheptatrienyl ML_3 complexes for the same reasons as given above.

In contrast, cyclopropenyliron tricarbonyl anion does not possess two perpendicular mirror planes nor δ orbitals in the π ligand, and thus a larger barrier is expected. A comparison of the nodal properties of e'' in cyclopropenyl (Figure 5) and e'' trimethylenemethane (Figure 3) shows the transparent relationship between the two complexes. The e'' set of cyclopropenyl will maximize its interaction with $2e$ in the staggered conformation, **23**, and maximize its repulsions with $1e$ in the eclipsed geometry, **24**. An x-ray structure of a related nickel complex has indicated that **23** is the preferred conformation;²⁶ however, there has been no experimental work on this barrier. For a planar cyclopropenyl ligand we calculate that **23** is more stable than **24** by 6.7 kcal/mol.



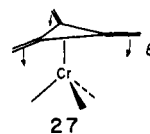
Cyclopropenyl and trimethylenemethane are both threefold rotors. Yet the computed barriers in their $Fe(CO)_3$ complexes are quite different. The reason that the calculated barrier is smaller in cyclopropenyl than that in TMM- $Fe(CO)_3$ lies in the fact that in **23** the overlap between the high-lying Walsh orbitals on cyclopropane²⁷ and $1e$ are maximized. Since both levels are filled, this constitutes a repulsive interaction which stabilizes **24** over **23**. Upon tilting the hydrogens on the cy-



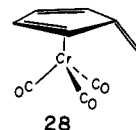
clopropenyl ring away from the iron, the barrier rises somewhat. This is due to the same rehybridization arguments as

given previously for TMM- $Fe(CO)_3$ (see also ref 10b). The optimized tilting angle for **23** and **24** was calculated to be approximately 20° (22° for **23** and 19° for **24**) which is in reasonable agreement with structural evidence for related molecules.^{26,28} At this geometry the barrier is calculated to be 8.5 kcal/mol.

One can think of other parallels to the cyclopropenyl and trimethylenemethane systems. For example, in the hypothetical trimethylenecyclopropanechromium tricarbonyl (**27**),

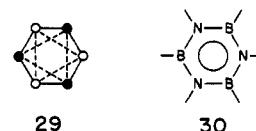


there are e sets completely analogous to those in the aforementioned cases. We find that the methylene groups bend down toward the chromium in the staggered geometry (**27**). However, they tend to remain planar in the eclipsed form. At a Cr-ring distance of 2.03 Å, θ optimizes to 14° . The total barrier was calculated to be 13.1 kcal/mol. Another similar complex that is expected to have a substantial rotational barrier is **28**.²⁹ In the 6,6-dimethyl derivative the carbonyl interchange



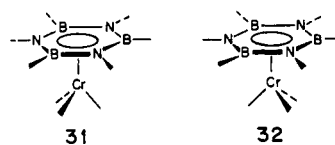
is frozen out at 183 K,^{29b} which probably corresponds to a barrier of 8–9 kcal/mol.

Perturbed Benzene Complexes. Another way to view the low barrier in benzenechromium tricarbonyl is obtained by noting that the molecule contains two interpenetrating trios, as shown schematically in **29**. Coupled with the three carbonyl groups



each trio fixes an octahedral coordination set. This is why there are relatively large rotational barriers in cyclopropenyl or trimethylenemethane complexes. When the trios are superimposed, as in the case of a sixfold symmetrical benzene, the threefold barrier is lost.

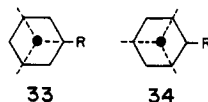
One can decouple the trios in benzene by changing the electronegativity of the atoms constituting one set relative to the other. An example is provided by borazine (**30**). The π levels will be markedly localized on nitrogen and the π^* on boron since nitrogen is more electronegative than boron.³⁰ Several borazine metal tricarbonyl complexes have been prepared by the Werner group³¹ and the x-ray results on the hexaethyl derivative³² show the conformation given by **31**. For the parent compound, borazinechromium tricarbonyl (with the borazine ring planar), we compute **31** to be more stable



than **32** by 18.3 kcal/mol. This represents a lower limit since there are slight puckering movements within the ring so that the Cr-N distance is slightly shorter than the Cr-B distance.³²

A more subtle manner to decouple the trios is by putting a substituent on the benzene ring. There exist structural studies on a fairly extensive series of substituted benzenechromium tricarbonyls. While the parent compound favors the staggered

conformation,¹⁸ **12**, substitution of electron-donating groups indicates that the syn-eclipsed structure **33** is favored over the anti-eclipsed, **34**, and staggered structures.^{33a-f} The reverse



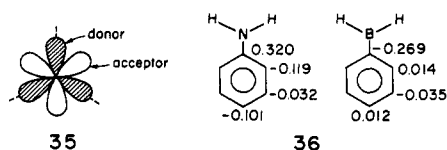
holds true for electron-withdrawing groups.^{33f-j} Finally, the $\text{Cr}(\text{CO})_3$ orients itself somewhere between these two geometries when the substituent pattern does not allow in a single structure complete satisfaction of the orientational preferences of each ligand taken individually (e.g., ortho or para electron donors).^{33k-n} This conformational preference cannot be a strong one judging from the available NMR evidence¹⁷ and the fact that substitution of bulky groups on the arene ring sometimes dominates the orientation.³⁴ There are also two cases where the pattern provided by **33** and **34** does not occur;³³ⁿ for example, the acetophenone complex adopts the staggered conformation.³⁵ Nevertheless, we feel that there is a decided electronic rationale, albeit a small one, for this pattern.

As models for π donation and π acceptance we have chosen aniline and phenylborane. To simplify our arguments still further we shall concentrate only on the HOMO and LUMO π levels of the arene fragment. The mixing of orbitals in a phenyl fragment upon interaction with a substituent is not only a first-order perturbation phenomenon, but there is considerable polarization by second-order mixing between the π levels. The second-order perturbation expression for this process has been discussed in some detail previously.³⁶ The important points are indicated in Figure 6. In the HOMO of aniline the mixing of π^*_s into π_s (recall that the antisymmetric recombinations are left unaffected by this perturbation) is given by the matrix element

$$\frac{\langle \pi^* | p \rangle \langle p | \pi \rangle}{(E_{\pi^0} - E_{\pi^*0})(E_{\pi^0} - E_p^0)}$$

If we choose our overlaps as being positive (as is the case in Figure 6), then the numerator is positive. Given that the relative energies for a normal π donor are $p < \pi_s < \pi^*_s$, then the denominator is negative and π^*_s mixes into π_s with the negative of the phase defined on the left of the interaction diagram in Figure 6. Similarly, π_s mixes into π^*_s in the reverse manner. The net effect of this perturbation is that the atomic coefficient at the para position is enhanced in the π_s level and decreased in π^*_s . The reverse situation occurs at the ipso carbon. The tilting of the e_s orbitals in chromium tricarbonyl, sketched on the right side of Figure 6, shows that the maximum overlap of $1e_s$ with π^*_s and $2e_s$ with π_s is achieved in conformation **33**. The same argument can be applied to phenylborane; it is readily apparent from Figure 6 that the most favorable conformation is now **34**. An analogous argument can be presented for the HOMO and LUMO interactions if the energy of the perturbing orbital lies between that of π_s and π^*_s .

Another way of indicating the conformational preferences of arenechromium tricarbonyls is by recalling that chromium tricarbonyl has three electron donor functions and three acceptor orbitals oriented 60° apart as shown in **35**. The charges



on the phenyl carbons in aniline and phenylborane, indicated in **36**, show the standard features. Allowing the acceptor functions to orient themselves toward regions of high negative

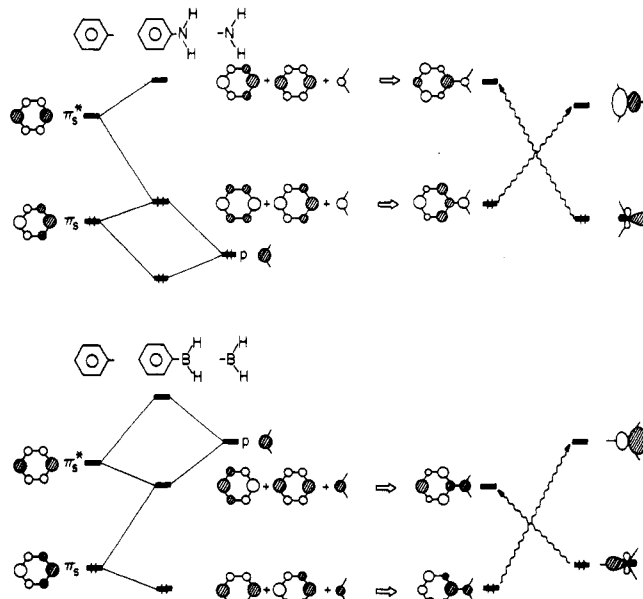
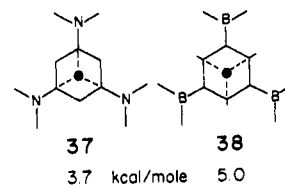


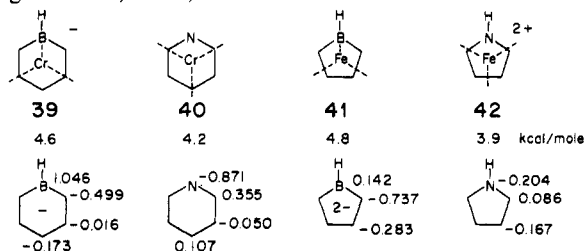
Figure 6. Interaction diagram for the model π donors and acceptors with a phenyl fragment. The resultant first- and second-order components are sketched in the center of the diagram and in turn the resultant π orbitals are interacted with the $\text{Cr}(\text{CO})_3$ fragment on the right.

density and donor functions to regions of low negative charge will lead to the preferred conformations.³⁷

It should be emphasized that the energy differences between **33** and **34** are likely to be quite small. The EHT calculations predict that the syn-eclipsed conformation, **33**, for anilinchromium tricarbonyl to be more stable than **34** by 1.3 kcal/mol. The phenylborane complex prefers **34** by 1.7 kcal/mol. Obviously, putting three substituents around the benzene nucleus in the pattern given by **29** will enhance this preference. The most stable conformations for **37** and **38** are shown below along with their calculated barriers of rotation.



The same treatment of conformational preferences can be applied to cyclic systems where the carbon atoms of the cyclic rings are substituted by different atoms. We shall consider borabenzene and pyridinechromium tricarbonyl along with borazole- and pyrroleiron tricarbonyl as model systems. Since the perturbation encountered in the π levels for these ligands has been treated in several standard texts³⁸ we shall not discuss it here. The levels corresponding to a_{2u} and b_{2g} of benzene must also be taken into consideration in these cases. The most expedient method to analyze the preferences is by matching regions of high and low electron densities with the donor and acceptor functions of $\text{Cr}(\text{CO})_3$ that were shown in **35**. The barriers for the model systems are given below (the most stable conformation is the one indicated) along with the calculated charges from the isolated fragments. The structures of analogues of **39**,^{39a} **40**,^{39b} and **42**^{39c-e} show the conformations



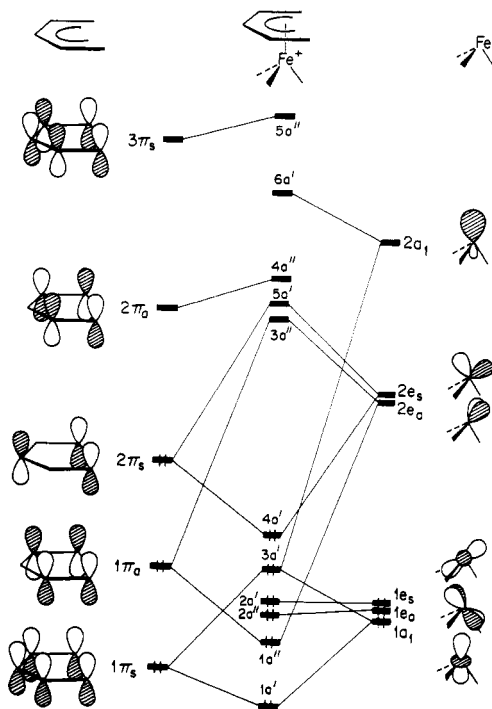
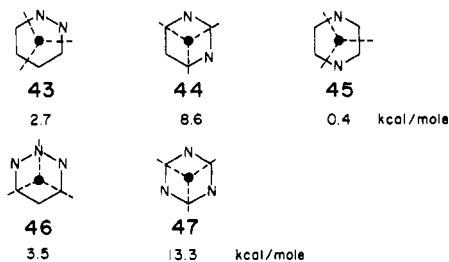


Figure 7. Interaction of the pentadienyl fragment with iron tricarbonyl in the conformation given by **37**.

which we calculate to be most stable; however, there has been no experimental work on the magnitude of these barriers.

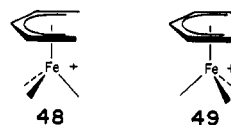
Another point of interest that we have investigated is what influence substituent patterns will have on these barriers. The most effective method to decouple the trios in **29** is by perturbing only the open or closed circles, but not both. Our calculations support this idea for the series of diazines and triazines, **43**–**47**. The preferred conformations along with the



associated barriers are given above. In **40**, **44**, and **47** the barrier increases in almost constant increments. In **43** the perturbation on one e set is canceled by that on the other so the barrier decreases in comparison to **40**. Finally there are two perpendicular mirror planes in the 1,4-diazine ligand of **45** and, therefore, only a very small barrier is predicted.

It was noted that a symmetry argument alone is sufficient to justify the small benzene–Cr(CO)₃ barrier. When the symmetry is reduced so that a threefold barrier remains, the impressive feature that our calculation reveals is how large the variation in that threefold barrier can become by perturbation of the π system.

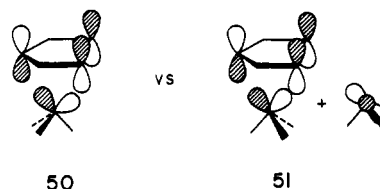
Acyclic Polyene Complexes. We shall again focus our attention on the interactions characteristic of one typical acyclic polyene complex, pentadienyliron tricarbonyl cation, before discussing the others in general. Let us assume an iron tricarbonyl fragment within the pseudo-octahedral geometry (C–Fe–C = 90°) and a planar pentadienyl unit. Of the two possible geometries, **48** has been shown by x-ray studies to be the preferred conformation.⁵ The same is true for the related cyclo-



hexadienyl complexes.⁴⁰ The barriers for these systems have been determined to lie in the range of 9–14 kcal/mol.^{7,41}

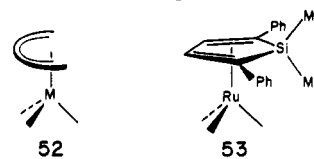
The orbital interaction diagram given for **48** in Figure 7 is similar to that for the cyclic polyene cases. The major interaction is of $2e_s$ with $2\pi_s$ and $2e_a$ with $1\pi_a$. Although there is only C_s symmetry in the complex, $1e_a$ interacts mostly with $2\pi_a$ and $1e_s$ with $3\pi_s$ because of the δ symmetry in the two polyene orbitals. However, the latter two interactions are really only of minor importance since $3\pi_s$ and $2\pi_a$ lie quite high in energy and, therefore, do not interact strongly with the $1e$ set.

Rigid rotation from **48** to **49** requires 10.9 kcal/mol. Most of this energy difference comes from the HOMO, $4a'$. In going from **50** to **51** the overlap between $2e_s$ and $2\pi_s$ decreases; likewise the interaction between $1e_s$ and $2\pi_s$ increases, stabilizing $2a'$ and further destabilizing $4a'$ as shown below.



The structures of pentadienyl ML₃ complexes indicate that the projection of the metal atom onto the plane of the polyene is not greatly altered from that in the corresponding cyclopentadienyl complexes. Therefore, there will be little or no difference in the energies of the a'' orbitals upon rotation. One could also express this conformational preference in terms of the perturbation in the π levels of the polyene in going from cyclopentadienyl to pentadienyl.⁴² Upon deleting the interaction of $1e_s$ with the pentadienyl fragment, we find that the energy rise in the $4a'$ level is due to approximately 30% from loss of overlap between $2e_s$ and $2\pi_s$ and 70% from increased repulsions of $1e_s$.

Hexatriene,⁴³ butadiene,^{44,22a} and allyl⁴⁵ complexes all adopt the conformation given by **52**, even when this is sterically difficult as in **53**.⁴⁶ When we explore the determinative factors



in the rotational barriers of these and other acyclic polyene complexes we find a picture very similar to that given above for pentadienyl. In Figure 8 the π levels of the polyenes are shown along with a top view of the e sets in an M(CO)₃ fragment. The first item to be noted is that ethylene possesses two perpendicular mirror planes and, as we have shown in the previous section, should have only a tiny barrier of 0.02 kcal/mol.⁴⁷ However, the rest of the molecules in Figure 8 do not have this feature. As the size of the polyene ribbon decreases, the energy of the $2\pi_s$ orbital increases, becoming progressively more decoupled from the $2e_s$ and $1e_s$ levels. Therefore, to a first approximation, the barrier in a hexatrienyl or pentadienyl complex should be larger than that found in an allyl complex. Our calculations and the available experimental data^{7,48–50} in Table I are in accord with this pattern. In the bicyclo[4.4.1]-undecatriene–Cr(CO)₃ series^{51,52} the Cr(CO)₃ unit is oriented in a manner opposite to all of the other hexatriene structures.⁴³ There appear to be electronic factors which favor this conformation, which will be discussed elsewhere.

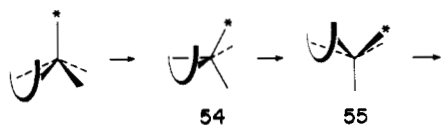
The reader must bear two caveats in mind when considering

Table I. Group Overlaps and Barriers For Acyclic Polyene Complexes

Compound		Group overlaps ^a		Barrier, kcal/mol		
		$\langle 2e_s 2\pi_s \rangle$	$\langle 1e_s 2\pi_s \rangle$	Calcd	Exptl	Ref
C ₆ H ₃ Cr(CO) ₃	Stag	0.2458	0.0029	10.4	11.3–11.9	<i>b</i>
	Eclip	0.2267	0.0961			
C ₅ H ₇ Fe(CO) ₃ ⁺	Stag	0.2153	0.0028	10.9	13.0–13.5	<i>c</i>
	Eclip	0.1867	0.1074			
C ₄ H ₆ Fe(CO) ₃	Stag	0.1863	0.0389	7.2	9.5	<i>d</i>
	Eclip	0.1378	0.1251			
C ₃ H ₅ Co(CO) ₃	Stag	0.1480	0.0247	2.9	≤5	<i>e</i>
	Eclip	0.1080	0.1034			
TMMFe(CO) ₃	Stag	0.2560	0.0092	20.8	19–20	<i>f</i>
	Eclip	0.2187	0.1333			
Me ₃ Fe(CO) ₃ ⁻	Stag	0.3097	0.0230	49.8		
	Eclip	0.2603	0.1632			

^a The designation of the orbitals is the same as given in Figure 8. The overlaps are for a planar polyene. ^b Reference 48b. ^c C. P. Lillya, personal communication. ^d Reference 49a. ^e Reference 50a. ^f Reference 8.

the results in Table I. Firstly, the barriers correspond to rotation of the polyene relative to a fixed M(CO)₃ group. We did not look for a Berry pseudorotation pathway, which can, in principle, make the carbonyls magnetically equivalent. However, an examination of the pseudorotation itinerary shows that it must always pass through a point given by the eclipsed structure, **55**. Therefore, one will not be able to distinguish



between the rotational and pseudorotational pathways by NMR measurements. The pseudorotation path has also been criticized because in **54** the ends of the polyene must span the axial and equatorial positions. The small “bite size” of an allyl and butadiene group, in particular, has been cited as evidence that this pathway can be excluded.^{49a} A careful analysis of pseudorotational itineraries for ligand site interchange in butadiene and pentadienyl complexes has been carried out by Lillya,^{7b} and by Cole-Hamilton and Wilkinson.^{49j}

The second point to consider is that while the carbonyl-metal-carbonyl bond angles in hexatriene and cyclopentadienyl complexes are close to 90°, as we have assumed for the data in Table I, this is not the case for butadiene and allyl complexes. Here there is a difference in the angles, as well as a tipping of the axis in the ML₃ fragment relative to the plane of the polyene. A detailed discussion of this for allyl-cobalt tricarbonyl has been given elsewhere.^{3k} The problem that we are concerned about is that these angles may vary upon rotation to **55**. Three parameters can be used to describe these geometrical deformations, within a mirror plane constraint. The angular variables are defined in **56**. For both allyl-cobalt



tricarbonyl and butadieneiron tricarbonyl, ω was set at the experimental value of 109^{45a} and 90°,^{44a} respectively. The optimized values for C₃H₅Co(CO)₃ were $\theta = 102^\circ$ and $\varphi = 130^\circ$ in the staggered geometry, **52**. This corresponds closely to the experimentally observed values.^{45a} Upon rotation to the eclipsed conformation, **56**, θ becomes 119° and $\varphi = 113^\circ$. The net barrier is calculated to be 3.8 kcal/mol, which is quite close to that given in Table I. Similarly in C₄H₆Fe(CO)₃ $\theta = 101^\circ$, $\varphi = 130^\circ$ in the staggered geometry and $\theta = \varphi = 120^\circ$ in the eclipsed. This corresponds to a barrier of 14.5 kcal/mol, a value which is too large in comparison to those given in Table I. It

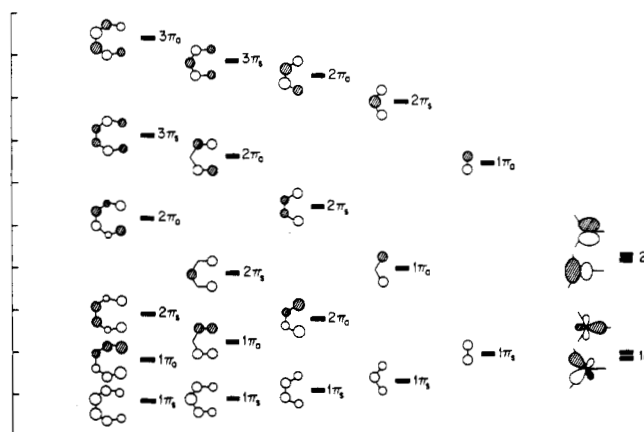
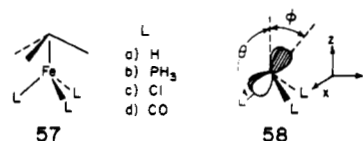


Figure 8. The energies and nodal properties for acyclic polyenes relative to those in an M(CO)₃ fragment. The energy scale is in units of electron volts.

is possible in this case that the Fe(CO)₃ unit may move with respect to the polyene. However, it should be emphasized that the stabilizations upon geometrical relaxation of both conformations nearly cancel each other. Therefore, the rationale for the origins of the barrier is not likely to change from that obtained within the restraints of a “pseudooctahedral” M(CO)₃ group.

Perturbations within the ML₃ Fragment. Thus far we have only considered an M(CO)₃ fragment within a fixed geometry. A logical extension is to examine the effect on the rotational barriers of varying L, for instance in the trimethylenemethane ML₃ complexes. We shall furthermore make all of the above compounds isoelectronic (i.e., **57a** and **c** have a 3- charge) and



initially all L–M–L angles are set at 90°. The barriers for **57**, given in Table II, show that there is a significant variation depending upon L. The largest barrier is calculated for **57c** where L is a π donor and the smallest for **57d** where L is a π acceptor. The barriers are linearly related to the orbital tilting, φ , of the 1e and 2e sets. φ is defined in **58**.

As φ for the 1e set goes to 90° (becoming chiefly $x^2 - y^2$ and xy) and φ for 2e approaches 0°, the left–right asymmetry in the e sets decreases, and therefore the barrier decreases. For a π donor the π orbitals on the ligand mix into 1e in an out of phase manner. As shown below, building more xz or yz char-

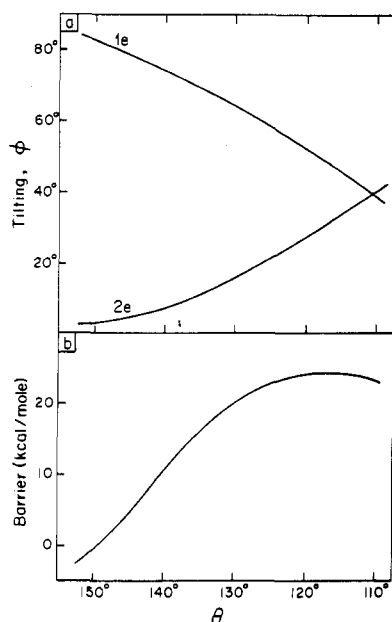


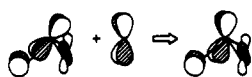
Figure 9. (a) Variation of the tilt angle for the e sets of $\text{Fe}(\text{CO})_3$ vs. θ , the C-Fe-C angle. (b) The calculated barrier of rotation in TMM $\text{Fe}(\text{CO})_3$ as a function of θ .

Table II. Variation of Tilting in ML_3 Groups and the Calculated Barrier in TMM FeL_3 ^a

L	Tilting ϕ ^b		Barrier, kcal/mol
	1e	2e	
H	54.7	35.3	38.7
PH_3	53.6	34.8	32.5
Cl	45.2	42.4	47.0
CO	58.4	22.9	23.6

^a All L-M-L angles were set at 90° . The TMM was nonplanar.
^b Defined in **58**.

acter into 1e reduces this antibonding. This is, of course, relative to a pure σ donor case, such as **57a**, where the tilting is



given exactly by the coefficients for an octahedron presented in the first section. Likewise, the 2e set will mix more $x^2 - y^2$ and xy character into itself. Conversely in the case of a π acceptor, π^* on L is mixed in xy and $x^2 - y^2$ in a bonding fashion so there is less tilting.

Experimental support for the hypothesis that the barrier of rotation in polyene- ML_3 should go in the order π donor $>$ σ donor $>$ π acceptor is rather tenuous. In a series of TMM $\text{Fe}(\text{CO})_n(\text{PF}_3)_{3-n}$ the coalescence temperature decreases as n decreases.¹³ However, PF_3 is stronger⁵³ or as strong a π acceptor as CO.⁵⁴ Likewise, in butadieneiron- $(\text{CO})_n(\text{PF}_3)_{3-n}$ complexes the barrier decreases from $n = 3$ (9.5 ± 0.2 kcal/mol) to $n = 1$ (8.8 ± 0.3 kcal/mol).^{49c} A number of cyclohexadienyl and cyclohexadiene $\text{M}(\text{CO})_n(\text{phosphine})_{3-n}$ have been studied,^{7a} but the role of electronic factors in determining the observed barriers is not clear. The barrier in cycloheptatrienechromium trimethylphosphine dicarbonyl or trimethylarsine dicarbonyl is, in fact, 1.9 and 2.4 kcal/mol, respectively, larger than that for the tricarbonyl compound.^{48a}

Another perturbation on the ML_3 framework to be considered is a variation of the L-M-L angles. It has been shown previously^{10a} that when θ in **58** is 90° , the 2e set is comprised solely of $x^2 - y^2$ and xz with 1e being xz and yz . As θ increases

Table III. Parameters Used in Extended Hückel Calculations

Orbital	H_{ii} , eV	ζ_1	ζ_2	C_1^a	C_2^a	
Cr	3d	-11.22	4.95	1.60	0.4876	0.7205
	4s	-8.66	1.70			
	4p	-5.24	1.70			
Fe	3d	-12.70	5.35	1.80	0.5366	0.6678
	4s	-9.17	1.90			
	4p	-5.37	1.90			
Co	3d	-12.11	5.55	2.10	0.6060	0.6060
	4s	-8.54	2.00			
	4p	-4.76	2.00			
Ni	3d	-12.99	5.75	2.00	0.5683	0.6292
	4s	-8.86	2.10			
	4p	-4.90	2.10			
B	2s	-15.20	1.30			
	2p	-8.20	1.30			
C	2s	-21.40	1.625			
	2p	-11.40	1.625			
N	2s	-26.00	1.95			
	2p	-13.40	1.95			
O	2s	-32.30	2.275			
	2p	-14.80	2.275			
Cl	3s	-26.30	2.033			
	3p	-14.20	2.033			

^a Contraction coefficients used in the double ζ expansion.

there is essentially an avoided crossing between the e levels; therefore, at large θ the tilting in 1e approaches 90° and 2e 0° . A consequence of this is that the rotational barrier in TMM $\text{Fe}(\text{CO})_3$ decreases as θ increases. This is shown in Figure 9 along with the variation of the tilt angle, ϕ , in the e sets of $\text{Fe}(\text{CO})_3$. A completely analogous trend occurs with the other ligands in ML_3 fragments.

The isolobal concept, relating metal fragments in which the number, extent in space, and symmetry properties of the valence orbitals are similar, has been shown to be of utility in predicting structural trends. For example, we have previously stressed the similarity in the valence orbitals of $\text{Fe}(\text{CO})_3$, $\text{Fe}(\text{C}_6\text{H}_6)$, and $\text{Co}(\text{C}_5\text{H}_5)$.^{10b} This correspondence does not, however, extend to barriers of rotation. The 1e set in $\text{Fe}(\text{C}_6\text{H}_6)$ and $\text{Fe}(\text{C}_5\text{H}_5)^-$ is almost exclusively $x^2 - y^2$ and xy . This is a result of the fact that the π^* levels of the rings have δ character. Likewise, 2e consists of xz and yz because of π character in the π orbitals. In other words, there will be no tilting in 1e and 2e for these fragments and, therefore, there will be no appreciable barrier in complexes of them.

Computed barriers in TMM- $\text{Fe}(\text{benzene})$ and TMM- FeCp^- are small, 0.05 and 0.002 kcal/mol, respectively, as would have been expected anyway from the manifold nature of the barrier. Sandwich complexes such as dibenzenechromium and ferrocene are also calculated to have small barriers, 0.9 and 0.3 kcal/mol, respectively. This is in accord with experimental findings.⁵⁵

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Appendix

All calculations were performed using the extended Hückel method.⁵⁶ The H_{ii} 's for chromium, iron, and cobalt were obtained from a charge iterative calculation on $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$, and $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$ using the experimental

geometries.^{19,44a,45a} The metal orbital exponents for the 3d functions are those given by Richardson et al.⁵⁷ while those for the 4s and 4p atomic orbitals are taken from previous work.⁵⁸ The values for the H_{ii} 's and orbital exponents are listed in Table III. The modified Wolfsberg-Helmholz formula was used^{42,59} throughout in these calculations. All C-C, C-H, and C-O distances were idealized at 1.41, 1.09, and 1.14 Å, respectively. Also all C-C-C, C-C-H (for the acyclic polyenes), and M-C-O angles were set at 120, 120, and 180°, respectively. The M-polyene bond lengths were taken from experimental values of closely related compounds. The M-C(O) distances were set to Cr, 1.84; Fe, 1.78; Co, 1.80; Ni, 1.82 Å. The values of ψ for the plots in Figures 1 and 2 were 0.4, 0.2, 0.1, 0.05, and 0.025. The solid lines indicate positive and the dashed lines negative values of ψ . In Figure 1, the slice of the wave functions for $1e_a$ and $2e_a$ were taken 0.5 Å out of the yz plane of the molecule.

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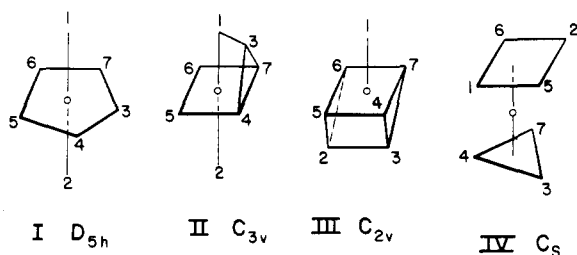
Neutron and X-Ray Diffraction Studies on Tris(dimethylphenylphosphine)osmium Tetrahydride

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Abstract: The crystal and molecular structure of $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ has been investigated by x-ray and neutron diffraction techniques. X-ray data collected at 298 K gave the unit cell parameters $a = 11.489$ (4) Å, $b = 12.441$ (4) Å, $c = 11.103$ (4) Å, $\alpha = 90.54$ (2)°, $\beta = 124.63$ (2)°, $\gamma = 89.93$ (2)°, $Z = 2$ in the triclinic space group $P\bar{1}$. Neutron data collected at 90 K gave the cell parameters $a = 11.409$ (2) Å, $b = 12.388$ (2) Å, $c = 11.098$ (2) Å, $\alpha = 90.36$ (5)°, $\beta = 125.07$ (1)°, and $\gamma = 90.06$ (4)°. Refinement against the x-ray data converged at $R = 0.055$ and $R_w = 0.060$ with 3486 reflections with $I \geq 3\sigma$. For the neutron study, agreement factors are $R = 0.044$ and $R_w = 0.042$ based on 3381 reflections. The complex is a distorted pentagonal bipyramid, the four hydride ligands, osmium, and one phosphorus atom being essentially coplanar. Important distances and angles in the molecule are as follows: Os–H = 1.663 (3), 1.648 (3), 1.644 (3), 1.681 (3) Å; Os–P = 2.317 (2), 2.307 (2), 2.347 (2) Å; H–Os–H = 67.9 (2), 69.4 (2), 70.0 (2)°; P–Os–P = 166.1 (1), 97.0 (1), 96.9 (1)°; H–Os–P(eq) = 73.0 (1), 79.7 (1)°.

There has been a great amount of interest in transition metal hydrides over the past two decades.² The structure of many hydride complexes is elusive because standard spectroscopic methods may fail to give useful information on the disposition of hydride ligands. Infrared spectra may be difficult to interpret and the metal–hydrogen stretching frequency is not always observed. NMR spectra of diamagnetic hydrides give information concerning the stoichiometry of the complex, but structural information is often lost owing to the fluxional nature of many complexes. The NMR of $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ ³ shows a high-field quartet, due to four equivalent hydrogens coupled to three equivalent phosphorus atoms. Four geometries may be considered for the seven-coordinate $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ complex: pentagonal bipyramid (I), face-capped octahedron (II), capped trigonal prism (III), and the piano stool geometry (IV). None of these, or any other, rigid geometry is consistent with the observed NMR spectrum. This complex, as well as many other MH_xL_y hydrides, is fluxional, with the chemically inequivalent protons interchanging at a rate that is rapid on the NMR time scale.



Interest in $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ comes not only from its fluxional properties, but also from the fact that seven-coordination is fairly uncommon, especially in complexes of group 8 metals. High coordination numbers are made possible in metal hydride complexes by the ability of the hydride ligand to stabilize high oxidation states and by its modest steric requirements. We report here the structure of $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$ as determined

by single crystal x-ray and neutron diffraction techniques. An x-ray diffraction analysis of the analogous $\text{H}_4\text{Os}(\text{PEt}_2\text{Ph})_3$ was earlier completed by Mason.⁴

Successful location and refinement of hydrogen atom positions by x-ray diffraction has been reported for several second- and third-row transition metal hydrides.⁵ The errors in these parameters are often large and probably frequently underestimated. In the present work, results from the x-ray study allowed geometries III and IV to be ruled out as possible structures for $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$. X-ray data alone were not adequate to distinguish unambiguously between configurations I and II, but I was strongly favored by the fact that the OsP_3 skeleton of the molecule is planar and T-shaped. Neutron data subsequently confirmed I as the correct geometry.

In addition to indicating the molecular geometry of $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$, the neutron diffraction study has made possible an accurate determination of the metal–hydrogen bond lengths. Precise knowledge of metal–hydrogen distances, although generally difficult to obtain, potentially offers more information concerning the covalent radius of the metal than do the lengths of other bonds. Interpretation of M–H bond distances is facilitated by the very simplicity of the hydride ligand, which is not able to participate in π bonding.

Experimental Section

X-Ray Diffraction. Tris(dimethylphenylphosphine)osmium tetrahydride was made by the published procedure³ and crystallized from absolute ethanol. A crystal with approximate dimensions $0.2 \times 0.25 \times 0.06$ mm was mounted along its $1\bar{1}0$ axis on a glass fiber. Preliminary precession photographs showed no systematic extinctions or symmetry of the diffraction pattern other than the center of inversion. Density measurements in aqueous zinc iodide agree well with the density calculated for two molecules per unit cell ($\rho_{\text{obsd}} = 1.51$, $\rho_{\text{calcd}} = 1.55$ g/cm³ for $\text{OsC}_{24}\text{H}_{37}\text{P}_3$), thus suggesting the space group to be $P\bar{1}$. Successful solution of the structure confirmed the correctness of this space group.

Data were collected at room temperature on an automatic Nonius