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Molecular Orbital Studies on Cyclobutadienemetal Complexes: The Concept of Metalloaromaticity

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Nonempirical molecular orbital calculations have been performed on a variety of cyclobutadienemetal complexes. For $C_4H_4Fe(CO)_3$, a detailed analysis of the frontier orbitals indicates that the molecule is best described as a C_4H_4Fe fragment perturbed by the carbonyls rather than as an $Fe(CO)_3$ moiety perturbed by the C_4H_4 ring. This description is more consistent with the photoelectron spectrum of $C_4H_4Fe(CO)_3$ than the Hartree–Fock description of the molecule. The C_4H_4–Fe bond is highly covalent resulting in a delocalization of six electrons in metal–ring π orbitals, a phenomenon which shall be referred to as metalloaromaticity. These concepts are extended to $C_4H_4Cr(CO)_4$ and $C_4H_4Ni(CO)_2$. The former species has been synthesized but the latter has not. Correlation of these facts with the calculations will be presented. Finally, a comparison will be made of C_4H_4 to C_5H_5 and C_6H_6 as ligands.

Introduction

There has long been interest in cyclobutadiene, the simplest example of a Hückel antiaromatic ($4n$ π-electron) molecule. Attempts to prepare cyclobutadiene via conventional organic synthesis have failed, and to date the molecule remains elusive, existing only in frozen inert-gas matrices.[1] However, shortly after the sandwich structure of ferrocene was recognized, Longuet-Higgins and Orgel proposed the existence of transition-metal complexes of cyclobutadiene.[2] This farsighted prediction, based primarily on symmetry arguments, was borne out within a few years as both (tetraphenylcyclobutadiene)iron tricarbonyl[3] and (tetramethylcyclobutadiene)nickel chloride dimer[4] were isolated. Since that time there has been rapid growth in the area of cyclobutadienemetal chemistry. In 1965 Pettit and co-workers synthesized the first unsubstituted cyclobutadiene complex, $C_4H_4Fe(CO)_3$.[5] This molecule, which lends itself to obvious comparison with $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$, is quite stable and undergoes a rich variety of ligand-substitution and -replacement reactions. Subsequent to the isolation of $C_4H_4Fe(CO)_3$, several other complexes of unsubstituted cyclobutadiene (which we shall denote Cb) have been synthesized, most notably $CbCr(CO)_4$[6] and $CbCoC_5H_5$.[7,8] The synthesis and chemistry of cyclobutadiene complexes have been thoroughly described in several review articles.[9-11]

It is one of the triumphs of organometallic chemistry that cyclobutadiene complexes should exist whereas the free hydrocarbon does not. Additionally, coordinated Cb often acts as if it were aromatic rather than antiaromatic.[11] The elucidation of the bonding in cyclobutadienemetal complexes therefore poses an intriguing question for theoreticians, viz., what is the mode of Cb–M bonding and why does it work? There have been some quantum chemical treatments of $CbFe(CO)_3$, including an ab initio Hartree–Fock calculation which shall be discussed later, but these have been more concerned with the energetics of the molecular orbitals rather than the mode or extent of metal–ring bonding.[12-14]

In this paper we present a detailed analysis of the bonding in $CbFe(CO)_3$. It is found that the stability and properties of the molecule can be explained by uniquely strong covalent bonding between the metal and the ring. The analysis is extended to $CbCr(CO)_4$ and $CbNi(CO)_2$ as well as to comparison of the complexation of C_4H_4 to that of C_5H_5 and C_6H_6.

Molecular Orbital Calculations

The Fenske–Hall nonempirical molecular orbital method has been described previously.[15] As the method has no adjustable parameters, the final results depend only upon the atomic basis set and internuclear distances.

Clementi's double ζ functions for neutral atoms were used for carbon and oxygen.[16] The 1s and 2s functions were curve-fit to single ζ by using the maximum overlap criterion, while maintaining their orthogonality.[17] For hydrogen, an exponent of 1.16 was used which corresponds to the minimum energy exponent for methane.[18] Metal functions were taken from the results of Richardson et al.[19] Single ζ functions were used for all orbitals except the 3d which was double ζ.

Table I. Bond Distances and Angles Used in $CbM(CO)_n$ Calculations[a]

C-H = 1.08 Å C-C = 1.46 Å C-O = 1.13 Å

	C_4H_4-$Fe(CO)_3$	$C_4H_4Cr(CO)_4$	$C_4H_4Ni(CO)_2$
M-X, Å	1.79	1.88	1.80
M-C(O), Å	1.82	1.92	1.84
C(O)-M-C′(O), deg	95.6	90 (see text)	109.5 (see text)

[a] X = the center of the C_4H_4 ring.

In all of the calculations the cyclobutadiene ring was assumed square, consistent with the observed diffraction data on cyclobutadiene complexes.[20,21] For $C_4H_4Fe(CO)_3$ the bond distances were extrapolated from the crystal structure of $C_4H_6Fe(CO)_3$,[22] as has been done by Hall et al.[12] The carbonyls are assumed to be staggered relative to the ring carbons, although it is expected that the results would be very similar for the eclipsed conformer.[21] For $C_4H_4Cr(CO)_4$ and $C_4H_4Ni(CO)_2$ it was assumed that the ring displaces two of the carbonyls in $Cr(CO)_6$ and $Ni(CO)_4$, respectively, with the metal–ring distances assumed proportional to the metal–carbonyl distances. The distances and angles are summarized in Table I.

Electronic Structure of $CbFe(CO)_3$

Symmetry Considerations.[23] Although the total symmetry of $CbFe(CO)_3$ is C_s, it is not unreasonable to expect the iron–cyclobutadiene and iron–tricarbonyl interactions to retain a large degree of their local symmetries. Thus, in order to clarify the principal interactions in $CbFe(CO)_3$, it is instructive to review the symmetry-allowed interactions of the C_4H_4 ring and of the $(CO)_3$ moiety.

For cyclobutadiene, it is expected that the σ system of the ring will play only a small role in the iron–cyclobutadiene bonding. When D_{4h} symmetry is assumed, the four π orbitals are as shown in Figure 1. The filled a_{2u} orbital, which is lowest in energy, is the totally symmetric linear combination of p_π orbitals on the ring. It can interact in a σ fashion with the z^2 orbital of the metal. Higher in energy is the doubly degenerate e_g level. If the free ligand existed and were square, the two e_g orbitals would be the highest occupied molecular orbitals, each orbital containing one electron. The two e_g orbitals can interact in a π sense with the metal xz and yz orbitals. Finally there is the empty b_{1u} orbital which is of

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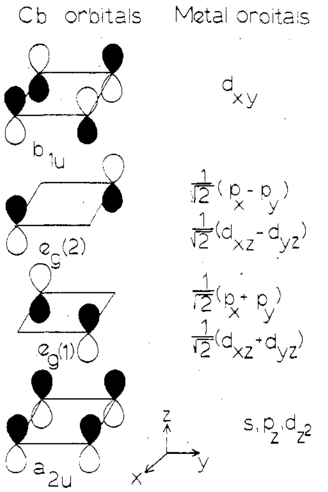


Figure 1. Symmetry-adapted linear combinations of the π orbitals of C_4H_4 and their allowed interactions with a metal.

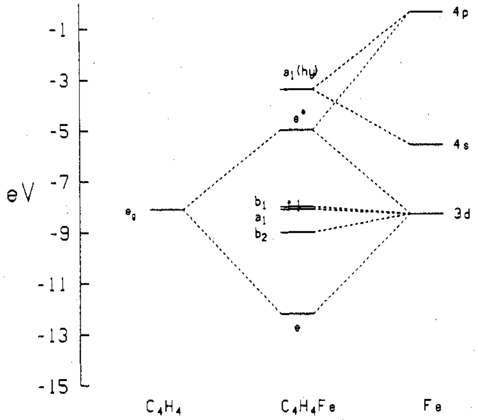


Figure 2. Molecular orbital diagram of C_4H_4Fe.

proper symmetry to interact in a δ fashion with the metal xy orbital. The metal $x^2 - y^2$ orbital cannot interact with the π system of the cyclobutadiene.

For comparison we shall consider the symmetry requirements of the C_{3v} $(CO)_3$ moiety. The important carbonyl orbitals will be the symmetry-adapted linear combinations of the σ-donating (5σ) and π-accepting (2π) orbitals. Under C_{3v} symmetry, the 5σ orbitals form a_1 + e combinations while the 2π orbitals reduce to $a_1 + a_2 + 2e$. The metal 3d orbitals transform as a_1 (z^2) + 2e ($x^2 - y^2,xy$; xz,yz). On the basis of the geometry of the three carbonyls relative to the metal, the e($x^2 - y^2,xy$) orbitals will interact primarily with the carbonyl 2π orbitals while the e(xz,yz) will interact mainly with the carbonyl 5σ orbitals.

CbFe and $Fe(CO)_3$. The study of the electronic structure of molecular fragments has proven very useful in the elucidation of metal–ligand bonding interactions. Hoffmann and co-workers have used frontier orbitals analysis to explain structural behavior, rotation barriers and unusual bonding modes.[24-26] In this section we shall investigate the bonding in the CbFe and $Fe(CO)_3$ fragments. The transferability of the frontier orbitals of these fragments to the molecular orbitals of $CbFe(CO)_3$ should indicate dominant effects in the bonding of the molecule.

The MO diagram for CbFe is shown in Figure 2. The resultant MO's have been transformed to a basis consisting of the Fe orbitals and the canonical orbitals of square cyclobutadiene. The metal $x^2 - y^2$,z^2 and xy orbitals interact minimally with the Cb ring in forming occupied b_1, a_1, and b_2 molecular orbitals which are all >90% metal d in character (Table II). The dominant metal–ring interaction is the formation of a very covalent, doubly degenerate e level representing π bonding between the metal xz and yz orbitals and the ring e_g orbitals. Inspection of Table II indicates the strong covalent nature of the e orbitals, viz., the nearly equal sharing of charge between the metal and ligand in this level. This high degree of covalency is a significantly different situation than that found in cyclopentadienyl or π-arene metal complexes, as shall be discussed later. The lowest unoccupied molecular orbital (LUMO) of CbFe is the antibonding counterpart of the e level. This e* level is quite diffuse due to major contributions from the metal 4p orbitals. Finally, there is a diffuse a_1 metal sp hybrid virtual orbital which is labeled "hy" in accordance with the convention of Hoffmann et al.[27]

Table II. Orbital Energies and Percent Characters of the Highest Valence Orbitals of C_4H_4Fe[a]

MO	ϵ, eV	Fe 3d	Fe 4s	Fe 4p	Cb π	Cb σ
e	−12.23	37		5	54	4
b_2	−8.95	94			6	0
a_1	−8.11	95	4	0	1	0
b_1	−8.00	99				1
e*	−5.02	49		33	18	0
hy	−3.44	1	67	31	1	0

[a] The b_1 level is the highest occupied orbital.

Table III. Orbital Energies and Percent Characters of the Highest Valence Orbitals of $Fe(CO)_3$[a]

MO	ϵ, eV	Fe 3d	Fe 4s	Fe 4p	CO 5σ	CO 2π
e_π	−12.53	76		0	0	19
a_1	−12.45	76	0	1	0	20
e_σ	−8.95	47		33	5	12
hy	−6.26	10	22	46	0	22

[a] The e_σ level is the highest occupied orbital.

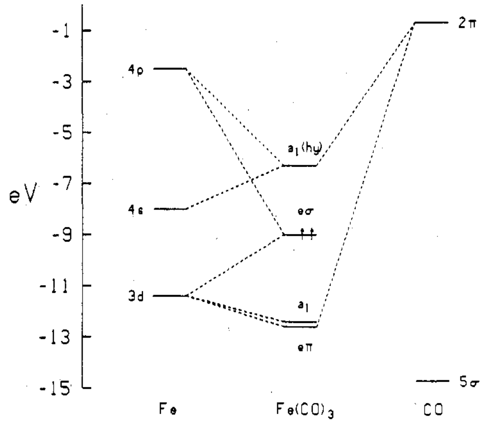


Figure 3. Molecular orbital diagram of $Fe(CO)_3$.

For comparison, the results for $Fe(CO)_3$ are presented in Figure 3 and Table III. The analysis is very similar to that of $Mn(CO)_3^+$ reported by Lichtenberger and Fenske, and only the salient features will be reiterated here.[28] The primarily metal a_1 and e_π orbitals, composed mainly of the z^2 and ($x^2 - y^2$,xy) orbitals, are stabilized by back-donation to the carbonyl 2π orbitals. Because $Fe(CO)_3$ is a d^8 system, however, the higher energy e_σ orbital is half-filled. This orbital consists primarily of the (xz,yz) orbitals with substantial mixing of the $4p_x$ and $4p_y$ orbitals. There is some back-donation into the carbonyl 2π orbitals, although this will be counteracted to some extent by the small destabilizing interaction with the filled carbonyl 5σ orbitals.

$CbFe(CO)_3$. The results on the two fragments provide a unique test of bonding dominance in $CbFe(CO)_3$. If the molecule is best considered as a CbFe fragment perturbed by three CO groups, the covalent metal–cyclobutadiene bonding levels should be below the metal–carbonyl back-bonding levels

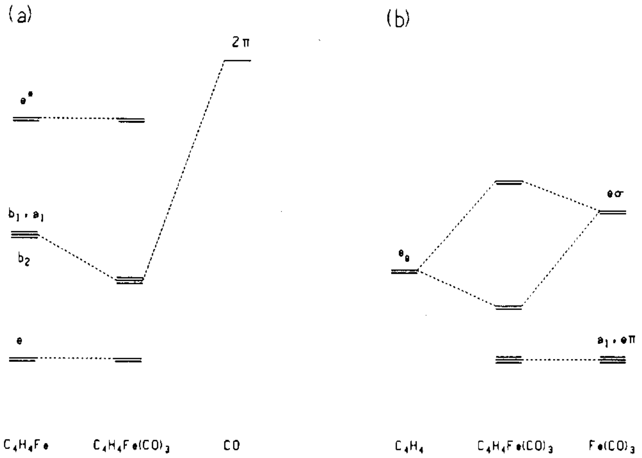


Figure 4. Molecular orbital diagram of the possible bonding dominances in $C_4H_4Fe(CO)_3$: (a) C_4H_4Fe interaction dominates, (b) $Fe(CO)_3$ interaction dominates.

Table IV. Orbital Energies and Percent Characters for the Highest Valence Orbitals of $CbFe(CO)_3$[a]

MO	ε, eV	Fe 3d	Fe 4s	Fe 4p	Cb σ	Cb π	Co 5σ	Co 2π
16a″	−13.38	44		4	9	33	1	6
29a′	−13.29	39	0	6	9	38	1	5
30a′	−11.92	67	0	4	0	2	0	23
17a″	−11.65	46		15	1	16	2	18
31a′	−11.21	53	0	12	2	10	1	20
32a′	0.21	18	11	18	0	13	0	40
18a″	1.27	14		5	1	38	1	42
33a′	1.28	14	0	5	1	38	1	42

[a] The 31a′ is the highest occupied orbital.

(Figure 4a). If on the other hand $CbFe(CO)_3$ is best thought of as an $Fe(CO)_3$ fragment perturbed by the ring, the metal–carbonyl levels should be below the metal–ring π interaction (Figure 4b). Table IV gives the orbital energies and characters of the highest occupied molecular orbitals of $CbFe(CO)_3$. It can be seen that there is remarkable transferability of the CbFe fragment. Aside from small contributions of the Fe xy and $x^2 - y^2$ orbitals (due to the lower symmetry of $CbFe(CO)_3$), the 16a″ and 29a′ MO's are essentially the e orbitals of CbFe. As expected, the "naked 3d" a_1, b_1, and b_2 orbitals of CbFe are stabilized by donation to the carbonyl 2π orbitals. The transferability is quite apparent in Figure 5, the MO diagram for $CbFe(CO)_3$ as compared to the results for CbFe and $(CO)_3$. It would thus seem that $CbFe(CO)_3$ is best described by Figure 4a, i.e., a CbFe fragment perturbed by three carbonyls. This is strikingly different from the usual description of cyclic metal–polyene carbonyl complexes where it is generally thought that the metal–carbonyl interaction dominates the metal–polyene bonding. Thus the use of frontier orbitals has led not only to a convenient description of $CbFe(CO)_3$ in terms of molecular fragments but also to a very different approach for explaining the existence of cyclobutadienemetal complexes vis-à-vis the nonexistence of cyclobutadiene.

It is of interest to compare the results of our calculation on $CbFe(CO)_3$ to ab initio Hartree–Fock results on the same molecule. Hall et al. performed an all-electron single-configuration Hartree–Fock calculation on $CbFe(CO)_3$ by using a limited basis of Gaussian-type functions.[12] Interestingly enough, based on Koopmans' theorem[29] the ab initio calculation predicts that the highest occupied orbitals are the metal–ring π bonds (the ordering of Figure 4b) and that there is an appreciable gap (~4.5 eV) between these two orbitals and the other three metal orbitals. When the ionization energies were calculated by using total energy differences between the ground state and the ion (the ΔSCF method), the ordering was the same as predicted by Koopmans' theorem although the gap decreased to ~0.2 eV. It would seem, therefore, that the ordering of levels according to our Fenske–Hall calculations contravene the order predicted by the ab initio calculations. However, unambiguous support for the ordering predicted by the Fenske–Hall method is given by the He I and He II photoelectron spectra of $CbFe(CO)_3$, which were recorded by Hall et al.[12] On the basis of intensity changes in the two spectra, the first ionization was attributed to levels primarily localized on the metal whereas the second ionization is assigned to levels with substantial ring character. Hence, Hall et al. conclude that the application of Koopmans' theorem to the interpretation of the bands arising from the metal MO's is inaccurate.

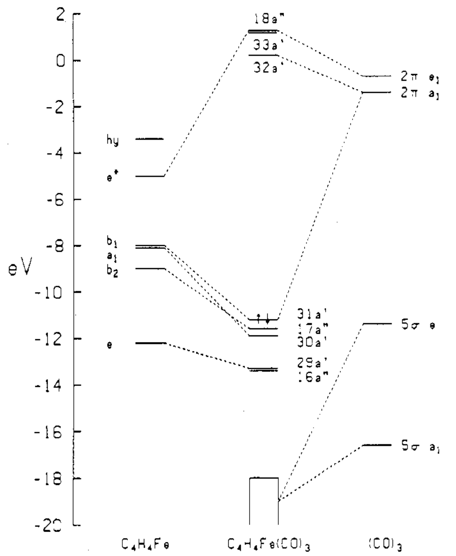


Figure 5. Molecular orbital diagram of $C_4H_4Fe(CO)_3$.

It is appropriate to point out that the inability of the Hartree–Fock method to properly order ionizations in $CbFe(CO)_3$ is not an isolated occurrence. The Fenske–Hall method has given more consistent ordering of levels with respect to ionization data than the Hartree–Fock method for $Mn(CO)_5H$, $Mn(CO)_5CH_3$, and $Mn(CO)_4NO$, as has been detailed by Fenske.[30] In fact, in recent years the validity of single-configuration Hartree–Fock calculations on transition-metal complexes has been severely questioned. In particular, the large one-center splitting of same-shell orbitals has been investigated as a source of the disparity between Hartree–Fock and approximate methods.[31] For a transition metal, the splitting of the d orbitals can result in a highly asymmetric charge distribution about the atom. This effect will be most pronounced in low-symmetry molecules since the electronic charge distribution is generally constrained to have the same symmetry as the nuclear framework. Thus, for $Mn(CO)_4NO$ there is a tremendous charge asymmetry along the Mn–NO axis resulting from the large (~12-eV) splitting of the Mn 3d orbitals.[30c] Interestingly enough, when configuration interaction (CI) is allowed, the ground configuration mixes strongly with excited configurations to yield a much more symmetric charge distribution along the Mn–NO bond axis.[30c] Our experience indicates that this effect is general; CI will tend to greatly "smooth out" the charge-distribution asymmetry so often found in Hartree–Fock calculations. By comparison, the Fenske–Hall method employs spherical averaging of one-center repulsive terms[15] (as does the Xα–SW method[32]) and, hence, does not suffer from the same difficulties as the Hartree–Fock method with respect to charge-distribution asymmetry. We fully expect, therefore, that a CI calculation on $CbFe(CO)_3$ would support the ordering of levels predicted

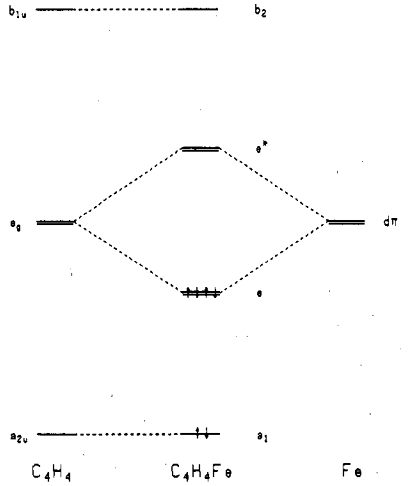


Figure 6. Qualitative molecular orbital diagram of the π system of C_4H_4Fe.

by the Fenske–Hall method.[33]

The Concept of Metalloaromaticity

The above interpretation of the bonding in $CbFe(CO)_3$ is quite a departure from the description of other $(CH)_nM(CO)_m$ complexes, e.g., $CpMn(CO)_3$ ($Cp \equiv \eta^5\text{-}C_5H_5$) and $C_6H_6Cr(CO)_3$. Lichtenberger and Fenske[28] performed a detailed molecular orbital analysis of $CpMn(CO)_3$ and found that the molecule is best described as an $Mn(CO)_3{}^+$ fragment interacting with a Cp^- ring. In order to better understand the unique nature of the iron–cyclobutadiene bond, we shall take a closer look at free cyclobutadiene and the CbFe fragment.

Square cyclobutadiene is the classic example of a Hückel antiaromatic compound. The half-filled e_g orbital contributes nothing to the stabilization of the π system (actually, the e_g orbital is antibonding across the diagonals, but it is expected that these interactions will be weak). Indeed, it is predicted theoretically that the minimum energy geometry of cyclobutadiene is rectangular, resulting in a singlet ground state.[34,35] It has been shown, however, that the cyclobutadiene moiety in $CbFe(CO)_3$ behaves as if it were aromatic; the ring is nearly square, and it readily undergoes Friedel–Crafts acylation and other electrophilic substitutions.[10] A simple explanation of these aromatic tendencies follows.

When the ring is allowed to interact with an iron atom, there are two additional π orbitals in the system, the *xz* and *yz*. Because the d_π orbitals overlap strongly with the ring e_g orbitals ($S = 0.183$) and are energetically similar, it is expected (and found) that there is strong mixing of the d_π and e_g orbitals. Figure 6 shows a simplified MO diagram for CbFe in which only the π system is shown. When the *total* π system of the CbFe fragment is considered, there are six electrons in bonding orbitals and none in antibonding orbitals, strongly suggesting satisfaction of Hückel's $4n + 2$ rule. Furthermore, the strong sharing of charge between the Cb e_g and Fe d_π orbitals results in a large delocalization of charge throughout the entire CbFe π system. Because this benzene-like π delocalization and stabilization depends intimately upon the metal–ring bonding interactions, we shall refer to it as "metalloaromaticity". In light of the controversy surrounding the term "aromaticity"[36] it is appropriate to comment on the nature of metalloaromaticity. The concept is intended to be primarily a heuristic device rather than a rigid definition. Thus it is not important that the metal atom is not in the plane of the ring; indeed, the explicit inclusion of d orbitals in an aromatic network allows a variety of geometric constructs consistent with the usual schemes of π delocalization. In addition, it must be stressed that interaction of the metal is crucial to the definition. Hence, as will be shown later, $C_5H_5Mn(CO)_3$ is not considered metalloaromatic despite the aromatic behavior of the Cp ring.

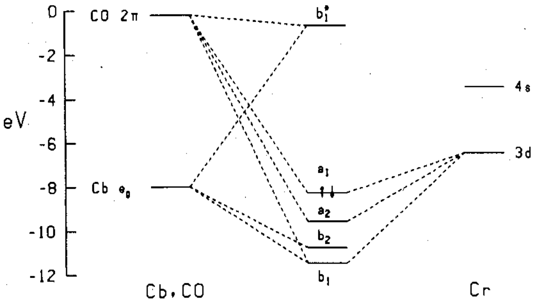
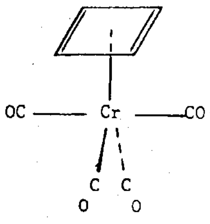


Figure 7. Molecular orbital diagram of $C_4H_4Cr(CO)_4$.

The Role of the Carbonyls. In the previous discussion we have ignored the crucial function of the carbonyls in holding $CbFe(CO)_3$ together. The ability of carbonyls to stabilize low oxidation state metals via back-acceptance into the empty 2π orbitals has been extensively discussed.[37] In the case of $CbFe(CO)_3$, however, the geometry of the metal–tricarbonyl fragment is critical. As can be seen in Figure 3, the z^2, $x^2 - y^2$, and *xy* orbitals are most favorably situated for back-bonding into the carbonyls. Thus, the three metal d orbitals which interact negligibly with the ring are those most stabilized by the presence of the carbonyls. This clean geometric separation has been generalized by Hoffman et al. for $M(CO)_3$ and $M(C_6H_6)$ fragments.[27]

CbCr(CO)$_4$ and CbNi(CO)$_2$. From the preceding discussion it is apparent that there are a number of unique features affecting the electronic structure of $CbFe(CO)_3$: (1) the near equality of the Cb e_g levels and the Fe 3d levels which results in the large mixing of e_g and d_π orbitals, (2) the d^8 configuration of Fe(0) which does not require metal–ring antibonding orbitals to be occupied, and (3) the geometry of the carbonyls which allows a good separation of metal–ring and metal–carbonyl interaction. It seems quite remarkable (and fortuitous) that all of these phenomena should come together in one molecule! In order to investigate the effects of changing the metal, we have performed calculations on $CbCr(CO)_4$, which has been isolated, and $CbNi(CO)_2$, which has not.

The d^6 complexes $CbM(CO)_4$ (M = Cr, Mo, W) have all been prepared by Pettit and co-workers.[6] Although it appears that the Cb ligand in these compounds is square, it does not undergo Friedel–Crafts acylation as $CbFe(CO)_3$ does. It would thus appear that the metalloaromaticity of the CbM unit is lost in the tetracarbonyl complexes. The MO diagram of $CbCr(CO)_4$ is presented in Figure 7. C_{2v} point symmetry has been assumed (**1**); the arguments presented should also apply to a C_{4v} structure (**2**). There are several noteworthy features in Figure 7. First of all, the Cr 3d levels are ~2 eV higher in energy than were the Fe 3d levels (cf. Figure 2). This will tend to increase 3d–CO 2π interaction while decreasing 3d–Cb e_g mixing. Second, and more important, the increased number of carbonyls forces a geometry (either C_{2v} or C_{4v}) in which the Cb ring must compete with the carbonyls for the (*xz*,*yz*) orbitals. For example, the b_1 orbital at −11.57 eV is 33% Cb e_g, 20% CO 2π, and 25% Cr *xz*. Indeed, when the results are transformed into the CbCr and $(CO)_4$ canonical



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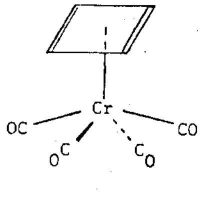

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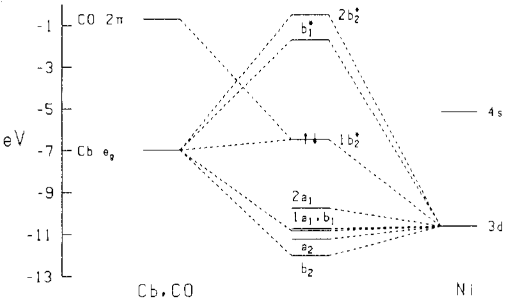
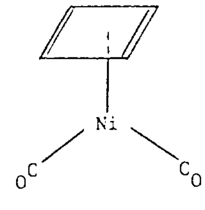


Figure 8. Molecular orbital diagram of $C_4H_4Ni(CO)_2$.

orbitals, it is found that neither fragment transfers very well to $CbCr(CO)_4$; the geometry and energetics of the molecule have forced a large degree of mixing between the fragments. Since the metalloaromaticity of $CbFe(CO)_3$ depended crucially on the transferability of the CbFe fragment, it would seem reasonable to expect $CbCr(CO)_4$ to *not* exhibit aromatic properties due to the competition between the ring and the carbonyls.

The other system we shall investigate is $CbNi(CO)_2$ (**3**),



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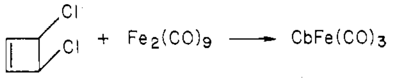
which has not been synthesized. In fact, no d^{10} complexes of cyclobutadiene have been made, an observation which can be rationalized quite easily from Figure 2. The extra two electrons of a d^{10} system would be expected to occupy the e* orbital, greatly weakening the metal–ring π bond. This is borne out in Figure 8, the MO diagram for $CbNi(CO)_2$. The b_2 and b_1 orbitals are essentially the π bonds between the metal and the ring; they contain virtually no carbonyl character. The $1b_2^*$ HOMO is antibonding between metal and ring, although there is a significant (18%) contribution from the CO 2π orbitals. It is expected that occupation of this high-energy, antibonding orbital precludes the formation of $CbNi(CO)_2$. This analysis is well supported by the known synthetic routes to cyclobutadiene complexes. Whereas $Fe_2(CO)_9$ and $Cr(CO)_6$ react with dihalocyclobutene to form the cyclobutadienemetal carbonyl complexes (eq 1 and 2)[5,38] $Ni(CO)_4$ does not. Rather,



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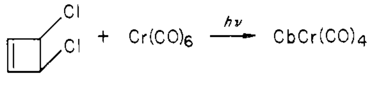
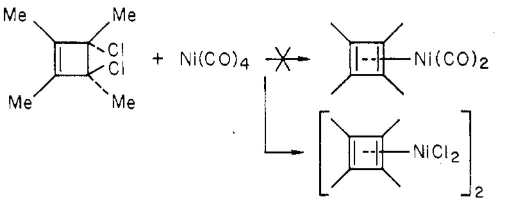


(2)

the reaction of $Ni(CO)_4$ with *trans*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene results in a chloride-bridged dimer in which the nickel atoms have been oxidized to Ni(II)[4] (eq 3).



(3)

Thus, a d^8 metal configuration has been achieved, and it is not necessary to occupy metal–ring antibonding orbitals. On the basis of this simple analysis, it seems unlikely that d^{10} complexes of Cb would be stable.

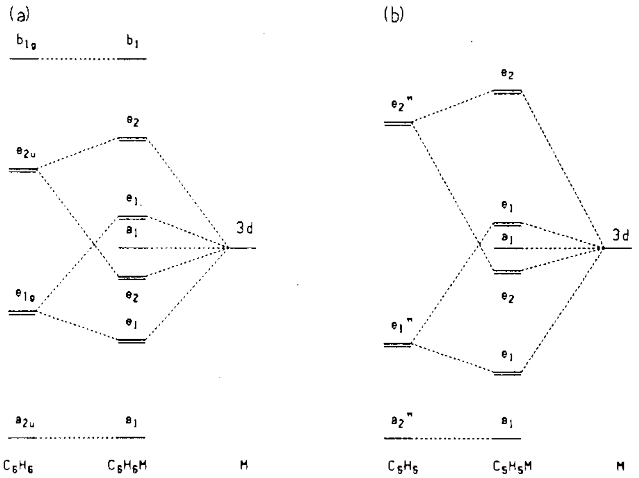


Figure 9. Qualitative molecular orbital diagram of C_nH_nM interactions: (a) C_6H_6, (b) C_5H_5.

Cyclobutadiene vs. Other Polyene Ligands. Now that the concept of metalloaromaticity has been introduced, it is of interest to see how it relates to other metal–polyene systems.

The first ligand to be considered will be benzene, the prototype aromatic molecule. The π system consists of filled a_{2u} and e_{1g} bonding orbitals and empty e_{2u} and b_{1g} antibonding orbitals. Complexation of benzene to a metal occurs via ligand-to-metal donation from the filled a_{2u} and e_{1g} orbitals and metal-to-ligand donation to the empty e_{2u} and b_{1g} orbitals (Figure 9a). It is apparent that the net effect of this synergic bonding is a transfer of some π-electron density from the bonding to the antibonding orbitals of benzene. Thus, even though there may be very little net change in the amount of benzene π-electron charge, it is expected that the aromatic nature of benzene will be greatly affected upon complexation. This is, in fact, reflected in the chemistry of π-arene metal complexes.[39] Friedel–Crafts acylation of $C_6H_6Cr(CO)_3$ does not proceed easily, and $(C_6H_6)_2Cr$ does not undergo any of the usual electrophilic substitution reactions characteristic of aromatic systems. Additional evidence is provided by a ^{13}C NMR study of substituted bis(arene)chromium complexes.[40] On the basis of the chemical shifts, Graves and Lagowski concluded that substituent effects are not transmitted across the ring as would be expected for an aromatic system. It is apparent that the metal atom, rather than enhancing the aromaticity of the ring, partially destroys the aromaticity which existed in the free ligand.

Metal–cyclopentadienyl complexes, on the other hand, possess many chemical properties typical of aromatic compounds. For example, ferrocene possesses a rich and varied organic chemistry, and, in general, the Cp rings are even more susceptible to electrophilic substitution than benzene. Our analysis shall be in terms of both the neutral radical species C_5H_5 and the closed-shell anion $C_5H_5^-$.

The primary M–Cp interactions are shown qualitatively in Figure 9b. The free ligand C_5H_5 has a π-electron configuration $a_2''^2e_1''^3$, one electron short of a Hückel $4n + 2$ configuration. It might be expected, therefore, that M–Cp fragments would exhibit covalency similar to that found in CbFe. This is not quite the case, however. Because the Cp e_1'' orbitals are strongly bonding, they are energetically lower than the metal 3d orbitals. Thus the M–Cp e_1 orbital is strongly localized on the ring, resulting effectively in a large charge transfer from the metal to the ring. (This description is of course equivalent to donation *from* the e_1'' of $C_5H_5^-$ *to* the metal 3d.) It is also important to note that the Cp e_2'' antibonding orbital is higher in energy than the corresponding

e_{2u} orbital of benzene; hence, there will be less aromaticity-destroying donation to the e_2'' orbital of Cp than there was to the e_{2u} orbital of benzene. In light of this qualitative analysis it appears that the usual description of metal–cyclopentadienyl interactions, an aromatic Cp^- ring stabilized primarily by ionic interaction with the metal, is quite accurate. The aromatic behavior of Cp complexes must therefore be attributed to the aromaticity of the Cp^- anion rather than metalloaromaticity of the CpM unit.

The above discussions indicate that, as expected, antiaromatic ligands have the most to gain by strong covalent metal–ligand bonding. In contrast to this, aromatic ligands must lose some of their aromaticity upon complexation. These trends are reflected in the ease of Friedel–Crafts acylation of the ring, the most commonly used chemical indicator of aromaticity. $CbFe(CO)_3$ is acylated much more easily than $C_6H_6Cr(CO)_3$, indicating that the metalloaromatic CbFe unit is "more aromatic" than complexed benzene. Empirically it might be expected that the ease of cyclopentadienyl compound acylation be intermediate between cyclobutadiene and benzene. Coordinated Cp is clearly more susceptible to electrophilic substitution than coordinated benzene (both ferrocene and $CpMn(CO)_3$ are easily substituted[41]). The comparison of Cb to Cp is more difficult, however, due to the lack of experimental comparisons between the two. Perhaps the best comparison of Cb to Cp occurs in $C_4H_4CoC_5H_5$ in which the Cb ring is preferentially acylated.[8] This would seem to indicate that the metalloaromatic CbCo moiety is "more aromatic" than the Cp ring. Clearly these conclusions could be tested by further experiments, for example, an acylation competition reaction between $CbFe(CO)_3$ and $CpMn(CO)_3$.

We have tried to demonstrate how the simple concept of metalloaromaticity can be used to explain chemical behavior in organometallic systems. As the concept rests largely on symmetry arguments, it can often be used qualitatively, obviating the need to perform quantitative molecular orbital calculations. In particular, it is hoped that the concept can provide insight into the bonding between metals and other antiaromatic or pseudoantiaromatic ligands (such as trimethylenemethyl or π-allyl).

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Registry No. $CbFe(CO)_3$, 12078-17-0; $CbCr(CO)_4$, 32678-96-9; $CbNi(CO)_2$, 70178-64-2.

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