lution (τ 28 ppm or σ 18 ppm). One notes that the spectrum narrows from 230 K to room temperature and then broadens as the temperature goes higher. This same trend was observed in data taken over a slightly wider temperature range, 178–333 K, at a 36-μs cycle time. ^{1}H dipolar spectra indicate the presence of proton motion[14] in this temperature range, and the multiple-pulse spectra are characteristic of a chemical shift powder pattern averaged by a restricted motion of the protons.[1]

$H_4Os_4(CO)_{12}$. Knox et al.[12] have concluded that the structure of $H_4Os_4(CO)_{12}$ is similar to that of $H_4Ru_4(CO)_{12}$ from spectroscopic data. Yet the dipolar spectra do not change from 100 to 300 K,[14] and one concludes that the reorientational motion of the protons present in the $H_4Ru_4(CO)_{12}$ is not present in $H_4Os_4(CO)_{12}$. The multiple-pulse spectrum for $H_4Os_4(CO)_{12}$ at 300 K is reproduced in Figure 4. The center of mass of the spectra furnishes an isotropic chemical shift of near 20 ppm (τ 30 ppm) in agreement with our earlier estimate,[14] and the solid line representing a nonlinear regressional fit of the spectra to that expected from chemical shift tensor with uniform Lorentzian broadening function furnishes principal values indicating an axially symmetric tensor with an asymmetry of 26 ppm and a large Lorentzian broadening function of 11-ppm half-width.

As discussed above, both heteronuclear dipolar interactions with the ^{189}Os and the proton chemical shift tensor contribute to the multiple-pulse spectrum, and thus the width of the multiple-pulse spectrum furnishes an upper limit to the proton chemical shift tensor. However, one expects the heteronuclear interaction to broaden the chemical shift spectra symmetrically, and thus the asymmetric tensor obtained from the computer fit to the $H_4Os_4(CO)_{12}$ can be associated with a proton chemical shift anisotropy. That is, since ^{189}Os has a large quadrupole moment and is located in a molecular site of less than cubic symmetry, one can assume that the spin $\frac{3}{2}$ ^{189}Os nuclei will be in Zeeman-perturbed quadrupolar state, and we have shown by explicit calculation[16] that the heteronuclear interaction in this limit will broaden the proton spectra symmetrically.

Acknowledgments. We thank Professor J. R. Shapley for providing the samples used in this study and for helpful discussions, and we appreciate enlightening discussion of structural information provided by Professor R. Bau. We wish to acknowledge financial support from the Department of Energy (EY-76-S-03-0767). A. T. Nicol wishes to acknowledge partial support from an IBM Fellowship.

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CpM(CO)$_2$(ligand) Complexes

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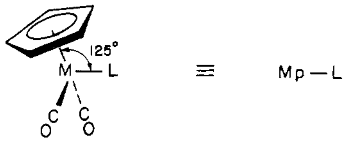
Abstract: The electronic structure of cyclopentadienyl metal dicarbonyl complexes of alkyls, carbenes, sulfur dioxide, acetylenes, and ethylenes is analyzed, with an emphasis on conformational preferences and rotational barriers.

The cyclopentadienyl metal dicarbonyl fragment, CpM(CO)$_2$, is a common constituent of a large class of organometallic complexes CpM(CO)$_2$L, Mp-L, **1**. These molecules have found widespread utility in transition metal aided organic synthesis, especially so the iron variant Fp, CpFe(CO)$_2$L.[2a] Structures have been determined for a range of CpM(CO)$_2$L complexes with L a σ-bonded ligand such as CO, PR$_3$, or CR$_3$,[2b–e,3,4] including related systems CpMLL′L″,[5] as well as complexes with conformationally more interesting ligands such as sulfur dioxide, carbenes, acetylenes, ethylenes, and allyls.[6–9] Examples are shown in **2**[7a] and **3**.[6a]



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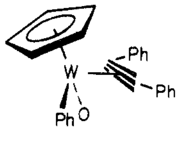

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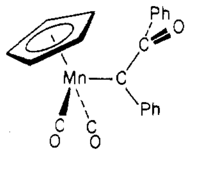

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Several studies have been made of the orientational preferences of the attached ligand, giving us some information on barriers to rotation about the metal to ligand bond.[10,11]

Systems containing more than one Mp unit can be put into two classes, those which contain the MpL moiety linked to

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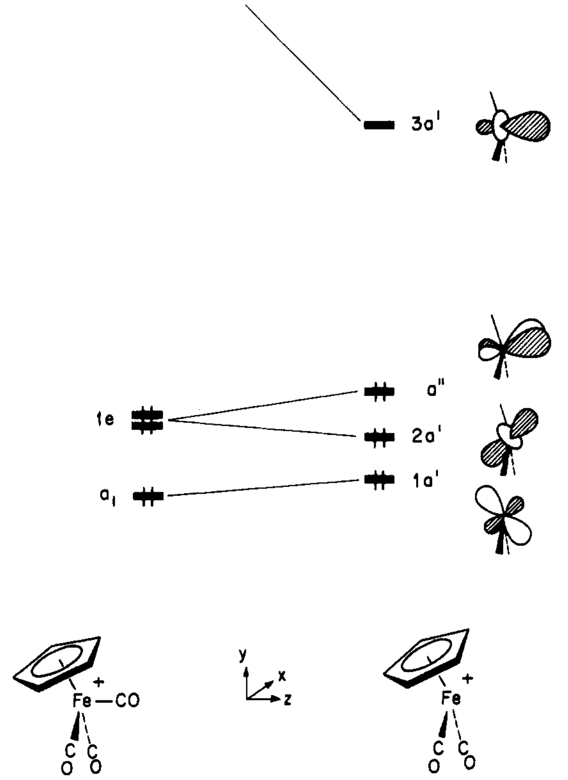
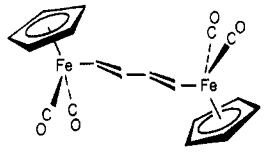


Figure 1. The valence orbitals of $CpFe(CO)_2^+$ generated from $CpFe(CO)_3$.

another Mp group by the ligand,[12] as exemplified by **4**,[12a] and those containing a metal-metal bond,[13] as in **5**.[13a] In com-



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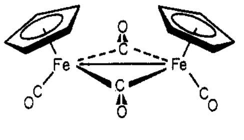

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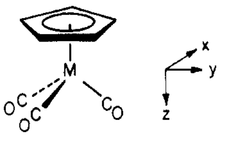
pounds of the latter category the Mp fragment often loses its integrity by bridging of the carbonyls.

This study aims at a general theoretical analysis of this interesting class of compounds. The fragment orbitals of $CpM(CO)_2$ are first constructed, using as a starting point previous studies of related systems such as $CpM(CO)_3$ and metal-carbonyl fragments.[14,15] This is then used as a basis for the description of the bonding with different ligands, with particular emphasis on understanding any conformational preferences and rotational barriers. The parameters of the extended Hückel method used in these calculations are specified in the Appendix.

The $CpM(CO)_2$ Fragment

The molecular orbitals of $CpM(CO)_2$ can be obtained in a number of ways,[16,17] but perhaps conceptually most instructive in the present case is to do so by removing one carbonyl group from $CpM(CO)_3$. The molecular orbitals of the latter have been extensively studied.[18] The natural coordinate system is, of course, one that orients the z axis along the fivefold axis of the Cp ring and the threefold axis of the $M(CO)_3$ fragment, as in **6**. The frontier levels of $CpM(CO)_3$ are easy to understand if it is remembered that the symmetry about the metal atom is approximately octahedral with near 90° C(O)-M-C(O) angles. There is a typical three below two splitting of the d block for the electronically pseudooctahedral complex. The three lower levels are an a_1 orbital, mainly metal z^2 in this coordinate system, and the 1e, mainly metal xy and $x^2 - y^2$. The a_1 orbital is slightly more stable than the 1e. The two higher orbitals, 2e, are mainly metal xz and yz. The orbital features of greatest consequence are already present in the orbital description of the $M(CO)_3$ portion of the molecule.[14] Interaction with the Cp ring causes some small mixing of the 1e and 2e orbitals and only slightly perturbs the energy of the a_1 and 1e.[18b]



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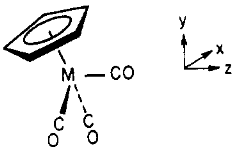
While coordinate system **6** is natural for the parent $CpM(CO)_3$, a choice more appropriate to the study of $CpM(CO)_2L$ with a wide variety of ligands is one which places the z axis along the M-L bond. The parent system is prepared for this in **7**. In this coordinate system the major contribution



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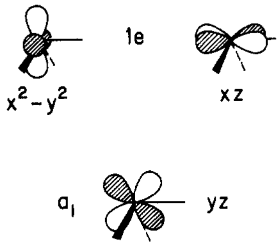
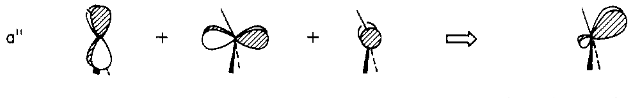
to the a_1 orbital of $M(CO)_3$ is yz, and the two 1e orbitals are predominantly $x^2 - y^2$ and xz.[14]



When a carbonyl group along the z axis is removed from $CpM(CO)_3$, the characters of the orbitals change only slightly. The valence orbitals of $CpFe(CO)_2^+$ are shown in Figure 1. The major effect of the loss of one ligand is the creation of a low-lying acceptor orbital, 3a', mainly z^2. This is what would be expected for a coordinatively unsaturated d^6 ML_5 fragment,[15] which $CpFe(CO)_2^+$ of course is, if one makes the isobal replacement of a Cp^- by three carbonyls. Removal of one CO also lowers the local symmetry about the metal, which necessitates a splitting of each e level into a' and a'', symmetric and antisymmetric orbitals with respect to the yz plane. Some mixing may occur between the 1a' orbital (originally a_1) and the 2a' orbital (originating from the 1e).

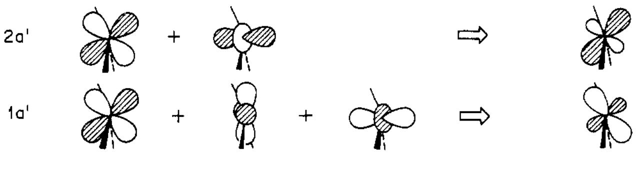
Contour plots of the four crucial orbitals are shown in Figure 2. The symmetric orbitals are plotted in the yz plane, the antisymmetric orbitals in a plane parallel and 0.2 Å from the yz plane. In order to anticipate the further discussion of the interaction of these orbitals with substituents bearing π-type donor or acceptor functions it is appropriate to comment here on the nature of the three lower orbitals.

The antisymmetric orbital a'' is particularly well set up for π interaction, as a result of some hybridization toward the vacant coordination site and its higher energy than 1a' and 2a'.

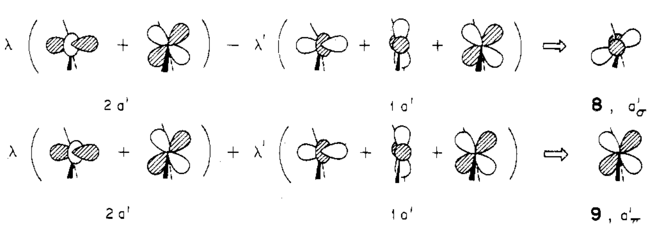


This is illustrated by the change in orbital energies shown in Figure 1, where removal of the stabilizing π interaction of one carbonyl group from $CpFe(CO)_3^+$ has the greatest effect on the a″ orbital energy. The 1a′ orbital is also slightly destabilized by removal of the CO from the z axis. This orbital has π interaction in the yz plane. The 1e orbital of $CpFe(CO)_3^+$, which correlates with the 2a′ orbital of $CpFe(CO)_2^+$, has much less π interaction with the leaving CO, and is the only orbital of the three which actually shows stabilization, albeit little.

The orbital contour diagrams are complicated by allowed mixing of the 1e and 2e in $CpM(CO)_3$, and by the further mixing of the 1a′ and 2a′ in $CpM(CO)_2$. The particular sense of hybridization in 1a′ and 2a′ shown below is worth noting. It will play a role when the incoming ligand is no longer "up-down" symmetric and so will probe the difference between 1a′ and 2a′.



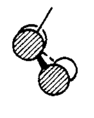
Both the symmetric orbitals will interact in σ and in π fashion with incoming ligands. This complicates the analysis, but a conceptual simplification of these interactions may be made by considering linear combinations of these orbitals, one that is set up mainly for σ bonding, **8**, the other for π bonding, **9**. The calculations show that the mixing specified by the coefficients λ and λ′ occurs to a different degree depending on the various ligands. But, as these combinations, to be called a'_σ and a'_π in the sequel, are simpler than 1a′ and 2a′, this viewpoint can be helpful in understanding the bonding pattern, and so will occasionally be utilized in the following discussion. One important point will emerge, and that is that a'_π, while it is well set up for π bonding, is not as effective at doing so as is a″.



σ Bonding

We studied a methyl complex, $CpFe(CO)_2CH_3$, as a prototype for a σ-bonding ligand. The interaction diagram is trivial in that the incoming CH_3^- base essentially restores the bonding pattern in $CpFe(CO)_3^+$ by a strong interaction between the CH_3^- lone pair and the low-lying 3a′ orbital. A similar analysis has been given in photoelectron studies of $CpM(CO)_2CH_3$, M = Fe, Ru.[17,19]

We also see some destabilization of a″ and a'_π by hyperconjugative interaction with the π-type orbitals of the methyl group,[20] one of which is shown in **10**. In a one-electron picture of the ethane barrier these methyl π-type orbitals play an important role.[21] The same orbitals are involved in producing a barrier to internal rotation around the Fe–C bond in $CpFe(CO)_2CH_3$. This we calculate is 2.9 kcal/mol, whereas a recent measurement[22a] gives 5.4 kcal/mol. Rotational isomerism in several complexes of this type has been studied.[22b]



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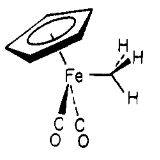

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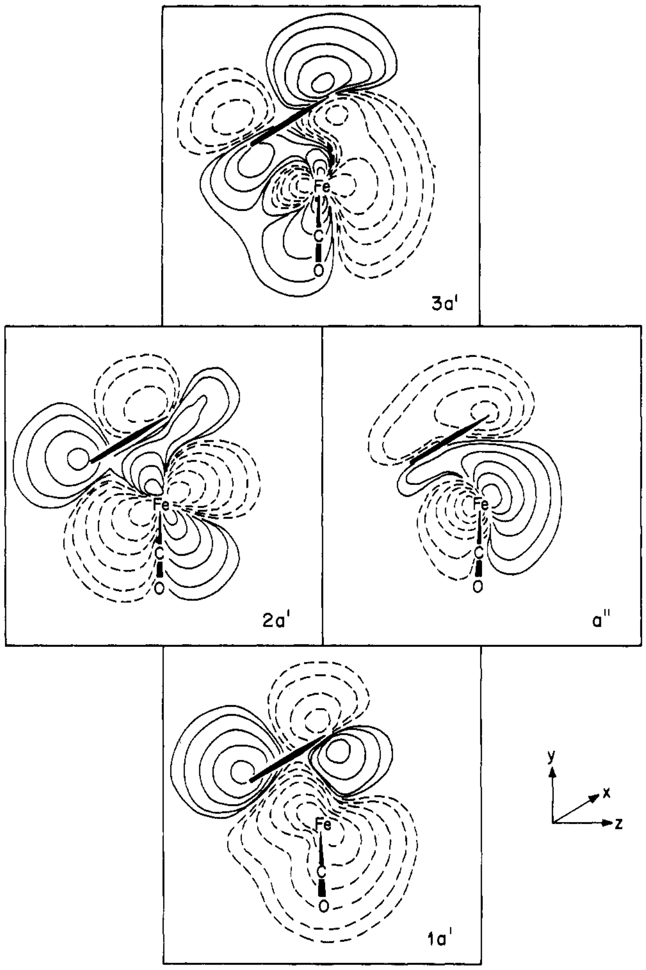
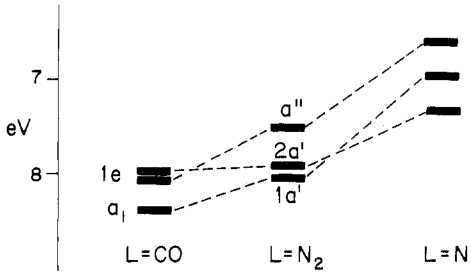


Figure 2. A plot of the four valence orbitals of a $CpFe(CO)_2^+$ fragment. The contour levels of ψ are 0.2, 0.1, 0.55, 0.025, 0.01, and 0.005. The symmetric orbitals are plotted in the yz plane, the antisymmetric orbitals in a plane parallel and 0.2 Å from the yz plane.

π Bonding and Sulfur Dioxide

The influence of ligands with π-back-bonding ability has been indicated. Basically, loss of π back-bonding along the z axis destabilizes the a″ and 1a′ orbitals relative to the 2a′. The relative shifts of these orbital energies are reflected in the metal ionization energies of $CpMn(CO)_2L$ in the series CO, N_2, NH_3.[17b,18b] The N_2 ligand is a slightly weaker σ donor and π acceptor than CO, and thus models the initial influences of removal of CO. The NH_3 ligand goes further in lacking π-acceptor ability. The observed metal ionization energies for these molecules are shown below. The metal ionizations of $CpMn(CO)_3$ indicate 1e slightly before a_1. The a″ and 1a′ ionizations are more affected by loss of π stabilization than the 2a



Sulfur dioxide in $CpMn(CO)_2SO_2$ also has π-acceptor orbitals, but the π* orbital normal to the plane of SO_2 is much

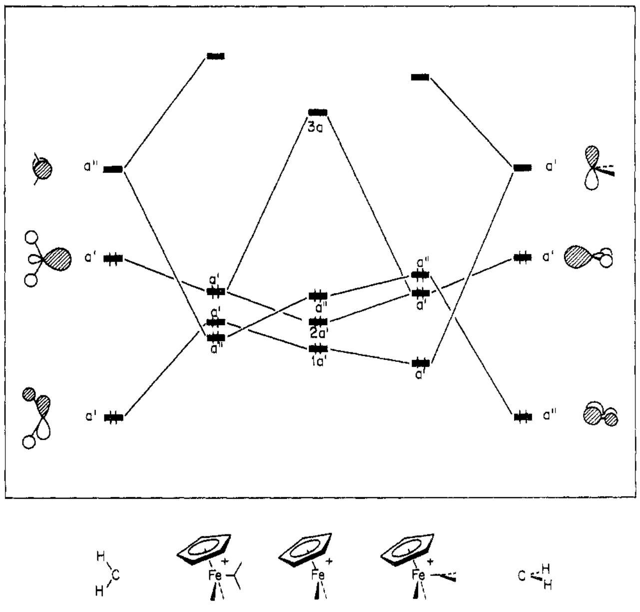
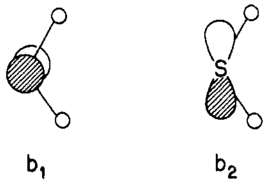
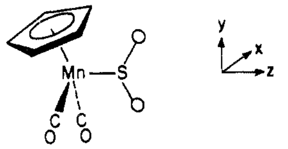


Figure 3. Orbital interaction diagram for $CpFe(CO)_2^+$ and a carbene in two different orientations, **12** and **13**.

lower in energy than the π orbital in the plane. Photoelectron spectroscopy combined with theoretical studies indicates that the b_1 is a better acceptor than one CO π orbital and the b_2 is poorer.[23] The crystal structure of $CpMn(CO)_2SO_2$ shows that the SO_2 portion is oriented in the *yz* plane.[6h] This orientation allows interaction between the best π-acceptor orbital of SO_2 and the best π-donor orbital of $CpMn(CO)_2$, the a″. The complete orbital interactions of SO_2 with $CpMn(CO)_2$ are very similar to the case of carbene complexes, discussed in detail in the next section.

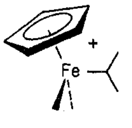




Carbene Complexes

In the carbene complex $CpMn(CO)_2(C(COPh)(Ph))$[6a]and the related acyl $CpMn(CO)_2(C(O)Ph)^-$ [6b] the orientation of the ligand is again such that the CR_2 plane coincides with the symmetry plane of the molecule, and in the latter the phenyl group is pointing toward the cyclopentadiene ring. This apparently sterically unfavorable orientation suggests that the factors governing the orientation of a carbene on a $CpMn(CO)_2$ fragment are electronic in character.

The interaction diagram for a CH_2 ligand and $CpFe(CO)_2^+$ is shown in Figure 3. The extreme orientations of the CH_2 plane relative to the Fp fragment are shown in **12** and **13** and in the two parts of the figure.



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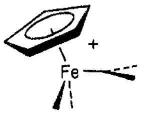

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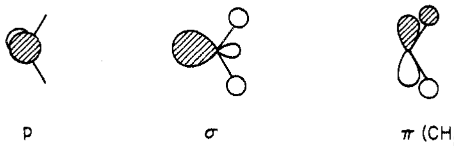
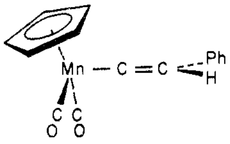
The important orbitals of the carbene are the empty p orbital, and the σ lone pair on carbon.[20b,24] Lower in energy is a π-type orbital of the CH_2 group.



The major factor governing the choice of orientation is the interaction of carbene p with a″ in orientation **12**, compared to its interaction with 1a′ in **13**. The relevant overlaps are shown in **14** and **15**. The energy criterion[25] also favors structural type **12**. The carbene lone pair, σ, interacts mainly with 3a′, the z^2 orbital. The bonding combination of these two is pushed up by the lower lying symmetric orbitals. This process, however, is very similar in the two orientations and does not contribute to the rotational barrier. The computed barrier is 6.2 kcal/mol favoring **12**, the "upright" conformation. This is in agreement with the equilibrium conformations indicated by the cited structural studies.

14 **15**

An interesting extension of the above analysis applies to the extended carbene or imine complexes in which several carbon atoms are interposed between the metal and the terminal CR_2 group.[26] Examples are the Mn and Mo systems **16**,[27] **17**,[28] and **18**.[29] In the first two complexes the structure determination indicates that the plane of the carbene bisects the molecular symmetry plane. In the case of **18** the structure is not known, but NMR evidence indicates that the two substituents are equivalent.



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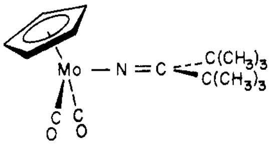

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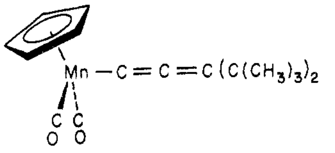


18

The characteristic feature of this type of complex is the presence of one or more π bonds between the metal fragment and the carbene. The preferred orientation, as was discussed above, will align an empty p orbital of the carbon fragment antisymmetric with respect to the mirror plane, so as to interact optimally with the metal a″. In the carbene, CH_2, this meant having the hydrogens in the plane of symmetry but, when π bonds are introduced, the preferred orientation is changed by a series of 90° twists. This is shown below, the carbene p orbital singled out in each case by an arrow.

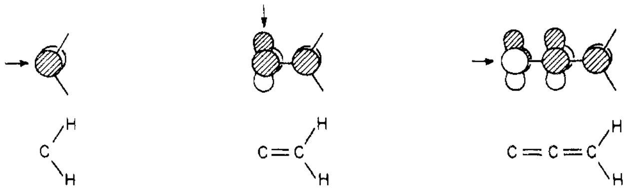


Table I. Acetylene Orbitals in CpM(CO)$_2$(acetylene)

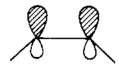
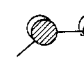
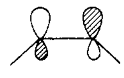
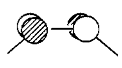
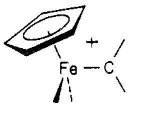
	 π_{a_1}	 π_{b_2}	 $\pi_{b_1}{}^*$	 $\pi_{a_2}{}^*$
22	a′	a″	a′	a″
23	a′	a′	a″	a″

Table II. Calculated Rotational Barriers (kcal/mol) in CpMo(CO)-L(acetylene)$^+$

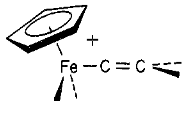
L	CO	CH_3	PH_3	NO^+	NO^-
barrier	13	17	17	4	22

The computed barriers and equilibrium conformations are shown below in **19–21.** The barriers decline along the series. The reason for this trend may be found in a detailed analysis of the balance of attractive interactions with carbene p and repulsive ones with π (CH$_2$), but is not given here. From this analysis we predict that the structure of the complex CpMn(CO)$_2$C=C=CR$_2$ should have the plane of the CH$_2$ group coinciding with the symmetry plane of the molecule. The NMR results[29] would indicate that either this is not the case or that rotation of the carbon fragment is fast. The actual calculated barrier is small, 3.2 kcal/mol, which suggests the latter.



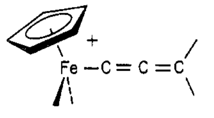
6.2 kcal/mole

19



3.6

20

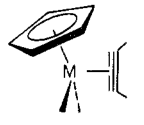


2.7

21

Acetylene and Ethylene Complexes

Rotational barriers in acetylene complexes of CpMLL′-(acetylene), M = Mo, Cr, W, have been studied[10] with conclusions that are not entirely consistent. The results seem to fall in two categories, a barrier of approximately 12–14 kcal/mol and a larger value of ~18 kcal/mol.[10] Some NMR investigations seem to indicate that the stable conformation of the acetylene is in the upright position, i.e., both carbons in the molecular symmetry plane,[10a] **22.** However, the configuration found in a crystal structure[7a] has the acetylene bisecting the symmetry plane of the molecule, **23,** with the hydrogens bent back in typical coordinated acetylene fashion. Our calculations[30] yield as the preferred conformation **23,** by an energy which varies with electron count, as will be discussed below.



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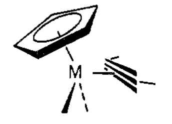


23

The acetylene orbitals which enter into the bonding are the two π and the two π^* levels. The local symmetry of the M-acetylene piece is C_{2v}, which is reduced in two different ways to C_s in conformations **22** and **23.** To simplify the group theoretical problem Table I shows the four orbitals, labels them in local C_{2v} symmetry, and shows the transformation properties in the two C_s modes.

One of the acetylene π^* orbitals is of local a$_2$ symmetry. Though it becomes a″ in the complex, the a$_2$ pseudosymmetry prevents it from significant interaction. Interaction with another one of the acetylene orbitals, π_{a_1}, is approximately balanced in the two geometries. The rotational preferences arise from the differential interaction of the π_{b_2} and $\pi_{b_1}{}^*$ orbitals. Figure 4 shows an interaction for CpMo(CO)$_2{}^-$ with an acetylene. The reason for examining Mo is that several of the known acetylene complexes contain this metal or Cr or W. The major change on going from Fe to Mo in the CpM(CO)$_2$ fragment is the reduction of splitting between a″ and 2a′, and less mixing between the d orbitals. The calculations were also carried out for Fe and the conclusions drawn were the same.

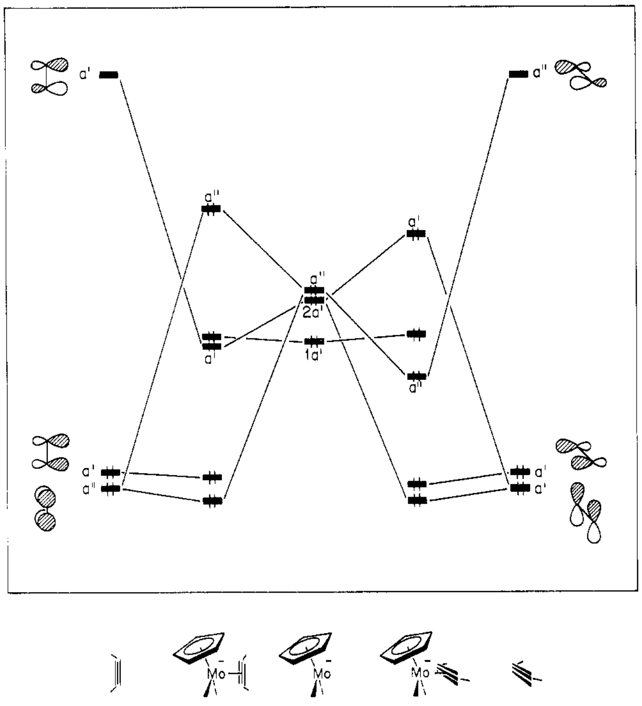


Figure 4. The orbital interaction diagram for CpMo(CO)$_2$(acetylene)$^-$ in the conformations **22** and **23.**

The governing factor again is the better overlap of a″, compared to a′$_\pi$, with the acetylene orbitals of the appropriate symmetry. In the upright conformation **22** the acetylene π acceptor orbital ($\pi_{b_1}{}^*$) is a′ and the π donor orbital (π_{b_2}) is a″. In geometry **23** the acetylene acceptor orbital is a″ and the donor orbital is a′. The maximum two-electron stabilizing interaction is thus achieved in the bisecting geometry **23.** At the same time the acetylene donor–metal fragment interaction is minimized. This interaction produces a relatively high-lying orbital, a″ in **22,** a′ in **23.**

The calculated barrier for the d^4 system CpMo(CO)$_2$-(acetylene)$^+$, where the highest lying MO in Figure 4 is vacant, is 13 kcal/mol, favoring geometry **23.** Only the first of the two factors mentioned above is operative here. Adding two further electrons to reach the d^6 system occupies the HOMO of Figure 4 and brings an additional repulsion into play favoring the bisected geometry **23.** The computed barrier is 23 kcal/mol for CpMo(CO)$_2$(acetylene)$^-$ or 19 kcal/mol for CpFe-(CO)$_2$(acetylene)$^+$.

The calculated equilibrium conformation agrees with that found in a crystallographic study. The systems studied in probing the rotational barrier, however, generally do not bear a symmetric fragment. This may have a serious effect on the rotational barrier.[31] In the context of a theoretical study of asymmetric complexes of this type, reported in the adjoining paper, we computed rotational barriers in CpMo(CO)-L(C$_2$H$_2$)$^+$ complexes with the range of results shown in Table II. Details of the role played by the other ligands will be given elsewhere.[32]

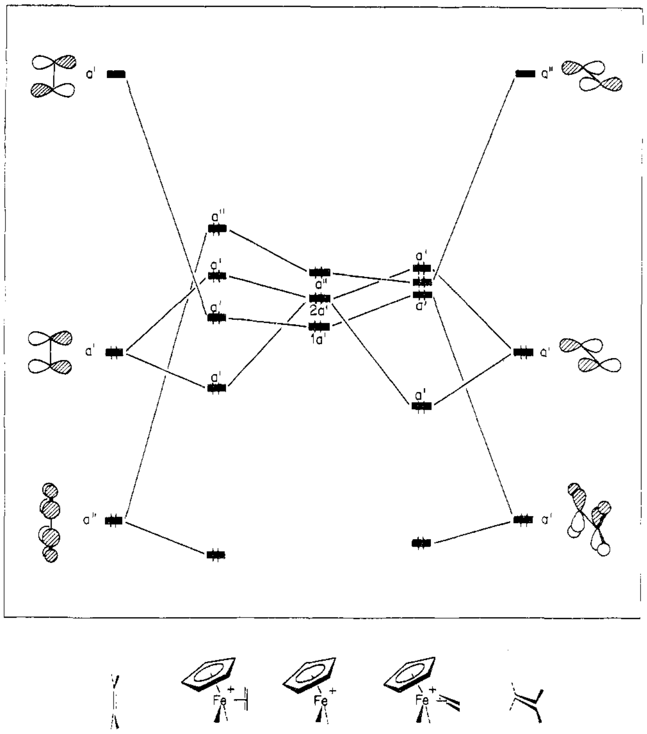
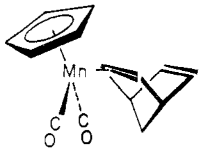


Figure 5. Interaction diagram for $CpFe(CO)_2^+$ and ethylene in the upright and bisecting position.

Rotational barriers in $CpM(CO)_2$-ethylene complexes have been found to be of the order of 8–10 kcal/mol.[11] The structural data cover a variety of complexes both with a conventional ethylene unit bonded to the metal,[8a–i] where **24** and **25**



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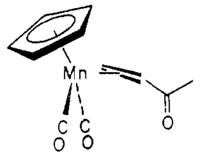
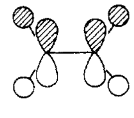


25

are examples, or complexes with heteroatoms involved in the π system, compounds such as $CpMo(CO)_2(RN{=}O)$ and $CpMo(CO)_2(H_2C{=}SR)$.[8j,k] The crystal structures uniformly have the ethylene bisecting the mirror plane of the fragment. This orientation is also observed when the carbon skeleton is an allene, which then bonds with one part in ethylene fashion.[33]

The bonding pattern of Fp-ethylene is in many ways similar to that in the acetylene complexes. One of the π orbitals is preserved, but the other is replaced by the lower lying σ_π orbital of ethylene,[20b] **26**. The interaction of the π^* and π is changed



26

only little from the acetylene system. The low-lying σ_π, which plays the same role as π_{b_2} in acetylene, is here far removed in energy, but the hybridization of a″ enhances overlap with this particular orbital. The interactions for ethylene in the two different orientations are shown in Figure 5. As in the acetylene case, the d^6 systems have the destabilized a″ or a′ filled, which gives a two-orbital four-electron repulsion. The result is a very large calculated barrier to rotation of 21 kcal/mol, larger by a factor of 5 than the observed rotational barriers.[11] The $CpM(CO)_2$ unit was not optimized during the rotation, which no doubt leads to an exaggerated barrier. In general extended Hückel energy differences are not reliable but must be viewed as indicative of trends.

Table III. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	$c_1{}^a$	$c_2{}^a$
Fe 3d	−12.70	5.35	1.80	0.5366	0.6678
4s	−9.17	1.90			
4p	−5.37	1.90			
Mo 4d	−10.50	4.54	1.90	0.6097	0.6097
5s	−8.34	1.96			
5p	−5.24	1.92			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
H 1s	−13.60	1.30			

[a] Contraction coefficients used in the double ζ expansion.

The bisected equilibrium geometry is to be expected only in the case of two identical ligands on the metal and a symmetrically substituted olefin. In other cases quite sizable deviations from this conformational extreme must be expected. These, along with the electronic structure of $CpM(CO)_2$(allyl) complexes and the intriguing role of asymmetry in the reactions of CpMLL′(allyl) compounds, are discussed in the adjoining paper.

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Appendix

The calculations were performed using the extended Hückel method[34] with parameters taken from earlier work.[14,35] H_{ii}'s and orbital exponents are listed in Table III. All C(O)–M–C(O) and C(O)–M–L angles were kept at 90°. In the $CpM(CO)_2$ fragment the angle between the normal to the Cp ring and the carbonyls was 127.6°. M–C(Cp) was taken as 2.09 Å, CC within the Cp ring as 1.43 Å. The M–C(O) distance was kept at 1.75 and 1.97 Å for Fe and Mo, respectively, and all M–L distances were set to 2.0 Å. The C–C distance in acetylene was 1.29 Å, in ethylene 1.37 Å, and all C–H distances were set to 1.09 Å.

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