

# Density Functional Theory Study of $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ , $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , and the Iron–Allyl Bond Energy

David L. Cedeño\*

Department of Chemistry, Illinois State University, Normal, Illinois 61790

Eric Weitz\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received November 5, 2002

Geometries and energies have been calculated for the pseudoaxial and pseudoequatorial isomers of singlet and triplet state  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  and three isomers of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  using density functional theory, with the BP86, BLYP, B3P86, and B3LYP functionals. The triplet state pseudoaxial olefin isomer is lower in energy than the pseudoequatorial isomer, while for the allyl hydride species the facial isomers are lower in energy than the meridional isomer. The energy of the Fe–allyl bond in  $\text{XFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{X} = \text{H}, \text{I}$ ) has been calculated, and an effective upper limit of 54 kcal/mol can be set for  $\text{X} = \text{H}$  and 45 kcal/mol for  $\text{X} = \text{I}$ . A comparison of the calculated  $\Delta H$  values with estimates for the Fe–allyl BDE, obtained via thermodynamic cycles, emphasizes that bond energies are not necessarily transferable from one complex to another. Comparison of our calculations with data obtained from matrix experiments, known gas phase experimental data, and data for ligand addition reactions to iron carbonyl complexes indicates that the reaction  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  is expected to preferentially occur from the triplet state pseudoaxial mono-olefin isomer to either or both of the facial-exo and endo allyl product isomers.

## I. Introduction

The isomerization of olefins is a reaction of importance in both synthetic organic chemistry and a number of industrial processes. It is well established that such a reaction can be homogeneously catalyzed by appropriate organometallic complexes.<sup>1–5</sup> Olefin isomerization processes are believed to take place via either of two prototypical mechanisms (see Scheme 1). The alkyl hydride mechanism involves a 16-electron metal hydride catalyst. Upon binding the olefin, hydrogen from the metal hydride migrates to the olefin to form an alkyl complex, which can undergo  $\beta$ -elimination of hydrogen to form an isomerized olefin. In the allyl hydride mechanism an olefin binds to a 14-electron metal complex and a  $\beta$ -hydrogen from the olefin is transferred to the metal, forming an  $\eta^3$ -allyl hydride complex. The reverse process leads to the aforementioned hydrogen being transferred back to the allyl moiety. If the hydrogen is transferred to a different carbon atom, olefin isomerization is effected.

Iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) and some of its olefin derivatives (i.e.,  $\text{Fe}(\text{CO})_3(\eta^2\text{-alkene})_2$ ) can participate in

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994; p 107.

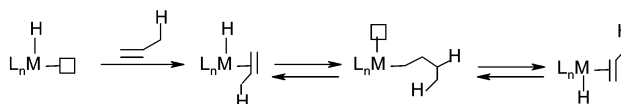
(3) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

(4) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992.

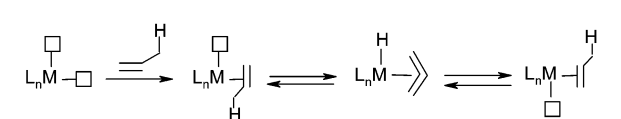
(5) Pruchnick, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum Press: New York, 1990; p 343.

## Scheme 1

Alkyl Hydride Mechanism - 16 electron metal hydride catalyst



Allyl Hydride Mechanism - 14 electron bare metal catalyst



the catalytic isomerization of olefins via the allyl mechanism.<sup>6–12</sup> The catalytically active carbonyl precursor is  $\text{Fe}(\text{CO})_3$ . Intermediates in the iron carbonyl-catalyzed isomerization of olefins have been experimentally detected. Barnhardt and McMahon<sup>11</sup> observed two  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers in a low-temperature matrix environment. One isomer was proposed to have the

(6) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

(7) Fleckner, H.; Grevels, F. W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

(8) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551. (b) Mitchner, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975. (c) Mitchner, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1065. (d) Wu, Y. H.; Bentsen, J. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530.

(9) Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 977.

(10) (a) Whetten, R. L.; Fu, K. J.; Grant, E. R. *J. Am. Chem. Soc.* **1982**, *104*, 4270. (b) Whetten, R. L.; Fu, K. J.; Grant, E. R. *J. Phys. Chem.* **1982**, *77*, 3769.

(11) Barnhardt, T. M.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5434.

(12) Long, G. T.; Wang, W.; Weitz, E. *J. Am. Chem. Soc.* **1995**, *117*, 12810.

olefin in a pseudoequatorial position and the other in a pseudoaxial position. The pseudoequatorial species was assigned as the more stable isomer on the basis of results for an analogous ethylene complex:  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_2\text{H}_4)$ .<sup>15</sup> Barnhardt and McMahon found that both of the  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers thermally convert to  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , thus demonstrating that the allyl hydride complex is thermodynamically favored versus the olefin complex under their experimental conditions. Detailed studies of the kinetics and energetics of the  $\text{Fe}(\text{CO})_5/\text{propene}$  and the  $\text{Fe}(\text{CO})_5/\text{pentene}$  systems, in the gas phase, have been subsequently reported in refs 12 and 16. These studies provide either direct measurements or estimates for the rate constants and energetics for the critical steps in the allyl mechanism depicted in Scheme 1. Mitchner and Wrighton<sup>8d</sup> detected two isomers of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , formed from the photolysis of iron tetracarbonyl propene complexes in a matrix at 77 K. Similar results were obtained from the photolysis of an iron tetracarbonyl pentene complex in a matrix.<sup>8d</sup> Although there are no experimental geometrical data on the isomers of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , there are X-ray data available for a related allyl iodide complex:  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ .<sup>13</sup> The preferred isomer in the solid state has a facial conformation with the iodide ligand in an endo position relative to the central hydrogen of the allyl moiety. However, there are two other possible isomers, a facial-exo and a meridional. Solution phase NMR reveals that the facial-endo and facial-exo isomers are in thermal equilibrium, but that in some solvents and at some temperatures the facial-exo isomer is predominant over the facial-endo complex.<sup>14</sup>

The  $\pi$ -allyl species is a critical intermediate in the isomerization of olefins and an important species in organometallic chemistry. However, there is very little experimental data regarding the energy of a metal–allyl bond. Knowledge of this bond energy could provide insights into differences in the catalytic activity of various organometallic complexes toward olefin isomerization.

Density functional theory has become an important tool that can be applied to gain insight into the mechanisms and energetics of organometallic reactions.<sup>17–19</sup> A growing set of calculations have reproduced available experimental data with very good accuracy and at a cost lower than that of the most advanced ab initio methods.<sup>20–25</sup> In the present work the Fe–allyl bond energy in both  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  and  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  is calculated using density functional theory and compared to estimates obtained from thermodynamical cycles based on available experimental data. The ener-

getics of the  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  to  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  transformation are also calculated and compared to the gas phase data for this system obtained by Long et al.<sup>12</sup>

## II. Computational Method

Equilibrium geometries and energies were calculated with the Jaguar quantum chemistry program.<sup>26</sup> All calculations were performed using density functional theory (DFT) with the BP86, BLYP, B3P86, and B3LYP functionals. Both B3P86 and B3LYP are hybrid methods using the three-parameter equation developed by Becke.<sup>27</sup> All of these methods use the local and nonlocal exchange functionals by Slater<sup>28</sup> and Becke,<sup>29</sup> respectively. B3P86 and BP86 use the local correlation of Perdew and Zunger (PZ81)<sup>30</sup> and Perdew's<sup>31</sup> (P86) nonlocal correlation functional. B3LYP uses local and nonlocal correlation functionals by Vosko et al.<sup>32</sup> (VWN) and Lee et al.<sup>33</sup> (LYP), respectively, while BLYP uses local and nonlocal correlation functionals by Lee et al.<sup>33</sup> Nonlocal density functionals were added self-consistently. Geometry optimization and energy minimization were run separately for every molecule using two different basis sets: LACVP\*\* and LACV3P\*\*. Both use Hay and Wadt's effective core potential (ECP)<sup>34</sup> to describe the metal and iodine, while other nonmetals are described using the 6-31G\*\* basis set<sup>35</sup> with LACVP\*\* and the 6-311G\*\* basis set<sup>36</sup> with LACV3P\*\*. In all computations the frozen core approximation was used, in which the outermost core orbitals are not frozen. Open shell calculations (both high and low spin) were run under unrestricted conditions.

Reaction energies ( $\Delta E$ ) are calculated by subtracting the sum of the reactant energies from the sum of the product(s) energies. They are then corrected for zero-point energy ( $\Delta ZPE$ ) and thermal contributions from molecular motion ( $\Delta E_{\text{th}}$ ) at  $T = 298$  K. Both  $\Delta ZPE$ s and  $\Delta E_{\text{th}}$  were obtained from unscaled vibrational frequency calculations on the optimized geometries. Reaction enthalpy changes ( $\Delta H$ ) are calculated from the

(13) Minasyants, M. K.; Struchkov, Y. T. *J. Chem. Struct. (Engl. Transl.)* **1968**, *9*, 577.

(14) (a) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71. (b) Nesmeyanov, A. N.; Ustynuk, Y. A.; Kristkaya, I. I.; Shchembelov, G. A. *J. Organomet. Chem.* **1968**, *14*, 395. (c) Nesmeyanov, A. N.; Fedorov, L. A.; Avakyan, N. P.; Petrovskii, P. V.; Fedin, E. I.; Arshavskaya, E. V.; Kristkaya, I. I. *J. Organomet. Chem.* **1975**, *101*, 121.

(15) Barnhart, T. M.; Fenske, R. F.; McMahon, R. J. *Inorg. Chem.* **1992**, *13*, 2679.

(16) Long, G. T.; Weitz, E. *J. Am. Chem. Soc.* **2000**, *122*, 1431.

(17) Laird, B. B.; Ross, R. B.; Ziegler, T. In *Chemical Applications of Density Functional Theory*; ACS Symposium Series 629; American Chemical Society: Washington, DC, 1996; Chapter 2.

(18) *Density Functional Theory Methods in Chemistry*; Labanowski, J. K.; Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991.

(19) (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (b) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743.

(20) Rosa, A.; Ehlers, A. W.; Baerends, E. J.; Snijders, J. G.; te Velde, G. *J. Phys. Chem.* **1996**, *100*, 5690.

(21) Radius, U.; Bickelhaupt, F. M.; Ehlers, A. W.; Goldberg, N.; Hoffmann, R. *Inorg. Chem.* **1998**, *37*, 1080.

(22) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(23) Nunzi, F.; Sgamelotti, A.; Re, N.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1999**, 3487.

(24) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653.

(25) (a) Cedeño, D. L.; Weitz, E.; Bérces, A. *J. Phys. Chem. A* **2001**, *105*, 8077. (b) Cedeño, D. L.; Weitz, E. *J. Am. Chem. Soc.* **2001**, *123*, 12857.

(26) *Jaguar 4.0 and 4.1*; Schrödinger Inc.: Portland, OR, 1998–1999.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(28) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

(29) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(30) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5058.

(31) (a) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(32) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(33) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(34) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(35) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233.

(c) Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 879. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (f) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (g) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223.

(36) (a) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, *4*, 294. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (d) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1989**, *72*, 5639.

**Table 1.** Calculated  $\Delta E$  and  $\Delta(\text{ZPE} + E_{\text{th}})$  (in parentheses) Relative to the Triplet Pseudoaxial Isomer for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  Species<sup>a</sup>

|                 | BP86   |        | BLYP  |        | B3P86  |        | B3LYP  |       |
|-----------------|--------|--------|-------|--------|--------|--------|--------|-------|
|                 | I      | II     | I     | II     | I      | II     | I      | II    |
| singlet         | -3.5   | -2.0   | 0.1   | 0.8    | 6.1    | 6.8    | 8.3    | 9.0   |
|                 | (-5.2) | (-0.8) | (1.6) | (-2.1) | (-0.1) | (-1.6) | (-1.4) | (0.2) |
| triplet pseudo- | 4.8    | 5.0    | 5.5   | 5.0    | 4.8    | 4.4    | 4.0    | 4.2   |
| equatorial      | (-1.1) | (1.1)  | (2.4) | (-4.6) | (-1.1) | (-1.4) | (-1.9) | (0.7) |

<sup>a</sup> In kcal/mol. I and II refer to full energy minimization results using the LACVP\*\* and LACV3P\*\* basis sets, respectively. Enthalpy differences are calculated using eq 1.

corrected  $\Delta E$  at 298 K by adding the  $\Delta(PV)$  term, which is equal to  $\Delta nRT$  assuming ideal gas behavior:

$$\Delta H(298 \text{ K}) = \Delta E + \Delta \text{ZPE} + \Delta E_{\text{th}} + \Delta nRT \quad (1)$$

In some cases, energy differences between isomers are within the computational error limits. It is generally accepted that the energy ordering of states of the same spin multiplicity is more reliable than specific energy differences. Thus, where energy differences between isomers are small, we focus on relative energy differences rather than absolute energies. In addition to the aforementioned calculations, natural bond order (NBO)<sup>37</sup> calculations were performed for the allyl complexes using Jaguar.

### III. Results and Discussion

**A. Energetics of the Reaction  $\text{Fe}(\text{CO})_3 + \text{C}_3\text{H}_6 \rightarrow \text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ .**  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  can be formed by the addition of propene to  $\text{Fe}(\text{CO})_3$ , where  $\text{Fe}(\text{CO})_3$  can be directly produced via photolysis:<sup>16</sup>



There is convincing evidence that the ground state of  $\text{Fe}(\text{CO})_3$  is a triplet.<sup>38,39</sup> Calculations (BP86/LACV3P\*\*) in this study agree with this conclusion and place the triplet state of  $\text{Fe}(\text{CO})_3 \sim 8$  kcal/mol lower than the lowest energy singlet state. Because  $\text{Fe}(\text{CO})_4$  is known to have a triplet ground state, and it has been inferred that other unsaturated tetracoordinate iron carbonyl complexes have triplet ground states,<sup>38,40</sup> it might be also inferred that  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  has a triplet ground state. However, to avoid biasing our results, unrestricted DFT calculations were run for both the triplet and the singlet multiplicities of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . The DFT calculated energy difference between the triplet and singlet states of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  differ from method to method. With both BP86 and BLYP, geometry optimizations for the singlet state typically converged to structures that are slightly lower than or quite similar to the energy of the lowest energy triplet state structure. The differences in enthalpy between the lowest energy singlet and triplet structures are within the expected error of the frequency calculations, which determine the  $\Delta(\text{ZPE} + E_{\text{th}})$  values (see Table 1). It

should be noted, however, that unrestricted DFT energy calculations of high spin systems often lead to elevated energies relative to corresponding low spin systems and also that the high-spin–low-spin energy differences are influenced by the way correlation effects are used by each functional when describing each spin state.<sup>41–47</sup> The manner in which spin in open shell systems is treated by the respective functionals can also influence energies. In the present case these effects would lead to the expectation that the triplet state is not as high in energy relative to the singlet state as the various calculations suggest. Interestingly, although both B3P86 and B3LYP give a triplet state that is lower in energy than the singlet state, both of these DFT methods fail to reproduce the experimental enthalpy for the reaction  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , while the BP86 method does a better job. These facts suggest that both the triplet and singlet states are close in energy. Given that DFT does not lead to a clear determination of the singlet–triplet energy difference, or even the energy ordering of these states, it is important to consider the available experimental data relevant to this issue.

There is published work that provides evidence in favor of a triplet ground state for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . Smaller rate constants for ligand addition reactions have been observed when there is a change in spin multiplicity relative to reactions where the addition reaction is spin-conserving.<sup>38b</sup> On the basis of this criterion the ground states of a number of  $\text{Fe}(\text{CO})_3\text{L}$  complexes, including  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ , have been imputed to be triplet states.<sup>38</sup> Given that the ground state of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  is a triplet, it is highly unlikely that the addition of one methylene group to  $\text{C}_2\text{H}_4$  to give propene would change the energy ordering of the ground state and the first excited state. There is additional data that favors a triplet ground state for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . Geometry optimizations under singlet multiplicity for both pseudoequatorial and pseudoaxial  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  converged to only one singlet isomer (with the olefin in the pseudoaxial position). In matrix experiments two distinct isomers were detected.<sup>11</sup> Thus, if there is only one stable isomer for a singlet ground state, an excited state of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  would have to account for the second isomer that is observed experimentally. Various isomers that can coexist on the ground state potential energy surface of a molecule have been observed, including less thermodynamically favored species.<sup>48,49</sup> However, there is little precedent for the long-term stability of an electronically excited state in a matrix environment since such states can potentially relax via both radiative and nonradiative processes.<sup>49,50</sup> Thus, we feel the most likely interpretation of this matrix experiment is that the two observed species are the two triplet isomers. On the basis of these data and the aforementioned data on rate constants for

(37) Glendenning, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 1996.

(38) (a) Weitz, E. *J. Phys. Chem.* **1994**, *98*, 11256. (b) House, P. G.; Weitz, E. *Chem. Phys. Lett.* **1997**, *266*, 239.

(39) Barnes, L. A.; Rossi, U.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1991**, *94*, 2031.

(40) Wang, J.; Long, G. T.; Weitz, E. *J. Phys. Chem. A* **2001**, *105*, 3765.

(41) Wang, W.; Weitz, E. *J. Phys. Chem. A* **1997**, *101*, 2358.

(42) Ricca, A.; Bauschlicher, C. W., Jr. *J. Phys. Chem.* **1994**, *98*, 12899.

(43) Young, D. *Computational chemistry: A practical guide for applying techniques to real world problems*; Wiley: New York, 2001.

(44) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 8582.

(45) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(46) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

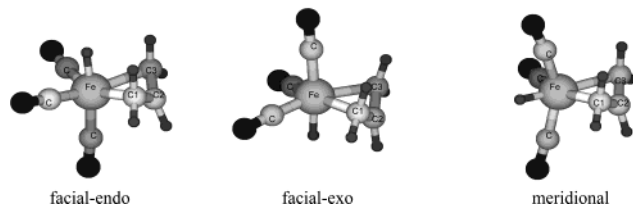
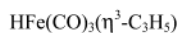
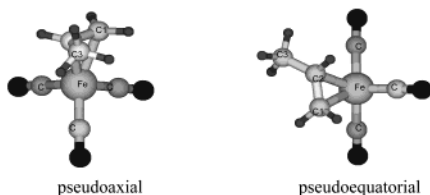
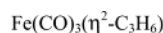
(47) Loew, G. H.; Harris, D. L. *Chem. Rev.* **2000**, *100*, 407.

(48) Knudsen, A. K.; Pimentel, G. C. *J. Phys. Chem.* **1991**, *95*, 2823.

(49) Varetti, E. L.; Pimentel, G. C. *J. Chem. Phys.* **1971**, *55*, 3813.



Scheme 2



addition reactions we feel that the weight of evidence is clearly on the side of a triplet ground state for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . As such, we have used the energy of the triplet as the ground-state energy of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  throughout the paper. This conclusion implies that the DFT calculations artificially elevate the energy of the triplet state relative to the energy of the singlet state of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . As previously mentioned, this elevation of energies of high spin systems in DFT calculations is well known.<sup>41–47</sup> This effect is also seen in our calculation of the energy difference between  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  and  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  (vide infra), for which there is experimental data.<sup>12</sup> Due to the artificial elevation of the triplet energy, it is expected that there is some computational error in the triplet state energies relative to singlet state energies. As such, we will consider and refer to energy values calculated relative to the triplet energy as limiting values.

BP86-optimized structures for the pseudoequatorial and pseudoaxial isomers of  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  are shown in Scheme 2. Calculated structural data for this complex could be found in the Supporting Information. To our knowledge there are no experimental geometric data for this complex. However, there are experimental data for the related saturated  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  complex.<sup>51</sup> Calculated geometrical data for  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  are in agreement with the available experimental data to within typical accuracy and are similar to calculated data for  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . Independent of the functional and the basis sets employed, the pseudoaxial  ${}^3\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  isomer is calculated to be lower in energy than the pseudoequatorial isomer (2–8 kcal/mol). Barnhardt et al.<sup>15</sup> report that for the analogous ethylene complex,  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_2\text{H}_4)$ , the isomer assigned as pseudoequatorial is more stable than the one assigned as pseudoaxial. However, their study on the propene system<sup>11</sup> did not provide conclusive quantitative data on the relative stability of the two observed  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers. Unscaled calculations of carbonyl stretching frequencies were performed on both complexes. Although the values calculated using the various functionals (see Supporting Information) are in at least qualitative agreement with

those observed in the matrix spectra, the results obtained with the BP86 functional provide the best agreement. However, both isomers have very similar spectra, and therefore frequency calculations alone do not provide enough information to allow for a clear determination of which set of absorptions belongs to each of the two anticipated isomers, pseudoaxial and pseudoequatorial.

For both the pseudoequatorial and pseudoaxial isomers, geometry optimizations (BP86/LACVP\*\*) were also carried out starting with isomeric structures in which the olefin is rotated 90°. During optimization these structures converted to the isomers shown in Scheme 2. This strongly suggests that the structures shown in Scheme 2 represent global minima for the respective isomers, and therefore these were the only isomers taken into consideration. In the case of the pseudoequatorial isomer all DFT methods yield structures in which the alkene binds to the metal with the C=C bond perpendicular to the pseudoequatorial plane. In the case of the pseudoaxial isomer, the olefin binds to the metal with the C=C bond aligned with the plane that bisects the pseudoequatorial CO ligands, although there are slight differences in the geometries obtained using different functionals (see Supporting Information, Table S1).

The calculated enthalpy for the addition of propene to  ${}^3\text{Fe}(\text{CO})_3$  ranges from 12 to 23 kcal/mol for the pseudoaxial isomer and 9–17 kcal/mol for the pseudoequatorial isomer, depending on the functional and basis set utilized (see Table 2). Although there is no experimental determination of this bond enthalpy, the enthalpies calculated using the BP86 functional, 23.3 (LACV3P\*\*) and 18.7 (LACVP\*\*) kcal/mol for the pseudoaxial isomer, are certainly reasonable when compared to the value estimated for the Fe–C<sub>3</sub>H<sub>6</sub> BDE value in the bisolefin  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$  complex of 19 kcal/mol.<sup>12</sup> The result obtained with the B3LYP functional yields the smallest bond enthalpy. Previous DFT calculations using the B3LYP functional for BDE determination in iron complexes are compatible with our results in this study in that they can be too low.<sup>52</sup> To corroborate the validity of the aforementioned estimate of the BDE for loss of the first olefin in  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$ , we also calculated (BP86/LACV3P\*\*) the Fe–C<sub>3</sub>H<sub>6</sub> BDE in the bis-propene complex relative to  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . The calculation yields 21.1 kcal/mol, which may be taken as an effective upper limit for the BDE since, as previously mentioned, the energy of the triplet state product,  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ , may be artificially elevated by a few kcal/mol relative to the ground singlet state of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$ . However, the magnitude of this effect would be anticipated to be only a few kcal/mol, and thus the agreement with the estimated value of 19 kcal/mol is still good.

**Energetics of the Reaction  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ .** Scheme 2 shows the optimized structures for the singlet ground state of the three allyl hydride isomers. Complete geometrical information can be found in the Supporting Information. Although there are no experimental data for any of these complexes, there is an X-ray structure<sup>13</sup> for an analogous allyl

(50) Kerins, P.; Healy, B.; McCaffrey, J. G. *Low Temp. Phys.* **2000**, 26, 756.

(51) Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, 21, 401.

(52) Cedeño, D. L.; Weitz, E.; Bérces, A. *J. Phys. Chem. A* **2001**, 105, 3773.

**Table 2.** Calculated  $\Delta E$  and  $\Delta(\text{ZPE} + E_{\text{th}})$  (in parentheses) for the Reaction  ${}^3\text{Fe}(\text{CO})_3 + \text{C}_3\text{H}_6 \rightarrow {}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)^a$ 

| product                                    | BP86           |                | BLYP           |                 | B3P86          |                | B3LYP          |                |
|--|----------------|----------------|----------------|-----------------|----------------|----------------|----------------|----------------|
|  | I              | II             | I              | II              | I              | II             | I              | II             |
| pseudoaxial                                | -22.3<br>(4.2) | -25.1<br>(2.4) | -18.6<br>(0.8) | -18.0<br>(3.7)  | -20.2<br>(3.9) | -22.8<br>(4.6) | -14.9<br>(3.5) | -17.1<br>(3.4) |
| pseudoequatorial                           | -17.5<br>(3.2) | -20.2<br>(3.5) | -13.1<br>(3.2) | -12.9<br>(-0.9) | -15.5<br>(2.9) | -18.4<br>(3.2) | -10.9<br>(1.6) | -12.9<br>(4.1) |
| exptl estimate ( $\Delta H$ ) <sup>b</sup> | -19            |                |                |                 |                |                |                |                |

<sup>a</sup> Energies and enthalpies in kcal/mol. I and II refer to full energy minimization results using the LACVP\*\* and LACV3P\*\* basis sets, respectively. Enthalpy differences are calculated according to eq 1. <sup>b</sup> Estimated from loss of  $\text{C}_3\text{H}_6$  from  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$  in ref 12; calculated value for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$  (BP86/LACV3P\*\*) is -21 kcal/mol.

**Table 3.** Calculated  $\Delta H_{298}$  for the Reaction  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)^a$ 

| reaction                               | BP86           |       | BLYP |      | B3P86 |      | B3LYP |      |
|--|----------------|-------|------|------|-------|------|-------|------|
|  | I              | II    | I    | II   | I     | II   | I     | II   |
| p-axial $\rightarrow$ facial exo       | -8.4           | -8.7  | 1.0  | -4.9 | 0.6   | -2.4 | 5.4   | 3.6  |
| p-axial $\rightarrow$ facial endo      | -7.9           | -7.7  | 1.6  | -4.0 | 1.7   | -1.9 | 6.8   | 4.7  |
| p-axial $\rightarrow$ meridional       | -3.9           | -4.7  | 5.6  | -0.6 | 3.9   | 1.2  | 10.3  | 7.6  |
| p-equatorial $\rightarrow$ facial exo  | -12.2          | -14.8 | -6.9 | -5.4 | -3.1  | -5.3 | 3.3   | -1.3 |
| p-equatorial $\rightarrow$ facial endo | -11.7          | -13.8 | -6.3 | -4.5 | -1.9  | -4.8 | 4.6   | -0.1 |
| p-equatorial $\rightarrow$ meridional  | -7.7           | -10.8 | -2.4 | -1.0 | 0.3   | -1.8 | 8.2   | 2.7  |
| exptl <sup>b</sup>                     | -7.2 $\pm$ 0.6 |       |      |      |       |      |       |      |

<sup>a</sup> In kcal/mol. I and II refer to full energy minimization results using the LACVP\*\* and LACV3P\*\* basis sets, respectively. <sup>b</sup> Gas phase at room temperature from ref 12.

iodide complex,  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , with a facial-endo conformation. A DFT calculation (BP86/LACV3P\*\*) of the structure of the facial endo- and exo- $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  isomers reproduces the available experimental structural data with typical accuracy (see Supporting Information, Table S5). This agreement suggests that calculated geometries for  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  should be similarly reliable.

All of the DFT calculations indicate that the facial-exo isomer of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  is the lowest in energy, although the facial-endo isomer has a similar energy ( $\sim 1$  kcal/mol above), while the meridional isomer is the highest in energy (3–5 kcal/mol above the endo isomer). Although there is experimental evidence<sup>8d</sup> for the observation of at least two isomers of the allyl hydride in a matrix, it has not been determined which of the three possible isomers they correspond to. As indicated, the allyl iodide complex prefers the facial-endo conformation in the solid state, but there is evidence that in solution there is an equilibrium between the endo and exo allyl iodide iron isomers.<sup>14</sup> The small energy differences calculated are consistent with the existence of an equilibrium between allyl hydride isomers, with the endo and exo isomers being the dominant species.

One of the interesting observations of Barnhardt and McMahon<sup>11</sup> is that one of the  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers converts thermally to the allyl hydride at a matrix temperature of 5 K, while the other isomer does not convert until the temperature of the matrix is raised to 50 K. Since there is evidence for two isomers of the reactant, and no definitive evidence as to the product isomer(s) that are formed, there are multiple possible pathways from reactants to products. Long et al.<sup>12</sup> report an experimentally determined gas phase enthalpy change for this reaction of  $-7.2 \pm 0.6$  kcal/mol, with the allyl hydride complex being more thermodynamically stable than the  $\eta^2$ -olefin complex. The experimental activation energy for the  $\beta$ -hydrogen transfer process was estimated to be  $< 3.5$  kcal/mol.<sup>12</sup> However,

the study in ref 12 does not distinguish between possible isomers of the reactants or products.

DFT calculations of  $\Delta H$  for the  $\beta$ -hydrogen transfer reaction from the propene complex to the allyl hydride complex were performed for a number of functionals and two basis sets (see Table 3). Of all the functionals and basis set combinations there are some values that agree reasonably well with the gas phase experimental value ( $-7.2 \pm 0.6$  kcal/mol). The best agreement (within 2 kcal/mol) with experiment is obtained for the enthalpy change in the following cases:

- The reaction goes from the axial olefin isomer to produce facial endo- and exo-products using BP86 (both basis sets) and BLYP/LACV3P\*\*.
- The reaction goes from the equatorial olefin isomer to the facial endo- and exo-products using B3P86/LACV3P\*\* and BLYP/LACVP\*\*.
- The reaction goes from the axial and equatorial olefin isomers to the meridional product using BP86/LACV3P\*\* and BP86/LACVP\*\*, respectively.

The last two may be, *a priori*, less likely scenarios since both the equatorial olefin complex isomer and meridional allyl hydride are the highest energy species. Although it is likely that a mixture of isomers is at equilibrium in the gas phase at room temperature, it is expected that the reaction mixture will be dominated by the pseudoaxial  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomer on the basis of the relative energies of the reactant isomers, assuming that there is not a significant difference in the entropies of the compounds. Consistent with this picture, the calculated values should then agree best with experimental gas phase data if the process is dominated by conversion of the pseudoaxial  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  complex to the facial-exo and/or endo  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  complexes. If this picture is accepted, the best agreement occurs for values calculated with the BP86 functional. B3P86 and, particularly, B3LYP undervalue the reaction enthalpy (see Table 3), to such an extent that in some cases the calculated enthalpy is no longer negative. This likely

**Table 4. Calculated  $\Delta H_{298}$  for the Reaction  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5) \rightarrow {}^2\text{HFe}(\text{CO})_3 + {}^2\text{C}_3\text{H}_5$ <sup>a</sup>**

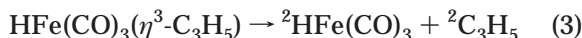
| $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$<br>isomer | BP86 |      | BLYP |      | B3P86 |      | B3LYP |      |
|--|------|------|------|------|-------|------|-------|------|
|  | I    | II   | I    | II   | I     | II   | I     | II   |
| facial exo   | 52.2 | 54.2 | 42.0 | 43.0 | 43.9  | 46.1 | 33.5  | 36.4 |
| facial endo  | 51.6 | 53.2 | 41.4 | 42.1 | 42.7  | 45.7 | 32.2  | 35.2 |
| meridional   | 47.7 | 50.2 | 37.5 | 38.7 | 40.5  | 42.6 | 28.6  | 32.4 |
| exptl <sup>b</sup>   | 52   |      |      |      |       |      |       |      |

<sup>a</sup> Enthalpies in kcal/mol. I and II refer to full energy minimization results using the LACVP\*\* and LACV3P\*\* basis sets, respectively. <sup>b</sup> This work, estimated using a thermodynamic cycle.

occurs because of the factors affecting the energy of high spin systems that have been alluded to previously.

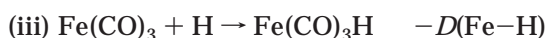
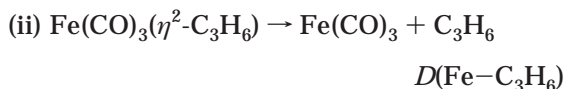
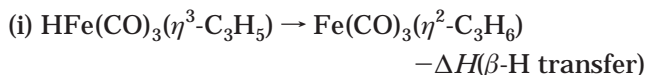
Considering that BP86 is the DFT method that best reproduces the enthalpy change in the  $\beta$ -hydrogen transfer reaction ( ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ ), and the vibrational spectrum of the  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers, and that it has been used to reliably reproduce BDEs in other iron carbonyl complexes, we consider this method to be the most reliable for a calculation of the Fe–allyl bond enthalpy in both  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  and  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ . Consistent with the above discussion, as seen in Table S7, the BP86 functional also has the smallest spin contamination in the calculation of the optimized structure of  ${}^3\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ .

**C. Fe–Allyl Bond Enthalpy.** Fe–allyl bond enthalpies were calculated for the reaction



These are in the 48–54 kcal/mol range (BP86, see Table 4) for all allyl hydride isomers. Calculations are relative to the doublet ground state of  $\text{HFe}(\text{CO})_3$ , which is 35 kcal/mol below the lowest energy quartet state. If the meridional allyl hydride is excluded, because it is the highest energy isomer, the range is narrowed to 52–54 kcal/mol. Thus, 54 kcal/mol represents an effective upper limit for the Fe–allyl BDE, even taking into account that there is the possibility of an artificial elevation of the energy of the high spin species.

To our knowledge there are no direct experimental determinations of the Fe–allyl bond energy. A previous estimate for the energy of this bond was based on the transferability of thermodynamic data from other processes. Long et al.<sup>12</sup> used the following thermodynamic cycle:

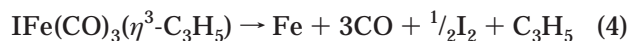


The only known experimental values for this cycle are steps i and iv:  $\Delta H(\beta\text{-H transfer})$  is  $-7$  kcal/mol and  $D(\text{C}-\beta\text{H})$  is  $88$  kcal/mol.<sup>53</sup> Given that the other steps in the cycle (ii and iii) are not known, the authors used

(53) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1973.

estimates. These were 19 kcal/mol for  $D(\text{Fe}-\text{C}_3\text{H}_6)$ , which was estimated from the bond dissociation energy for  $\text{C}_3\text{H}_6$  in  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$ , and 37.5 kcal/mol for the  $D(\text{Fe}-\text{H})$ , which was taken from the BDE for the diatomic FeH molecule.<sup>54</sup> With this set of values Long et al. obtained an estimate of 76 kcal/mol for the Fe–allyl bond energy, which is  $\sim 20$  kcal/mol above the calculated DFT/BP86 values. The  $D(\text{Fe}-\text{H})$  value in  $\text{Fe}(\text{CO})_4(\text{H})_2$  is likely to be a more accurately transferable thermodynamic parameter because the electronic environment around the metal in the allyl hydride is likely to be more similar to the environment in  $\text{Fe}(\text{CO})_4(\text{H})_2$  than in FeH. If the available average for the Fe–H bond energy ( $D(\text{Fe}-\text{H})$ ) in  $\text{Fe}(\text{CO})_4(\text{H})_2$  of 62 kcal/mol<sup>55</sup> is used instead of 37.5 kcal/mol for the Fe–H BDE in FeH, the estimated Fe–allyl BDE is then 52 kcal/mol, which is in very good agreement with the DFT/BP86 calculations. The desirability of using the  $D(\text{Fe}-\text{H})$  value from  $\text{Fe}(\text{CO})_4(\text{H})_2$  is further supported by enthalpy calculations of step iii ( $D(\text{Fe}-\text{H})$  in  ${}^2\text{HFe}(\text{CO})_3$ ), which is in the 59–63 kcal/mol range.

Another estimate of the Fe–allyl bond energy that was based on thermodynamic data was provided by Connor et al.,<sup>56</sup> and yields a value of  $42 \pm 3$  kcal/mol. This was obtained using the experimental heat of disruption ( $168 \pm 3$  kcal/mol) of the allyl iodide complex,  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ :



In their determination they employed an Fe–CO bond energy of  $28.1 \pm 0.5$  kcal/mol (the indicated bond energy is the average value for an Fe–CO bond in  $\text{Fe}(\text{CO})_5$ ) and an Fe–I bond energy of  $42 \pm 2$  kcal/mol, which is obtained from the heat of disruption of  $\text{Fe}(\text{CO})_4(\text{I})_2$ . This thermodynamically derived value of  $\sim 42$  kcal/mol for the Fe–allyl bond in  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  is 10 kcal/mol below the value obtained using the thermodynamic cycle for the Fe–allyl bond in  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  using the Fe–H BDE taken from data on the  $\text{Fe}(\text{CO})_4(\text{H})_2$  complex. This 10 kcal/mol difference in the estimated energy is perhaps not surprising in light of the fact that what is being compared are Fe–allyl bond energies in two different complexes: the iodide and the hydride. Clearly the nature of the ligands around the metal center may affect this BDE.

To further investigate the bond energies in these complexes the Fe–allyl bond energy in the facial exo and endo-allyl iodide complex was calculated using a reaction analogous to reaction 3:



The  $\Delta H$  value obtained (BP86/LACV3P\*\* for the facial isomers) is in the 43–45 kcal/mol range, which is in good agreement with the estimate of Connor et al.<sup>56</sup> The calculated Fe–allyl BDE in the allyl iodide complex is  $\sim 9$  kcal/mol smaller than the calculated Fe–allyl bond energy in the allyl hydride complex (52–54 kcal/mol). As indicated above, estimated values for these BDEs,

(54) Schultz, R. H.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *94*, 2262.

(55) Wang, W.; Narducci, A. A.; House, P. G.; Weitz, E. *J. Am. Chem. Soc.* **1996**, *118*, 8654.

(56) Connor, J. A.; Demain, C. P.; Skinner, H. A.; Zafarani-Moattar, M. T. *J. Organomet. Chem.* **1979**, *170*, 117.



**Table 5.** Calculated  $\Delta H_{298}$  for Hydrogen Loss from  ${}^2\text{HFe}(\text{CO})_3$  and  $\text{C}_3\text{H}_6$ <sup>a</sup>

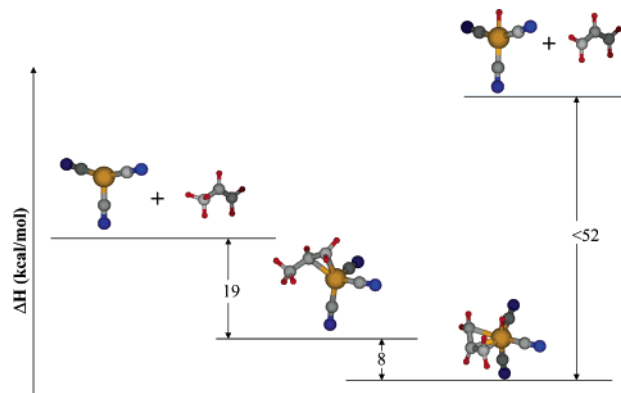
| reaction  | BP86 |      | B3LYP |      | BP86 |      | B3LYP |      | exptl             |
|---|------|------|-------|------|------|------|-------|------|-------------------|
|   | I    | II   | I     | II   | I    | II   | I     | II   |                   |
| ${}^2\text{HFe}(\text{CO})_3 \rightarrow {}^2\text{H} + {}^3\text{Fe}(\text{CO})_3$ | 63.3 | 63.4 | 59.7  | 59.7 | 61.8 | 61.8 | 58.9  | 58.7 | 62 <sup>b</sup>   |
| $\text{C}_3\text{H}_6 \rightarrow {}^2\text{H} + {}^2\text{C}_3\text{H}_5$          | 88.4 | 85.6 | 84.4  | 83.0 | 89.4 | 86.7 | 85.8  | 84.4 | 88.3 <sup>c</sup> |

<sup>a</sup> In kcal/mol. I and II refer to full energy minimization results using the LACVP\*\* and LACV3P\*\* basis sets, respectively. <sup>b</sup> Estimated Fe–H average energy from  $\text{H}_2$  loss from  $\text{Fe}(\text{CO})_4(\text{H})_2$  from ref 55. <sup>c</sup> From ref 53.

based on experimental data and an appropriate thermodynamic cycle, differ by a very similar amount:  $\sim 10$  kcal/mol.

The subject of transferability of bond energies is an important one in organometallic chemistry and has been reviewed by other authors.<sup>57–60</sup> Differences in the nature of the interactions between a given ligand (i.e., the allyl) and two similar but yet different metal fragments (i.e.,  $\text{IFe}(\text{CO})_3$  and  $\text{HFe}(\text{CO})_3$ ) may lead to different bond energies. The results of NBO calculations are consistent with the electronegativity of the iodine atom being a major contributory factor to the smaller Fe–allyl bond energy in the iodide complex relative to the hydride. These calculations indicate that the greater electronegativity of iodine results in there being less electron density available for the Fe–allyl bond in the iodide complex relative to the hydride complex, leading to a weaker bond in the iodide complex. The results of the NBO calculations are summarized in Scheme S1 in the Supporting Information. The difference in the estimated and calculated Fe–allyl bond energies in these two complexes ( $\sim 9$ – $10$  kcal/mol) suggests that transferability of bond energies from one complex to another must be done with caution and upon considering the effect of “spectator” ligands. However, it is interesting to note that the estimates of BDEs in each complex, at least when the average value of the Fe–H BDE in  $\text{H}_2\text{Fe}(\text{CO})_4$  is used as an input, agrees well with the value for the respective BDE calculated using DFT.

This agreement could come about as a result of selecting input data that agrees well with the actual BDEs in the complexes of interest and/or due to fortuitous cancellation of errors. To further investigate this issue the energy for each step (i to iv) in the cycle used as an input for  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  was calculated using the BP86 functional. The first reaction is the net olefin-allyl complex transformation (eq 3), which is calculated (vide supra) to be  $\sim 8$  kcal/mol exothermic on going from the axial olefin to the facial-endo/exo allyl hydride complexes. This value is only about 1 kcal/mol larger than the experimental value. The Fe– $\text{C}_3\text{H}_6$  bond energy in the axial  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  complex is calculated as 19–23 kcal/mol, which is 0–4 kcal/mol larger than the Fe– $\text{C}_3\text{H}_6$  BDE in  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)_2$ , which was used to estimate the BDE of  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)$ . The Fe–H bond energy in  $\text{HFe}(\text{CO})_3$ , which is calculated to be 63 kcal/mol (BP86, see Table 5), is only  $\sim 1$  kcal/mol larger than the average Fe–H value in  $\text{Fe}(\text{CO})_4(\text{H})_2$  (62 kcal/mol). The dissociation of a hydrogen atom from propene



**Figure 1.** Schematic depiction of the calculated (BP86/LACVP\*\*) energies for the formation and dissociation of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ .

to produce the allyl species is calculated to be in the range 86–88 kcal/mol (Table 5), in good agreement with the experimental value of 88.3 kcal/mol. From this comparison it is clear that the agreement between the estimate discussed above and the calculated value for the Fe–allyl BDE in  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  results from the fact that the input data generally agrees well with the calculated values for the BDEs that are needed for the cycle used to determine the Fe–allyl BDE. However, we emphasize that this is a result of good (or possibly fortuitous) choices of data that have been used as inputs to the cycle. It has already been pointed out that using the Fe–H BDE in  $\text{Fe}-\text{H}$  gives much poorer agreement with the calculated BDE. Similarly, if one were to use the Fe–H BDE in  $\text{CpFe}(\text{dpe})\text{H}$  of 70 kcal/mol, as calculated (BP86) by Tilset et al.,<sup>61</sup> one would obtain an Fe–allyl BDE that is 8 kcal/mol smaller than our best value. Thus, our conclusion is that the differences in  $\pi$ -allyl BDEs in  $\text{HFe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_5)$  and  $\text{IFe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_5)$  and the differences in the estimates for the BDE of  $\text{HFe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_5)$ , based on alternative but plausible data for the Fe–H BDE, make it clear that any attempt to transfer a BDE from one organometallic complex to another should be viewed with caution.

The bonding energetics calculated for the formation and dissociation of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  are shown schematically in Figure 1. It should be noted that the reactions that involve changes in spin are the overall loss of H from  $\text{HFe}(\text{CO})_3$  (doublet to triplet) and the BDE for the  $\beta$ -H in propene. This latter number is of course well established. In the former reaction the fact that both molecules are open shell systems could effectively cancel any potential offset in energy of one moiety relative to the other. Another interesting observation is that Fe–allyl energy computed as the sum of the calculated values for each step in the cycle yields

(57) Marks, T. J. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symp. Ser. 428; American Chemical Society, Washington, DC, 1990.

(58) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(59) Pilcher, G. *Pure Appl. Chem.* **1989**, *61*, 855.

(60) Calhorda, M. J.; Dias, A. R.; Minas da Piedade, M. E.; Salema, M. S.; Martinho Simões, J. A. *Organometallics* **1987**, *6*, 734.

(61) Tilset, M.; Fjeldhal, I.; Hamon, J.-R.; Hamon, P.; Toupet, L.; Saillard, J.-Y.; Costuas, K.; Haynes, A. *J. Am. Chem. Soc.* **2001**, *123*, 9984.

essentially the same value that is calculated directly from reaction 3. This of course is necessary if the DFT results are to be self-consistent.

In closing, it would be interesting to consider whether the value of a BDE that is calculated for a specific system of interest is intrinsically more reliable than an estimate based on the best available data, albeit data from different organometallic complexes. Of course there may be no general a priori answer to this question, but that itself is worthy of note.

#### IV. Conclusion

The energy of the Fe–allyl bond in  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  has been calculated using density functional theory and the BP86 functional. Within the error limits of the calculation an effective upper limit of 54 kcal/mol is obtained for the Fe–allyl bond in  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  with a triplet ground state for  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$ . This value agrees well with an estimate (52 kcal/mol) of this bond energy that has been obtained on the basis of a thermodynamic cycle that involves the transfer of thermochemical information from other molecules. Similar computations of the Fe–allyl bond in the  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  resulted in an upper limit of 45 kcal/mol, which is also in agreement with an estimate (42 kcal/mol) obtained using a thermochemical cycle. However, despite the agreement between calculations and estimates from thermodynamic cycles, the fact that both the estimated and calculated bond energies for  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  and  $\text{IFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  are significantly different ( $\sim 9\text{--}10$  kcal/mol) clearly indicates that the nature of the surrounding ligands influences the energy of a given bond. Therefore, caution has to be exercised when transferring available experimental bond energies from a given complex to estimate bond energies in a different complex using a thermodynamic cycle. NBO calculations indicate that the difference in electronegativity of iodine and hydrogen is a major contributor to this difference in Fe–allyl bond energies.

The enthalpy for conversion of the low-energy axial alkene isomer to either or both of the facial exo- and endo-product isomers ( $-8$  kcal/mol) is consistent with enthalpy changes for the reaction  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  ( $-7.2 \pm 0.6$  kcal/mol), as measured in the work reported in ref 12. Calculations support the existence of two  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6)$  isomers with the pseudoaxial 4–5 kcal/mol lower energy in energy than the pseudoequatorial isomer. The calculated energy ordering of these isomers is opposite the energy ordering suggested in a prior study,<sup>11</sup> which was based on IR assignments extrapolated from the ethylene complex.<sup>15</sup> BP86 calculations of the enthalpy of the reaction  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_3\text{H}_6) \rightarrow \text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  agree best with experiment for the pseudoaxial isomer as the principal reactant. The matrix experiments of Mitchner and Wrighton<sup>8d</sup> and other studies of allyl iron complexes<sup>13,14</sup> observed two isomers of the complexes under consideration. For  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  our calculations demonstrate these are likely to be the facial-endo and facial-exo isomers. These two isomers have similar energies (the exo isomer is lower by 1 kcal/mol) and are thermodynamically more favorable than the meridional isomer (by 4–5 kcal/mol).

**Acknowledgment.** We acknowledge the support of this work by the National Science Foundation under grant NSF 97-34891. We thank Les Kismartoni for sharing data with us from his calculations of the energies of a number of unsaturated iron carbonyl and iron carbonyl olefin complexes.

**Supporting Information Available:** Information on energies, geometries and frequencies of relevant complexes (as indicated in the text) and an NBO calculation for  $\text{XFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020920L