(38) H. W. Vos, Y. W. Bakker, C. MacLean, and N. H. Velthorst, *Chem. Phys. Lett.*, **25**, 80 (1974).
(39) P. S. O'Sullivan and H. F. Hameka, *J. Am. Chem. Soc.*, **92**, 1821 (1970).
(40) (a) Davies[41] has stated the opinion that ". . . the comparative success of London's method for aromatic hydrocarbons may be attributed to the dependence of the theoretical anisotropy on the square of the area of the rings in a molecule" and that ". . . any method that takes this into account is likely to give reasonable results for the ratio . . ." of a given calculated anisotropy to that calculated, by the same method, for benzene. We might also add that, at least for paramagnetic systems of the type considered here, another important requirement for obtaining 'reasonable' ratios is the use of a π-electron wave function which is iteratively self-consistent with respect to atomic charges and bond orders. (see subsection 4 of this section).
(41) D. W. Davies, *Trans. Faraday Soc.*, **57**, 2081 (1961).
(42) These are the quantities which, in ref 32, are called the "integrated π-electron current densities" associated with the various rings of a given polycyclic, conjugated system.
(43) J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, Oxford, 1932.
(44) Such a connection has been suggested[45a] and the proposal has been much taken up, the latest instance being in a recent study[45b] of the "aromatic character" of certain five-membered heterocyclic systems. For a vehement criticism of the idea, see ref 45c and 45d and, for a less forceful (though equally cogent) one, based on calculations of the type presented here, see ref 14b. In a very recent paper[45e] Benassi et al. address themselves to the whole question of magnetic criteria for aromaticity. (See also ref 6f and 45f,g.)
(45) (a) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961); (b) E. Corradi, P. Lazzeretti, and F. Taddei, *Mol. Phys.*, **26**, 41 (1973); **27**, 1439 (1974); (c) J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965); (d) *Adv. Magn. Reson.*, **2**, 177 (1966); (e) R. Benassi, P. Lazzeretti, and F. Taddei, *J. Phys. Chem.*, **79**, 848 (1975); (f) J.-F. Labarre and F. Crasnier, *Fortschr. Chem. Forsch.*, **24**, 33 (1971). (g) See also several articles in the "Jerusalem Symposium: Aromaticity, Pseudo-Aromaticity and Anti-Aromaticity", E. D. Bergman and B. Pullman, Ed., Israel Academy of Sciences and Humanities, Jerusalem, 1971.
(46) NOTE ADDED IN PROOF (by R.B.M., December, 1975). (a) In a very recent article in this journal, Wilcox et al.[46b] have given a discussion (very similar to that in section 4 of the present Results and Discussion, and in Conclusions) concerning the occurrence of paramagnetic "ring currents" in the polycyclic hydrocarbon, cyclooctа[*def*]biphenylene. They have also examined the inferences which may, or may not, properly be drawn on this basis about the "aromaticity", or otherwise, of that conjugated system. (b) C. F. Wilcox, J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *J. Am. Chem. Soc.*, **97**, 1914, (1975). (c) In order to test the predictions made in the present paper about the π-electron magnetic properties of the (as yet hypothetical) molecule, dipleiadiene (VI), my colleagues I. P. Field, D. Franks, and M. C. Grossel (Christ Church, Oxford) are currently engaged on a synthesis of this molecule. It is hoped that their findings will be published in a future issue of the journal.

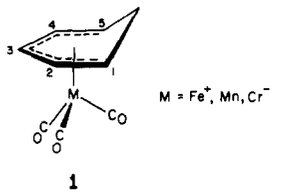
The Electronic Origin of Geometrical Deformations in Cyclohexadienyl and Cyclobutenyl Transition Metal Complexes

Roald Hoffmann* and Peter Hofmann

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received May 19, 1975*

Abstract: A case is presented for an electronic factor in the out-of-plane bending of the saturated carbon in cyclohexadienyl-$M(CO)_3$ complexes, M = Fe^+, Mn, Cr^-. In the cyclohexadienyl ligand hyperconjugation extends the nonbonding MO wave function to the methylene hydrogens. The phase of the CH_2 hydrogen contributions to that MO is such that when the C_6H_7 ligand is bound to the $M(CO)_3$ group there arises a secondary M-CH_2 interaction which is destabilizing. In cyclobutenyl and cyclooctatrienyl complexes this interaction is lacking and thus these should be less bent than cyclohexadienyl complexes. A similar analysis rationalizes the bending away from the metal in cyclopentadiene-$Fe(CO)_3$ complexes, its lessening in cyclopentadienone complexes, and the bending toward the metal in fulvene or cyclopentadienyl-carbonium ion complexes. The charge distribution and substituent effects in $C_6H_7M(CO)_3$ complexes are examined, as well as a case of hypothetical isomerism in benzyl-$M(CO)_3$.

There exists a substantial chemistry of transition metal complexes of cyclohexadienyl and cyclobutenyl ligands, exemplified by structure **1**. Examples exist for M = Fe^+, Mn, Cr^-, and their lower transition series analogues. The assign-



1

ment of a formal charge to the metal is, of course, arbitrary. Nevertheless it focuses on the basic electronic similarity of these complexes, an aspect that might be obscured by an argument over the cationic or anionic nature of the coordinated cyclohexadienyl ligand.

In all known structures of type **1** the six-membered organic ring is highly nonplanar, and distorted in the same way—atoms 1 through 5 remain in an approximate plane, but the saturated carbon 6 moves out of that plane and away from the metal. The dihedral angle between planes 165 and 12345 takes on values of 43° in $C_6H_7Mn(CO)_3$,[1] 39° in dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron,[2] 50° in $C_6(CH_3)_6HRe(CO)_3$,[3] 40° in (2-methoxycyclohexadienyl)$Fe(CO)_3^+$,[4] 41° in tricarbonyl(bis(ethoxycarbonyl)methyl)cyclohexadienylmanganese,[5] 43° in a complex of a somewhat different but related type, bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyliron),[6] and angles of approximately 45° in structures of three substituted 1,2-dihydropyridinechromium tricarbonyl complexes.[7,8]

It should be noted that the free organic ligand is either planar or only moderately distorted. In the crystal structure of the tetrachloroaluminate salt of the heptamethylbenzenonium cation, **2**, the six-membered ring is essentially planar.[9] However, in three recent structures of stabilized σ complexes, **3**,[10] dihedral angles up to 17° have been found.[11] Stabilized anionic σ complexes, that is Meisenheimer complexes, have been known for some time.[12] Several crystal structures of such highly substituted cyclohexadienyl anions are available,[13] and in all the six-membered ring is approximately planar. The problem of potential nonplanarity of cyclohexadienyl radicals has been discussed recently.[14]

At any rate it is clear that upon formation of a transition metal complex there is a significant enhancement of the

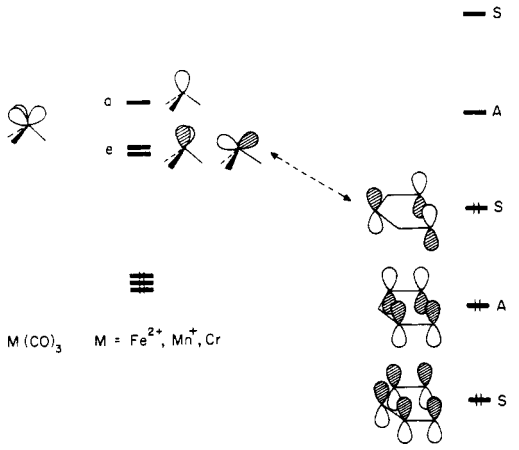
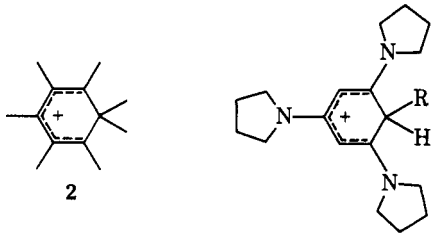


Figure 1. Interaction diagram for pentadienyl-$M(CO)_3$. At right are the pentadienyl π orbitals, at left the $M(CO)_3$ valence orbitals. The dashed line marks the strongest interaction.



2 3

a, R = H
b, R = CH_3
c, R = Br

nonplanarity of a cyclohexadienyl ring. If one inquired after the reasons for this distortion, it is likely that the deformation would be attributed to one of the following causes. (a) "Rehybridization for better metal–ligand overlap." The reference is to the termini of the π-electron system. A rehybridization from trigonal toward tetrahedral coordination at carbons 1 and 5 and/or a rotation around the 12 and 45 bonds might produce a better overlap between the metal orbitals and those of carbons 1 and 5. Such distortions are common in transition metal complexes.[15] In the specific case of pentadienyl complexes there exists a structure of an open chain pentadienyl-$Mn(CO)_3$ complex in which the terminal methylene is reported to be significantly twisted out of the plane of the five carbon atoms.[16] (b) "Steric hindrance between the metal and the saturated carbon, with its bonded atoms." (c) "Readjustment of ligand geometry to changes imposed by metal complexation." The reference here is to the abnormally large 612 and 456 angles that would result unless the CH_2 group moves out-of-plane.[7] The purpose of this contribution is to suggest that there is an electronic component which contributes significantly to the observed deformation.

Figure 1 shows an interaction diagram for the formation of a pentadienyl–metal tricarbonyl complex. The electronic configurations of the fragments are to some extent arbitrary, but are shown for $Fe(CO)_3^{2+}$ and a pentadienyl anion. The number, position in energy, and shape of $M(CO)_3$ valence orbitals have been discussed in a previous paper.[17] Figure 1 singles out one of the many interactions in the complex bonding pattern, in fact the most important one, between the nonbonding MO of pentadienyl and an acceptor orbital of $Fe(CO)_3$. The occupied bonding combination which results from this interaction is shown in **4**.[18] But the nonbonding MO of cyclohexadienyl differs somewhat from that of pentadienyl. The saturated CH_2 group σ and

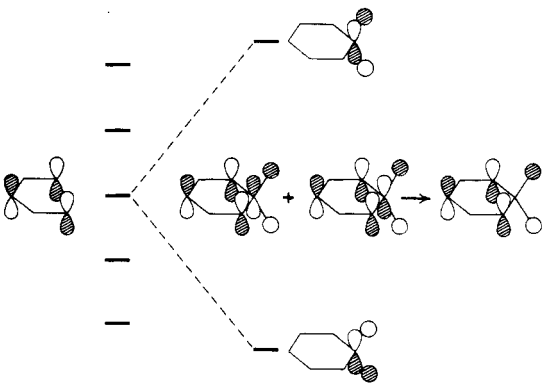
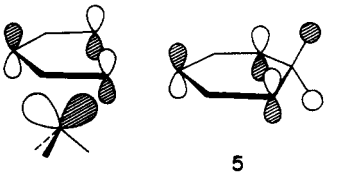


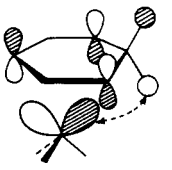
Figure 2. A perturbation theoretic construction of the cyclohexadienyl nonbonding orbital. It arises from the mixing of the CH_2 σ in an antibonding way and CH_2 σ^* in a bonding way into the pentadienyl nonbonding MO.



4 5

σ^* orbitals have the correct symmetry to mix into the pentadienyl nonbonding MO, and so they do, in a manner easy to analyze[19] (Figure 2). The orbital resulting from this hyperconjugative interaction is shown in **5.** It has a contribution at the saturated methylene group, especially at the hydrogens. The experimental confirmation of a significant density at those hydrogens comes from the large hyperfine splitting of 48 G of the methylene protons in the EPR spectrum of the cyclohexadienyl radical.[20]

Most important, the phase relationship of the methylene hydrogens is *opposite* to that of the 2p orbital contributions at carbons 1 and 5 of the pentadienyl chain. It follows that when the cyclohexadienyl is complexed by an $M(CO)_3$ group that there is a secondary antibonding interaction between the metal and the lower methylene hydrogen, as illustrated in **6.** Molecular orbital calculations which will now



6

be described lead us to the conclusion that the significant out-of-plane bending of the methylene group can be traced in a large part to efforts by the molecule to avoid this secondary antibonding interaction.

The molecular orbital calculations are of the extended Hückel type, and are described in the Appendix. The conclusions we draw are based on the following observations.

(1) Assuming a somewhat idealized geometry for $C_6H_7Fe(CO)_3^+$, but one based on the available crystal structures, we computed a potential energy curve for moving the CH_2 group out of the plane of the five other carbons. The results are shown in Figure 3. Two alternative assumptions were made concerning the location of the hydrogens at positions 1 and 5. In the first case, marked by a solid line in Figure 3, the hydrogen positions were kept fixed in the five carbon plane as the CH_2 group swung up above that plane. In the second case, the dashed line of Figure 3,

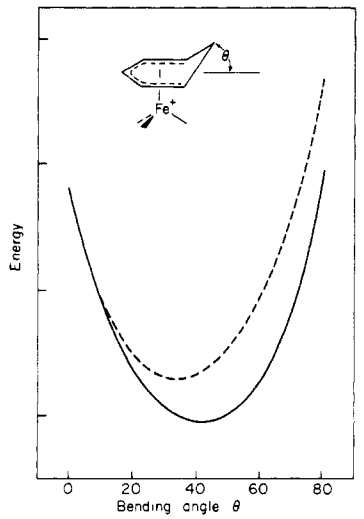


Figure 3. Calculated energies for CH_2 bending up in $C_6H_7Fe(CO)_3^+$. Solid line = hydrogens at 1 and 5 kept fixed in their original positions in five carbon plane. Dashed line = hydrogens allowed to follow bending motion as described in text. The vertical scale markings are separated by 1.0 eV.

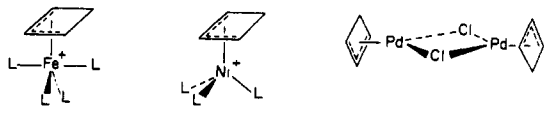
the hydrogens were allowed to follow the CH_2 bending in a restricted way. They were placed in the 1-2-6 (or 4-5-6) plane, along the bisector of the 126 angle, and in that fashion moved down below the five carbon plane as the bending proceeded. From the figure it is seen that the restricted hydrogen relaxation we allowed is not a stabilizing motion.[21] The computed bending minimum, at approximately 40°, is in reasonable agreement with the available structural information. Incidentally, a calculation on the free $C_6H_7^+$ ligand shows a preference for a planar geometry, though the barrier to small excursions from planarity is soft.[22]

(2) Assuming a "planar" ligand structure, we optimized the position of the $Fe(CO)_3$ group with respect to lateral displacements in the mirror plane of the complex. If the reference point is defined as Fe below the center of the ring (in turn defined by the intersection of the 13, 24, and 35 vectors), then if the ring was kept planar, the $Fe(CO)_3$ preferred to move over 0.5 Å toward C_3, that is away from the methylene group. When the methylene group was bent up 40°, the $Fe(CO)_3$ moved back, finding a minimum displaced only 0.2 Å toward C_3 from the center reference position. We interpret this behavior as a manifestation of a repulsive interaction between the metal and the saturated site in the planar geometry.

(3) A detailed analysis of the overlaps and orbitals shows that in the case of a planar ring there are significant overlaps between metal orbitals and the lower hydrogen at C_6. Furthermore, the repulsive interaction, which is diminished as the CH_2 group bends up, can be traced orbital by orbital to the highest occupied MO of the complex, which has just the shape of **6**. A breakdown of the AO contributions to the destabilization of this orbital confirms the importance of the postulated secondary effect.

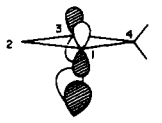
While we are convinced that this secondary destabilizing effect is what dominates the bending, we doubt if anyone else would abandon the "rehybridization for better metal–ligand overlap" argument on the basis of what we have presented up to this point. But there is more to our case.

Consider the family of cyclobutenyl complexes, represented by three idealized structures **7**, **8**, and **9**, where L is a neutral ligand such as CO. The structures are drawn with a neutral allyl group, and the charge on the metal, but of course this is a formalism. Representatives of **7**,[23] **8**,[24] and **9**[25] are known, with only a few crystal structures available.



7 8 9

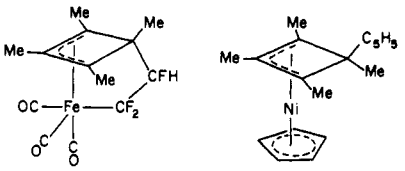
In these complexes the most important bonding interaction will be between the nonbonding allyl MO and a matching metal fragment orbital, **10**.[26] The allyl orbital, being an-



10

tisymmetric with respect to the plane containing the metal, C_2, and C_4, has no contribution at the methylene hydrogens. The antibonding secondary interaction used by us above is not present. In these molecules the methylene group should bend up less than in cyclohexadienyl complexes.

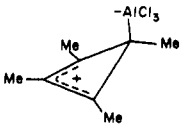
The structural evidence at hand is the following. A molecule of type **7**, specifically structure **11**, exists and must have a small dihedral angle.[27] However, the trifluoroethylene bridge imposes a strong structural constraint. In a



11 12

structure of type **8**, 1-keto-2,3,4-triphenylcyclobutenyl-$Co(CO)_3$, the bending angle is 11°.[24c] Two structures of type **9** are available, being an isomeric compound with respect to the attachment of phenyl and ethoxy groups at the saturated carbons. The molecular structures show dihedral angles of 22° and 27°. A third structure is of compound **12**, related to structural type **8** if one replaces three ligands by a pentahaptocyclopentadienide. The angle of bending in that structure is 25°.[28]

The range of these angles is not impressive until one compares them with the free ligand. There is a general dearth of structural data on cyclobutenyl cations or anions, but we do have some information. From NMR studies of various cyclobutenyl cations in strong acid media there comes evidence that these cations are nonplanar.[29] Theoretical studies indicate the same.[30] One available molecular structure is that of the σ complex of tetramethylcyclobutadiene and aluminum trichloride, shown in **13**.[31] The observed dihedral angle is 31.5°. Electrostatic factors could contribute to the bending in this zwitterion. Another structure is that of the 4-chloro-1,2,3,4-tetraphenylcyclobutenium cation, and that has a planar four-membered ring.[32] The two structures do not give us a consistent picture of the bending tendencies of



13

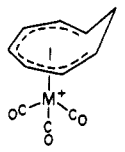
the free ligand. Concerning the cyclohexadienyl case, we could clearly say that in the metal complex the ligand is more bent than when it is free. In the cyclobutenyl case we

must reserve judgment, but we do note that the net bending in the complex is less than in the cyclohexadienyl case.

The contrast between the four- and six-membered ring cases is thus more impressive than either case by itself. It should be noted that one might have expected the cyclobutenyl complexes to be more bent. This expectation is based on the known geometrical preferences of coordinated allyl groups. In such complexes the metal atom is not directly below the allyl plane, but displaced to the side, so that the dihedral angle between the planes formed by the three allyl carbons and the metal plus the two terminal carbons is greater than 90°.[33] Such a positioning of the metal atom would in the cyclobutenyl case lead to a still shorter metal–CH_2 contact. It should be noted that we do not claim that bending should be absent in the cyclobutenyl complexes. Model molecular orbital calculations indicate bending, though less than in the cyclohexadienyl complexes. Moreover, the bending in the cyclobutenyl complexes can be traced to four-electron destabilizing interactions between lower-lying filled symmetric orbitals. Such interactions are the molecular orbital equivalent of steric repulsions.

A referee has pointed out that a remarkable feature of the cyclohexadienyl complex structures is the relatively small angle at the saturated carbon. This angle ranges between 100 and 104° in the observed structures,[1-7] compared to 114–115° in uncomplexed cyclohexadienyl cations.[9,11] Our theory does not appear to provide an explanation for the smaller angle, while the considerations of Churchill and Scholer[1] and of Huttner and Mills[7] do furnish a rationalization.

Returning to the experimental implications, an obvious extension of our arguments is to the class of cyclooctatrienyl or homotropylium complexes with $M(CO)_3$, M = Cr, Mo, W, illustrated in **14.** The heptatrienyl nonbonding MO



14

is antisymmetric, and so we would not expect a repulsive secondary interaction enhancing bending. Such complexes are known.[34] No structural information is available on either the free homotropylium ion[35-37] or its metal complexes. The NMR spectra of the complexes strongly resemble those of the uncomplexed cation,[34a,d,38] especially in the large differential between the chemical shifts of the two saturated protons. This has been reasonably interpreted as indicating similar homoaromatic and therefore presumably significantly bent structures for the free ligand and its complex. Whether the orbital effect we propose plays a role must await more detailed structural investigation.

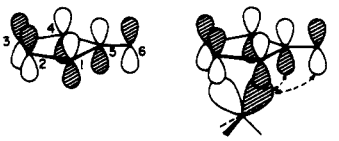
The bending of a saturated bridge away from the metal fragment is not peculiar to polyenyl–transition metal complexes, but is a common occurrence in complexes of polyenes as well. To a variable extent the saturated bridge in all cyclopentadiene and 1,3-cyclohexadiene complexes is bent in just such a manner. Some typical dihedral angles are 38° in $(CH_3)_2Re(Cp)(\eta^4$-methylcyclopentadiene),[39] 36.5° in $CpCo(\eta^4$-phenylcyclopentadiene),[40] and 47.3° in (octafluorocyclohexadiene)$Fe(CO)_3$.[41] The bending has been perfectly well interpreted in terms of rehybridization at the polyene termini for better metal–ligand bonding, associated with increasing donation into ψ_3 of butadiene, its symmetric LUMO.[42]

The secondary effect we discuss for cyclohexadienyl complexes is also present in these molecules. First the interaction diagram for a butadiene–$Fe(CO)_3$ resembles Figure 1. The most important interaction is between one component of the $Fe(CO)_3$ fragment e orbital and the LUMO of butadiene, ψ_3. The LUMO of cyclopentadiene or cyclohexadiene is modified from ψ_3 of butadiene in a way that is very similar to the cyclohexadienyl case. There is significant hyperconjugation with the CH orbitals of the saturated bridge. In the specific case of cyclopentadiene the LUMO is shown schematically below. Note the resemblance to **5.** We

15

would anticipate the secondary effect to be somewhat smaller in cyclopentadiene than in cyclohexadienyl complexes, because the crucial orbital of the former lies higher in energy and thus interacts less with the $Fe(CO)_3$. The observed bending, however, is comparable in the two types of complexes. An analysis similar to this one can be carried through for cyclic ligands containing a conjugated triene complexed to $Cr(CO)_3$. The crucial hyperconjugated orbital in these is the symmetric HOMO of the triene.

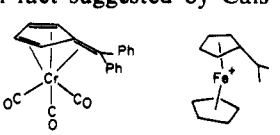
In cyclopentadienone complexes less bending is observed. By way of example one has dihedral angles of 9° in CpCo(tetramethylcyclopentadienone),[44] 21.3° in CpCo(tetra(trifluoromethyl)cyclopentadienone),[44] and 20.1° in $(CO)_3$Fe(tetra(trifluoromethyl)cyclopentadienone).[45] The cyclopentadienone LUMO is known to lie at very low energy.[46] It can be described as an in-phase mixture of ψ_3 of butadiene and the carbonyl π^* orbital, as shown below in **16.** Let



16 17

us reason as before, dividing up the interaction between the $Fe(CO)_3$ and the cyclopentadienone into a primary one, involving carbons 1, 2, 3, and 4, and a secondary one with carbon 5 and oxygen 6. As indicated in **17,** the secondary interaction has a bonding ($Fe–C_5$) and an antibonding ($Fe–O_6$) component, and should certainly be less antibonding than in the case of a methylene replacing the CO. This is then in accord with the lesser degree of bending in cyclopentadienones. We would not be surprised if a structure of a metal complex of a cyclopentadienone is found in which C_5 remains in the plane of the four other carbons, or even moves below it, while the exocyclic oxygen bends out of the plane, away from the metal.

Distortions by substituents on a polyene or polyenyl complex are not limited to motions away from the metal. It is clear that if the secondary interaction is a bonding or stabilizing one that the substituent involved may move toward the metal center. Such distortions have been observed for fulvene complexes, **18,**[47] and ferrocenyl carbonium ions, **19,**[48] and were in fact suggested by Cais[49] and predicted



18 19

from extended Hückel calculations by Gleiter and Seeger.[50] A detailed analysis of these systems, viewing both molecular types **18** and **19** from the starting point of a cyclopenta-

dienyl group carrying a carbonium ion substituent, finds two stabilizing secondary interactions responsible for the geometry change. The first is direct overlap of the carbonium ion center with metal z^2,[50] and the second is an improvement of the overlap of a cyclopentadienyl–carbonium ion fragment orbital with metal xz.

In the course of our studies of the cyclohexadienyl complexes we examined the electron distribution in the complexes as well as the effect of substitution at various sites. The following observations were made.

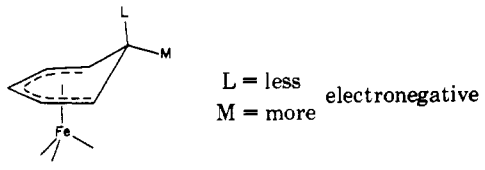
(1) As the metal atom in $C_6H_7M(CO)_3$ is changed from Cr^- to Mn to Fe^+, the calculated dihedral angle of bending increases slightly.

(2) The calculated charge distribution in the pentadienyl segment of the three complexes, all bent up 40°, is compared in Table I with the charge distribution in the anionic, radical, and cationic forms of the free ligand distorted in the same way. The total charges in the C_5H_5 segment show the expected—that the pentadienyl ribbon is more negative in $C_6H_7Cr(CO)_3^-$ than in $C_6H_7Fe(CO)_3^+$, but that the accumulation of charge is considerably attenuated in the complexes. In going from $C_6H_7^+$ to $C_6H_7^-$ the C_5H_5 ribbon gains 1.848 electrons, but in going from $C_6H_7Fe(CO)_3^+$ to $C_6H_7Cr(CO)_3^-$ it gains only 0.645 electron. The charge densities at the individual carbons are interesting—note that a strong charge alternation in the pentadienyl anion direction is maintained in $C_6H_7Mn(CO)_3$ and even $C_6H_7Fe(CO)_3^+$.

(3) When the cyclohexadienyl group is bent upon complexing, the two CH bonds at the CH_2 group become nonequivalent, and can be classified as exo (axial) or endo (equatorial). A concern with an anomalous CH stretching frequency assigned to the exo bond formed part of the motivation for the early structural studies of these complexes.[1] In our calculations there appeared a differential between the two C–H bonds consistent with a weaker exo bond, but the magnitude of the effect was small. For instance in $C_6H_7Fe(CO)_3^+$ the overlap populations of the CH bonds were 0.8062 endo, 0.7915 exo.

(4) We studied briefly the effect on the tendency of the cyclohexadienyl moiety to bend of substituents at the saturated site and the pentadienyl ribbon. This was carried out for substituted $C_6H_7Fe(CO)_3^+$ by computing the difference in energy between C_6H_7 planar and bent 40° and comparing that difference to the stabilization calculated in the absence of substitution. This procedure is no substitute for the computation of a full surface, but should be indicative. In all cases the effects were relatively small, but the direction interesting.

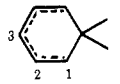
The primary factor influencing substituent site preferences at the saturated site appears to be ligand electronegativity. If L = a ligand less electronegative than H and M = a ligand more electronegative than H, then the favored substituent pattern is with L exo and M endo, as shown in **20.**



20

That pattern is preferred for both L and M present, or for either substituent alone. According to our calculations, there should be a greater degree of bending associated with the substitution pattern of **15,** while the opposite pattern should produce less bending. The substituent at the endo site appears to control the energetic situation to a greater extent.

Table I. Atomic and Total Charges in Free and Complexed Cyclohexadienyls

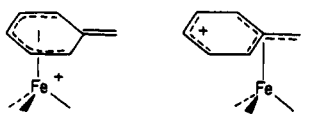


	3	2	1	Total[a]
$C_6H_7Cr(CO)_3^-$	−0.156	+0.031	−0.287	−0.568
$C_6H_7Mn(CO)_3$	−0.094	+0.070	−0.216	−0.289
$C_6H_7Fe(CO)_3^+$	−0.011	+0.113	−0.119	+0.077
$C_6H_7^-$	−0.352	−0.047	−0.373	−1.019
C_6H_7	−0.049	−0.046	−0.064	−0.095
$C_6H_7^+$	+0.255	−0.045	+0.244	+0.829

[a] Total charge on the five pentadienyl carbons and their bonded hydrogens.

In the case of substitution on the pentadienyl ribbon the π-donor or acceptor character of the substituents seems to influence the bending preference. There is more bending indicated with 1 or 3 substitution by donors, and the reverse effect for acceptor substitution at the same sites.

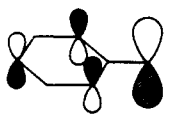
In the course of thinking about this problem we were led to consider substitution at the 6 position by a methylene group. The resulting structure, **21,** would still be expected to be bent. But an interesting point arises when one realizes that **21** describes an $Fe(CO)_3$ complex of the benzyl cation. An alternative structure for such a complex is **22,** in which



21 **22**

part of the benzyl ligand is complexed in a trimethylenemethane type mode and part is left as an allyl cation.

Our first inclination was to think that either **21** or **22** would be the stable point in the system. But consideration of the nonbonding benzyl orbital **23** reveals that while there



23

is good interaction between the $Fe(CO)_3$ acceptor orbital (the same one shown previously in **4, 6,** or Figure 1) and the nonbonding benzyl orbital when the iron fragment is under the center of the ring (corresponding to **21**) or under carbon 6 (**22**), the passage between these two geometries puts the iron fragment in a position where its interaction with the benzyl orbital is minimal. This was probed with a model calculation where the $Fe(CO)_3$ was moved along the molecular plane under a rigid benzyl group (Figure 4). There are two minima, corresponding to **21** and **22,** and a sizable barrier in-between them. The minima will deepen when geometric relaxation is allowed. Whether a barrier large enough to allow observation of both coordination modes will survive once structural relaxation is allowed remains to be seen. Another interesting possibility is the coordination of an $Fe(CO)_4$ fragment to the exocyclic double bond in **21** and the allyl cation in **22.** Incidentally our calculations for **22** indicate little positive charge on the allyl segment. While some benzyl complexes are known, for instance (η^3-benzyl)(η^5-Cp)M(CO)$_2$, M = Mo, W,[51] we have not been able

Table II. Parameters in Extended Hückel Calculations

	Orbital	ζ^a	H_{ii}(eV)		
	Fe 4s	1.575	−10.56		
	Fe 4p	0.975	−6.19		
	Mn 4s	1.450	−10.03		
	Mn 4p	0.900	−6.06		
	Cr 4s	1.325	−9.58		
	Cr 4p	0.825	−5.94		
Orbital	$\zeta_1{}^a$	$c_1{}^b$	$\zeta_2{}^a$	$c_2{}^b$	H_{ii}(eV)
Fe 3d	5.35	0.53659	1.80	0.66779	−13.50
Mn 3d	5.15	0.51391	1.70	0.69291	−12.43
Cr 3d	4.95	0.48761	1.60	0.72051	−11.38

[a] Slater exponent. Two are listed for the 3d functions. [b] Expansion coefficients in the double zeta function.

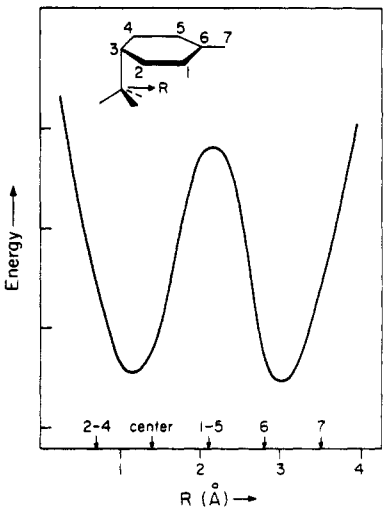


Figure 4. Potential energy curve for moving an $Fe(CO)_3$ fragment under a benzyl cation. The vertical scale markings are separated by 0.5 eV. The horizontal scale is marked in Å away from the initial position under C_3 (see inset-structure). The internal arrows mark special sites—"center" refers to a position under the center of the six-membered ring, "1-5" under midpoint of line joining C_1 and C_5, etc.

Acknowledgment. The stimulus to this work came from the Baker Lectures of J. Lewis and conversations with M. F. Semmelhack, whose group has demonstrated the synthetic utility of a set of reactions which likely proceeds through $C_6H_6LCr(CO)_3^-$ intermediates. We are grateful to the members of our research group for their comments. The stay of P.H. at Cornell was made possible by a fellowship from the Deutsche Forschungsgemeinschaft. Our work at Cornell was generously supported by the National Science Foundation and was assisted by the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

Appendix

All calculations were performed using the extended Hückel method.[54] Reasonable diagonal matrix elements for iron were obtained by a charge iterative calculation on $(C_6H_7)Fe(CO)_3^+$ with a geometry taken from an x-ray structure determination of (2-methoxycyclohexadienyl)-$Fe(CO)_3^+$.[4] The basis set of valence AO's for Fe consisted of 3d, 4s, and 4p, the latter being single Slater-type orbitals whereas the 3d functions were taken as contracted linear combinations of two Slater-type wave functions. The orbital exponents are those of Richardson et al.[55] H_{ii}'s as well as orbital exponents for carbon, oxygen, and hydrogen were those used previously[54] and were kept fixed during charge iteration. A quadratic dependence of the H_{ii}'s of Fe was assumed.[56] A modified Wolfsberg-Helmholz formula was used,[57] with $K = 1.75$.

$$H_{ij} = \frac{[K - (K-1)\Delta^2]S_{ij}}{2}[(1+\Delta)H_{ii} + (1-\Delta)H_{jj}]$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}$$

Separate charge iterations were carried out for $C_6H_7Mn(CO)_3^-$. The converged H_{ii} values and other parameters used are given in Table II.

All calculations for ligand distortions, etc., were then done by a noniterative usual extended Hückel scheme. The following geometrical assumptions were made. (A) Cyclohexadienyl ligand: pentadienyl fragment CC, 1.40 Å; C-H 1.08 Å; $C-CH_2$, 1.50 Å; HC-H, 1.10 Å, angle HCH, 109°; angle CCC in pentadienyl fragment 120°. (B) Cyclobutenyl ligand: allyl fragment CC and CH as in pentadienyl fragment above, $C-CH_2$, 1.50 Å; HC-H, 1.09 Å; angle HCH, 109°; angle CCC in allyl fragment 90°. (C) $Fe(CO)_3$: octahedral fragment; Fe-C, 1.82 Å; C-O, 1.15 Å. (D) Benzyl ligand: all CC, 1.40 Å; CH, 1.08 Å, 120° angles. In the centered structures all Fe-C (pentadienyl) were taken as 2.2 Å, as were the Fe-C (allyl) distances. This placed the iron atom 1.697 Å below the pentadienyl fragment plane, and that was the perpendicular separation maintained in the benzyl-$Fe(CO)_3^+$ calculations.

References and Notes

(1) M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, **8**, 1950 (1969).
(2) P. J. Van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *Chem. Commun.*, 883 (1970); *J. Am. Chem. Soc.*, **93**, 4394 (1971).
(3) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).
(4) P. M. Harrison, Ph.D. Thesis, University of Sheffield, 1968, as cited by R. Mason in XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, Special Lectures, Vol. 6, 1971, p 31.
(5) A. Mawby, P. J. C. Walker, and R. J. Mawby, *J. Organomet. Chem.*, **55**, C39 (1973).
(6) M. Mathew and G. J. Palenik, *Inorg. Chem.*, **11**, 2809 (1972).
(7) G. Huttner and O. S. Mills, *Chem. Ber.*, **105**, 3924 (1972).
(8) C. A. Bear, W. R. Cullen, J. P. Kutney, V. E. Ridaura, J. Trotter, and A. Zanarotti, *J. Am. Chem. Soc.*, **95**, 3058 (1973).
(9) N. C. Baenziger and A. D. Nelson, *J. Am. Chem. Soc.*, **90**, 6602 (1968). The compound was prepared by W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).
(10) P. Menzel and F. Effenberger, *Angew. Chem.*, **87**, 71 (1975), and references therein.
(11) J. J. Stezowski, University of Stuttgart, Abstracts, 2nd European Crystallographic Meeting, 1974, and private communication. Preliminary studies indicate a dihedral angle of 3° for **3a**, 17° for **3b**, and 14° for **3c**.
(12) For a review see M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).
(13) (a) R. Destro, C. M. Gramaccioli, and M. Simonetta, *Acta Crystallogr., Sect. B*, **24**, 1369 (1968); (b) H. Ueda, N. Sakabe, J. Tanaka, and A. Furasaki, *Bull. Chem. Soc. Jpn.*, **41**, 2866 (1968); (c) G. G. Messmer and G. J. Palenik, *Chem. Commun.*, 470 (1969).
(14) M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, **97**, 1004 (1975).
(15) Among leading references we cite F. A. Cotton and J. M. Troup, *J. Organomet. Chem.*, **77**, 369 (1974); A. Immirzi, *Ibid.*, **76**, 65 (1974).
(16) The structure is of tricarbonyl-1-*syn*-(1′,2′-dihydro-2′-oxo-1′-oxaazulen-3′-yl)pentadienylmanganese: M. J. Barrow, O. S. Mills, F. Haque, and P. L. Pauson, *Chem. Commun.*, 1239 (1971).
(17) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(18) In our calculations this is the highest occupied MO of the cyclohexadienyl complex. Other molecular orbital calculations, on cyclohexadienyl, cycloheptadienyl, and cycloheptatrienyl $Mn(CO)_3$ complexes, place this combination below the metal "t_{2g}" set: T. H. Whitesides, D. L. Lichtenberger, and R. A. Budnik, *Inorg. Chem.*, **14**, 68 (1975).
(19) The perturbation theoretic arguments behind the construction of Figure 2 are described in R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971). The specific case of cyclohexadienyl was discussed by R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).
(20) I. I. Chkeheidze, Yu. N. Molin, N. Ya. Buben, and V. V. Voevodskij, *Dokl.*

Akad. Nauk SSSR, **130**, 1291 (1960); H. Fischer, *Z. Naturforsch. A*, **17**, 693 (1962); *J. Chem. Phys.*, **37**, 1094 (1962); R. W. Fessenden and R. H. Schuler, *ibid.*, **38**, 773 (1963); **39**, 2147 (1963).
(21) Indeed there appears to be no indication from the structures known of such a distortion. See for example ref 3.
(22) (a) To bend 20° out-of-plane requires approximately 4 kcal/mol. The surface is softer still as one moves to the anion. (b) A C_{2v} equilibrium structure for $C_6H_7^+$ is calculated by MINDO/2 by W. W. Schoeller and G. E. Schenck, *Tetrahedron*, **29**, 425 (1973). (c) Ab initio calculations on planar $C_6H_7^+$ species are reported by W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 6901 (1972). See also W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 7163 (1974). (d) An INDO calculation for the out-of-plane deformation of the cyclohexadienyl radical is reported in ref 14.
(23) (a) A. Bond and M. Green, *J. Chem. Soc. Dalton Trans.*, 763 (1972); (b) A. Bond, M. Green, and S. H. Taylor, *J. Chem. Soc., Chem. Commun.*, 112 (1973).
(24) (a) C. E. Coffey, *J. Am. Chem. Soc.*, **84**, 118 (1962); (b) R. B. King and A. Efraty, *J. Organomet. Chem.*, **24**, 241 (1970); (c) J. Potenza, R. Johnson, D. Mastropaolo, and A. Efraty, *ibid.*, **64**, C13 (1974).
(25) (a) L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); (b) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).
(26) The importance of frontier orbital interactions has been previously stressed in this context by B. R. Bonazza and C. P. Lillya, *J. Am. Chem. Soc.*, **96**, 2298 (1974).
(27) J. A. Howard, R. A. Marsh, and P. Woodward, cited in footnote 2 of ref 23b.
(28) W. Oberhansli and L. F. Dahl, *Inorg. Chem.*, **4**, 150, 629 (1965).
(29) G. A. Olah, J. S. Staral, and G. Liang, *J. Am. Chem. Soc.*, **96**, 6231 (1974).
(30) (a) A. J. P. Devaquet and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 3644 (1974). An STO-3G optimization of the cyclobutenyl cation yields a bending of 10°. (b) W. W. Schoeller and G. E. Schenck, *Tetrahedron*, **29**, 425 (1973).
(31) C. Krüger, P. J. Roberts, Y.-H. Tsay, and J. B. Koster, *J. Organomet. Chem.*, **78**, 69 (1974); see also G. M. Whitesides and W. H. Ehmann, *J. Am. Chem. Soc.*, **91**, 3800 (1969), and H. Hogeveen, H. Jorritsma, P. A. Wade, F. van Rantwijk, J. B. Koster, J. J. Prooi, A. Sinnema, and H. van Bekkum, *Tetrahedron Lett.*, 3915 (1974).
(32) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964), and private communication.
(33) M. R. Churchill and R. Mason, *Adv. Organomet. Chem.*, **5**, 93 (1967); S. F. A. Kettle and R. Mason, *J. Organomet. Chem.*, **5**, 573 (1966); P. Heimbach and R. Traunmüller, "Chemie der Metall-Olefin Komplexe", Verlag Chemie, Weinheim/Bergstr., 1970.
(34) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (c) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966); (d) R. Aumann and S. Winstein, *Tetrahedron Lett.*, 903 (1970).
(35) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2482 (1962).
(36) Reviewed by S. Winstein in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, p 965.
(37) For some molecular orbital calculations on homotropylium see W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974), and R. C. Haddon, *Tetrahedron Lett.*, 863 (1975).
(38) See also L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *J. Am. Chem. Soc.*, **95**, 3386 (1973), and ref 29.
(39) N. W. Alcock, *Chem. Commun.*, 177 (1965).
(40) M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, **279**, 191 (1964).
(41) M. R. Churchill and R. Mason, *Proc. Chem. Soc., London*, 226 (1964).
(42) (a) M. R. Churchill and R. Mason, *Adv. Organomet. Chem.*, **5**, 93 (1967); (b) M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 72.
(43) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **83**, 752 (1961).
(44) M. Gerloch and R. Mason, *Proc. R. Soc. London, Ser. A*, **279**, 170 (1964).
(45) N. A. Bailey and R. Mason, *Acta Crystallogr.*, **21**, 652 (1966).
(46) (a) See E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **91**, 6785 (1969), and references therein; (b) for a theoretical account of cyclopentadienone complexes see D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 49(1959).
(47) V. G. Andrianov, Y. T. Struchkov, V. N. Setkina, V. I. Zdanovich, A. Z. Zhakaeva, and D. N. Kursanov, *J. Chem. Soc., Chem. Commun.*, 117 (1975).
(48) (a) S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem.*, **84**, 1104 (1972); (b) R. L. Sime and R. J. Sime, *J. Am. Chem. Soc.*, **96**, 892 (1974).
(49) M. Cais, *Organomet. Chem. Rev.*, **1**, 435 (1966).
(50) R. Gleiter and R. Seeger, *Helv. Chim. Acta*, **54**, 1217 (1971).
(51) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966); F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 5418 (1968); F. A. Cotton and T. J. Marks, *ibid.*, **91**, 1339 (1969).
(52) (a) D. J. Ehntholt and R. C. Kerber, *Chem. Commun.*, 1451 (1970); R. C. Kerber and D. J. Ehntholt, *J. Am. Chem. Soc.*, **95**, 2927 (1973); J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 329 (1972); (b) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(53) G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *J. Organomet. Chem.*, **30**, C22 (1971); B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *Chem. Commun.*, 177 (1971); *J. Chem. Soc., Dalton Trans.*, 2076 (1972).
(54) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3179, 3489 (1962); **37**, 2872 (1962).
(55) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
(56) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, New York, N.Y., 1964.
(57) The rationale for this modification will be described elsewhere: J. C. Thibeault and R. Hoffmann, to be submitted for publication.