

0.07 mmol) and $\text{Cp}^*_2\text{ZrH}_2$ (25 mg, 0.07 mmol) at -196°C in an NMR tube. The tube was sealed and warmed to room temperature and the reaction monitored by NMR spectroscopy. The product was identified as $\text{Cp}(\text{PMe}_3)_2\text{Ru}-\text{CH}_2\text{O}-\text{Zr}(\text{H})\text{Cp}^*_2$ by the similarity of its ^1H NMR spectrum to that of 11a.

$\text{CpFe}(\text{CO})_2\text{CH}_3 + \text{Cp}^*_2\text{ZrH}_2$. NMR samples of 1 (50 mg, 0.14 mmol) and 12a (30 mg, 0.15 mmol) were prepared in C_7D_8 with and without PMe_3 (0.25 mmol) at -196°C . After being sealed, the samples were warmed to -78°C to liquify the solvent and then to 25°C . The reactions were monitored by ^1H NMR spectroscopy, the products being identified by comparison to previously reported spectra.^{1b,24} A similar procedure to that above was employed by using 1 (30 mg, 0.08 mmol), 12b (20 mg, 0.08 mmol), and PMe_3 (0.10 mmol).

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Registry No. 1, 61396-34-7; 1-*d*₂, 83708-61-6; 2a, 12078-25-0; 2b, 12192-97-1; 2b (^{13}C enriched), 87985-74-8; 3a, 76545-15-8; 3b, 87985-75-9; 3b (^{13}C enriched), 87985-76-0; 4, 77299-72-0; 5a, 87985-77-1; 5b, 87985-78-2; 6, 87985-79-3; 7a, 87985-80-6; 7b, 87985-81-7; 8, 57349-59-4; 9, 87985-82-8; 10a, 35796-54-4; 10a-*d*₁, 87985-83-9; 10b, 87985-84-0; 11a, 87999-37-9; 11b, 87999-38-0; 12a, 12080-06-7; 12b, 53449-90-4; 13, 77309-18-3; $[\text{Cp}^*_2\text{ZrN}_2]_2\text{N}_2$, 54387-50-7.

Comparison of Isolobal Fragments: Bonding of Tricarbonyliron and Cyclopentadienylcobalt to Cyclobutadiene and Cyclopentadienone

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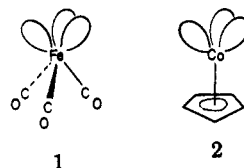
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Generalized molecular orbital and configuration interaction calculations are reported for $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_3$, $(\eta^4\text{-C}_4\text{H}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, $(\eta^4\text{-C}_4\text{H}_4\text{CO})\text{Fe}(\text{CO})_3$, and $(\eta^4\text{-C}_4\text{H}_4\text{CO})\text{Co}(\eta^5\text{-C}_5\text{H}_5)$. The results suggest that $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ bonds more strongly to the C_4H_4 ligand than to the $\text{C}_4\text{H}_4\text{CO}$ ligand, while the opposite behavior is seen for $\text{Fe}(\text{CO})_3$. Both Co complexes have a more covalent diene-M bond than the Fe complexes. Deformation density plots suggest that previous conclusions concerning how the two isolobal fragments $\text{Fe}(\text{CO})_3$ and $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ perturb the C-C bonds in a 1,3-diene may be inaccurate.

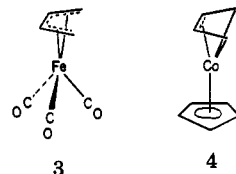
Introduction

Part of the challenge in synthetic chemistry is to find reaction schemes that have general applicability. In organometallic chemistry, the interest focuses on the similarities and differences in the chemical and physical behavior of organic ligands complexed to similar transition-metal fragments. One simple way of investigating such effects is to gradually change the nature of the transition-metal moiety, while keeping its theoretically equivalent bonding ability the same. This theoretical equivalence is termed isolobal. Two metal fragments are isolobal if they afford the same number of bonding electrons and orbitals to the complexed organic ligand.¹ In this sense, $\text{Fe}(\text{CO})_3$ and $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ are isolobal fragments, even though they are composed of quite different atoms. Hoffmann and co-workers have already examined the structure and bonding of the $\text{M}(\text{CO})_3$, $\text{M}(\text{C}_5\text{H}_6)$, and $\text{M}(\eta^5\text{-C}_5\text{H}_5)$ fragments with extended Hückel calculations and concluded that $\text{M}(\text{CO})_3$ is a better π -bonding group than $\text{M}(\text{Bz})$ or $\text{M}(\text{Cpd})$, whereas the latter two have stronger σ interactions.² From our work on (polyene) ML_n complexes,³ it is a logical extension to consider a comparison of the effects of isolobal fragments on the same polyenes.

We are primarily interested in examining the bonding effects of two different, but isolobal, fragments [$\text{Fe}(\text{CO})_3$, 1, and $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, 2] on the same polyene. On the basis of a number of X-ray diffraction studies performed on complexes of 1 and 2 containing 1,3-butadienes and bu-



tadiene-like ligands (which we will collectively refer to as dienes), Churchill, Mason, and co-workers concluded that dienes have three approximately equal C-C bond lengths when bound to 1, as in 3, but one short and two long C-C bond lengths when complexed to 2, as in 4.⁴ Though this



principle has been repeated in at least one textbook for a number of years,⁵ it is of questionable validity in light

(1) See, for example: (a) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, 99, 7546. (b) Albright, T. A.; Hoffmann, R.; Tse, Y.; D'Ottavio, T. *Ibid.* 1979, 101, 3812. (c) Hoffmann, R. *Science (Washington, D.C.)* 1981, 211, 995.

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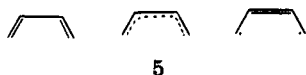
Table I. Molecular Parameters for the (Diene) ML_n Complexes^a

parameter	(Cbd)Fe(CO) ₃	(Cbd)Co(C ₅ H ₅)	(Cbdo)Fe(CO) ₃	(Cpdo)Co(C ₅ H ₅)
$r_{\text{C-C}}$ (diene)	1.437	1.437	1.432	1.432
$r_{\text{C-C}}$ (C ₅ H ₅)		1.390		1.390
$r_{\text{C-CO}}$ (dienone)			1.466	1.466
$r_{\text{C-O}}$ (dienone)			1.224	1.224
$r_{\text{C-O}}$ (carbonyl)	1.137		1.137	
$r_{\text{M-C}}$ (diene)	2.065	1.9645	2.105, 2.044	
$r_{\text{Fe-C}}$ (carbonyl)	1.793		1.793	
$r_{\text{Co-C}}$ (C ₅ H ₅)		2.038		2.038
CCC (diene)	90	90	107.3, 109.3	

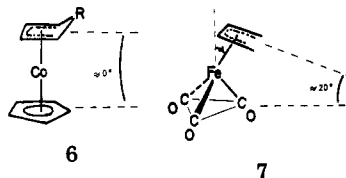
Ketonic group forms 20° angle with diene plane in dienone

^a Bond lengths are in angstroms (Å), and bond angles are in degrees (deg).

of the vast number of diene structures now available in the literature. Indeed, a recent statistical analysis by Herbstein and Reisner⁶ demonstrated that dienes complexed to 1 span the range of one long and two short C-C bonds (as in free butadiene), through three equal C-C bonds, to one short and two long C-C bonds, 5.

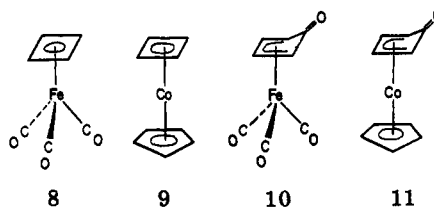


Furthermore, it seems that $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ prefers to coordinate to dienes that are four- or five-membered rings, with the diene portion being nearly coplanar to the opposite cyclopentadienyl ring on the cobalt, 6.⁷ On the other hand, $\text{Fe}(\text{CO})_3$ prefers to complex either to open dienes or to diene units in larger membered rings, such that the diene portion is tilted forward and downward over one of the carbonyls about 20°, 7.^{6,8} These variations in structural form suggest that there are significant differences in the chemical reactivity of $\text{Fe}(\text{CO})_3$ and $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ with dienes.



In making the kind of comparison that Churchill and Mason made, one needs to find structures in which 1 and 2 are bound to the same diene. There are only a few such complexes to be found: those with cyclobutadiene⁹ and those with cyclopentadienone.^{7a,10} With these as model compounds, we will compare the electronic structure of $(\eta^4\text{-cyclobutadiene})\text{tricarboxyliron}(0)$, 8, to that of $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{cobalt}(I)$, 9, and the electronic structure of $(\eta^4\text{-cyclopentadienone})\text{tri}$

carbonyliron(0), 10, to that of $(\eta^4\text{-cyclopentadienone})(\eta^5\text{-cyclopentadienyl})\text{cobalt}(I)$, 11, to examine the similarities and differences in the bonding effect of the two metal fragments on the two polyenes. Variations in reactivity will also be correlated with electron structure.



Theoretical Considerations

Methods. Ab initio calculations were performed on 8, 9, 10, and 11 at the Hartree-Rock-Roothaan (HFR) and at the generalized molecular orbital (GMO)-configuration interaction (CI) levels to investigate the orbital interactions between the metal 3d and diene 2p_π orbitals. The GMO approach¹¹ provides a simple way of obtaining a set of orbitals optimized for a CI calculation. The GMO and CI calculations were performed over a four orbital space involving the primary bonding and antibonding combinations of the metal d_{zz} and d_{yz} and the corresponding diene π orbitals. Full CI was performed in this space and included all possible spin- and symmetry-adapted configurations. The CI orbitals in this limited GMO space were also used to construct pseudo-GVB pairs by carrying out the procedure described previously.¹²

All of the computations were carried out on the Texas A&M University Amdahl 470 V/6 and V/7 computers. The integrals and HFR calculations at the ab initio level were performed with the ATMOL3 systems of programs,¹³ while the GMO calculations were done with programs written by Dr. M. B. Hall. The CI package from the University of Wisconsin¹⁴ was modified by T. E. Taylor and M. B. Hall for use on the Amdahl.

The calculated wave functions were then used in program MOPLOT¹⁵ to generate total density, $\rho(r)$, deformation

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(15) Lichtenberger, D. L., Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1974. Program available from QCPE, Chemistry Department, Indiana University, Bloomington, IN 47401.

Table II. Calculated Total Energies (in au) for the (Diene)ML_n Complexes and Their Composite Fragments

complex	HFR	GMO	GMO-CI ^a
(C ₄ H ₄)Fe(CO) ₃	-1737.709 02	-1737.728 07	-1737.758 90
(C ₄ H ₄)Co(C ₅ H ₅)	-1711.304 54	-1711.364 55	-1711.434 28
(C ₄ H ₄ CO)Fe(CO) ₃	-1849.239 19	-1849.260 48	-1849.320 01
(C ₄ H ₄ CO)Co(C ₅ H ₅)	-1822.836 54	-1822.882 35	-1822.938 58
Fe(CO) ₃ (³ A ₁)	-1585.827 68 ^b		
Co(C ₅ H ₅) (³ A ₁)	-1559.526 67 ^b		
C ₄ H ₄ CO	-263.322 65		
C ₅ H ₅ (³ A _{1g})	-151.802 72 ^b		
CO (¹ Σ ⁺)	-111.431 13		

^a Results are for the four-orbital space. ^b Restricted Hartree-Fock.

Table III. Computed Stabilization Energies (in kcal/mol) for the Complexes Relative to Their Fragments

complex	Δ(HFR-frags)	Δ(CI-frags)
(C ₄ H ₄)Fe(CO) ₃	-49.30	-80.58
(C ₄ H ₄)Co(C ₅ H ₅)	15.57	-65.77
(C ₄ H ₄ CO)Fe(CO) ₃	-55.72	-106.40
(C ₄ H ₄ CO)Co(C ₅ H ₅)	8.01	-55.97
C ₄ H ₄ CO	-55.68	

density, Δρ(*r*), and orbital maps for planes of interest. These were drawn on a Versatec Model 1200 plotter by using program CONTOUR.¹⁶ In the maps, positive density contours are represented by solid lines and negative contours by dashed lines. Contouring values (when present) are in units of millielectrons au⁻³, and adjacent contours of the same sign differ by a factor of 2 in all maps. The smallest contours plotted are ±2⁻¹⁰.

Geometry. The geometry of 8 and 9 were averages of several structures.⁹ The geometries of the Fe(CO)₃ and Co(C₅H₅) fragments were carried over into the rest of the complexes without change. The geometry of the dienone fragment and the metal-to-dienone distances were taken from an average of several structures.^{7a,8c,17} All four dienes were kept periplanar to the counterligand group on the metal fragments and were in the eclipsed conformations. These molecular parameters are tabulated in Table I.

Basis. The basis functions used in the ab initio calculations were obtained from a least-squares fit¹⁸ of a linear combination of Gaussians to near Hartree-Fock quality Slater-type functions.¹⁹ Three Gaussians were used for all fits except the carbon and oxygen 2p and the metal 3d. For C and O the 2p function was fit to four Gaussians. For cobalt and iron, five Gaussians were used to fit the 3d function. The metal basis sets were also augmented by a single exponent of 0.20 for a 4s function and a single exponent of 0.25 for a 4p. In the molecular calculations, the most diffuse components of the 2p functions on the dienes and of the 3d functions on the metals were split off to form double-ζ representations.

Results and Discussion

Energies. The calculated total energies for the converged HFR, GMO, and CI wave functions for the four model (diene)ML_n complexes are given in Table II. This

(16) An in-house program that uses CONREC, a special smoothing routine for drawing contours, developed at the National Center for Atmospheric Research (NCAR), Boulder, CO, and adapted for use on the Amdahl 470V/6 by Thomas Reid, Data Processing Center, Texas A&M University.

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Table IV. Most Important Configurations from a Full GMO-CI Calculation of (C₄H₄)Fe(CO)₃ and (C₄H₄)Co(C₅H₅) over a Four-Orbital Space

configuratn	CI coeff
(1) Starting Orbital Space for (C ₄ H ₄)Fe(CO) ₃	
(16a'') ² (32a') ² (33a'*) ⁰ (17a'*) ⁰	
(12 possible configurations)	
(aa'') ² (a') ²	0.9676
(a'') ² (a'*) ²	-0.1520
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × αββ	-0.1437
(a'') ² (a'*) ²	-0.1366
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × ααββ	0.1236
(2) Starting Orbital Space for (C ₄ H ₄)Co(C ₅ H ₅)	
(15a'') ² (30a') ² (16a'*) ⁰ (31a'*) ⁰	
(12 possible configurations)	
(a'') ² (a') ²	0.9321
(a'') ² (a'*) ²	-0.2083
(a') ² (a'*) ²	-0.2083
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × ααβββ	-0.1414
(a'*) ² (a'*) ²	0.0797
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × αβββ	-0.0714

Table V. Most Important Configurations from a Full GMO-CI Calculation of (C₄H₄)Fe(CO)₃ and (C₄H₄)Co(C₅H₅) over a Four-Orbital Space

configuratn	CI coeff
(1) Starting Orbital Space for (C ₄ H ₄)Fe(CO) ₃	
(19a'') ² (36a') ² (20a'*) ⁰ (37a'*) ⁰	
(12 possible configurations)	
(a'') ² (a') ²	-0.9465
(a'') ² (a'*) ²	0.1719
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × ααββ	0.1622
(a') ² (a'*) ²	0.1294
(a'') ² (a') ¹ (a'*) ¹	0.0730
(a'') ¹ (a') ² (a'*) ¹	0.0706
(a'*) ² (a'*) ²	-0.0635
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × αβββ	0.0603
(2) Starting Orbital for (C ₄ H ₄)Co(C ₅ H ₅)	
(18a'') ² (34a') ² (35a'*) ⁰ (19a'*) ⁰	
(12 possible configurations)	
(a'') ² (a') ²	-0.9305
(a'') ² (a'*) ²	0.2705
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × αβββ	-0.2188
(a') ² (a'*) ²	0.1210
(a'') ¹ (a') ¹ (a'*) ¹ (a'*) ¹ × ααββ	0.0986
(a'*) ² (a'*) ²	-0.0752

table also contains the total energies for the component fragments of the complexes. For C₄H₄, Fe(CO)₃, and Co(C₅H₅), the open-shell restricted Hartree-Fock procedure was used and yielded triplet states for these fragments.

With use of the total energies in Table II, we can compute stabilization energies for the four (diene)ML_n complexes, relative to their component fragments. These are listed in Table III. It is interesting to observe that the cobalt complexes are unstable with respect to dissociation to their fragments at the Hartree-Fock level, whereas the

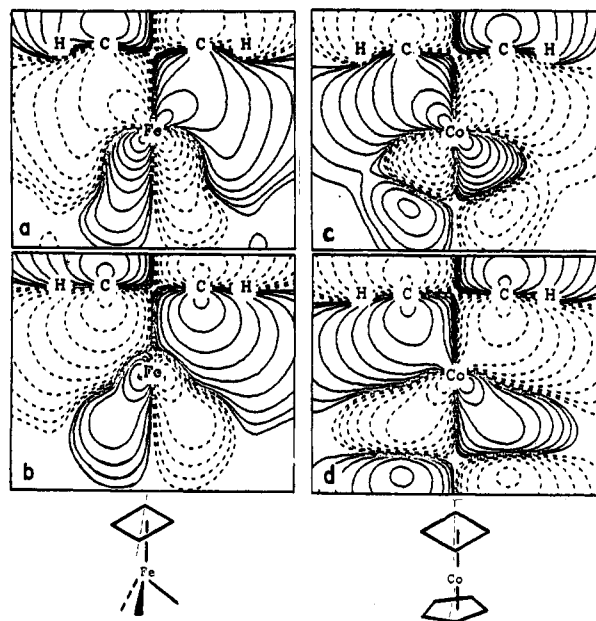


Figure 1. Orbital plots of the PGVB pairs of a'' symmetry for (cyclobutadiene)metal fragments. a and b are for $(\text{Cbd})\text{Fe}(\text{CO})_3$ while c and d are for $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$.

iron complexes are quite stable. The incorporation of correlation stabilizes all complexes, to a significant degree. In general, the $\text{Fe}(\text{CO})_3$ complexes appear more stable than then the corresponding $\text{Co}(\text{C}_5\text{H}_5)$ complexes. If one compares the relative stability of the two $\text{Fe}(\text{CO})_3$ complexes, one finds that the $\text{Fe}-\text{Cpd}$ bond appears stronger than the $\text{Fe}-\text{Cbd}$ bond. However, for the $\text{Co}(\text{C}_5\text{H}_5)$ complexes the $\text{Co}-\text{Cbd}$ bond appears stronger than the $\text{Co}-\text{Cpd}$ bond.

Wave Functions. The most important configurations in the CI wave functions are listed in Tables IV (for the cyclobutadiene complexes) and V (for the cyclopentadienone complexes). In each complex, the three most important excited-state configurations involve paired double excitations from one of the bonding a' or a'' orbitals to its antibonding partner (a'^* or a''^*), and the split double excitation that places one electron in each orbital of the CI space. Of even greater significance is the fact that the addition of CI is more important to the description of the wave function for the cobalt complexes than for the iron ones. The larger coefficients for the excited configurations attest to this. In general, this is found to be true for molecules whose bonding is very covalent (e.g., H_2) where the addition of CI is necessary to properly describe the molecule. Molecules that are more ionic are not as dependent on CI for a correct description.

By diagonalizing the one-electron density matrix, one can form the natural orbitals (NO) of this wave function. These are approximations to the true natural orbitals for which the CI expansion converges most rapidly to the true wave functions. From the occupation numbers of these natural orbitals one can generate pseudo-generalized-valence-bond (PGVB) orbitals.¹² The latter orbitals emphasize the fragment parentage of the orbitals. Each PGVB orbital is occupied by one electron.

Plots of the PGVB orbitals of a'' symmetry for $(\text{Cbd})\text{Fe}(\text{CO})_3$ and $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$ are shown in Figure 1. The orbitals in Figure 1a show a $\text{Fe}(\text{CO})_3$ fragment orbital strongly polarized into the p_x orbitals of cyclobutadiene. The companion orbital (Figure 1b) shows a cyclobutadiene orbital polarized to a small degree into the $\text{Fe}(\text{CO})_3$. By comparison the corresponding orbitals for $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$, shown in parts c and d of Figure 1, suggest a more covalent

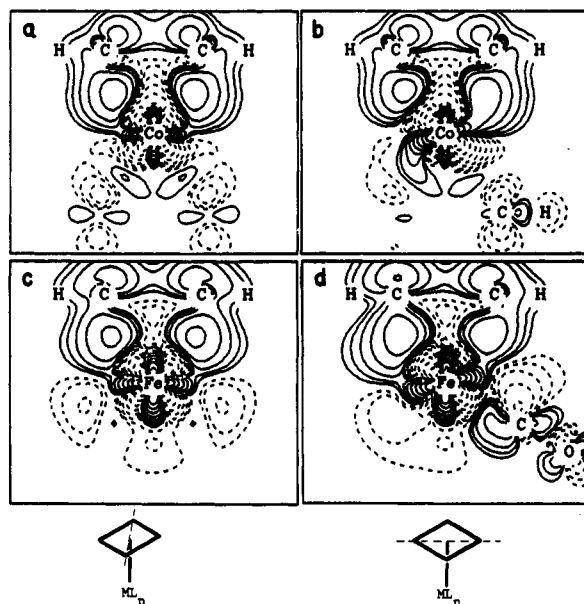


Figure 2. Fragment deformation density plots for the $(\text{Cbd})\text{ML}_n$ complexes in the vertical XZ and YZ planes. Maps a and b are the XZ and YZ plane plots for $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$, while maps c and d are the XZ and YZ plane plots for $(\text{Cbd})\text{Fe}(\text{CO})_3$. The deformation densities were formed by subtracting the restricted HFR fragments from the CI total densities for the complexes.

$\text{Cbd}-\text{Co}$ interaction. The orbital in Figure 1c is similar to that in Figure 1a, but the orbital in Figure 1c contains more M and less C character than the orbital in Figure 1a. Hence, the $\text{Co}(\text{C}_5\text{H}_5)$ fragment orbital is less polarized onto the cyclobutadiene than are the $\text{Fe}(\text{CO})_3$ orbitals. The orbital in Figure 1d is also similar to that in Figure 1b, but, again the orbital in Figure 1d contains more M and less C character than the orbital in Figure 1b. Thus, the cyclobutadiene fragment orbital is more strongly polarized onto the $\text{Co}(\text{C}_5\text{H}_5)$ fragment than the $\text{Fe}(\text{CO})_3$ fragment. Overall the less electronegative $\text{Fe}(\text{CO})_3$ fragment has pushed more electrons onto the cyclobutadiene and produced a more polar $\text{Cbd}-\text{M}$ bond. The a' orbitals show similar differences as do the cyclopentadienone orbitals, but the differences are not as apparent in the latter. Alternatively, if one begins with Cbd^{2-} and $\text{Fe}(\text{CO})_3^{2+}$ or CoCp^{2+} , then $\text{Fe}(\text{CO})_3^{2+}$ accepts less electron density than CoCp^{2+} and the $\text{Cbd}-\text{Fe}$ bond is more ionic. Similar conclusions were reached by Elian et al.²

Electron Densities. If we now examine fragment deformation density plots ($\Delta\rho$) for these complexes in the vertical XZ and YZ planes, we see further differences in the bonding behavior of $\text{Fe}(\text{CO})_3$ vs. $\text{Co}(\text{C}_5\text{H}_5)$. In these plots we have subtracted the electron density of the fragments (Cbd , Cpd , $\text{Fe}(\text{CO})_3$, or $\text{Co}(\text{C}_5\text{H}_5)$) from the total density of the molecule. These deformation densities emphasize the bonding between the two fragments. For the Cbd complexes (Figure 2), the XZ plane is similar, but the accumulated density between the Cbd and M is larger for Co. In the YZ plane there is substantially greater electron density gain at the uneclipsed carbon in $(\text{Cbd})\text{Fe}(\text{CO})_3$, while $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$ has slightly more electron density at the eclipsed carbon. Thus, the uneclipsed carbon should move toward the metal in the iron complex and the eclipsed carbon should move toward the metal in the cobalt complex. This prediction is observed in the structure of $(\text{C}_4\text{Ph}_4)\text{Fe}(\text{CO})_3$,^{9a} but not yet in $(\text{Cbd})\text{Co}(\text{C}_5\text{H}_5)$.^{9c} We believe that low-temperature (78 K) structures of both 2 and 9 would confirm these predictions.

For the Cpd complexes (Figure 3), the XZ plane of the cobalt complex has slightly more electron density in the

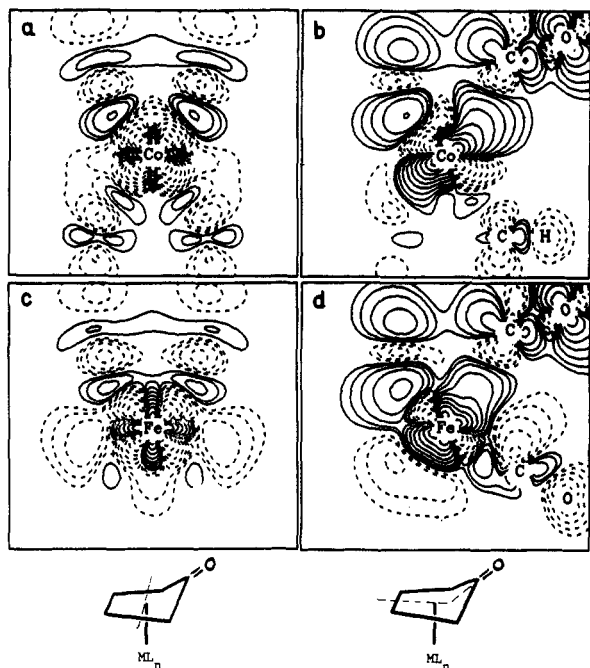


Figure 3. Fragment deformation density plots for the $(\text{Cpdo})\text{ML}_n$ complexes in the vertical XZ and YZ planes. Maps a and b are the XZ and YZ plane plots for $(\text{Cpdo})\text{Co}(\text{C}_5\text{H}_5)$, while maps c and d are the XZ and YZ plane plots for $(\text{Cpdo})\text{Fe}(\text{CO})_3$. The deformation densities were formed by subtracting the restricted HFR fragments from the CI total densities for the complexes.

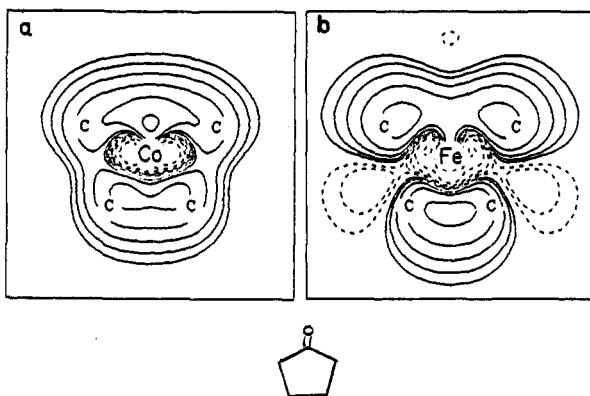


Figure 4. Deformation density plots for the $(\text{Cpdo})\text{ML}_n$ complexes in the π -maximum plane. Map a is for the cobalt complex, and map b is for the iron complex. The deformation densities were formed by subtracting the restricted HFR fragments from the CI total densities for the complexes.

π region (positive region above metal) than the iron complex, but the reverse is true for the YZ plane. The differences are subtle and suggest that the diene in the Fe complex looks more like 12, whereas the diene in the Co complex looks more like 13. These differences are made



more dramatic by examining $\Delta\rho$ plots taken near the diene π -maximum plane (Figure 4). The fragment deformation densities show the density changes, relative to the free diene, which has an electronic structure as in 14 (one long and two short bonds). Both complexes show a gain in π density for the "back" C-C bond (the single bond in 14). The $\text{Fe}(\text{CO})_3$ complex actually shows π density loss in the two "side" C-C bonds (the double bond in 14). Thus the Fe complex should be substantially distorted from 14 to 13 or even toward 12. The $\text{Co}(\text{C}_5\text{H}_5)$ complex shows no such loss in the two "side" C-C bonds. The structural work on the perfluoromethyl derivatives^{7a,10} shows essentially equal C-C diene bonds for both the $\text{Fe}(\text{CO})_3$ and $\text{Co}(\text{C}_5\text{H}_5)$ complexes. The estimated standard deviations of these early structure preclude any conclusions regarding the experimental differences.

Conclusions

We have shown that the addition of CI makes an important contribution to the predicted stability of these diene complexes. The CI appears to be more important for the $\text{Co}(\text{C}_5\text{H}_5)$ dienes than the $\text{Fe}(\text{CO})_3$ dienes, and the analysis of the wave functions suggests that the diene-Co bond is more covalent than the diene-Fe bond. The more ionic diene- $\text{Fe}(\text{CO})_3$ complexes appear to have the electron density shifted toward the diene.

The $\text{Co}(\text{C}_5\text{H}_5)$ fragment makes a stronger bond to the cyclobutadiene ligand than to the cyclopentadienone. The reverse is true for the $\text{Fe}(\text{CO})_3$ fragment. One important contribution to this difference arises from the difference in the electron repulsions for the two metal fragments. Because of the larger electron repulsions for the more compact d orbitals of cobalt, the Co fragment's singlet excited state is higher in energy than the Fe fragments' singlet excited state. As both states are important in binding the diene ligand, the Co fragment would prefer the ligand with the lower energy triplet state, the cyclobutadiene. This smaller energy difference is superimposed on the larger difference arising from the smaller diene-Co overlap that makes all the diene-Co bonds weaker than the diene-Fe bonds.

Examination of the $\Delta\rho$ plots suggests that the differences between the diene-M bonding for the two isolobal fragments $\text{Fe}(\text{CO})_3$ and $\text{Co}(\text{C}_5\text{H}_5)$ may not be as clear-cut as previously suggested. As one "fine-tunes" organometallic systems the small differences between the structure and reactivity of isolobal fragments will become as important as their similarities. Clearly, high-quality, low-temperature structures and reactivity studies are needed on identical dienes to delineate the real differences between the isolobal fragments $\text{Fe}(\text{CO})_3$ and $\text{Co}(\text{C}_5\text{H}_5)$.

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