

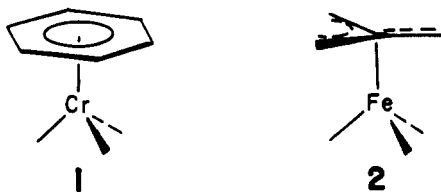
Rotational Barriers and Conformations in Transition-Metal Complexes

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The study of rotational barriers and conformations has been a long-standing subject of concern to chemists. Perhaps the main reason for this is that the magnitude of a rotational barrier is directly related to the bonding within the molecule. Thus, theory and experiment are intimately connected in these simple "reactions". Although the magnitudes and physical origins of rotational barriers in organic molecules have been extensively studied,¹ not nearly so much is known about organometallic compounds. One has the intuitive feeling, and this turns out to be the case, that rotation about a metal-carbon σ bond will be facile. However, rotation about the polyene-metal axis in a transition-metal polyene- ML_n complex is intuitively less clear. We have been concerned with this problem, both in the experimental arena (NMR measurements) and in the theoretical domain. The latter area will be of chief concern in this Account.

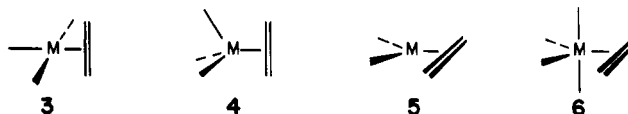
Experimental studies on the magnitude of these barriers have shown that there is an extensive range for polyene- ML_n complexes. For example, the barrier in benzene- $Cr(CO)_3$, **1**, is very small, perhaps in the region



of ~ 0.5 kcal/mol.^{2a} On the other hand, the barrier in trimethylenemethane- $Fe(CO)_3$, **2**, is much larger, ~ 20 kcal/mol.^{2b} It will be shown that the barrier in **1** can actually be tuned over an unprecedented 40 kcal/mol range by electronic perturbations within the benzene ring. It was this tremendous susceptibility of the polyene-metal bonding to electronic effects that initially sparked out interest. Perhaps more importantly, theoretical studies of reactions have shown that the conformation of a polyene with respect to the ML_n axis has a crucial bearing on the reactivity of the complex or the regioselectivity of attack by external reagents on it.

While our primary interest is focused on the polyene-metal axis, we cannot forget the other ligands at the metal. The ancillary ligands set the energy of the metal-centered orbitals and tailor them to specific shapes. Consequently, their number and geometrical disposition will directly influence conformational preferences and rotational barriers. For example, the

barrier about the metal-olefin axis in compounds of type **3** is 10-15 kcal/mol^{3a} while that in **4** is extremely



small (less than 5 kcal/mol).^{3b} Notice that both are nominally four-coordinate; however, **3** has a square planar geometry and **4** is tetrahedral. The barrier in trigonal **5** with one less auxiliary ligand is larger than 20 kcal/mol.⁴ Finally, the rotation process in **6** does not involve simple rotation about the metal-olefin axis. As we shall see, that would require a large activation energy; instead rotation is accompanied by specific geometrical motions of the other ligands, and moderate barriers in the neighborhood of 10-15 kcal/mol are actually found.⁵ It is this kind of structural and energetic diversity in organometallic complexes that makes the interplay of experimental and theoretical studies interesting.

Our theoretical strategy to analyze these barriers has been to utilize the fragment molecular orbital approach.⁶ The basic idea here is to develop the valence orbitals of an ML_n unit. These are interacted with the π orbitals of a polyene in two or more limiting conformations. Utilization of symmetry-based overlap arguments⁷ allows us to decide which conformation shows the largest stabilizing interaction between the polyene and ML_n fragments. The magnitude of this stabiliza-

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(7) (a) For a very lucid description of group theory and symmetry, see: Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley: New York, 1971. (b) An excellent introduction to the interaction of orbitals may be found in: Hoffmann, R. *Acc. Chem. Res.* 1971, 4, 1.

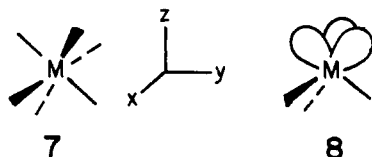
Tom Albright received his B.S. from North Dakota State University and his Ph.D. from the University of Delaware; he did postdoctoral work at Cornell University. In 1977 he joined the faculty of the University of Houston where he is an Assistant Professor. In 1979 he received a Camille and Henry Dreyfus Teacher-Scholar Award. His primary research interests are in experimental and theoretical studies of organometallic compounds.

tion difference is directly related to the barrier size. The actual molecular orbital technique we have used is the extended Hückel method.⁸ This has given us consistently reliable barriers for the polyene- ML_n class in comparison to experiment. The reason behind this is that extended Hückel normally does well at energetically describing overlap differences, and this is at the heart of the barrier problem. Calculations at the ab initio level have been carried out for a few cases and, as shall be mentioned, agree well with the extended Hückel values. The fragment molecular orbital approach can be utilized quantitatively at either computational level,⁶ but we shall only use it here in a qualitative way. The physical origins of the barriers and qualitative indications of their magnitudes will be stressed in a simple, pictorial way.

Trimethylenemethane- ML_3

The rotational barrier in trimethylenemethane- $Fe(CO)_3$ derivatives has been found to be 19–20 kcal/mol by Magyar and Lillya.^{2b} Molecular orbital calculations at the extended Hückel level give a barrier of 23.6 kcal/mol for the parent compound.⁹ The most stable conformation is experimentally found to be that shown in **2** for the parent compound as well as all derivatives.¹⁰ In order to see how this comes about we need the orbitals of an $Fe(CO)_3$ group or that of an $M(CO)_3$ fragment, and then the number of electrons can be adjusted according to our needs.

The most expedient way to develop the valence orbitals of an $M(CO)_3$ group^{9,11} starts from octahedral $M(CO)_6$, **7**. Three *fac* carbonyls are removed, yielding



the $M(CO)_3$ group (**8**). This is done for $Cr(CO)_6$ in Figure 1. On the left side the metal-centered orbitals, t_{2g} and e_g , are sketched. The derivation of the symmetry labels for these orbitals would be too lengthy to present here.^{7a} Our use of them is motivated by two factors. The cardinal rule of perturbation theory is that only orbitals of the same symmetry (symmetry labels, if each set is labeled with respect to the total symmetry of the molecule) can interact.^{7b} In addition, they are used to provide a label for the reader. In all cases the orbital in question shall be explicitly drawn out. The atomic composition of t_{2g} and e_g is a little different than that normally given for octahedral complexes because of the unusual coordinate system, shown at the top center of Figure 1. Notice that the z axis lies on one of the threefold faces of the octahedron. One member of the t_{2g} is z^2 . The other two members are mainly x^2

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(11) See also: (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Burdett, J. K. *Ibid.* **1975**, *14*, 375; *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599. (c) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

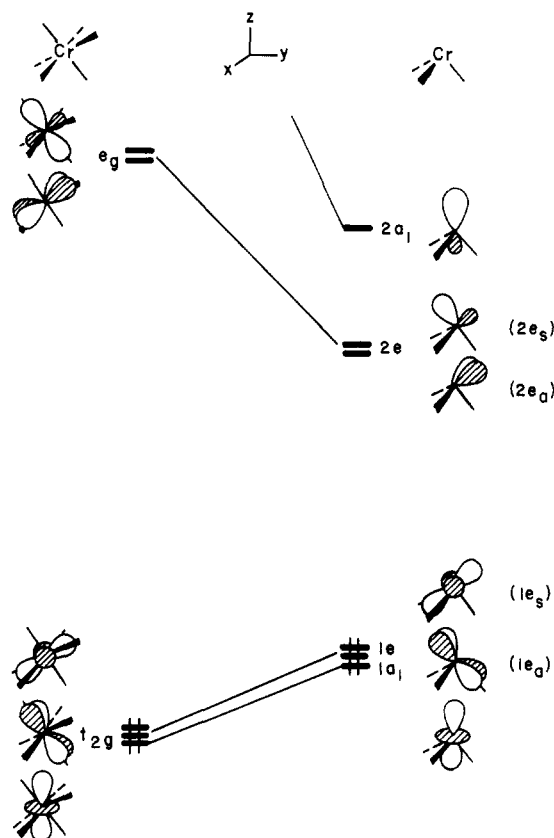
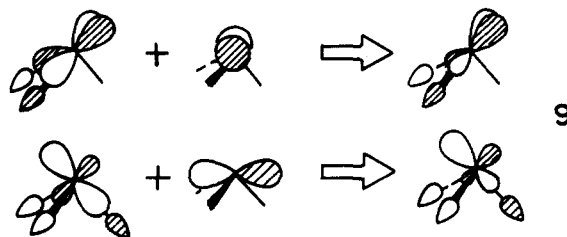


Figure 1. Derivation of the valence orbitals of a C_{3v} $Cr(CO)_3$ fragment from octahedral $Cr(CO)_6$.

– y^2 and xy , with some yz and xz , respectively, mixed into them. The intermixing of atomic functions maximizes back-bonding to carbonyl π^* . At higher energy is e_g . It is mainly of yz and xz character antibonding to carbonyl σ , with some $x^2 - y^2$ and xy mixed in. This bothersome intermixing of atomic functions is a consequence of the coordinate system chosen. But it leads to an easy analysis of $Cr(CO)_3$. When three carbonyls are removed from $Cr(CO)_6$ the t_{2g} set, now $1a_1 + 1e$ in C_{3v} symmetry (see the right side of Figure 1), rises slightly in energy. Some of the bonding to carbonyl π^* is lost. But the shape of $1e$ and $1a_1$ is the same as that for the parent t_{2g} . When the three carbonyls are removed, those levels corresponding to e_g , now labeled $2e$ on the right side of Figure 1, fall in energy (the s and a subscripts in $1e$ and $2e$ refer to whether the individual members of the e sets are symmetric or antisymmetric to the plane of the paper). Half of the antibonding to carbonyl σ is removed. There is also a hybridization that ensues. Upon lowering of the symmetry of the complex, metal x and y can mix into $2e$. They do so, shown in **9**, in a way which is bonding to carbonyl σ .



This hybridizes $2e$ away from the carbonyls, toward the polyene. Finally, there is another orbital, $2a_1$, which comes into the picture. It started in the octahedron as

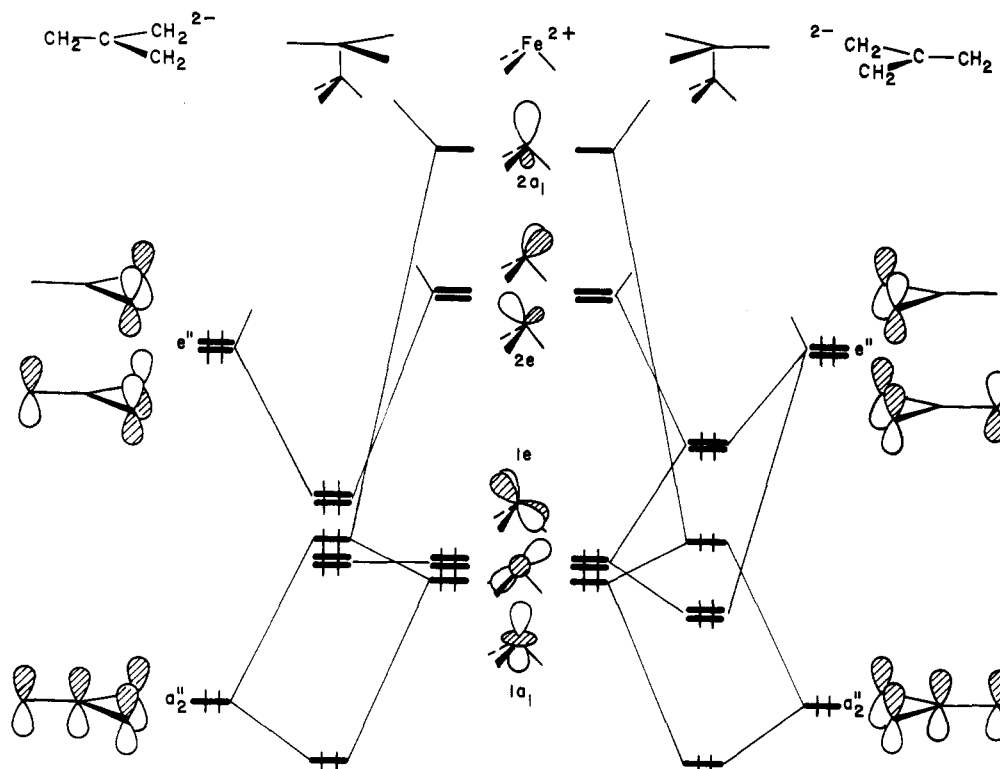


Figure 2. Orbital interaction diagram for TMM-Fe(CO)₃ in the staggered (left) and eclipsed (right) conformation.

a metal s orbital. In Cr(CO)₃ a substantial portion of z (and z²) mix into it. We could have derived these orbitals in a different fashion. One way would be to remove the three carbonyls from Cr(CO)₆. This leaves three empty hybrid orbitals pointing toward the missing carbonyls, as indicated in 8.¹² Symmetry-adapted linear combinations^{7a} of these localized hybrids leads to 2a₁ + 2e.

There are two further points about M(CO)₃ that should be brought up at this point. Maximal interactions with polyene π levels will come from the 2a₁ + 2e triad. The orbitals lie at moderate energy and are hybridized toward the polyene. For Cr(CO)₃ or any d⁶ fragment, 2a₁ + 2e are formally empty and will interact with filled π levels of a polyene. The 1a₁ + 1e set is always filled for a d⁶ fragment. They will participate in bonding to a lesser extent because of their pseudo-δ overlap with empty polyene π* levels. In addition, 2e and 1e are tilted. That is, they are asymmetric with respect to the xz in 1e and 2e, which, in turn, came from the octahedron. This tilting will play a primary role in setting rotational barriers. As we shall see, if a polyene has π orbitals that are tilted, then they will overlap more with M(CO)₃ orbitals in one conformation, and a rotational barrier will be created.

Trimethylenemethane (TMM) is one such ligand where the π orbitals are tilted, and TMM-Fe(CO)₃ nicely illustrates the origins of a rotational barrier in the polyene-M(CO)₃ class. Figure 2 shows orbital interaction diagrams for TMM-Fe(CO)₃ in the two limiting conformations. On the left side is what we shall call the staggered orientation. It is the experimentally observed one.¹⁰ On the right side is the eclipsed geometry. The relevant π orbitals of TMM, e'' + a₂'', are displayed on the far right and left. The complex has been arbitrarily divided into TMM²⁻ and Fe(CO)₃²⁺.

This makes the M(CO)₃ fragment d⁶, isoelectronic to Cr(CO)₃. All of the electronic details that result from the union of these two sets of fragment orbitals will not be given here.⁹ Suffice it to say that three molecular orbitals are formed from the combination of the fragment orbitals labeled a₂'', 1a₁, and 2a₁. The important point is that these fragment orbitals are cylindrically symmetrical. Therefore, the overlap between them will be the same in any conformation, and this cannot be the source of the rotational barrier. In the staggered geometry there is a strong interaction between the 2e set on Fe(CO)₃ and e'' of TMM. The bonding combination is filled, and the antibonding combination (not shown in Figure 2) is empty. Notice that the tilting in 2e matches the left-right asymmetry in e''. For example, 2e_a points directly toward the two p orbitals in the antisymmetric member of e'', its bonding partner. Precisely the same occurs between 2e_b and the symmetric member of e''. The 1e set of Fe(CO)₃ is basically nonbonding. The tilting in 1e minimizes its overlap with TMM orbitals. In the eclipsed geometry on the right side of Figure 2 there are substantial differences. Now the 2e set loses overlap with e''. Notice that 2e_a is pointed to the right side and e''_a has its electron density concentrated on the left side. This is one reason why the highest occupied molecular orbital (HOMO) in the eclipsed geometry is higher in energy for the eclipsed conformation that it is in the staggered form. Overlap is also now turned on between 1e and e'', and this also destabilizes the HOMO. Inorganic readers will see that a far easier way to express this barrier problem is that the union of TMM²⁻ and Fe(CO)₃²⁺ creates an octahedron in the staggered arrangement. The eclipsed conformation is analogous to the less stable trigonal prismatic geometry for saturated ML₆ complexes. We shall pursue this more fully in a later section. The barrier is calculated⁹ to be 20.8 kcal/mol with a planar

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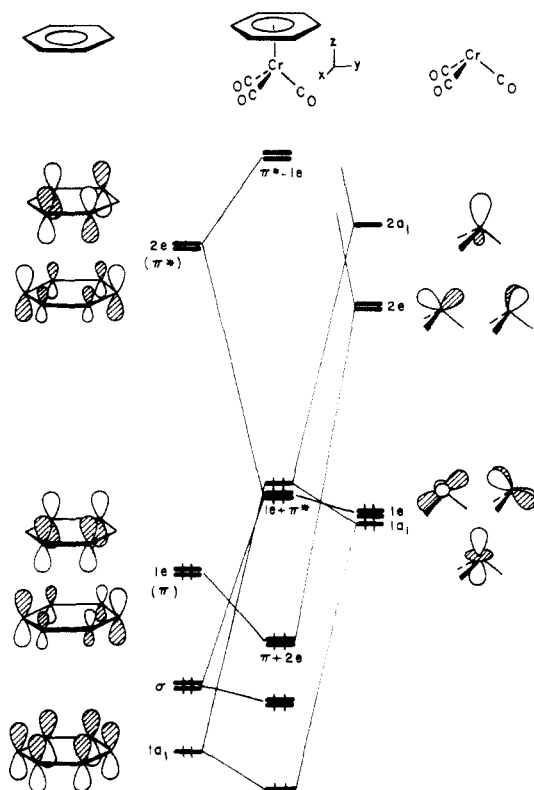


Figure 3. Orbital interaction diagram for benzene–Cr(CO)₃. The conformation shown is the eclipsed one, but identical energies are found in the staggered geometry.

TMM geometry. Puckering TMM to the experimental geometry causes the calculated barrier to rise to 23.6 kcal/mol. The TMM e'' set becomes directed more toward the metal, and a greater differential of the overlap between $2e$ and e'' is set up.⁹

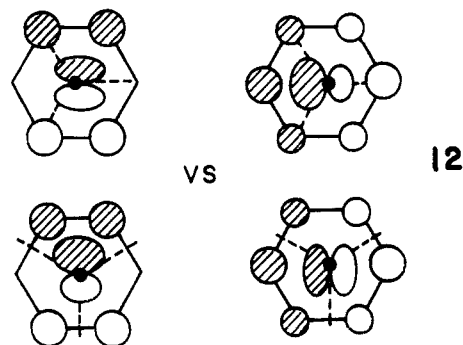
The tilting in Fe(CO)₃ is directly responsible for the rotational barrier. Had $1e$ and $2e$ not been tilted ($1e$ purely $x^2 - y^2$ and xy and $2e$ purely xz and yz), then the rotational barrier would be very small. The amount of tilting, therefore, will influence the size of the barrier. For example, the rotational barrier is approximately doubled by replacing the π acceptor CO ligands by π donors like Cl.⁹ The tilting is also sensitive to the pyramidalicity of the ML₃ unit.^{9,11a} By a decrease in the C–Fe–C angle in TMM–Fe(CO)₃ the barrier can actually be made to drop to zero.⁸ These modifications will work in the same fashion for other polyene–ML₃ compounds, so there is a way to tune the barrier by electronic and geometric means within the ML₃ portion.

Polyene–ML₃ Complexes

Let us now turn to the opposite extreme, a polyene–ML₃ complex that has a very small barrier of rotation. The example that we shall develop in some detail is benzene–Cr(CO)₃. As mentioned in the introduction, the barrier has been found by electron diffraction to be very small.^{2a} Its structure in the solid state has been determined¹³ to be staggered, 10, rather than eclipsed, 11. There are also three isoelectronic η^6 -C₆H₆–RuL₃ complexes,¹⁴ two of which are eclipsed and one is

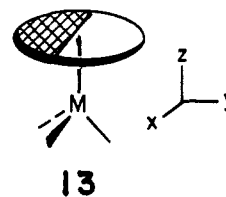


staggered. Packing forces apparently are causing the different conformations, so this too points to a small barrier. An interaction diagram for benzene–Cr(CO)₃ is shown in Figure 3. The degenerate π set of benzene is stabilized considerably by the empty $2e$ set on Cr(CO)₃, yielding the orbitals labeled $\pi + 2e$. The filled $1e$ set of Cr(CO)₃ is also stabilized by benzene π^* . However, this overlap is of δ type and certainly is not nearly strong as the π overlap in $\pi + 2e$. This means that more electron density is transferred from benzene to Cr(CO)₃ in $\pi + 2e$ than is back-donated from $1e + \pi^*$. The benzene ligand is rendered electron deficient and is susceptible to attack by nucleophiles. This reaction has been synthetically exploited by Semmelhack and co-workers.¹⁵ The important point to be noted is that the overlap of π with $2e$ and π^* with $1e$ is identical in the staggered and eclipsed conformations. This is shown in 12 for the $\pi + 2e$ combinations. The calcu-



lated barrier⁹ is 0.3 kcal/mol, which favors the staggered geometry.

There are two ways to generalize the rotational barrier problem in polyene–ML₃ complexes. If there is to be a substantial barrier, then the polyene must have a left–right asymmetry as in 13. The π orbitals will then



be tilted, and the tilting in the two fragments can reinforce or cancel each other in the two limiting conformations. Putting this in another way, the polyene cannot have two real or effective perpendicular mirror planes in the xz and yz planes of 13 to create a large barrier. Clearly benzene does, and TMM does not, so we are left with small and high, respectively, barriers in complexes of them. A slightly different but related perspective starts from a localized picture of ML₃. The set of three hybrids in 8, shown from a top view in 14, stagger the M–L bonds. A combination of $1a_1 + 1e$ gives a set of three localized hybrids, which, as shown by 15, eclipse the M–L bonds. The two trios are different; that is, they have different radial extent in the

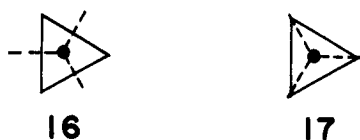
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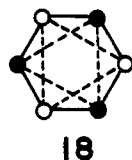
z direction of 13 and different electron occupancy. For a d^6 fragment 14 is empty and 15 is filled. It is easy to see by 14 and 15 that the ML_3 fragment fixes an octahedron. The better the filled π orbitals of a polyene topologically match 14 (and avoid 15), the larger will be the barrier when the fragments are rotated against each other.

These guidelines point to the fact that low barriers will be found for η^4 -cyclobutadiene- ML_3 ,¹⁶ η^5 -cyclopentadienyl- ML_3 , and η^7 -cycloheptatrienyl- ML_3 . In η^3 -cyclopropenyl- ML_3 complexes, though, one should get a sizeable barrier. We calculate it to be at least 7 kcal/mol ($ML_3 = Co(CO)_3$), with conformation 16 more

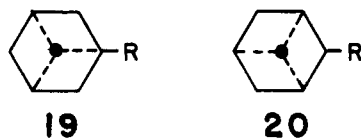


stable than 17.⁹ Notice the resemblance to an octahedron in 16. The barrier for this system is unknown; however, all structures¹⁷ do possess a conformation like that in 16.

The barrier in benzene- $Cr(CO)_3$ can be dramatically increased by electronic perturbations within the benzene ring. One can think of the π orbitals of benzene as being constructed from the two interpenetrating trios diagrammed in 18. If these could be uncoupled, then



a rotational barrier is created. Substituents of either a π -donor or π -acceptor type will do this. A maximum barrier will be seen for a 1,3,5 trisubstitution pattern. For one substituent either a syn-eclipsed, 19, or anti-

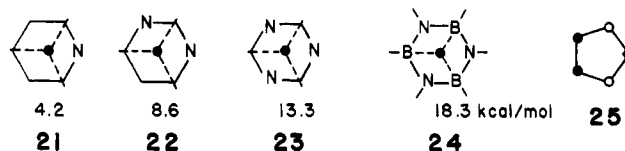


eclipsed, 20, may be the ground state. A prediction can be made by matching regions of high electron density on the arene ring (induced by the substituent) to the empty trio of 14 and regions of low electron density with the filled trio of 15. Therefore, when R is an electron donor 19 is more stable than 20. In this orientation 14 is pointed at the electron rich ortho and para positions. Likewise, 20 is the most stable geometry when R is a π acceptor. A perturbation approach can also be used to make these predictions and most structures conform

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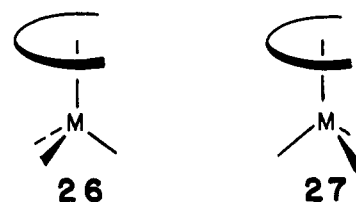
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to this pattern.⁹ Even larger perturbations result when more electronegative atoms are substituted for the carbons in 18. There is a regular increase in the barrier when one, two, or three CH groups are replaced by nitrogens. The predicted conformations and barriers are given by 21-23.⁹ The structures of two complexes



related to 21 have been determined.¹⁸ Both lutidine and collidine- $Cr(CO)_3$ have the orientation given in 21. Work is currently under way to prepare derivatives of 22 and 23 and measure the rotational barriers in this series.¹⁹ Making one trio in 18 more electronegative and the other trio less electronegative than carbon will create a substantial barrier of rotation. An example is borazine- $Cr(CO)_3$, 24. An X-ray structure²⁰ of the hexaethyl derivative has the geometry indicated, but there has been no measurement of the barrier. The way to maximize the barrier in cyclopentadienyl-based complexes is shown in 25.²¹ Either a 1,3,4 or 1,3 perturbation pattern will give the largest barriers. This has been convincingly demonstrated by Hawthorne and co-workers for related carborane complexes.²² In eclipsed arene- $Cr(CO)_3$ complexes the $Cr(CO)_3$ group is not an electronically innocent bystander, either. The $Cr(CO)_3$ group itself polarizes the electron density on specific carbons in an arene ring. This in turn will influence the regioselectivity of attack by nucleophiles and electrophiles on the ring.²³ The polarization can be related again to the tilting on 1e and 2e or the orientation of 14 and 15. Localizing the C-C single and double bonds in benzene- $Cr(CO)_3$ also will create an enormous barrier of 19.4 kcal/mol.⁹

Acyclic polyene- ML_3 complexes have an orbital pattern very similar to the TMM- $Fe(CO)_3$ example.⁹ All 18-electron complexes, and there are hundreds of X-ray structures to back this up, are more stable in the conformation given by 26 rather than 27. Actually here



it is only $2e_s$ and $1e_s$ that are at the origin of the barrier. $2e_a$ and $1e_a$ overlap with the appropriate π orbitals to an approximately equivalent extent in 26 and 27. The amount of interaction between $2e_s$ and the relevant π orbital sets the barrier size. Barriers of about 3 kcal/mol for π -allyl- $Co(CO)_3$ to about 13 kcal/mol for pentadienyl- $Mn(CO)_3$ have been calculated and observed.⁹

(18) Zawortoko, M. J.; Shakir, R.; Atwood, J. L.; Onnuch, A.; Reynolds, S. D.; Albright, T. A., manuscript in preparation.

(19) Onnuch, A.; Reynolds, S. D.; Albright, T. A., work in progress.

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(22) Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1981, 103, 2988.

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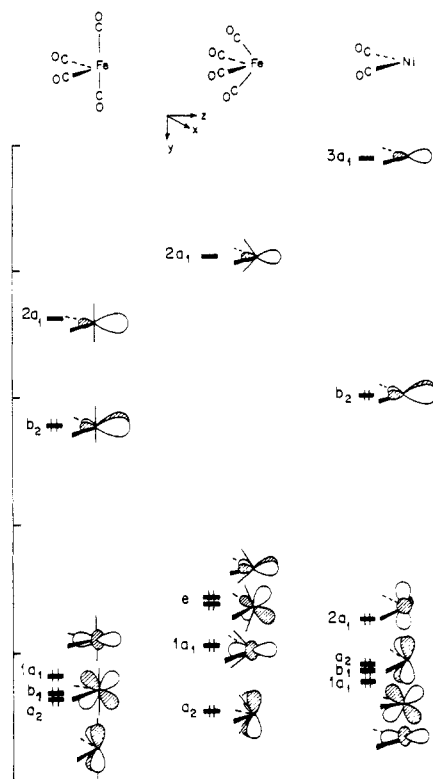


Figure 4. The valence orbital of a C_{2v} $\text{Fe}(\text{CO})_4$ (left), C_{4v} $\text{Fe}(\text{CO})_4$ (middle), and C_{2v} $\text{Ni}(\text{CO})_2$ fragment (right). The energy scale on the left is in units of eV.

Notice that there will be only a tiny barrier in ethylene- ML_3 complexes, 4.^{3b} The olefin has two perpendicular mirror planes.

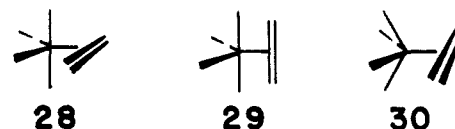
It can be shown²⁴ that 16-electron complexes will prefer 27 as the ground-state geometry. There is some evidence for this in a π -allyl- $\text{Mn}(\text{CO})_3$ derivative.²⁵ The 18-16 electron dichotomy can be used also to predict equilibrium conformations and changes in the magnitude of rotational barriers in cycloheptatriene- $\text{Cr}(\text{CO})_3$ complexes. The barrier here is tied to cycloheptatriene-norcaradiene equilibrium,²⁴ and this has been demonstrated from NMR studies of the barriers in 7-substituted cycloheptatriene and derivatives of 1,6-methano[10]annulene- $\text{Cr}(\text{CO})_3$.²⁶

Polyene- ML_2 and - ML_4 Complexes

The ML_2 and ML_4 fragments also have specific requirements for the establishment of a rotational barrier.²⁷ The valence orbitals of a C_{2v} ML_4 fragment are displayed on the left side of Figure 4. They can easily be constructed by removal of two cis carbonyls from an octahedron.^{11a} Likewise, ML_2 can be derived from a square-planar ML_4 complex. In each fragment it is the b_2 orbital (see Figure 4) that sets the equilibrium conformation. Notice that in both fragments b_2 is hybridized out away from the remaining carbonyls and lies at a moderate energy. The hybridization comes out in a way that is analogous to that described for the 2e set in $\text{M}(\text{CO})_3$. Both fragments also have an orbital of b_1

symmetry, which is orthogonal to b_2 . b_1 is not hybridized and lies at a much lower energy. This competition between b_2 and b_1 sets the rotational barrier.

An example of this tension between b_2 and b_1 is provided by ethylene- $\text{Fe}(\text{CO})_4$. The equilibrium geometry is drawn in 28.²⁸ Here the ethylene π^* orbital



stabilizes b_2 . In 29 ethylene π^* stabilizes b_1 ; b_2 is left nonbonding. The $b_2 + \pi^*$ interaction in 28 provides much greater stabilization to the system than $b_1 + \pi^*$ in 29. b_2 lies at higher energy and is, therefore, closer to π^* than is b_1 . Also, b_2 is hybridized and overlaps to a greater extent with π^* than that from b_1 . Therefore, both energy gap and overlap factors favor 28 over 29. The energy difference is calculated to be about 30 kcal/mol at the extended Hückel^{27a} and ab initio²⁹ levels. Going from 28 to 29 is *not* the pathway for rotation. There is an additional degree of freedom in the $\text{Fe}(\text{CO})_4$ unit. It can pseudorotate to a C_{4v} structure, the valence orbitals of which are displayed in the middle of Figure 4. b_2 and b_1 become an e set. Both members will overlap with ethylene π^* to an equal extent. Therefore, along with rotation of the olefin there is pseudorotation motion which leads to the transition state, 30. The calculated barrier of 10.1 kcal/mol^{27a} lies within the 10-15 kcal/mol range measured for derivatives.⁵ The analysis for d^{10} ethylene- ML_2 complexes is identical. Rotation from the geometry shown in 5 will be difficult since there is now no way to make b_2 equivalent to b_1 .

It can be shown^{27b} that any 18-electron acyclic polyene- ML_4 complex will have a geometry like that in 31.



Polyene rotation will be accompanied by pseudorotation of ML_4 . To be fair, an alternative mechanism for equivalencing the ligands would be a turnstile path. Here, the two equatorial and one axial ligand are rotated. Work is currently under way on π -allyl and butadiene complexes to differentiate these mechanisms and measure the barrier.³⁰ Sixteen-electron ML_2 complexes will be most stable with the conformation given by 32. Rotation to 33 requires large energies.^{27b} Cyclic polyenes can also be handled and substitution patterns constructed for maximizing the barrier.^{27b} Larger barriers are created the more polyene- ML_4 resembles the octahedron and polyene- ML_2 a square-planar complex. The ML_2 compounds are especially interesting because the b_2 - b_1 difference cannot be resolved by ligand distortion. In many 18-electron cases the polyene

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distorts or the ML_2 unit slips to a lower coordination number.^{21,27b,31}

Conclusions and Extensions

No matter which way one dissects these barriers, it is the electronic asymmetry at the metal (tailored by the other ligands) that causes them. There is a threefold pattern for C_{3v} ML_3 complexes and a twofold one in the C_{2v} ML_2 and C_{2v} ML_4 compounds. A δ orbital can also create a barrier for a C_{4v} ML_4 or C_{4v} ML_5 complex (the a_2 orbital for C_{4v} ML_4 in Figure 4).²⁷ We have neglected steric effects in this review. They are minimal for the cases presented here, but this is not always the case. The orientation and the source of rotational barriers in the Zeise's salt complexes, **3**, are actually set by steric factors.^{27a,32} It takes something as large as a *tert*-butyl group on, for example, a benzene ring to cause an appreciable effect on the rotational potential for a compound where there is normally a small barrier.^{23,33} In systems possessing a much larger barrier such as the acyclic polyene- ML_3 class there are a number of examples³⁴ where extremely close contacts exist between substituents on the polyene ring and the

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L groups in the electronically favored conformation **26**. The steric problems could have been relieved by rotation to **27**, but structural studies still find **26** as the ground state conformation.

The fragment orbital analysis of rotational barriers can be extended to transition-metal dimers and trimers.³⁵ It is easy to see how a barrier from L_3M-ML_3 or L_4M-ML_4 complexes can be created. There are a large number of other fragments that can be considered; each have specific electronic properties. One particularly nice example is given by $CpML_2$ complexes of polyenes.³⁶ It can be shown that the regioselectivity of attack by nucleophiles on $CpMo(CO)(NO)(allyl)^+$ is determined by the orientation of the allyl ligand with respect to the $CpMLL'$ unit.^{36b} The many coordination geometries available to transition metals and the countless ways that electronic perturbations can be incorporated make this an exciting field where there is still much work to be done.

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Formation and Stabilities of Cobalt Dioxygen Complexes in Aqueous Solution[†]

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The earliest known synthetic dioxygen complex is probably $[(NH_3)_{10}Co_2O_2]^{4+}$, described by Werner and Myelius in 1893,¹ but this discovery was not pursued further until the report by Tsumaki² on the properties of the cobalt(II) chelate of bis(salicylal)ethylenediamine, "salcomine". This development was followed by a period of activity involving three research groups. Calvin and co-workers³⁻⁹ published a series of papers on the properties of the salcomine-type chelates in 1946-1947, and a series of papers on similar compounds by Diehl and co-workers¹⁰ appeared at about the same time. Much of the early incentive for investigating the

salcomine-type oxygen-carrying chelates was to develop a practical system of preparing pure oxygen from gaseous mixtures with light-weight equipment. Recently, the fluorine-substituted salcomine chelate, "fluomine", has been employed as the basis of a successful oxygen supply system.¹¹⁻¹⁴ Further interest in cobalt dioxygen

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