Articles

Density Functional Study of $Fe(CO)_3$ and $Fe(CO)_3(L)$ with H_2 and C_2H_4, where L = H_2 or C_2H_4: Reactions Relevant to Olefin Hydrogenation

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Received January 21, 2004

The bonding and geometries of $H_2Fe(CO)_3$, $H_2Fe(CO)_3(C_2H_4)$, and $HFe(CO)_3(C_2H_5)$, which are species relevant to iron carbonyl-catalyzed olefin hydrogenation, are analyzed using density functional theory (DFT). These calculations indicate that $H_2Fe(CO)_3$ and $H_2Fe(CO)_3(C_2H_4)$ are respectively triplet and singlet dihydrogen complexes with $H_2Fe(CO)_3(C_2H_4)$ lower in energy than $HFe(CO)_3(C_2H_5)$ by a modest amount (10.2 kcal/mol with BP86/LACV3P**). Further, it is likely that when $H_2Fe(CO)_3(C_2H_4)$ forms, it can rearrange to form the $HFe(CO)_3(C_2H_5)$ complex. The reductive elimination of C_2H_6 from $HFe(CO)_3(C_2H_5)$ is exothermic, whether it is accompanied by or precedes ethylene addition.

I. Introduction

Density functional theory has been used to investigate the mechanism and the species responsible for the iron carbonyl-catalyzed hydrogenation of ethylene. Prior experimental work in this area has focused on the gas-phase kinetics of iron carbonyls, ethylene-substituted iron carbonyls, and hydrogen complexes of iron carbonyls.[1−14] Time-resolved IR spectroscopy has played a primary role in these studies. It has been used to observe processes involved in the evolution of the catalytic cycle for olefin hydrogentation.[3,5,15] The following mechanism, which is depicted in Scheme 1 and discussed below, was proposed by Wrighton[13] and studied by Grant,[6] to explain olefin hydrogenation by iron carbonyls.

Iron pentacarbonyl ($Fe(CO)_5$) can be photolyzed in the gas phase, by ultraviolet light in the 300 nm range, to generate triplet iron tricarbonyl ($Fe(CO)_3$).[1−3] When $Fe(CO)_3$ is generated in the presence of ethylene and hydrogen, it can react with both C_2H_4 and H_2 as part of the catalytic cycle involved in the hydrogenation of ethylene.[3,5] Addition of ethylene to $H_2Fe(CO)_3$ or H_2 to $Fe(CO)_3(C_2H_4)$ results in what has been alluded to by Hayes and Weitz as singlet $H_2Fe(CO)_3(C_2H_4)$.[3] Hayes and Weitz attribute an IR absorption near 2051 cm^{-1} to this complex, which has been regarded as "the postulated crucial intermediate in the hydrogenation of ethylene".[3,5,6] It has been "conventional wisdom" that ethane formation proceeds by reductive elimination after transfer of a hydrogen from the iron carbonyl-bound ethylene moiety to form an iron carbonyl-bound alkyl (C_2H_5) hydride.[6] The reductive elimination of ethane could be driven by the association of a second ethylene, or ethylene could add to $Fe(CO)_3$ after ethane loss. Both scenarios generate $Fe(CO)_3(C_2H_4)$, which can react with hydrogen to regenerate $H_2Fe(CO)_3(C_2H_4)$.

II. Computational Methods

The application of computational methods can provide valuable insights into complexes that are not observable using current experimental methodologies. For example, compounds may exist as steady-state intermediates in a chemical reaction at concentrations that are too low to observe. In addition, computational methods can provide insights into unobservable properties of reactive species: for example, localized charges or electron densities.

Interestingly, a crucial postulated intermediate in ethylene hydrogenation, $HFe(CO)_3(C_2H_5)$, has *not* been observed ex-

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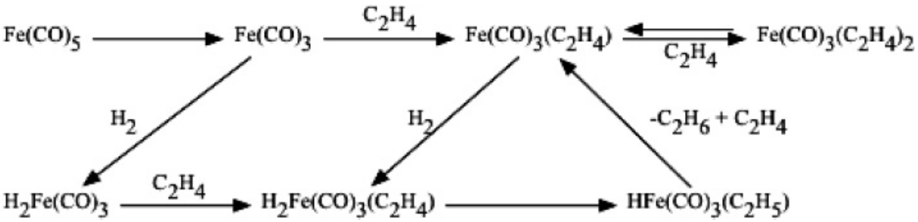
10.1021/om0499411 CCC: $30.25

Scheme 1



perimentally. It has been hypothesized that formation of this species could be the rate-limiting step in the loss of ethane from $H_2Fe(CO)_3(C_2H_4)$, and therefore $HFe(CO)_3(C_2H_5)$ would not be present in significant concentrations.[6]

Over approximately the past decade, DFT methods have emerged as preferred alternatives to both semiempirical and HF methods when applied to problems in organometallic chemistry.[16−20] The particular attraction of this method is that minimization of the energy requires only three spatial coordinates, thus scaling as N^3 (where N is the number of basis functions). The most successful DFT methods have centered on gradient-corrected (also referred to as "nonlocal" or "generalized-gradient approximation" (GGA) functionals) and hybrid methods. Gradient-corrected methods attempt to account for the variation of electron density with position, leading to lower exchange−correlation energies, while hybrid methods mix some amount of the exact Hartree−Fock exchange energy into the exchange−correlation.

In this study, geometries, energies, and frequencies were calculated using the Jaguar quantum chemistry program.[21] All calculations were run using unrestricted DFT. Two basis sets, LACVP** and LACV3P**, were employed. LACVP** is a double-ζ basis set that employs the 6-31G** basis set for C, O, and H atoms. LACV3P** is a triple-ζ basis set that employs the 6-311G** basis set for C, O, and H atoms. Both basis sets make use of Hay and Wadt's effective core potentials,[22] which have been shown to give results similar to the corresponding all-electron calculations on transition metals, but at a reduced computational cost.[23] Generally, the smaller basis set was used to calculate the initial properties and geometries. Geometries optimized in this way were used as starting points for energy calculations using the larger basis set.

A calibration of enthalpies was performed by employing four different functionals (B3LYP, BLYP, B3P86, and BP86) to calculate the bond dissociation enthalpy for the C_2H_4−$Fe(CO)_3(C_2H_4)$ complex, for which this enthalpy has been experimentally measured. BP86 has been shown to often give excellent results for the geometries and energetics of iron carbonyl complexes,[24−26] while B3LYP gives good geometries, but the energetics are usually less accurate than those obtained with BP86.[24−26] Results from the present calibration calculations support these observations and indicate that the BP86 method is the most reliable of the functionals indicated above for the systems in this study. BP86 is a gradient-corrected functional that uses Becke's 1988 functional for exchange,[27] Perdew's 1986[28] functional, and Vosko, Wilk, and Nusair's functional for nonlocal correlation and local correlation, respectively.

In this study thermochemical data come from unscaled frequency calculations that use the same functional and basis set as the corresponding energy minimization calculations. DFT can typically compute vibrational frequencies for transition metal carbonyls within 2−10% of the observed frequency.

Bond energies are calculated using the following scheme[29] (eqs 1 and 2):

$$\mathrm{ML}_n \leftrightarrow \mathrm{ML}_{n-1} + \mathrm{L} \tag{1}$$

$$\Delta E_{\mathrm{elec}} = E(\mathrm{ML}_{n-1}) + E(\mathrm{L}) - E(\mathrm{ML}_n) \tag{2}$$

Bond enthalpies at 298 K are calculated by factoring in the relevant thermochemical data. In the following scheme, the ΔZPE is the change in the zero-point energy of the products versus the reactants. The same treatment is applied to obtain the change in the thermal energy, which is a sum of rotational, vibrational, and translation energies. The factor ΔPV is equal to RT for every mole of gas formed and accounts for the molar work term when assuming ideal gas behavior (eq 3).

$$\Delta H_{298} = \Delta E_{\mathrm{elec}} + \Delta \mathrm{ZPE} + \Delta E_{\mathrm{th}} + \Delta(PV) \tag{3}$$

Basis set superposition error (BSSE) corrections, obtained from counterpoise calculations, are included for the results obtained using the BP86 method and the LACV3P** basis set. The BSSE correction for the reactions under study was in the 1.6−4.1 kcal/mol range. A BSSE calculation was carried out for the dissociation of ethylene from $Fe(CO)_3(\eta^2\text{-}C_2H_4)_2$ using the BP86 method and the smaller basis set. As expected, the BSSE obtained with the smaller basis set is larger. For this specific reaction it was 4.6 kcal/mol, which is 0.8 kcal/mol larger than what was obtained using the LACV3P** basis set.

A Mulliken population analysis (MPA) has been performed along with a natural population analysis (NPA), since MPA is often basis set dependent. The stand-alone NBO 4.0 program was used to calculate NPA using the "bndidx" keyword to display bond indices between nuclear centers,[30] while Wiberg indices are used to compare bond orders.[31]

III. Results and Discussion

A. Calibration Calculations. Though the bond energy has been experimentally determined for only one of the complexes discussed in the work, several systems provide data for calibrations for basis sets and functionals for the complexes studied in this work.

The energy of the (C_2H_4)−$Fe(CO)_3(C_2H_4)$ bond, which is discussed in more detail in Section III.D, has been experimentally determined to be 21.3 ± 2 kcal/mol.[32] The data in Table 1 show that with the BP86 functional a bond dissociation enthalpy (BDE) is calculated that

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Table 1. Enthalpy of the Reaction $^3Fe(CO)_3(C_2H_4) + C_2H_4 \rightarrow Fe(CO)_3(C_2H_4)_2$

Δ*H* BP86/LACV3P**	−26.2 kcal/mol (−22.4)[a]
Δ*H* B3P86/LACV3P**	−21.6 kcal/mol
Δ*H* BLYP/LACV3P**	−16.3 kcal/mol
Δ*H* B3LYP/LACV3P**	−11.6 kcal/mol

[a] The value in parentheses includes the BSSE correction.

is ~5 kcal/mol higher than the experimental value. When the BSSE correction of 3.8 kcal/mol is included, the value calculated using the BP86 function is within the reported error of the experimental value. With B3P86, BLYP, and B3LYP the uncorrected enthalpies are 0.4 kcal/mol higher and ~ 5 and ~11 kcal/mol lower than the experimental value, respectively.

The data clearly show that there is a dependence on both the correlation gradient used and whether hybridization is included. The BLYP and B3LYP values are already lower than the experimental value, and application of a BSSE correction would lead to even poorer agreement. Thus, we conclude that as previously observed, the use of the LYP gradient is generally not favorable for systems of this type.[25] The BSSE correction for the B3P86 result would be expected to be of magnitude similar to the BP86 result and thus would be expected to give comparable though somewhat poorer agreement with experiment than the BP86 result.

The bond energy for the (C_2H_4)−Fe bond in $Fe(CO)_4(C_2H_4)$ has been experimentally determined, and based on an analysis of the experimental results in ref 32 it was concluded that the experimental BDE is in the range 36 ± 2.5 kcal/mol, independent of whether the singlet or triplet state of $Fe(CO)_4$ is the appropriate reference state. The calculated results for this BDE using BP86 is again quite close to the experimental value: 35 kcal/mol without the BSSE correction. The good agreement between experimental results and DFT calculations using the BP86 functional and the LACV3P** basis set was not surprising based on prior experience with Fe and Cr complexes.[24,25] It was anticipated that the combination of the BP86 functional and the LACV3P** basis set would give the most reliable data on bond energies.

Since $Fe(CO)_3(C_2H_4)$ is a triplet and the product, $Fe(CO)_3(C_2H_4)_2$, is a singlet, it is quite plausible that DFT overestimates the energy of $Fe(CO)_3(C_2H_4)$ relative to the product. Interestingly, the hybrid methods underestimate the bond enthalpy. As can be seen in Table 1, the hybrid DFT methods yield enthalpies that are ~5 kcal/mol lower than the nonhybrid DFT methods, and the values obtained with the methods including the LYP nonlocal correlation gradient are ~10 kcal/mol below the values obtained using the corresponding non-LYP gradient. Similar behavior has been noted by Cedeño and Weitz for calculations on the reaction $Fe(CO)_3 + C_3H_6 \rightarrow Fe(CO)_3(\eta^2\text{-}C_3H_6)$ using the same DFT methods.[25] Further, Table S1 contains a calculation for $\langle S^2 \rangle$ for $^3Fe(CO)_3(C_2H_4)$ for the different functionals and basis sets employed in this work. As expected, the BP86/LACVP** combination gives a value of $\langle S^2 \rangle$ that is closest to 2.0, the exact value expected for a triplet state complex.

We conclude from the above comparisons and discussion that the results obtained with the BP86 functional are likely to be more accurate than those obtained with any of the other three functionals. Thus, further discussion will focus on results obtained with the BP86 functional and the LACV3P** basis set.

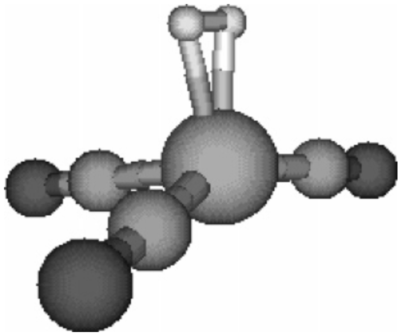

Figure 1. η^2-$H_2Fe(CO)_3$.

B. Energetics and Details of the Reaction $^3Fe(CO)_3 + H_2 \rightarrow {}^3H_2Fe(CO)_3$. $H_2Fe(CO)_3$ is formed by the addition of hydrogen to triplet $Fe(CO)_3$.[3,5] The structure of this compound is unknown, but has been hypothesized to be a trigonal bipyramidal *cis* dihydride. Calculations starting with this structure optimized to a C_s symmetry triplet η^2-H_2 complex.

A clear indication of the dihydrogen character of this complex is the calculated H−H bond length (0.78−0.83 Å), which is in general agreement with accepted values for a dihydrogen complex bond length of 0.82−0.90 Å.[33] Frequency calculations with BP86/LACV3P** yield an H−H stretch at 3768 cm^{-1}. A reduction in the stretching frequency relative to the fundamental of H_2 at 4159 cm^{-1} is expected as a result of the weakening (but not absence) of the H−H bond due to participation of H_2 in σ^*-bonding with the Fe center. The structure of the complex is shown in Figure 1, with geometric details reported in Table S2 in the Supporting Information.

It is interesting to note that an increase in the number of two-electron-donating π-accepting ligands, such as CO, usually *stabilizes* a dihydrogen ligand due to the π^*-accepting ability of the added CO ligands.[34] In this situation, an increase in the number of π^* orbitals around a metal center would normally be expected to lead to a lower electron density around the metal center, thus decreasing the relative population in the σ^* orbitals of the hydrogen and stabilizing the dihydrogen ligand. In $H_2Fe(CO)_4$ and $H_2Fe(CO)_3$, however, this trend is reversed. $H_2Fe(CO)_4$ is a true dihydride, while $H_2Fe(CO)_3$ is a *dihydrogen* complex.[34] A Mulliken population analysis, which is an arithmetic sum of the electron density in the overlapping orbitals between two nuclei (density is negative in antibonding orbitals and positive in bonding orbitals), of $H_2Fe(CO)_4$ and $H_2Fe(CO)_3$ for all functionals and all basis sets confirms this reversal. The iron in $H_2Fe(CO)_3$ has a significantly lower partial negative charge than the corresponding iron in $H_2Fe(CO)_4$. This is consistent with the iron in $H_2Fe(CO)_4$ possessing sufficient electron density to populate the σ^* orbitals of hydrogen. A population analysis also shows $H_2Fe(CO)_3$ to have significant bonding character in the H−H bond, while $H_2Fe(CO)_4$ has nonbonding character in the H−H bond. $H_2Fe(CO)_3$ also has a lower population in the Fe−H bonding orbitals than $H_2Fe(CO)_4$.

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Table 2. Mulliken Analysis of $H_2Fe(CO)_3$ and $H_2Fe(CO)_4$[a]

	$H_2Fe(CO)_3$				$H_2Fe(CO)_4$			
parameter	I	II	III	IV	I	II	III	IV
Fe chg.	−0.1206	0.0789	−0.1458	0.2480	−0.4376	−0.3721	−0.5379	−0.3401
H chg.	0.0738	0.0799	0.0602	0.0550	0.1541	0.1236	0.1259	0.0684
Fe−H pop.	0.087	0.126	0.074	0.105	0.204	0.142	0.231	0.178
H−H pop.	0.264	0.216	0.297	0.198	−0.003	−0.007	−0.002	−0.007

[a] I = BP86/LACVP**, II = BP86/LACV3P**, III = B3LYP/LACVP**, IV = B3LYP/LACV3P**.

Table 3. NBO Analysis of $H_2Fe(CO)_3$ and $H_2Fe(CO)_4$[a]

	$H_2Fe(CO)_3$				$H_2Fe(CO)_4$			
parameter	I	II	III	IV	I	II	III	IV
Fe chg.	−0.0586	−0.0691	0.0317	0.3353	−0.7541	−0.7859	−0.7253	−0.7455
H chg.	0.0385	0.0478	0.0168	0.0249	0.0573	0.0852	0.0086	0.0281
Fe−H order	0.127	0.159	0.091	0.110	0.383	0.388	0.431	0.435
H−H order	0.764	0.707	0.840	0.806	0.025	0.029	0.028	0.031

[a] I = BP86/LACVP**, II = BP86/LACV3P**, III = B3LYP/LACVP**, IV = B3LYP/LACV3P**.

Additionally, the charge on the hydrogens increases from $H_2Fe(CO)_3$ to $H_2Fe(CO)_4$, indicating that the hydrogens *lose* electron density to the metal (see Table 2).

An NBO comparison of $H_2Fe(CO)_3$ and $H_2Fe(CO)_4$ points to a conclusion similar to the Mulliken populations. There is an increase in the charge on the iron in $H_2Fe(CO)_4$, which is consistent with an increase in electron density around the metal. The NBO analysis also provides insights into the nature of the H_2 bond (see Table 3). In $H_2Fe(CO)_3$, there is considerable donation of electron density from the "classic" σ-bonding orbital to the empty iron *sd* hybrid orbital. In addition, the NBO analysis indicates there is a small amount of electron donation from the iron d orbitals to the H_2 "classic" σ^* orbital.

In $H_2Fe(CO)_4$, the NBO orbital analysis shows that there are strong couplings between the Fe−H (these are hybrid metal sd orbitals interacting with hydrogen s orbitals) bonds and the corresponding *trans* Fe−C (sd−sp hybrid interactions) bonds. This is probably indicative of an interaction where electron density is funneled into the Fe−H bonds from *trans* Fe−C bonds, thus stabilizing the Fe−H bonds and weakening the H−H bond.

The calculated enthalpies for the reaction of H_2 with $Fe(CO)_3$ range from ~ −2 to ~ −7 kcal/mol, depending on the functional and the basis set used (see Table S3). The enthalpy calculated using BP86/LACV3P** is −5.9 kcal/mol with the BSSE correction. The magnitude of this enthalpy is somewhat smaller than the bond enthalpy reported for the dihydrogen complex, $(\eta^2\text{-}H_2)Cr(CO)_5$, of 15.0 ± 1.3 kcal/mol.[35] Clearly the bond between dihydrogen and the metal center in this complex is weaker than in the corresponding Cr complex.

C. Energetics and Details of the Reaction $^3Fe(CO)_3 + C_2H_4 \rightarrow {}^3Fe(CO)_3(C_2H_4)$. Formation of $Fe(CO)_3(C_2H_4)$ occurs when ethylene complexes with $Fe(CO)_3$. The $Fe(CO)_3(C_2H_4)$ complex was hypothesized to have a triplet ground state because $Fe(CO)_3$, with a triplet ground state,[3,36] complexes with a ligand with a singlet ground state and also because $\eta^2\text{-}H_2Fe(CO)_3$ is calculated to have a triplet ground state. We have optimized the structure of $Fe(CO)_3(C_2H_4)$ as both a singlet and a triplet and note that the triplet ground state is lower in energy than the corresponding singlet minima by ~9 kcal/mol. The structure of $Fe(CO)_3(C_2H_4)$ can be described as a C_s symmetry distorted tetrahedron. The molecule is depicted in Figure 2, with structural details in Table S4.

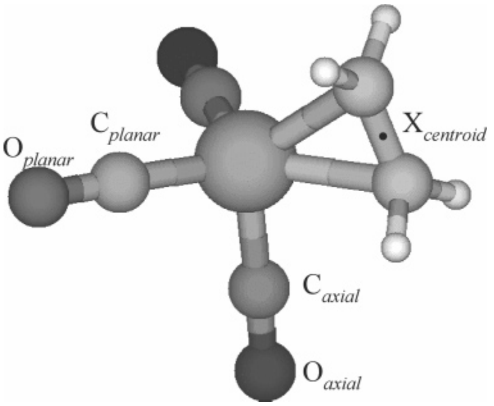

Figure 2. $Fe(CO)_3(C_2H_4)$.

However, we also note that prior calculations by Cedeño produced results in which $Fe(CO)_3(\eta^2\text{-}C_3H_6)$, an analogous complex, has a structure that converges to a slightly lower energy as a singlet than as a triplet.[25] Nevertheless, there is experimental evidence, which is summarized in ref 25, involving the kinetics of the reaction of $Fe(CO)_3$ that is consistent with $Fe(CO)_3(\eta^2\text{-}C_3H_6)$ being a triplet. The contrary computational result was attributed to the fact that energy calculations using DFT methods on open shell systems are sometimes elevated compared to the corresponding closed shell systems. This is likely due to the inclusion of higher order spin states in the wave function of the open shell systems.[37,38] The BP86/LACV3P** enthalpy calculated for the association of ethylene and $Fe(CO)_3$ is −20.2 kcal/mol (−23.1 kcal/mol without BSSE correction), which is very similar to the value of −22.7 kcal/mol (without BSSE correction) obtained in a prior calculation by Cedeño for $^3Fe(CO)_3 + C_3H_6 \rightarrow {}^3Fe(CO)_3(\eta^2\text{-}C_3H_6)$.[25]

D. Energetics and Details of the Reaction $^3Fe(CO)_3(C_2H_4) + C_2H_4 \rightarrow Fe(CO)_3(C_2H_4)_2$. $Fe(CO)_3(C_2H_4)_2$ results from the addition of ethylene to $^3Fe(CO)_3(C_2H_4)$. Singlet $Fe(CO)_3(C_2H_4)_2$ can be described as having a C_{2v} trigonal-bipyramid structure with the

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Table 4. Mulliken Analysis of $H_2Fe(CO)_3(C_2H_4)$[a]

	$H_2Fe(CO)_3(C_2H_4)$				$H_2Fe(CO)_4$			
parameter	I	II	III	IV	I	II	III	IV
Fe chg.	−0.4144	−0.2059	−0.4848	−0.1948	−0.4376	−0.3721	−0.5379	−0.3401
H chg.	0.1129	0.1094	0.1038	0.0909	0.1541	0.1236	0.1259	0.0684
Fe−H pop.	0.094	0.121	0.088	0.103	0.204	0.142	0.231	0.178
H−H pop.	0.225	0.216	0.258	0.255	−0.003	−0.007	−0.002	−0.007
$C_{(CO)}$−Fe pop. (equit.)	0.309	0.153	0.311	0.176	0.248	0.146	0.250	0.174
$C_{(C_2H_4)}$−Fe pop.	0.123	0.122	0.132	0.136				

[a] I = BP86/LACVP**, II = BP86/LACV3P**, III = B3LYP/LACVP**, IV = B3LYP/LACV3P**.

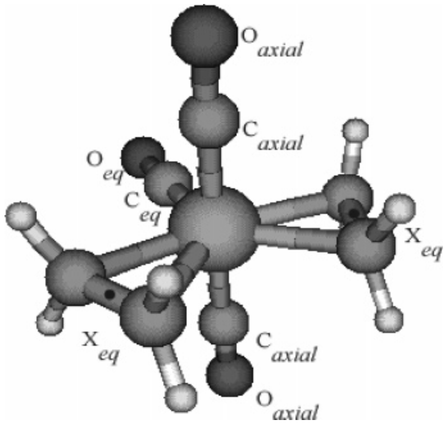

Figure 3. $Fe(CO)_3(C_2H_4)_2$.

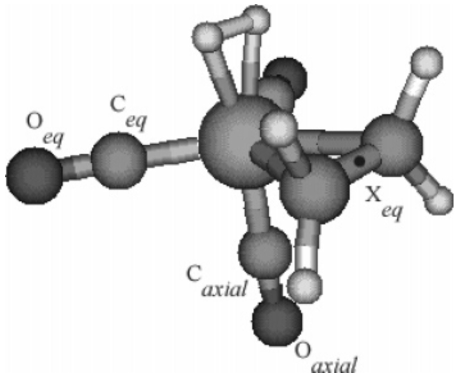

Figure 4. η^2-$H_2Fe(CO)_3(C_2H_4)$.

ethylene ligands in the equatorial plane. This structure is shown in Figure 3, with structural parameters in Table S5.

The title reaction involves a spin-forbidden transformation to form a singlet product from the triplet $Fe(CO)_3(C_2H_4)$ and singlet C_2H_4 reactants. The bond enthalpy calculated for the addition of a second ethylene ligand using the four different functionals ranges from ~ -12 to ~ -26 kcal/mol (without BSSE corrections). A value of −22.4 kcal/mol was obtained for the enthalpy for this process from a BP86/LACV3P** calculation including the BSSE correction. This calculated value is within the experimental error of the enthalpy of −21.3 ±2.0 kcal/mol reported for this reaction by House and Weitz.[1] The bond enthalpy calculated with the other functionals used in this study is in Table S6.

E. Energetics and Details of the Reaction $H_2Fe(CO)_3 + C_2H_4 \rightarrow H_2Fe(CO)_3(C_2H_4)$. It has been speculated that $H_2Fe(CO)_3(C_2H_4)$ is a singlet *cis* dihydride with a *fac* carbonyl octahedral structure.[6] If this species acted like Wilkinson's hydrogenation catalyst, $H_2RhCl(PPh_3)$, insertion of the first hydride would be the rate-limiting step, followed by a fast insertion of the second hydride.[6] However, calculations for the $H_2Fe(CO)_3(C_2H_4)$ dihydride complex fail to find a minimum for this species.

Onda and co-workers proposed that $H_2Fe(CO)_3(C_2H_4)$ may be a singlet trigonal bipyramidal dihydrogen species.[14] Calculations on such a complex result in a minimum that has a trigonal bipyramidal structure with C_s symmetry. Again, evidence for the dihydrogen character comes from the H−H bond length (~0.80−0.85 Å) and the presence of an H−H stretching mode near 3164 cm^{-1} (BP86/LACV3P**). Compared to $H_2Fe(CO)_3$, which has a calculated bond length of 0.78−0.83 Å and a frequency of 3768 cm^{-1}, the H−H bond in $H_2Fe(CO)_3(C_2H_4)$ is longer and at a lower frequency. Thus, it can be concluded that it is somewhat weaker. Results describing the structure of η^2-$H_2Fe(CO)_3(C_2H_4)$ are presented in Figure 4 and Table S7.

It is interesting to note that $H_2Fe(CO)_3(C_2H_4)$ is a dihydrogen complex, while $H_2Fe(CO)_4$, which also has four two-electron-donating ligands (CO), is a dihydride. In comparing the results of the Mulliken population analysis for $H_2Fe(CO)_3(C_2H_4)$ to that for $H_2Fe(CO)_4$, it can be seen that the charge around the metal in $H_2Fe(CO)_3(C_2H_4)$ is slightly lower, the populations of the Fe−CO bonds are higher, implying increased back-bonding, and there is significant population in the H−H bonding orbital (see Table 4). A comparison of the equatorial CO-bonding $H_2Fe(CO)_4$ to the C_2H_4 σ bond in $H_2Fe(CO)_3(C_2H_4)$ shows that C_2H_4 is a poorer σ donor than CO, which likely accounts for the lack of sufficient electron density around the metal in $H_2Fe(CO)_3(C_2H_4)$ to break the H−H bond.

The NBO analysis of $H_2Fe(CO)_3(C_2H_4)$ and $H_2Fe(CO)_4$ is again consistent with the results of the Mulliken analysis (see Tables 4 and 5). Further, the NBO analysis shows there is a greater tendency for the dihydrogen ligand σ^* orbital in $H_2Fe(CO)_3(C_2H_4)$ to back-donate to the empty metal *sd* hybrid orbitals, consistent with retention of the dihydrogen character of the H_2 ligand.

The formation of $H_2Fe(CO)_3(C_2H_4)$, by addition of C_2H_4 to $H_2Fe(CO)_3$, involves a spin-forbidden transition from a triplet reactant to a singlet product. To our knowledge there are no experimental values for the enthalpy change associated with this addition reaction. The value calculated using BP86/LACV3P** is −35.2 kcal/mol (−39.3 kcal/mol without the BSSE corrections).

F. Energetics and Dynamics of the Reaction $HFe(CO)_3(C_2H_5) + C_2H_4 \rightarrow Fe(CO)_3(C_2H_4) + C_2H_6$. Although it is plausible that the $HFe(CO)_3(C_2H_5)$ complex could be a triplet alkyl hydride, calculations

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Table 5. NBO Analysis of $H_2Fe(CO)_3(C_2H_4)$[a]

	$H_2Fe(CO)_3(C_2H_4)$				$H_2Fe(CO)_4$			
parameter	I	II	III	IV	I	II	III	IV
Fe chg.	−0.5191	−0.5319	−0.4525	−0.4575	−0.7541	−0.7859	−0.7253	−0.7455
H chg.	0.1034	0.1183	0.0883	0.1004	0.0573	0.0852	0.0086	0.0281
Fe−H pop.	0.181	0.192	0.170	0.180	0.383	0.388	0.431	0.435
H−H pop.	0.606	0.585	0.671	0.651	0.025	0.029	0.028	0.031

[a] I = BP86/LACVP**, II = BP86/LACV3P**, III = B3LYP/LACVP**, IV = B3LYP/LACV3P**.

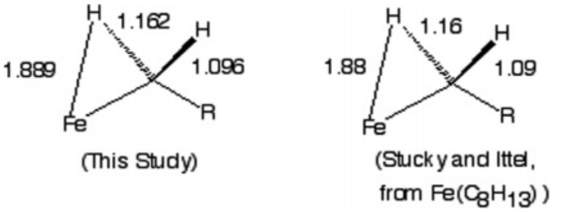


Figure 5. Agostic hydrogen interactions.

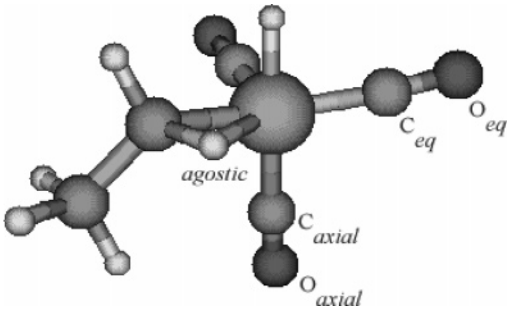


Figure 6. $HFe(CO)_3(C_2H_5)$.

Table 6. Enthalpy of the Reaction $HFe(CO)_3(C_2H_5) + C_2H_4 \rightarrow Fe(CO)_3(C_2H_4) + C_2H_6$

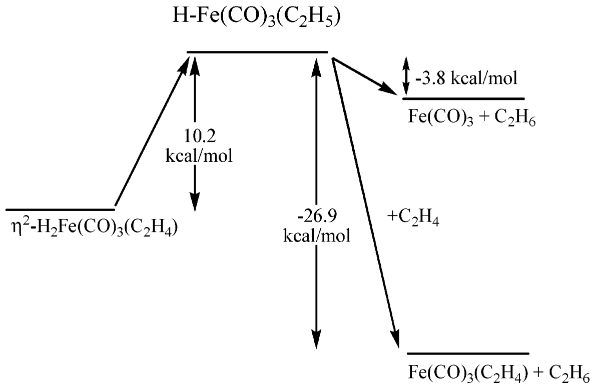
	association included	loss of ethane
ΔH BP86/LACV3P**	−26.9 kcal/mol	−3.8 kcal/mol
ΔH B3LYP/LACV3P**	−36.3 kcal/mol	−20.6 kcal/mol

indicate that it is a singlet alkyl hydride with one of the alkyl hydrogens participating in an agostic interaction with the iron center. The bond lengths are summarized in Figure 5 and compared to corresponding bond lengths reported by Stucky and Ittel for an iron complex exhibiting agostic interactions.[33,39] The relevant structural data are summarized in Figure 6 and Table S8.

In the gas phase, if reductive elimination of C_2H_6 occurs, it is an effectively irreversible process since the ethane is free to exit the complex into the gas phase, where in the absence of added ethane, it will be present at low concentrations. The possibility that association of ethylene precedes the reductive elimination of the alkane or that elimination of the alkane precedes the association of ethylene has been considered. Although our methods do not provide insights into the reaction dynamics, they can be used to calculate the energetics of these processes. In either case, the reactions are exothermic (see Table 6), favoring the formation of the alkane and $Fe(CO)_3(C_2H_4)$.

Scheme 2

Hydrogenation Step
(BP86/LACV3P** Enthalpy Differences Reported)



The results of the calculation with the BP86 and B3LYP functionals are indicated in Table 6. In all the other calculations reported in this study, the enthalpies calculated for a process using the BP86 functional have a larger absolute magnitude than the enthalpies calculated using B3LYP. However, all the other calculations were for a ligand association process, where the reaction in Table 6 involves bond scission as well the formation of a new bond (the $H-C_2H_5$ bond). To understand the source of the differences in the BP86 and B3LYP results, we consider the steps involved in a thermodynamic cycle leading from $HFe(CO)_3(C_2H_5)$ to $Fe(CO)_3 + C_2H_6$.

Breaking the $Fe-C_2H_5$ bond in $HFe(CO)_3(C_2H_5)$ is calculated to require 34.6 kcal/mol using BP86/LACV3P**, while with B3LYP/LACV3P** the energy required is 19.9 kcal/mol. Breaking the $H-Fe(CO)_3$ bond is calculated to require 65.4 kcal/mol with BP86/LACV3P**, while with B3LYP/LACV3P** the calculated enthalpy is 62.0 kcal/mol (all results are without the BSSE correction and all bond enthalpies were calculated on the basis of enthalpies of the relevant fragments in their optimized minimum energy geometry). Thus, once again, the bond enthalpy calculated for these iron complexes using B3LYP is actually smaller than the corresponding energy calculated using BP86. The sum of the two bond energies does not exactly equal the energy reported for the loss of ethane in Table 6 due to differences in the calculated energy of ethane. Although the energies for breaking the $H-Fe(CO)_3$ bonds are similar and close to the experimentally determined value for the average bond enthalpy of an Fe−H bond in $(H)_2Fe(CO)_4$,[2] an enthalpy of ~34 kcal/mol is a much more reasonable value for an $Fe-C_2H_5$ bond than ~20 kcal/mol.[40]

G. Reaction Scheme. Scheme 2 is a diagram of the relative energies of the complexes involved in the hydrogenation reaction in this system. Enthalpies for

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Table 7. Enthalpies of the Reaction $(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4) \rightarrow \text{HFe(CO)}_3(\text{C}_2\text{H}_5)$

ΔH BP86/LACVP**	8.7 kcal/mol
ΔH BP86/LACV3P**	10.2 kcal/mol
ΔH B3LYP/LACVP**	11.4 kcal/mol
ΔH B3LYP/LACV3P**	14.2 kcal/mol

the reaction $(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4) \rightarrow \text{HFe(CO)}_3(\text{C}_2\text{H}_5)$ are also given in Table 7.

The barrier height for the reaction $(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4) \rightarrow \text{HFe(CO)}_3(\text{C}_2\text{H}_5)$ has not been calculated. However, at equilibrium at room temperature, on the basis of the differences in enthalpy, the relative population of the two species $\text{HFe(CO)}_3(\text{C}_2\text{H}_5)/(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4)$ would be on the order of 3×10^{-8} (assuming no significant difference in entropy).

Similar ratios of reactants to intermediate concentrations were seen for the mechanism for iron carbonyl-induced olefin isomerization.[15,41] This ratio was sufficient to allow olefin isomerization to become a facile process at room temperature. The kinetics for such a process are outlined by Weitz and Long for Fe(CO)_3 and 1-pentene.[15]

IV. Conclusion

The structures and energetics of intermediates relevant to hydrogenation of ethylene by iron carbonyls have been calculated using density functional theory (DFT). Calibration results using four DFT methods (BP86, B3P86, BLYP, and B3LYP) and the LACVP3** basis set indicate that BP86 yields values for enthalpies that are preferable. Deviations from available experimental data may be larger when the reaction involves a change in spin of one of the reactants.

$(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4)$ is calculated to be a singlet dihydrogen complex. The reductive elimination of ethane from $(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4)$ proceeds through an $\text{HFe(CO)}_3(\text{C}_2\text{H}_5)$ intermediate, which is calculated to have an enthalpy that is 10.2 kcal/mol higher than $(\eta^2\text{-H}_2)\text{Fe(CO)}_3(\text{C}_2\text{H}_4)$ (BP86/LACV3P**). Once this alkyl hydride intermediate is accessed, reductive elimination of ethane is an exothermic process even in the absence of ethylene addition. Thus, we conclude that while ethylene addition may occur in concert with, or after elimination of, ethane, it is not required for the elimination of ethane to be exothermic.

Finally, calculations indicate that $\text{H}_2\text{Fe(CO)}_3$ is a triplet dihydrogen complex. When compared to $\text{H}_2\text{Fe(CO)}_4$, these results show a reversal of the generally expected trend in which an increase of two electron-donating ligands that are good π-acceptors stabilize a dihydrogen ligand. However, they are readily rationalized when the results of a Mulliken population analysis and an NBO analysis are considered.

Acknowledgment. We acknowledge support of this work by the National Science Foundation under Grant NSF 97-34891.

Supporting Information Available: This material, which is described in the text, is available free of charge via the Internet at http://pubs.acs.org.

OM0499411

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