Gas-Phase Study of the Formation and Dissociation of $Fe(CO)_4H_2$: Kinetics and Bond Dissociation Energies

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Abstract: Time-resolved IR spectroscopy has been used to study the oxidative addition of H_2 to $Fe(CO)_4$ and its reverse reaction, the reductive elimination of H_2 from $Fe(CO)_4H_2$, in the gas phase. The rate constant for oxidative addition of H_2 shows little temperature dependence, indicating that if there is an activation barrier for this process it is small (<4 kcal mol^{-1}). The activation barrier for the reductive elimination of H_2 is 20.5 ± 2.1 kcal mol^{-1}. From these measurements, the average of the dissociation energies for the two Fe−H bonds in $Fe(CO)_4H_2$ is calculated to be 62 ± 2 kcal mol^{-1}. Kinetic measurements employing D_2 indicate small kinetic isotope effects for both the oxidative addition and reductive elimination reactions.

I. Introduction

The oxidative addition and reductive elimination of hydrogen are of great importance in organometallic chemistry. They represent fundamental steps in many catalytic systems.[1] Factors influencing the mechanism of hydrogen addition to a transition-metal complex have been the subject of extensive experimental and theoretical studies,[2] and the magnitude of metal−hydrogen bond dissociation energies (BDEs) is a central factor governing reaction pathways in many processes.[3] However, experimental measurements of metal−hydrogen BDEs can be difficult, and relatively few metal−hydrogen BDEs have been reported.[4] Over the past decade time-resolved IR spectroscopy has been successfully applied to determine BDEs in systems of ligands weakly bound to coordinatively unsaturated metal carbonyls.[5] Such measurements can be done in the gas phase, which provides an environment free of solvent effects. Here we report a study of the kinetics of the reversible oxidative addition of hydrogen to $Fe(CO)_4$, in the gas phase, by time-resolved IR spectroscopy, which provides information on the BDE of the Fe−H bonds in $Fe(CO)_4H_2$ and the mechanism for this reaction.

II. Experimental Section

Two types of time-resolved IR setups, which have been described in detail previously, were used in the current study.[6,7] For measurements of the rate of oxidative addition of hydrogen to $Fe(CO)_4$, a pulsed Nd:YAG laser, operating at 355 nm, was used to photolyze mixtures of $Fe(CO)_5$ and H_2/D_2, with or without added He, and a tunable infrared diode laser was used to monitor the decay of $Fe(CO)_4$ and the rise of $Fe(CO)_4H_2$. Helium is used to increase the heat capacity of the system to suppress shock waves that could result from inhomogeneous deposition of energy by the excitation pulse and a sufficient quantity is added to ensure that the bimolecular association reactions under study are in the high-pressure limit.

For measurements of the rate of reductive elimination of hydrogen from $Fe(CO)_4H_2$, an FTIR spectrometer was used to monitor the decay of $Fe(CO)_4H_2$ and the recovery of $Fe(CO)_5$. In the FTIR experiments, $Fe(CO)_4H_2$ was initially produced by photolysis of a mixture of $Fe(CO)_5$, H_2, and CO using ∼200 laser pulses. In all experiments the $Fe(CO)_5$ pressure was approximately 100 mTorr. Errors are reported as ±2σ.

III. Results and Discussion

The 355-nm photolysis of $Fe(CO)_5$ generates $Fe(CO)_4$ as a significant product. In the presence of added H_2, $Fe(CO)_4$ decays, accompanied by the formation of a new broad absorption, peaked at 2052 cm^{-1}. The rate of rise of the absorption at 2052 cm^{-1}, monitored by the diode laser, depends on H_2 pressure and matches the decay of $Fe(CO)_4$. The 2052-cm^{-1} absorption was also present in FTIR spectra taken following photolysis of mixtures of $Fe(CO)_4$ and H_2 with multiple laser pulses (Figure 1). At higher resolution (see inset to Figure 1) the 2052-cm^{-1} absorption can be seen to be composed of multiple peaks, with the largest peaks at ∼2057 and 2052 cm^{-1}. In addition to the band at 2052 cm^{-1}, a weak, broad absorption was observed at ∼1880 cm^{-1} in the FTIR spectra.

The only $Fe(CO)_4/H_2$ species that has been characterized is dihydridotetracarbonyliron, $Fe(CO)_4H_2$. In the gas phase $Fe(CO)_4H_2$ has been reported to have strong, ν(C−O), absorptions at 2056 and 2050 cm^{-1}.[8a] In hexane solutions, $Fe(CO)_4H_2$ shows strong, ν(C−O), absorptions at 2053 and 2042 cm^{-1} and a weak, broad, ν(Fe−H), absorption around 1880 cm^{-1}.[8b] Thus the species associated with the absorptions at ∼2056, ∼2052, and ∼1880 cm^{-1}, formed by the addition of H_2 to $Fe(CO)_4$, was assigned as $Fe(CO)_4H_2$. The ν(C−O) absorptions of another potential product, $Fe(CO)_4(\eta^2\text{-}H_2)$, a dihydrogen species,

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994. (c) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (d) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992.

(2) For recent reviews, see: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(3) (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(4) *Bonding Energetics in Organometallic Compounds;* ACS Symposium Series *V428*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990.

(5) (a) For a recent review, see: Weitz. E. *J. Phys. Chem.* **1994**, *98*, 11256. (b) Bogdan, P. L.; Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1991**, *113*, 1294. (c) McNamara, B.; Becher, D. M.; Towns, M. H.; Grant, E. R. *J. Phys. Chem.* **1994**, *98*, 4622.

(6) Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 3343.

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

(8) (a) Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2162. (b) Farmery, K.; Kilner, M. *J. Chem. Soc. A* **1970**, 634.

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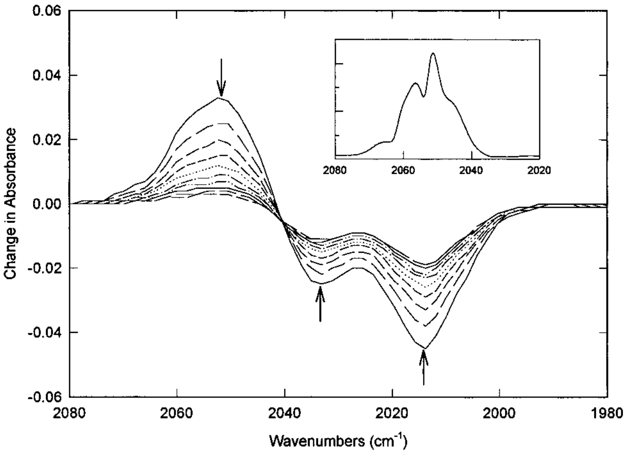

Figure 1. Time-resolved FTIR spectrum of the C−O stretching region following photolysis of a mixture of $Fe(CO)_5$ (100 mTorr), H_2 (15.0 Torr), CO (85.0 Torr), and He (390 Torr) by ~200 355-nm laser pulses. The spectrum is shown in 5.0-min increments for times of 0−45.0 min. Arrows indicate the direction of the change of absorbance with time. The inset is a higher resolution FTIR spectrum (0.5-cm^{-1} resolution) showing multiple peaks in the 2052-cm^{-1} band. The spectrum in the inset is a result of subtraction of the residual $Fe(CO)_5$ spectrum from the spectrum recorded immediately following photolysis of a mixture of $Fe(CO)_5$ (100 mTorr), H_2 (197 Torr), and CO (6.5 Torr) by ~200 355-nm laser pulses.

would be expected to be at significantly lower frequency since formation of the dihydride species is expected to require the transfer of more electron density from iron to hydrogen orbitals than in the formation of the dihydrogen species.

The rate constant for addition of H_2 to $Fe(CO)_4$, k_a, was measured to be $1.97 \pm 0.15 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 296.5 K and $2.47 \pm 0.49 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 315 K, over a range of H_2 pressure from ~50 to ~500 Torr (Figure 2). Though the rate constant at 315 K is slightly higher than that at 296.5 K, the two values are within experimental error of each other. This indicates that if there is an activation barrier for the addition of H_2 to $Fe(CO)_4$, it is small: less than ~2 kcal/mol based on the mean and ~4 kcal/mol based on the extremes of these two data points. The rate constant for addition of D_2 to $Fe(CO)_4$ is $2.27 \pm .28 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 296.5 K, slightly higher than but within the error limits of that for H_2. Thus the addition of hydrogen to $Fe(CO)_4$ has a small and possibly inverse kinetic isotope effect. Small kinetic isotope effects have been observed for related systems in solution.[9a−c]

The rate constant for addition of hydrogen to $Fe(CO)_4$ is about 3 orders of magnitude smaller than is typical for addition of hydrogen to other coordinatively unsaturated species.[6,10] The ground state of $Fe(CO)_4$ is known to be a triplet.[11] As with $Fe(CO)_4 + CO \rightarrow Fe(CO)_5$,[5a] the small rate constant for addition of hydrogen to $Fe(CO)_4$ is presumably a result of the system crossing from a triplet to a singlet potential energy surface during the course of the reaction.

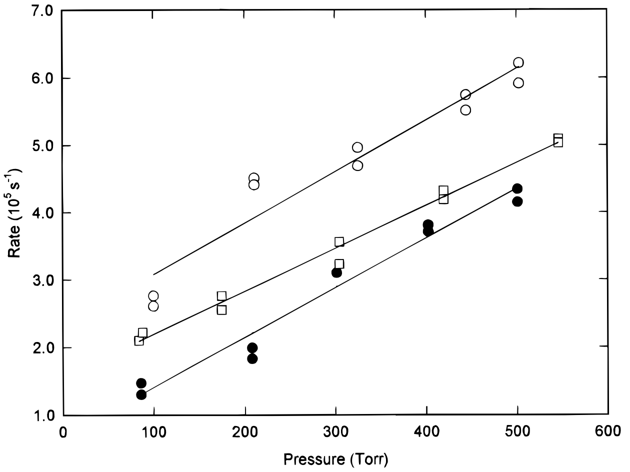

Figure 2. Rate of formation of $Fe(CO)_4H_2$ at 2052 cm^{-1} as a function of H_2 (□, at 296.5 K; ○, 340 K) or D_2 (●, 296.5 K) pressure. The total pressure ($Fe(CO)_5 + H_2/D_2 + He$) is 550 Torr.

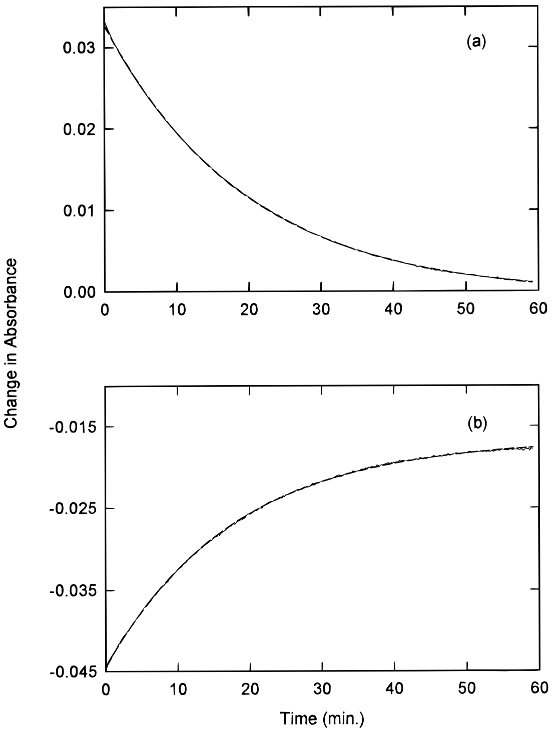

Figure 3. The decay of $Fe(CO)_4H_2$ at 2052 cm^{-1} (a) and recovery of $Fe(CO)_5$ at 2014 cm^{-1} (b). The experimental conditions are as for Figure 1. Solid fine lines are experimental results and dashed lines are single exponential fits. The rates (k_{obs}) from the fits are 0.051 ± 0.004 min^{-1} at 2052 cm^{-1} and 0.056 ± 0.002 min^{-1} at 2014 cm^{-1}.

In the presence of a suitable amount of CO the decay of $Fe(CO)_4H_2$, as monitored by FTIR, is single exponential and has the same rate, within experimental error, as the recovery of $Fe(CO)_5$ (Figure 3). Although $Fe(CO)_4$ is a significant product on 355-nm photolysis, $Fe(CO)_3$ is also expected to be produced in significant concentrations and has been reported as the dominant product on 351-nm photolysis.[12] Both $Fe(CO)_3$ and $Fe(CO)_4$ can potentially react with $Fe(CO)_5$ to produce polynuclear species.[12b] As a result of these reactions, complete recovery of parent, in Figure 1, is not expected. However, there was no indication that the production of $Fe(CO)_3$ or its subsequent reactions interfered with the current measurements.

The simplest mechanism that is consistent with these observations is the reductive elimination of hydrogen: where reactions 1 and 2 represent elementary steps.

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(9) (a) Vaska, L.; Werneke, F. *Trans. N.Y. Acad. Sci.* **1971**, *94*, 7364. (b) Zhen, P.; Vitale, A. A.; Filippo, J. S., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8047. (c) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353. (d) Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jesperson, K. *J. Phys. Chem.* **1993**, *97*, 5890.

(10) (a) Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1989**, *93*, 652. (b) Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K.-J. *J. Phys. Chem.* **1992**, *96*, 9821.

(11) For a recent review, see: Poliakoff, M.; Weitz, E. *Acc. Chem. Res.* **1987**, *20*, 408.

(12) (a) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 1977. (b) Ryther, R. J.; Weitz, E. *J. Phys. Chem.* **1992**, *96*, 2561.

$$\mathrm{Fe(CO)_4H_2} \underset{k_\mathrm{a}}{\overset{k_\mathrm{d}}{\rightleftarrows}} \mathrm{Fe(CO)_4} + \mathrm{H_2} \tag{1}$$

$$\mathrm{Fe(CO)_4} + \mathrm{CO} \xrightarrow{k_\mathrm{CO}} \mathrm{Fe(CO)_5} \tag{2}$$

The above mechanism predicts

$$k_\mathrm{obs} = k_\mathrm{d}\left(\frac{1}{1 + \dfrac{k_\mathrm{a}[\mathrm{H_2}]}{k_\mathrm{CO}[\mathrm{CO}]}}\right) \tag{3}$$

where k_obs is the rate of decay of $\mathrm{Fe(CO)_4H_2}$ or the rate of recovery of $\mathrm{Fe(CO)_5}$. Consistent with this mechanism, k_obs did not change, within experimental error, when the total pressure ($[\mathrm{H_2}] + [\mathrm{CO}]$) was varied by a factor of 5 with the $[\mathrm{H_2}]/[\mathrm{CO}]$ ratio fixed. Rearranging eq 3 gives the rate constant for reductive elimination of $\mathrm{H_2}$:

$$k_\mathrm{d} = k_\mathrm{obs}\left(1 + \frac{k_\mathrm{a}[H_2]}{k_\mathrm{CO}[\mathrm{CO}]}\right) \tag{4}$$

Figure 4 is an Arrhenius plot of $\ln(k_\mathrm{d})$ versus $1/T$. Since k_a and k_CO[12a] have negligible temperature dependencies, the values of k_a and k_CO at 296.5 K were used for all data points. From the slopes in Figure 4, activation energies, $E_\mathrm{a}{}^\mathrm{d}$, of 20.5 ± 2.1 and 19.0 ± 1.1 kcal $\mathrm{mol^{-1}}$ were obtained for the reductive elimination of $\mathrm{H_2}$ and $\mathrm{D_2}$ from the corresponding dihydrides. (Use of temperature-dependent rate constants, derived from an interpolation of the measurements at 296.5 and 315 K, gives a value for the activation energy that differs from these values by less than 1%.) The enthalpy difference between $\mathrm{Fe(CO)_4} + \mathrm{H_2}$ and $\mathrm{Fe(CO)_4H_2}$, ΔH^0, is equal to $E_\mathrm{a}{}^\mathrm{d} + \mathrm{RT} - E_\mathrm{a}{}^\mathrm{a}$, where $E_\mathrm{a}{}^\mathrm{d}$ and $E_\mathrm{a}{}^\mathrm{a}$ are activation energies for the forward and backward reactions in eq 1, respectively. The average Fe−H bond dissociation energies in $\mathrm{Fe(CO)_4H_2}$, defined as $D(\mathrm{Fe{-}H}) = [D(\mathrm{H{-}H}) + \Delta H^0]/2$, is then 62 ± 2.0 kcal $\mathrm{mol^{-1}}$ for both H and D.[13] These error limits include errors in the activation barrier for dissociation and in the temperature dependence of the association rate constant, assuming that, as expected, the temperature dependence of the association rate constant for $\mathrm{D_2}$ is the same as that for $\mathrm{H_2}$. Note that the average BDE could be significantly different from the individual BDE's. Though limited data are available for Fe−H BDE's of hydride complexes, an upper limit of 65 kcal $\mathrm{mol^{-1}}$ has been estimated[3a] for the average Fe−H BDE in $\mathrm{Fe(CO)_4H_2}$ from the activation enthalpy for its thermal decomposition in solution.[14] The Fe−H BDE in $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2H}$ has been estimated to be 50 kcal $\mathrm{mol^{-1}}$.[15a] The BDE in FeH[15b] and Fe−H BDE's in $\mathrm{HFe(CO)}_n{}^+$ ($n = 0{-}5$)[15c] have also been measured as have the BDE's for Fe−H bonds in a number of 18 $\mathrm{e^-}$ ionic species in solution.[15d]

The reductive elimination of $\mathrm{H_2/D_2}$ has a weak, normal kinetic isotope effect in the experimental temperature range, as indicated in Figure 4. $k_\mathrm{d}{}^\mathrm{H}/k_\mathrm{d}{}^\mathrm{D}$ is 1.1 ± 0.1 at 296.5 K and 1.3 ± 0.1 at 315.5 K. This measurement is also consistent with measurements on related systems.[9c] The pre-exponential factors, obtained from the y intercepts in Figure 4, are $(2.7 \pm 0.3) \times 10^{11}$ and $(1.9 \pm 0.2) \times 10^{10}$ $\mathrm{s^{-1}}$ for the elimination of $\mathrm{H_2}$ and $\mathrm{D_2}$, respectively, many orders of magnitude smaller than those for typical dissociation reactions of metal carbonyl species.[7] This is presumably a result of intersystem crossing from a singlet to a triplet potential energy surface that accompanies dissociation leading to $^3\mathrm{Fe(CO)_4}$. Thus, these BDEs are assumed to be relative to the triplet ground state of $\mathrm{Fe(CO)_4}$.

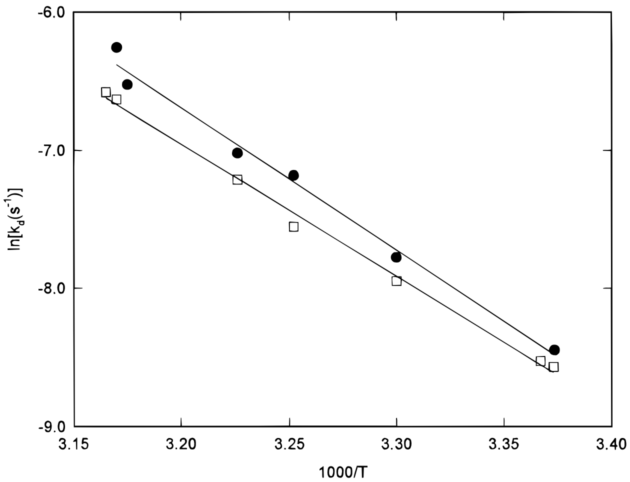

Figure 4. Arrhenius plots of the rate constants for reductive eliminations of $\mathrm{H_2}$ (●) and $\mathrm{D_2}$ (□) from $\mathrm{Fe(CO)_4H_2}$ and $\mathrm{Fe(CO)_4D_2}$, respectively. The plot is the ln of k_d from eq 4 vs $1000/T$.

In the above treatment it was assumed that the oxidative addition and the reductive elimination of hydrogen are elementary reactions. However, dihydrogen species have been found to exist in equilibrium with dihydrides[16] and are often proposed as intermediates in the formation of dihydrides. Since the studied reaction has a minimal activation energy, the energy necessary to break the $\mathrm{H_2}$ bond must come from formation of the Fe−H bonds. Thus, initiation of the formation of the Fe−H bonds must precede breakage of the dihydrogen bond. This implies that this system goes through a complex which resembles a dihydrogen species. Though our data do not allow us to determine whether this "dihydrogen-like species" is a local minimum on the potential energy surface, calculations at Hartree−Fock and density functional theory levels indicate that a dihydrogen species is located in a local minimum along the reaction pathway toward oxidative addition of $\mathrm{H_2}$.[17] Any equilibrium between dihydride and dihydrogen species in this system must significantly favor the dihydride since we see no spectroscopic evidence for $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$. If $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$ is in equilibrium with $\mathrm{Fe(CO)_4H_2}$, the rate for the reductive elimination of $\mathrm{H_2}$ can be expressed by an effective rate constant which is the product of an equilibrium constant and the rate constant for the elementary reaction leading to loss of $\mathrm{H_2}$. The transition state for such a process would involve addition of $\mathrm{H_2}$ to form $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$. However, even if there is an equilibrium between a dihydrogen species and the dihydride, it can

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[13] On the basis of $D(\mathrm{H{-}H}) = 104.2$ kcal $\mathrm{mol^{-1}}$ and $D(\mathrm{D{-}D}) = 106.0$ kcal $\mathrm{mol^{-1}}$. *CRC Handbook of Chemistry and Physics*, 51st ed.; Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1970−1971; p F177.

[14] Pearson, R. G.; Mauerman, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.

[15] (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (b) Schultz, R. H.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *94*, 2262. (c) Ekeberg, D.; Hagen, S. I.; Hvistendehl, G.; Schulze, C.; Uggerud, E.; Vedde, J. *Org. Mass. Spectrom.* **1993**, *28*, 1547. (d) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996,** *118*, 935

[16] (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855.

[17] Wang, W.; Weitz, E. Manuscript in preparation.

[18] For this mechanism the effective rate constant for reductive elimination of $\mathrm{H_2}$ is $k_\mathrm{d} = K_\mathrm{eq}k_\mathrm{d}'$, where K_eq is the equilibrium constant between $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$ and $\mathrm{Fe(CO)_4H_2}$ and k_d' is the rate constant for dissociation of $\mathrm{H_2}$ from $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$. Since $K_\mathrm{eq} = \mathrm{e}^{\Delta S/R}\mathrm{e}^{-\Delta H/RT}$ and $k_\mathrm{d}' = (kT/h)\mathrm{e}^{\Delta S^\ddagger/R}\mathrm{e}^{-(\Delta H^\ddagger)/RT}$, $k_\mathrm{d} = (kT/h)\mathrm{e}^{\Delta S^\ddagger}\mathrm{e}^{-\Delta H^\ddagger \mathrm{RT}}$, where $\Delta S^\ddagger = \Delta S + (\Delta S^\ddagger)'$ and $\Delta H^\ddagger = \Delta H + (\Delta H^\ddagger)'$ (see: Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: NJ, 1989). This is an effective Arrhenius equation with the transition state being that for loss of $\mathrm{H_2}$ from $\mathrm{Fe(CO)_4}(\eta^2\text{-}\mathrm{H_2})$. Thus even if this mechanism was operative the ΔH measured in the present experiments would still correspond to the enthalpy difference between the activated complex and $\mathrm{H_2Fe(CO)_4}$.

be shown that this equilibrium will not effect the conclusions regarding the energy difference between $Fe(CO)_4 + H_2$ and H_2-$Fe(CO)_4$ or the average BDE for the H−Fe bond in $H_2Fe(CO)_4$.[18]

Above, the small rate constants for addition of H_2 to $Fe(CO)_4$ and elimination of H_2 from $Fe(CO)_4H_2$ were assumed to be a result of intersystem crossing between $H_2 + Fe(CO)_4$, the latter with a triplet ground state, and $Fe(CO)_4H_2$, which is calculated to have a singlet ground state.[19] The dissociation products for the H_2 elimination reaction were not directly observed. Rather, what is observed experimentally is the decay of $Fe(CO)_4H_2$ and the recovery of $Fe(CO)_5$, which forms as a result of addition of CO to $Fe(CO)_4$ as in reaction 2. In the above discussion it has been assumed that $Fe(CO)_4H_2$ dissociates directly to $^3Fe(CO)_4 + H_2$. This assumption is compatible with all available evidence and leads to self-consistent results. Since $^1Fe(CO)_4$ is higher in energy than $^3Fe(CO)_4$, the dissociation of $Fe(CO)_4H_2$ to $^1Fe(CO)_4 + H_2$ will have a higher activation barrier than for dissociation to $^3Fe(CO)_4 + H_2$. However, if the singlet−triplet separation is small enough, there is a possibility that the rate constant for dissociation of $Fe(CO)_4H_2$ to $^1Fe(CO)_4 + H_2$ may be larger than that to $^3Fe(CO)_4 + H_2$: the latter processes occurring via intersystem crossing. If dissociation of $H_2Fe(CO)_4$ to $^1Fe(CO)_4 + H_2$ were a dominant process in the elimination of H_2, eqs 1−4 could still be used to describe the kinetics except that, in this case, k_d, k_a, and k_{CO} are the rate constants associated with $^1Fe(CO)_4$. Since the ratio k_a/k_{CO} associated with $^1Fe(CO)_4$ is not expected to be dramatically different from that associated with $^3Fe(CO)_4$, from eq 4 and Figure 4, we can conclude that the pre-exponential for k_d, the rate constant for the dissociation of $Fe(CO)_4H_2$ to $^1Fe(CO)_4 + H_2$, would be on the order of 10^{10} s^{-1}, many orders of magnitude smaller than is typical for dissociation of small molecules from metal carbonyl species. This would imply a transition state that is more restricted and tighter than $Fe(CO)_4H_2$. Although H_2 elimination is likely to proceed through a multicenter transition state, such an unusual, tight, transition state has, to our knowledge, not been observed before. In addition, thermochemical properties of several stationary points on the lowest singlet potential energy surface for the reductive elimination of H_2 from $Fe(CO)_4H_2$ have been calculated at the Hartree−Fock level.[17] As indicated above, a dihydrogen species, $Fe(CO)_4(\eta^2\text{-}H_2)$, is an intermediate in the elimination process. The entropy difference between $Fe(CO)_4(\eta^2\text{-}H_2)$ and $Fe(CO)_4H_2$ is 8.3 J mol^{-1} K^{-1} and that between $^1Fe(CO)_4 + H_2$ and $Fe(CO)_4H_2$ is 117.6 J mol^{-1} K^{-1}. Though the transition state between $Fe(CO)_4(\eta^2\text{-}H_2)$ and $^1Fe(CO)_4 + H_2$, which governs the rate constant for the H_2 elimination, was not optimized, and the results of calculations of the entropy differences may not be quantitatively correct, it seems unlikely that the transition state would be “tighter” than $Fe(CO)_4(\eta^2\text{-}H_2)$. Therefore, a restricted and tight transition state is unlikely to be responsible for the small rate constant for elimination of H_2. This further implies that the measured BDE is most likely relative to the ground state, $^3Fe(CO)_4$.

The deuterium kinetic isotope effect (KIE) for oxidative addition of hydrogen to transition metal complexes has been the subject of many experimental and theoretical investigations. Weak, normal KIEs ranging from 1 to 2 have been observed for H_2/D_2.[9a−c] The weak KIEs were initially considered to be indicative of early transition states. Recent studies have pointed out that even if the transition state occurs extremely early, based solely on the large H_2/D_2 mass-moment of inertia (MMI) contribution, which will be about 5.66, a strong KIE would be expected.[9b,d] On the other hand, zero-point energy (ZPE) and excitation (EXC) terms contribute in reversing the effect of the large MMI term to produce a weak KIE. The origin of the strong inverse effect of ZPE and EXC lies in the five additional isotope-sensitive vibrational modes present in the transition state. These arguments can be applied to the addition of H_2 to $Fe(CO)_4$ to account for the weak KIE. There have been fewer studies regarding the KIEs for reductive elimination of H_2/D_2. A KIE of 2 has been observed for the reductive elimination of H_2 from $W(PMe_3)_4I_2H_2$.[9c] This modest value is consistent with our observation on the $Fe(CO)_4H_2$ system.

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[19] Daniel, C. *J. Phys. Chem.* **1991**, *95*, 2394.