

### Conclusions

We believe the foregoing shows that surface-related processes play an important role in controlling the rate of reaction and stereochemical behavior of the semiconductor photoinduced dimerization of PVE. Simple kinetic analysis based upon Langmuir-Hinshelwood treatment has been successfully applied. This procedure can rationalize the different effects of various quenchers on the reaction, and the overall pathway emerges as a complex sequence of steps involving both surface reaction and reaction in solution.

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**Registry No.** 7, 35370-71-9; 8, 35370-70-8; PVE, 766-94-9; TMB, 621-23-8; TMB, 2441-46-5; EVE, 109-92-2; ZnO, 1314-13-2; TiO<sub>2</sub>, 13463-67-7; CdS, 1306-23-6; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; Ta<sub>2</sub>O<sub>5</sub>, 1314-61-0; SnO<sub>2</sub>, 18282-10-5; Bi<sub>2</sub>O<sub>3</sub>, 1304-76-3; WO<sub>3</sub>, 1314-35-8; isoprene, 78-79-5; furan, 110-00-9; 2-methylfuran, 534-22-5;  $\beta$ -bromophenethole, 589-10-6.

## Structure, Conformation, and Ligand Binding in Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) and Some Derivatives. A Theoretical Study

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**Abstract:** Iron-olefin complexes of the general formula Fe(CO)<sub>4</sub>(C<sub>2</sub>X<sub>4</sub>), where X = H, F, Cl, and CN, were studied by molecular orbital methods. Calculated  $\Delta E$ 's for the reactions Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) + C<sub>2</sub>X<sub>4</sub> → Fe(CO)<sub>4</sub>(C<sub>2</sub>X<sub>4</sub>) + C<sub>2</sub>H<sub>4</sub> are found to vary in the order F ≫ CN > Cl and are consistent with available experimental data on related systems. The conformational preferences of these complexes have also been investigated. All derivatives studied here were found to prefer a trigonal-bipyramidal structure with the ethylene occupying a position in the equatorial plane. The nature of the metal-olefin bond is discussed and illustrated with electron density difference contour maps and localized molecular orbitals (LMO's) in the metal-olefin region. The relative binding energies of cis and trans 1,2-disubstituted olefins were also calculated and are discussed.

The chemistry of olefins in transition-metal complexes has been a topic of discussion for some time. As a result, numerous theoretical studies of metal-olefin complexes have appeared in the literature.<sup>1-13</sup> These studies have employed a large variety of quantum chemical methods ranging from empirical and semi-empirical schemes such as extended Hückel, CNDO, INDO, and HFS(X- $\alpha$ ) to all electron ab initio calculations. While approximate methods provide a means of systematically studying real olefin complexes, they are often insufficient for the prediction of molecular properties, particularly the total energy. First-principle calculations on real transition-metal-olefin systems are difficult, however, because the formidable size of such computations places them out of reach of most quantum chemists. Recently, the PRDDO approximations<sup>14</sup> have been extended through the first

transition series.<sup>15</sup> Although PRDDO is an approximate method, it closely reproduces ab initio minimum basis set calculations with only a fraction of the computational effort. This allows a systematic study of real olefin complexes without sacrificing the quantitative accuracy of the ab initio approach. In this paper, we present the first PRDDO calculations on metal-olefin systems.

The most widely accepted scheme of metal-olefin bonding comes from Dewar<sup>16</sup> and Chatt and Duncanson.<sup>17</sup> They proposed that the bonding consists of a two-way donor-acceptor mechanism:  $\sigma$  donation of the  $\pi$ -bonding electrons of the olefin to vacant orbitals on the metal, and  $\pi$  back donation of metal d electrons to the  $\pi^*$  orbital of the olefin. Their picture has served as the starting point for rationalizing olefin site preference, rotational barriers, and substituent effects observed in a wide range of metal-olefin systems. Many of these arguments were pioneered by Hoffmann et al.<sup>1,2</sup>

Limited to the first transition series, some of the most interesting olefin complexes to study are iron-olefin complexes of the general formula Fe(CO)<sub>4</sub>(C<sub>2</sub>X<sub>4</sub>), where X = H, F, Cl, or CN. Experimentally, all are known to exist;<sup>18-22</sup> however, they are thermally

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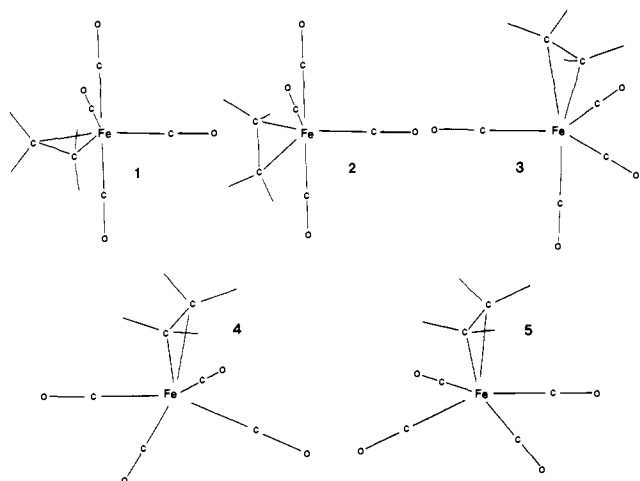
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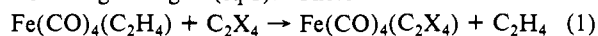
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**Figure 1.** Molecular conformations considered in this study: (1) ground-state structure, (2) ground-state structure with olefin rotated  $90^\circ$ , (3) axially substituted trigonal bipyramid, (4) square-pyramidal structure with the olefin eclipsing two of the basal carbonyls, (5) square-pyramidal structure with the olefin staggered with respect to the basal carbonyls.

unstable, making them difficult to synthesize and characterize. Although the instability of these complexes greatly hinders experimental inquiries, some information has been uncovered about them. As early as the first synthesis of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  (which we shall refer to as the parent complex throughout the rest of this paper) and similar derivatives, it was noted that intramolecular rearrangement occurs in these compounds.<sup>23-25</sup> Also, the tetracarbonyl-iron moiety is capable of catalyzing certain nucleophilic additions to olefins,<sup>26,27</sup> and it is an important simple prototype for metal-olefin systems. For these reasons, it is not surprising to find prior theoretical work<sup>1,2,4,10-13</sup> on the parent complex. We present here a study of the bonding in these systems by means of our approximate method through a systematic approach. As a means of probing the metal-olefin bond, we have varied substituents on the olefin as well as olefin conformation within the complex. By studying a series of related complexes, in which substituents have been changed, we can elucidate details of the electronic structure in the metal-olefin region using several different approaches.

To make quantitative estimates of the effect of various substituents on the iron-olefin bond strength, we have calculated ligand-exchange energies (eq 1). These values will be correlated



with various electronic properties, such as the energy and degree of localization of the  $\pi^*$  orbital in the free substituted ethylene. Our calculated ligand exchange energies will also be compared to the experimental values for related systems.

For the nature of metal-olefin bonding to be further probed, an additional effort was made to study the differences between cis and trans 1,2-disubstituted olefins in these complexes. A series of ligand exchange energies between cis and trans 1,2-disubstituted olefins was calculated. The results of these calculations will be compared to experimental values for related transition-metal-olefin complexes.

Analysis of olefin conformational preferences will be accomplished by calculating a series of isomerization energies between the structures shown in Figure 1.

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**Table I.** Optimized Bond Lengths and Angles in  $\text{Fe}(\text{CO})_4(\text{C}_2\text{X}_4)^a$

	Fe-C, Å	C-C, Å	X-C-X, deg	Fe-C-X, deg
H	1.90 (2.12) <sup>b</sup>	1.46 (1.46)	109	120
F	1.90 (1.99) <sup>c</sup>	1.52 (1.53)	111 (111.3)	120 (122)
Cl	1.93	1.54	110	120
CN	1.93	1.50	112	120

<sup>a</sup> Experimental values are in parentheses. <sup>b</sup> Reference 33. <sup>c</sup> Reference 34.

Electron density difference maps between the parent compound and various derivatives will be presented. These plots will enable us to correlate changes in the charge distribution with the corresponding ligand-exchange energy, and thus gain a more complete understanding of how substituents can affect the bonding. In addition to density difference maps, localized molecular orbitals were calculated, permitting for the first time the study of localized bonding in these types of complexes. Contour plots of the localized molecular orbitals will also be presented.

### Calculations

In all calculations each atom excluding the iron was represented by a minimum basis set, with exponents given by Hehre et al.<sup>28,29</sup> The iron basis set was minimum as well, except for the 3d's, which were described by a fixed-contracted linear combination of two Slater orbitals. For computational efficiency,<sup>15</sup> the exponents of the following orbitals were constrained to be equal: 2s-2p, 3s-3p, 4s-4p. The values of these exponents and contraction coefficients were obtained from ab initio atomic SCF calculations, except for the 4s and 4p exponents, which were set equal to 2.0. Previous work<sup>30,31</sup> has indicated this to be a reasonable value.

Localized molecular orbitals were calculated via the Boys method,<sup>32</sup> which has been used previously to study localized bonding patterns in octahedral transition-metal complexes.<sup>30</sup> The Boys method accomplishes localization by minimizing the orbital self-extension  $E$ .

$$E = \sum_{i=1}^{\text{OCC}} \langle \phi_i(1)\phi_i(2) | r_{12}^{-2} | \phi_i(1)\phi_i(2) \rangle \quad (2)$$

Only the one-electron dipole-moment integrals are needed for this transformation, making the method computationally fast, hence ideal for the study of LMO's in large molecules.

Each calculation yields the total energy, overlap populations, degrees of bonding, atomic charges, molecular-dipole moment, and both canonical and localized molecular orbitals. The MO coefficients can then be used as input to a series of contouring routines which then make contour plots of the individual MO densities or the sum of any MO densities. All PRDDO calculations were carried out on an IBM 4341 computer. All graphics were prepared on a DEC 2060 interactive system.

### Geometries

All  $\Delta E$ 's for ligand-exchange reactions and isomerization energies were calculated from partially optimized geometries.<sup>31</sup> While the estimated errors in optimized bond lengths and angles are large ( $\pm 0.03$  Å and  $\pm 2^\circ$ , respectively), the total energy is estimated to be within 2 kcal/mol of the absolute minimum with respect to the four critical parameters optimized. This was deemed satisfactory since our primary motivation was to obtain reliable energies for the calculation of the ligand-exchange energies. The optimized parameters included the Fe-C and C-C distances, along with the X-C-X and Fe-C-X angles. The results of these op-

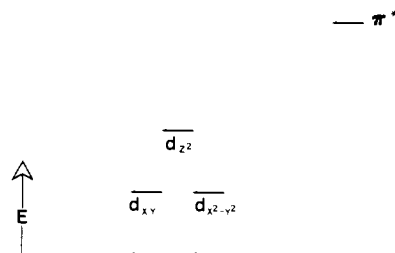
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**Figure 2.** Qualitative diagram showing the relative splitting of the d orbitals and their relation to the olefin  $\pi^*$  orbital. The d-orbital splitting is for a complex with its axial ligands along the z axis and the olefin in the xy plane, parallel to the y axis.

**Table II.** Ligand-Exchange Energies for the Tetrasubstituted Species

$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4) + \text{C}_2\text{X}_4 \rightarrow \text{Fe}(\text{CO})_4(\text{C}_2\text{X}_4) + \text{C}_2\text{H}_4$	
X	$\Delta E$ , kcal/mol
F	+1
Cl	-45
CN	-36

timizations for the ground-state conformation **1** are given in Table I. The Fe-C distances for  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  and  $\text{Fe}(\text{CO})_4(\text{C}_2\text{F}_4)$ , for which the structures have been determined by electron diffraction,<sup>33,34</sup> are short by  $\sim 0.1\text{--}0.2$  Å. The remaining two complexes (Cl, CN) have not been characterized structurally. Ab initio calculations on tetracarbonyl(ethylene)iron employing a minimal basis set of Gaussian functions<sup>4</sup> also yielded an optimized Fe-C distance which was  $\sim 0.2$  Å too short. The remaining optimized geometrical parameters compare well with experimental values. To test the effect of geometry variations on our calculated isomerization and ligand-exchange energies, we recalculated the isomerization energies of the parent compound and the ligand-exchange energies (eq 1) with the Fe-C distances set at the experimental value for the parent system; however, the qualitative trends reported here were not seriously affected.

All carbonyl-iron distances and angles in **1-3** were taken from the experimental parameters of the parent compound.<sup>33,34</sup> The carbonyl C-O distance was also fixed at the experimental value of 1.145 Å. It was not considered necessary to optimize these parameters, since PRDDO has been shown to yield excellent iron-carbonyl distances in  $\text{Fe}(\text{CO})_5$ .<sup>31</sup> For conformations other than **1**, the Fe-C and C-C distances and the X-C-X and Fe-C-X angles were fixed at the optimized values of **1**. Preliminary optimizations of the parent complex in the remaining four conformations (**2-5**) gave values similar to those obtained in the optimizations of **1**. Square-pyramidal geometries (**4** and **5**) were arrived at by averaging axial and equatorial iron-carbonyl distances, followed by the optimization of the basal carbonyl angles in both **4** and **5**.

The free olefin structures were determined by optimizing the C-C distance and X-C-X angle in the tetrasubstituted species. Averages of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{X}_4$  geometries were then used to construct the cis and trans 1,2-disubstituted isomers.

Geometries for the 1,2-disubstituted complexes were taken as an average between the parent complex and the corresponding tetrasubstituted species. Only the ground-state structure (**1**) was considered. All substituent-carbon distances were taken as averages of experimental values and are as follows: C-F (1.32 Å), C-Cl (1.72 Å), C-CN (1.46 Å), C-N (1.16 Å), and C-H (1.09 Å).

## Discussion

**Ligand-Exchange Energies.** The calculated ligand-exchange energies (Table II) indicate that tetrachloroethylene and tetracyanoethylene stabilize the  $\text{Fe}(\text{CO})_4$  complex relative to ethylene,

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**Table III**

X	energy $\pi^*$ , <sup>a</sup> au	% population in $\pi^*$ <sup>b</sup>
H	0.34	100
F	0.29	86
Cl	0.17	92
CN	0.05	58

<sup>a</sup>PRDDO eigenvalues of the  $\pi^*$  orbital in the free olefins. <sup>b</sup>Percent population on the carbon for the  $\pi^*$  orbital in the free olefins.

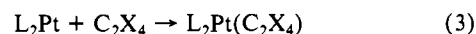
**Table IV**

X	orbital population <sup>a</sup>	free olefin <sup>b</sup>	complexed olefin <sup>c</sup>	$\Delta^d$
H	0.79	-0.13	-0.31	0.18
F	0.73	+0.29	+0.09	0.20
Cl	0.49	+0.14	-0.11	0.25
CN	0.49	+0.12	-0.14	0.26

<sup>a</sup>Orbital population of back-bonding d orbital. <sup>b</sup>Atomic charges on the olefin carbon in the free olefin. <sup>c</sup>Atomic charges on the olefin carbon in the complex. <sup>d</sup>Difference between second and third columns.

whereas tetrafluoroethylene does little energetically. As has been discussed previously,<sup>1,2</sup> stabilization of the iron-ethylene bond can be accomplished via enhanced  $\sigma$  donation, or increased  $\pi$  back-bonding. For the parent system, it is generally acknowledged<sup>1,2</sup> that back-bonding is the dominant effect. Therefore, substituents that change the level of the  $\pi^*$  orbital in the olefin should exhibit a noticeable effect on the strength of the iron-olefin bond. A qualitative sketch (Figure 2) shows the relative positions of the interacting orbitals in the metal and the olefin. If the energy of the unoccupied  $\pi^*$  orbital is lowered it will interact to a greater extent with the occupied metal 3d orbitals of local  $\pi$  symmetry. The net result is a strong bonding interaction. PRDDO calculations on the free olefins show the LUMO, which corresponds to the  $\pi^*$ , decreases in energy in the order  $\text{H} > \text{F} \gg \text{Cl} > \text{CN}$ . These values (Table III) are consistent with the large stabilization effect seen for the chloro and cyano derivatives. Further analysis of the orbital populations of the d orbital involved in back-bonding (Table IV) shows a far greater depopulation for the chloro and cyano species compared to the parent complex. The very same effect can be seen in the atomic charges (Table IV). A secondary effect which must be invoked to fully rationalize the trends seen in Table II is the degree of metal-olefin orbital overlap. For two orbitals to mix efficiently, they must not only be close in energy but they must also overlap well. From the population analysis for the free olefin calculations (Table III) it is clear that the  $\pi^*$  orbital in tetrafluoroethylene is not well localized on the carbons. This would tend to decrease the overlap between the metal 3d orbitals and the ethylene  $\pi^*$ . Hence, stabilization is not as great in this case. This same argument also explains why tetracyanoethylene, which has a lower  $\pi^*$  than tetrachloroethylene, stabilizes the complex less.

There are no direct experimental data available on the tetracarbonyl(ethylene)iron system. However, there are data on related platinum and iridium systems, which indicate that our results are reasonable. The  $\Delta H$  for the reaction



has been measured for X = H and CN, and tetracyanoethylene binding is favored by 35 kcal/mol.<sup>35,36</sup> Tetracyanoethylene exhibits a similar but smaller stabilization effect of 8 kcal/mol in  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{C}_2\text{X}_4)$  systems.<sup>37,38</sup> Furthermore, tetrafluoroethylene produces stabilization of 4 kcal/mol<sup>37,39</sup> relative to ethylene in the same system.

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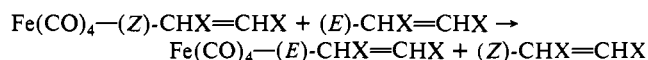
**Table V.** Calculated Isomerization Energies (kcal/mol)<sup>a</sup>

X	1-2	1-3	1-4	1-5
H	28 (31)	31 (21)	14 (12)	22 (13)
F	56	52	27	37
Cl	76	84	31	51
CN	66	70	30	42

<sup>a</sup> Ab initio values (ref 12) are in parentheses.

**Conformational Analysis.** Typically, pentacoordinate  $d^8$  transition-metal complexes are stereochemically nonrigid. Many are believed to undergo rearrangement between trigonal-bipyramidal and square-pyramidal conformations. NMR spectra have also shown that pentacarbonyliron exhibits intramolecular rearrangement.<sup>40,41</sup> The most widely embraced mechanism for this process is the Berry pseudorotation process.<sup>42</sup> When an olefin is introduced to the pentacoordinate sphere, the pathway for rearrangement becomes more complicated. Although pure rotation about the metal olefin axis is thought to occur in many transition-metal olefin complexes,<sup>43-53</sup> olefin rotation in  $\text{Fe}(\text{CO})_4(\text{C}_2\text{X}_4)$  complexes is believed to be coupled with carbonyl pseudorotation in most cases.<sup>24</sup> Major evidence supporting this view comes from NMR spectra of the parent complex and related systems.<sup>18,24,33</sup> Various schemes have been proposed for this process,<sup>12,24</sup> and structures **3**, **4**, and **5** have been suggested to be important in these mechanisms. As a means of investigating the feasibilities of these mechanisms, we have calculated the energy difference between structures **1** and **2-5**, respectively. We include isomerization energies for structure **2** since it is derived from **1** by pure olefin rotation—the simplest possible rearrangement in this system. In addition, we have also calculated the same isomerization energies for the tetrasubstituted complexes. The results of these calculations are listed in Table V.

For the parent complex, structure **2** is found to be 28 kcal/mol less stable than **1**. This is a rather large value compared to values of experimentally known olefin rotation barriers.<sup>43-52</sup> However, this quantity is in good agreement with ab initio calculations by Veillard,<sup>28</sup> which predict a 31-kcal/mol isomerization energy. The same value of 31 kcal/mol was also reported by Hoffmann using extended Hückel calculations.<sup>1</sup> Hoffmann<sup>2</sup> argued earlier that the olefin  $\pi^*$  would prefer interaction with the equatorial d orbitals due to 3d-4p hybridization toward the olefin. Overlap and orbital energy considerations lead to the same conclusion.<sup>1</sup> Essentially, the equatorial d's are preferred because they are closer in energy to the olefin  $\pi^*$  than the set of d orbitals perpendicular to the equatorial plane. If we locate the complex in the manner indicated in Figure 2, the d orbitals will split roughly as if they were in a trigonal-bipyramidal environment. The d orbital interacting with the olefin  $\pi^*$  in **1** is  $d_{xy}$ . Turning the olefin 90° forces the interacting d orbital to be  $d_{xz}$  and increases the energy separation between the interacting orbitals. This will have the effect of decreasing the amount of ethylene back-bonding in **2** relative to **1**, making **1** the energetically preferred conformer. This decrease in the amount of ethylene back-bonding is clearly evident in the population analyses, which show that the group charge of the

**Table VI.** Ligand-Exchange Energies for *cis*- and *trans*- $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_2\text{X}_2)$ 

X	$\Delta E$ (kcal/mol)
F	-3
Cl	-6
CN	-3

**Table VII.** Populations of Back-Bonding d Orbital in *cis*- and *trans*- $\text{Fe}(\text{CO})_4(\text{CHX}=\text{CHX})$ 

X	population		$\Delta$
	<i>cis</i>	<i>trans</i>	
F	0.78	0.76	0.02
Cl	0.63	0.61	0.02
CN	0.62	0.60	0.02

ethylene is  $\sim 0.2 e$  less in **2** than in **1** for all four tetrasubstituted species.

If a particular substituent enhances the  $\pi$ -acceptor ability of an olefin, the energy difference between **1** and **2** will increase.<sup>1,2</sup> The calculated values of the  $\pi^*$  in the free tetrasubstituted olefins (Table III) correlate well with the calculated barriers for pure olefin rotation. Differences in overlap populations and atomic charges between the two geometries indicate a weakening of the Fe-C bond in going from **1** to **2**. In general these same results hold in going from **1** to **2-5**. We should note that the large isomerization energies calculated for the chloro and cyano derivatives are probably competitive with the Fe-olefin bond energy, and therefore should only be used as a qualitative guide, indicating that these structures are not involved in the pseudorotation process. In fact, it seems highly likely that the tetrachloro and tetracyano complexes are stereochemically rigid. Our analysis of the relative energies of structure **1-5** for the parent complexes indicates that structures **4** and **5** are the most likely participants in the rearrangement process.

While our calculated isomerization energies are in general accord with Hoffmann's qualitative predictions, the magnitude of the substituent effects seen here is much larger. Extended Hückel calculations predict a 10.1 kcal/mol energy difference between **1** and **5** for the parent system, rising to only 12.8 kcal/mol for the tetracyano-substituted species.<sup>1</sup> Our predicted values (Table V) are 22 and 42 kcal/mol, respectively. Part of this discrepancy arises from our somewhat higher value for the internal rotation barrier in the apically substituted square pyramid (8 kcal/mol compared to 1-3 kcal/mol in other calculations<sup>1,28</sup> on the parent system). However, experimental evidence<sup>25</sup> does imply that PRDDO is overestimating the barriers by as much as 100% in some cases. We note here that the PRDDO value for the internal rotation barrier in the square-pyramid structure is reduced to  $\sim 5$  kcal/mol if the Fe-C distance is lengthened to 2.1 Å, close to the experimental distance. Similarly, all calculated isomerization energies are reduced at this longer distance, but the qualitative conclusions discussed here remain unchanged.

**Cis-Trans Effects.** It has been known for some time now that *cis*-disubstituted olefins are generally more stable thermodynamically and electronically than the *trans* isomer.<sup>54,55</sup> Also,  $\pi$  to  $\pi^*$  transitions lie at lower energies in the *trans* species relative to the *cis* in many 1,2-disubstituted olefins.<sup>56-58</sup> Therefore, it is not surprising to find that *cis*- and *trans*-disubstituted olefins bind metal centers with measurable energy differences. Thermochemical measurements<sup>56</sup> confirm this for *cis*- and *trans*-1,2-diphenylethylene in  $\text{L}_2\text{Pt}$ -olefin complexes, which show a 4-kcal/mol

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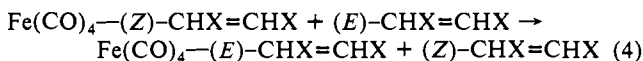
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**Table VIII.** Hybridizations, Bond Angle Deviations, and Percent Delocalizations in  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  and  $\text{C}_3\text{H}_6$ 

LMO	bond angle deviations, deg	hybridizations <sup>a</sup>	percent delocalization
Fe-C	18.7	$s^{1.0}p^{2.2}d^{14.5}$	14.9
C-Fe	21.3	$s^{1.0}p^{3.6}$	14.9
C-C	26.5	$s^{1.0}p^{2.6}$	12.4
C-C <sup>b</sup>	28.4	$s^{1.0}p^{3.8}$	9.3

<sup>a</sup> For the atom listed first. <sup>b</sup>  $\text{C}_3\text{H}_6$ , ref 59.

preference for the trans isomer over the cis. To test this effect in the tetracarbonyl-iron olefin systems, we have calculated  $\Delta E$ 's for reactions of the type



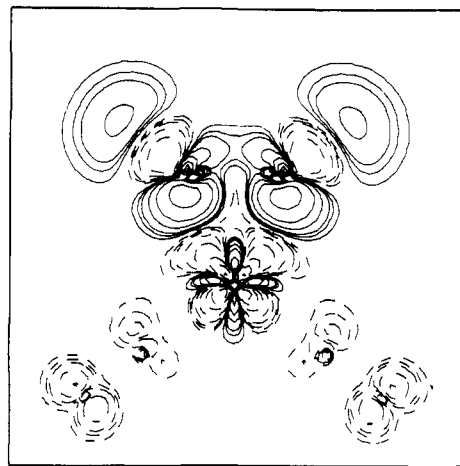
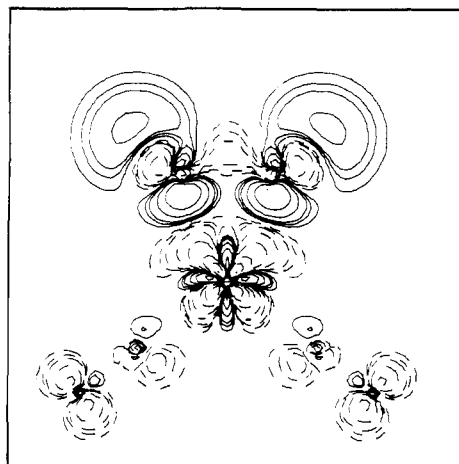
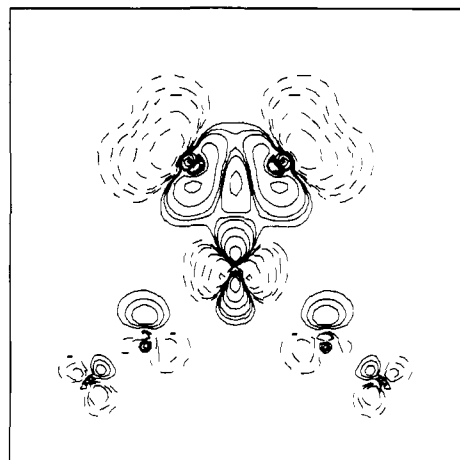
The calculated ligand-exchange energies (Table VI) show a slight preference for the trans olefin over the cis in all cases, consistent with the experimental trends discussed above. This trend seems to be directly related to the degree of back-bonding. For each disubstituted olefin, the trans complex shows  $\sim 0.02 e$  greater depopulation of the d orbital involved in back-bonding (Table VII).

**Density Difference Plots.** Density difference plots provide a convenient means of graphically illustrating the variation of electron density in the metal-olefin region as a function of the substituent on the ethylene. The difference density  $\rho_D$  is defined as

$$\rho_D = \rho_{\text{Fe}(\text{CO})_4(\text{C}_2\text{X}_4)} - \rho_{\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)} \quad (5)$$

To avoid effects due purely to geometry changes, the densities of the parent and substituted complexes were calculated with identical geometrical parameters for the olefinic unit (obtained by averaging the Fe-C and C-C distances and X-C-X and Fe-C-X angles in the parent and substituted species). Plots for the tetrachloro and tetracyano complexes (Figure 3, parts a and b) show obvious signs of increased back-bonding relative to the parent complex. Both plots exhibit a sizable redistribution of charge density from the region of the iron back-bonding d orbital to the region of the olefin  $\pi^*$ . In contrast, the difference plot for the tetrafluoro complex (Figure 3c) displays a pattern which is markedly different and clearly consistent with charge redistribution among the forward bonding orbitals. Thus, the density difference plots are entirely consistent with the population analysis, particularly the orbital populations of the back-bonding d orbital (Table IV), and again suggest that the dominant factor in determining the ligand exchange energies is the degree of back-bonding.

**Localized Molecular Orbitals.** Although the localized molecular orbital approach has proven useful in understanding the bonding patterns in a wide variety of organic<sup>59-61</sup> and inorganic<sup>62-64</sup> systems, little LMO work has been done on transition-metal complexes.<sup>30</sup> We present here the first localized description of metal-olefin bonding based on the objective Boys<sup>31</sup> criteria and our PRDDO wave functions. The LMO's obtained for the parent complex are illustrated in Figure 4 along with the corresponding canonical molecular orbitals. These orbitals are representative of those obtained for all four complexes. The localized iron-olefin interaction is best described as a three-member metallocyclopropane ring, as has been suggested from simple qualitative arguments.<sup>1</sup> The two Fe-C orbitals show a small amount of delocalization into the adjacent equatorial carbonyl's  $\pi^*$  orbital, which has been

**a****b****c**

**Figure 3.** Density difference plot between the tetrachloro- (a), tetracyano- (b) and tetrafluoro- (c) substituted complexes and the parent complex in the equatorial plane. (Contour values:  $\pm 0.5, \pm 0.4, \pm 0.3, \pm 0.2, \pm 0.1, \pm 0.05, \pm 0.02, \pm 0.01, \pm 0.005, \pm 0.0035, \pm 0.002 e/\text{au}^3$ .)

previously observed in other metal-carbonyl systems.<sup>65</sup> Hybridizations for the carbons and the iron, derived from the LMO's

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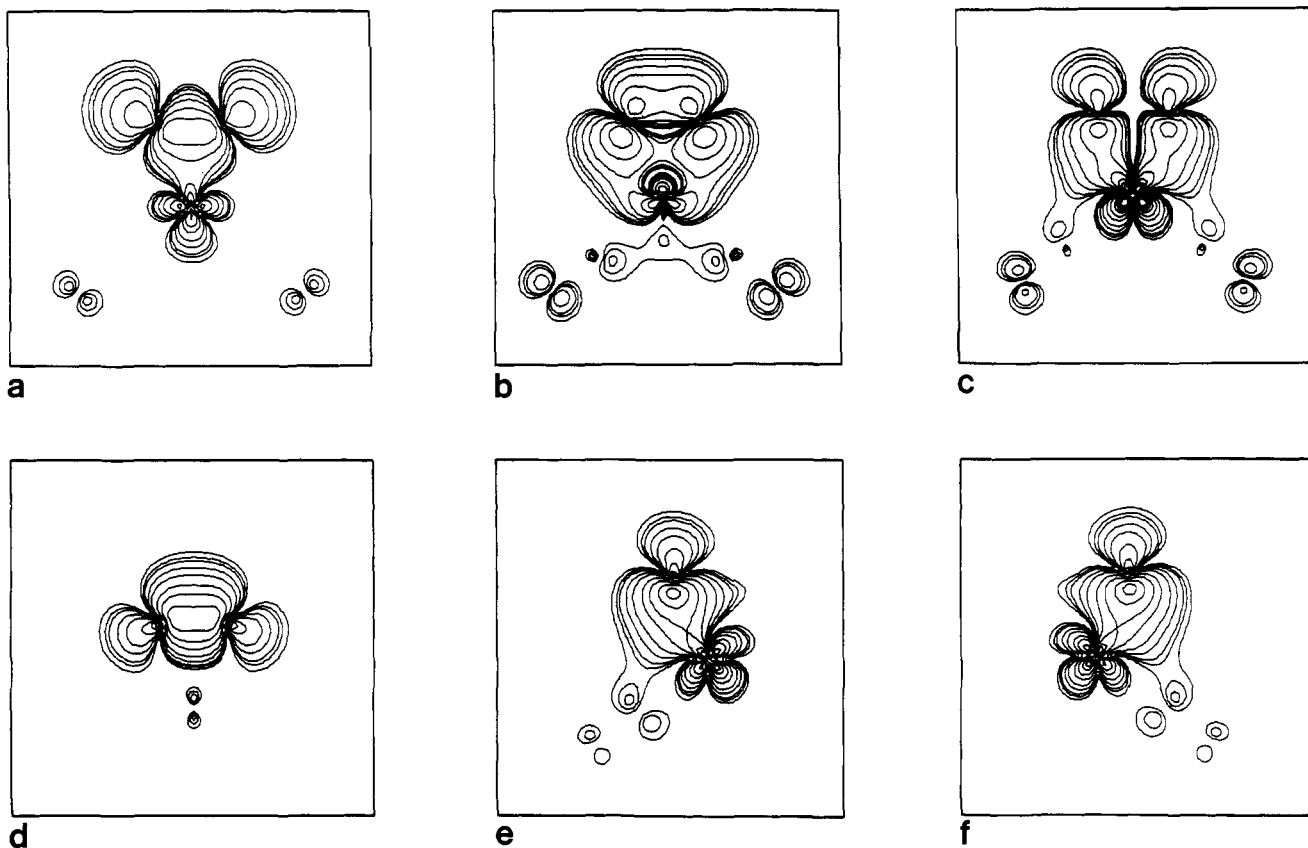
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**Figure 4.** Canonical and localized molecular orbital densities of the iron-olefin region in the equatorial plane. The three canonical MO's (a-c) roughly correspond to the carbon-carbon single bond, the forward bonding orbital, and the back-bonding orbital, respectively. Orbital plots d-f are the localized analogues of a-c and correspond to the carbon-carbon single bond (d) and two iron-carbon single bonds (e and f). (Contour values: 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.0035, 0.002  $e/\text{au}^3$ .)

in the usual fashion,<sup>66</sup> along with bond angle deviations and percent delocalizations for the parent system and cyclopropane,<sup>59</sup> are listed in Table VIII. The bond angle deviations indicate that the Fe-C-C ring is somewhat less strained than the C-C-C ring in cyclopropane, consistent with the high d orbital character on Fe and increased C-C-Fe bond angle ( $67^\circ$  compared to  $60^\circ$  in cyclopropane).

### Conclusion

The relative binding energies of various substituted ethylenes in  $\text{Fe}(\text{CO})_4(\text{C}_2\text{X}_4)$  have been shown to vary as  $\Delta E_{\text{H}} \approx \Delta E_{\text{F}} \gg \Delta E_{\text{CN}} > \Delta E_{\text{Cl}}$ . Back-bonding effects clearly dominate the trends found here. This was illustrated by population analyses, difference density plots, and correlations with the energy of the free ligand  $\pi^*$  orbitals. An important quantity which must be taken into consideration to fully understand the trends seen here is the degree of metal-olefin overlap. Ligands such as tetracyanoethylene have very low lying  $\pi^*$  orbitals, indicating strong metal-ligand bonding, but at the same time the  $\pi^*$  is highly delocalized. This results in relatively poor d- $\pi^*$  overlap and reduces the degree of back-bonding somewhat. Still, the single most important quantity needed for an understanding of our ligand exchange energies is the energy of the free ligand  $\pi^*$ .

For each complex examined, the ground-state structure has the ethylene in the equatorial plane, and the next lowest energy structure is **4**, the eclipsed square pyramid. In agreement with Hoffmann,<sup>1</sup>  $\pi$ -accepting substituents raise the isomerization energies. For tetrachloro- and tetracyanoethylene, this effect is so pronounced that the complexes may well be stereochemically rigid at room temperature.

The relative binding energies of cis and trans 1,2-disubstituted olefins have been examined. In each case the trans isomers are slightly (3-6 kcal/mol) more stable, consistent with experimental results in other systems.

Finally, localized molecular orbitals were calculated for the ground-state structure of all tetrasubstituted derivatives. The localized description of the iron-olefin interaction is essentially that of a three-member metallocyclopropane ring.

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**Registry No.**  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ , 71423-55-7;  $\text{Fe}(\text{CO})_4(\text{C}_2\text{F}_4)$ , 92077-27-5;  $\text{Fe}(\text{CO})_4(\text{C}_2\text{Cl}_4)$ , 71423-56-8;  $\text{Fe}(\text{CO})_4(\text{C}_2(\text{CN})_4)$ , 71423-57-9;  $\text{Fe}(\text{CO})_4$ -(Z)-CHF=CHF, 92011-75-1;  $\text{Fe}(\text{CO})_4$ -(E)-CHF=CHF, 92077-28-6;  $\text{Fe}(\text{CO})_4$ -(Z)-CHCl=CHCl, 52614-34-3;  $\text{Fe}(\text{CO})_4$ -(E)-CHCl=CHCl, 52646-80-7;  $\text{Fe}(\text{CO})_4$ -(Z)-CH(CN)=CH(CN), 92011-76-2;  $\text{Fe}(\text{CO})_4$ -(E)-CH(CN)=CH(CN), 92077-29-7;  $\text{C}_2\text{F}_4$ , 116-14-3;  $\text{C}_2\text{Cl}_4$ , 127-18-4;  $\text{C}_2(\text{CN})_4$ , 670-54-2.

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