MeC_2NMe_2. Compounds 4–6 formed by the coupling of two ynamine ligands and contain metallacyclopentadienyl groupings. These compounds appear to be unrelated since the coupling of the ynamine ligands in each occurs in a different way (i.e. tail-to-tail coupling in 4, head-to-head coupling in 5, and head-to-tail coupling in 6). Although 3 could conceivable be a precursor to one or more of these products, our efforts to convert 3 to them independently have been unsuccessful. The triosmium clusters were evidently formed by fragmentation of some tetraosmium species, but this precursor has not been identified.

In all cases, where the ynamine ligands were not coupled, there is structural and spectroscopic evidence for a strong C–N π-bonding interaction between the nitrogen atom and the amine-substituted carbon atom of the alkynyl group. This bonding appears to disrupt the anticipated metal–carbon bonding and causes this carbon atom to adopt a structural form that resembles an aminocarbene ligand. In those cases where the ynamine ligands have been coupled, there still appears to be evidence for significant, albeit weaker, π-bonding interactions between the amino groups and the adjacent carbon atoms that appear to lead to a weakening of the metal-carbon bonding.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy (Grant No. DEFG84ER13296).

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for all five crystal structure analyses (21 pages); tables of structure factor amplitudes (106 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Halide, Hydride, and Alkyl Derivatives of (Pentamethylcyclopentadienyl)(bisphosphine)iron(II)

Rocco A. Paciello,[1a] Juan M. Manriquez,[1b] and John E. Bercaw*,[1a]

Arnold and Mabel Beckman Laboratories of Chemical Synthesis,[†] California Institute of Technology, Pasadena, California 91125, and Universidad Tecnica Federico Santa Maria, Casilla 110-V, Valparaiso, Chile

Received July 6, 1989

Reaction of $[Fe(acac)_2]_x$ (acac = η^2-acetylacetonate) with LiCp* (Cp* = η^5-pentamethylcyclopentadienyl) in the presence of PMe_3 or DMPE (DMPE = $Me_2PCH_2CH_2PMe_2$) yields Cp*LFe(acac) (L = PMe_3 (1), η^1-DMPE (2)). Compounds 1 and 2 can be isolated or treated in situ with $ClSiMe_3$ (in the presence of PMe_3 for 1) to afford Cp^*L_2FeCl (L = PMe_3 (3), L_2 = DMPE (4)). Reaction of 1 with Grignard reagents, RMgX (X = Cl, Br), in the presence of PMe_3 yields either $Cp^*(PMe_3)_2FeR$ (R = CH_3, CH_2CH_3) or $Cp^*(PMe_3)_2FeX$ (R = CMe_3, $CH_2C_6H_5$, C_3H_5). Compounds of the general formula Cp^*L_2FeX react with RMgX to yield Cp^*L_2FeR (R = H, CH_3, $CH_2C_6H_5$) or $Cp^*(PMe_3)Fe(\eta^3\text{-}C_3H_5)$. Routes to the cationic species $[Cp^*(PMe_3)_2FeL]^+PF_6^-$ (L = PMe_3, CO) are described. Reaction of 1 with CH_3CH_2MgX in the absence of PMe_3 yields $Cp^*(PMe_3)(C_2H_4)FeH$. Treatment of this complex with dihydrogen yields a highly unstable Fe^{IV} complex, $Cp^*(PMe_3)FeH_3$. The reactivity of these complexes is discussed and proposed to involve highly reactive, 16-electron unsaturated intermediates, $[Cp^*(PMe_3)FeR]$ (R = H, alkyl, aryl, etc.).

Introduction

Electron-rich, half-sandwich complexes of the type $Cp^*(PMe_3)_2RuX$ (Cp* = (η^5-C_5Me_5); X = halide, alkoxide, alkyl, hydride, etc.)[2] exhibit a rich and varied chemistry. For example, several of these derivatives are precursors to highly reactive, 16-electron species, $[Cp^*(PR_3)RuX]$, capable of activating C–H bonds both intramolecularly and intermolecularly.[3] Utilizing equilibrium methods, we have determined relative Ru–X bond strengths for $Cp^*(PMe_3)_2RuX$[4] and have investigated factors influencing the loss of trimethylphosphine from these compounds.[5] The analogous iron system with the same electron-donating ligand set, $Cp^*(PMe_3)_2FeX$, also offers the potential for high reactivity. Although the synthesis and reactivity of $Cp(CO)_2FeX$ derivatives (Cp = η^5-C_5H_5)) have been extensively investigated,[6] synthetic routes to the pentamethylcyclopentadienyl–bis(phosphine) complexes have been reported only recently. For example, the reaction of C_5Me_5H with (η^6-C_6H_6)$(PMe_3)_2Fe$ yields $Cp^*(PMe_3)_2FeH$, which is readily converted to $Cp^*(PMe_3)_2FeCl$ upon treatment with CH_2Cl_2.[7] The requirement for an apparatus for the metal vapor synthesis of the precursor, (η^6-C_6H_6)$(PMe_3)_2Fe$,[8] prompted a search for "wet" chemical

---

[†] Contribution No. 7973.

[1] (a) California Institute of Technology. (b) Universidad Tecnica Federico Santa Maria.

[2] Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

[3] (a) Togni, A.; Tilley, T. D.; Paciello, R. A.; Bercaw, J. E.; Grubbs, R. H. Manuscript in preparation. (b) Merola, J.; Bercaw, J. E. Unpublished results.

[4] Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

[5] (a) Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron Symposium in Print* **1988**, *6*, 1441. (b) Bryndza, H, E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

[6] See for example: Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 8, pp 959–968.

[7] (a) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1984**, 1442. (b) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1987**, 411.

[8] Ittel, S. D.; Tolman, C. A. *Organometallics* **1982**, *1*, 1432.

0276-7333/90/2309-0260$02.50/0

routes to members of this series of compounds.

Very recently, a report of the synthesis of a variety of cyclopentadienyl–bis(phosphine) iron complexes, CpL_2FeR ($Cp = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$, $\eta^5\text{-}C_5Me_5$; $L = P(CH_3)_n(C_6H_5)_{3-n}$ (n = 0–3); R = alkyl), based on precursors such as $(PMe_3)_2FeCl_2$ and Cp(COD)FeCl (COD = 1,5-cyclooctadiene), has been published.[9] In other developments, one of us (J.M.M.) has reported the synthesis of Cp*Fe(acac)[10] via treatment of $[Fe(acac)_2]_x$ with LiCp* and its reaction with CH_3MgI under CO to yield $Cp^*(CO)_2FeCH_3$.[11] The latter suggested another synthetic pathway to such cyclopentadienyl–bis(phosphine) complexes. Accordingly, we have extended this synthetic route to both PMe_3[12] and DMPE complexes and now wish to report the facile synthesis of the pentamethylcyclopentadienyl–mono(phosphine)–acetylacetonate complexes and their utility in the synthesis of a variety of electron-rich iron(II) complexes.

Results and Discussion

Preparation of base-free, oligomeric $[Fe(acac)_2]_x$ is carried out by sublimation of the commercially available product. Treatment of this material with LiCp* in the presence of 1 equiv of phosphine, PMe_3 or DMPE, at −78 °C in THF, yields Cp*LFe(acac) on warming to room temperature (eq 1). Complexes **1** and **2** are most easily

$$[\mathrm{Fe(acac)_2}]_x \xrightarrow[\text{THF}]{\text{LiCp*, L}} \underset{\mathbf{1,\,2}}{\mathrm{Cp^*LFe(acac)}} \qquad (1)$$

$$L = \mathrm{PMe_3}\ (\mathbf{1}),\ \eta^1\text{-}\mathrm{Me_2PCH_2CH_2PMe_2}\ (\mathbf{2})$$

used in situ but may be isolated. $Cp^*(PMe_3)Fe(acac)$ is very soluble; nevertheless, it may be obtained as a dark red, crystalline solid in 71% yield from petroleum ether at low temperatures. $Cp^*(PMe_3)Fe(acac)$ exhibits a ^1H NMR spectrum indicative of a paramagnetic compound, i.e. with very broad peaks and chemical shifts that are very temperature dependent.[13] Treatment with carbon monoxide (1 atm) yields the known diamagnetic complex Cp*(CO)Fe(acac).[12]

Treatment of **1** or **2** with $ClSiMe_3$ (and 1 equiv of PMe_3 in the case of **1**) in THF at −78 °C affords Cp^*L_2FeCl on warming to room temperature (eq 2). $Cp^*(PMe_3)_2FeCl$

$$\mathrm{Cp^*LFe(acac)} \xrightarrow[\text{THF}]{\text{ClSiMe}_3} \underset{\mathbf{3,\,4}}{\mathrm{Cp^*L_2FeCl}} \qquad (2)$$

$$L = \mathrm{PMe_3}\ (\mathbf{3}),\ L_2 = \mathrm{Me_2PCH_2CH_2PMe_2}\ (\mathbf{4})$$

is moderately soluble and can be most easily isolated as a dark blue crystalline compound in 58% yield by toluene extraction, reduction of solvent, and addition of petroleum ether. Cp*(DMPE)FeCl is quite insoluble but can be isolated as a slate blue powder in 20% yield by a toluene extraction followed by recrystallization from diethyl ether.

Treatment of **1** with CH_3MgCl in the presence of PMe_3 at −78 °C yields the methyl complex $Cp^*(PMe_3)_2FeCH_3$ on warming to room temperature (eq 3). $Cp^*(PMe_3)_2FeCH_3$, originally reported by Green and coworkers,[7] is very soluble but may be isolated as a dark red crystalline complex from petroleum ether at low temperature in 55% yield based on $[Fe(acac)_2]_x$. Treatment of

$$\mathrm{Cp^*(PMe_3)Fe(acac)} \xrightarrow[\text{THF}]{\text{CH}_3\text{MgCl}} \mathrm{Cp^*(PMe_3)_2FeCH_3} \qquad (3)$$

$Cp^*(PMe_3)_2FeCH_3$ with hydrogen quantitatively yields $Cp^*(PMe_3)_2FeH$ (^1H NMR spectroscopy). The hydride is less soluble and is readily isolated (74% yield based on $[Fe(acac)_2]_x$) as an orange crystalline complex by hydrogenation of crude $Cp^*(PMe_3)_2FeCH_3$ in petroleum ether.

Unexpectedly, treatment of $Cp^*(PMe_3)Fe(acac)$ with 1 equiv of Me_3CMgCl or $C_6H_5CH_2MgCl$ in the presence of PMe_3 affords $Cp^*(PMe_3)_2FeCl$ in high yields. Similarly, treatment of $Cp^*(PMe_3)Fe(acac)$ with 1 equiv of C_3H_5MgBr and PMe_3 gives violet $Cp^*(PMe_3)_2FeBr$, although in rather low isolated yield (39%). $Cp^*(PMe_3)Fe(acac)$ reacts with 1 equiv of CH_3CH_2MgX (in the absence of PMe_3) to yield only $Cp^*(PMe_3)(C_2H_4)FeH$ (^1H NMR spectroscopy) (eq 4). $Cp^*(PMe_3)(C_2H_4)FeH$ is obtained

$$\mathrm{Cp^*(PMe_3)Fe(acac)} \xrightarrow[\text{THF}]{\text{CH}_3\text{CH}_2\text{MgX}} \mathrm{Cp^*(PMe_3)(C_2H_4)FeH} \qquad (4)$$

(with some difficulty due to its high solubility) as an off-white, crystalline solid in 46% yield. Synthetic and spectral data for this fluxional complex have been reported previously.[7]

Reaction of Cp^*L_2FeCl with RMgX occurs cleanly to yield the alkyl derivatives (eq 5). In contrast, reaction

$$\mathrm{Cp^*L_2FeCl} \xrightarrow[\text{THF}]{\text{RMgX}} \mathrm{Cp^*L_2FeR} \qquad (5)$$

$$R = \mathrm{CH_3,\ C_3H_5,\ CH_2C_6H_5,\ CH_2SiMe_3}$$

of Cp^*L_2FeCl with CH_3CH_2MgCl yields Cp^*L_2FeH, presumably by β-H abstraction. Reaction of **3** with C_3H_5MgBr is accompanied by phosphine loss to give the η^3-allyl complex $Cp^*(PMe_3)Fe(\eta^3\text{-}C_3H_5)$, which can be isolated as an orange crystalline complex in 76% yield. The benzyl complex $Cp^*(PMe_3)_2FeCH_2C_6H_5$ can be isolated as a dark red crystalline complex at 0 °C from petroleum ether in low yield (25%). Formation of this complex is accompanied by production of bibenzyl, which crystallizes from petroleum ether at −78 °C in about 20% isolated yield. The (trimethylsilyl)methyl complex can be obtained at low temperature as well-formed, very dark red crystals in ca. 50% yield. This complex has proved difficult to characterize, decomposing in solution rapidly. In addition, it is not very stable in the solid state (at −40 °C, the crystal faces dull and the edges degrade in ca. 12 h).

$Cp^*(DMPE)FeCH_3$ can be isolated as red orange crystals in 55% yield. Unlike the other alkyl derivatives, which readily undergo hydrogenation to Cp^*L_2FeH, this complex is unreactive toward hydrogen (3 atm, 160 °C). Treatment of Cp*(DMPE)FeCl with Me_3CMgCl does, however, yield the hydride complex cleanly as yellow-orange crystals in 52% yield.[14]

Treatment of $Cp^*(PMe_3)_2FeCl$ with $K^+PF_6^-$ in methanol in the presence of PMe_3 cleanly yields $[Cp^*(PMe_3)_3Fe]^+PF_6^-$, analogous to $[Cp^*(PMe_3)_3Fe]^+BF_4^-$, reported by

---

[9] Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C.; Raabe, E. *Chem. Ber.* **1987**, *120*, 1987.

[10] This complex has been found to have a piperidine coordinated to the metal center under the conditions described: Bunel, E. Personal communication.

[11] Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

[12] Synthesis of the complex $Cp^*(PMe_3)_2FeCH_3$ with use of this method has been previously communicated: Morrow, J.; Catheline, D.; Desbois, M.-H.; Manriquez, J. M.; Ruiz, J.; Astruc, D. *Organometallics* **1987**, *6*, 2605.

[13] The extreme air sensitivity and the highly labile nature of the PMe_3 ligand in this complex have prevented a detailed examination of its magnetic properties. It is not clear if the observed paramagnetism occurs because of phosphine loss to yield a paramagnetic 5-coordinate species or if a process such as spin equilibrium is occurring. Such behavior has been previously observed for octahedral Fe(II); for a comprehensive review, see: Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83.

[14] This process may not occur via a β-H elimination process; a concerted process has been proposed in an analogous system, Cp(Prophos)RuCl: Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202.

Green and co-workers.[7] The expected ethylene adduct $[Cp^*(PMe_3)_2Fe(C_2H_4)]^+PF_6^-$ is *not* formed by treating $Cp^*(PMe_3)_2FeCl$ with $K^+PF_6^-$ in methanol under 1 atm of ethylene; rather, $[Cp^*(PMe_3)_3Fe]^+PF_6^-$ is again obtained (57%), presumably by disproportionation of the starting material. Under an atmosphere of carbon monoxide $[Cp^*(PMe_3)_2Fe(CO)]^+PF_6^-$ is obtained as a yellow powder in 83% yield. Protonations of $Cp^*(PMe_3)_2FeCl$ or $Cp^*(PMe_3)_2FeH$ with $HBF_4{\cdot}Et_2O$ do not occur cleanly, but reaction of $Cp^*(DMPE)FeH$ with $HBF_4{\cdot}Et_2O$ yields $[Cp^*(DMPE)FeH_2]^+BF_4^-$ as a white, analytically pure precipitate in 81% yield; however, this complex proved to be extremely unstable in solution.

Whereas in benzene the reaction of $Cp^*(PMe_3)_2FeCH_3$ with H_2 (80 °C, 3 atm. 1 h) cleanly yields $Cp^*(PMe_3)_2FeH$, heating $Cp^*(PMe_3)_2FeH$ in benzene-d_6 leads to loss of the hydride signal concurrent with an increase in the signal due to benzene-d_5 (^1H NMR spectroscopy). As noted previously by Green and co-workers,[7] when the compound is heated with H_2, catalytic H–D exchange is observed to produce $C_6D_nH_{6-n}$, HD, and D_2, albeit the rate is rather slow (6–7 turnovers after 1 week at 80 °C). Unlike the analogous ruthenium alkyls, which react cleanly with benzene-d_6 to yield RD and $Cp^*(PMe_3)_2RuC_6D_5$,[3] heating $Cp^*(PMe_3)_2FeCH_3$ or $Cp^*(PMe_3)_2FeCH_2C_6H_5$ in benzene-d_6 results only in decomposition.

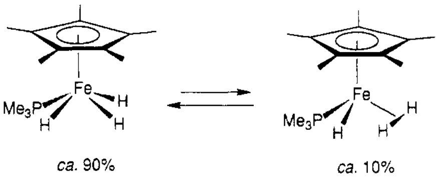
Other differences between the reactivities of iron and ruthenium compounds have also been noted. Whereas $Cp^*(PMe_3)_2RuH$ readily reacts with H_2 to afford $Cp^*(PMe_3)RuH_3$ and PMe_3, no evidence for $Cp^*(PMe_3)FeH_3$ is obtained (^1H NMR spectroscopy, <5%), even at 80 °C under 3 atm of H_2. Treatment of $Cp^*(PMe_3)(C_2H_4)FeH$ with 3 atm of H_2 at room temperature does, however, lead to a clean conversion to a compound with a ^1H NMR spectrum (THF-d_8: η^5-$C_5(CH_3)_5$, δ 1.90; $P(CH_3)_3$, δ 1.10 ($^2J_{P-H}$ = 8.4 Hz); FeH_3, δ −12.4 ($^2J_{P-H}$ = 42.9 Hz)) characteristic of $Cp^*(PMe_3)FeH_3$ (eq 6). $Cp^*(PMe_3)FeH_3$ is

$$Cp^*(PMe_3)(C_2H_4)FeH + 2H_2 \rightarrow Cp^*(PMe_3)FeH_3 + C_2H_6 \quad (6)$$

a highly fluxional and unstable molecule (vide infra) whose structure is probably that of a four-legged piano stool. It can be directly compared to the structurally characterized Fe^{IV} complex $Cp(CO)Fe(SiCl_3)_2H$.[15] It joins the latter, tetrakis(1-norbornyl)iron,[16] and $[P(CH_2CH_3)(C_6H_5)_2]_3FeH_4$[17] as members of a very small family of neutral Fe^{IV} organometallic complexes.

Removal of the dihydrogen atmosphere from solutions containing $Cp^*(PMe_3)FeH_3$ causes rapid decomposition. A disproportionation product, $Cp^*(PMe_3)_2FeH$, is observed among the products (^1H NMR and infrared spectroscopy). Attempts to grow crystals under H_2 have been unsuccessful. An infrared spectrum of $Cp^*(PMe_3)FeH_3$ has been obtained by generating the trihydride in pentane, quickly blowing off the solvent with H_2, and measuring the infrared spectrum of the resulting oil (ν(FeH) = 1905 cm^{-1} vs polystyrene).[18] An infrared spectrum in solution also has been obtained by the generation of $Cp^*(PMe_3)FeH_3$ in tetrahydrofuran and subsequent cannulation under H_2 into a infrared cell with CsCl windows. The same new ν(FeH) band is observed, along with that for the decomposition product $Cp^*(PMe_3)_2FeH$.

Scheme I



When $Cp^*(PMe_3)FeH_3$ is prepared in benzene-d_6, deuterium is incorporated into the hydride positions. The partially deuterated complexes $Cp^*(PMe_3)FeH_2D$ ($^2J_{H-D}$ = 4.8 Hz) and $Cp^*(PMe_3)FeHD_2$ may be resolved from $Cp^*(PMe_3)FeH_3$ by ^1H NMR and ^{31}P NMR spectroscopy.[19] If the different gyromagnetic ratios for the proton and deuteron are taken into account, the value of the H–D coupling constant for $Cp^*(PMe_3)FeH_2D$ can be used to estimate that for H–H: $^2J_{H-H}$ = 30 Hz. This value is larger than those commonly observed for "classical" transition-metal polyhydrides (<15 Hz),[20] yet smaller than those observed for a growing number of transition-metal dihydrogen ("nonclassical" hydride) complexes (~200 Hz).[21] Extremely large, temperature-dependent J_{H-H} values have been reported for the isoelectronic ruthenium complexes $Cp^*(PR_3)RuH_3$[22] and the isoelectronic cationic species $[Cp(L)IrH_3]^+$ (L = PMe_3, PPh_3, $AsPh_3$; e.g. 410 Hz for L = $AsPh_3$).[23] In no case, however, has the expected large, thus readily resolvable, J_{H-D} value been observed. An explanation to this dilemma has recently been offered: these very large "J_{H-H}" values are, in fact, attributable to quantum-mechanical exchange coupling[24] and, as such, depend primarily on nuclear position and vibrational modes involving the hydride ligands and, importantly, require identical exchanging particles. Thus, the sizable (4.8 Hz) $^2J_{H-D}$ value for $Cp^*(PMe_3)FeH_2D$ stands in contrast to these other situations and implicates either a nonclassical hydride structure or, more likely in view of the intermediate value for $^2J_{H-H}$ indicated, an equilibrium between classical and nonclassical forms.

Unusually short NMR relaxation times (T_1) may often be used to identify η^2-H_2 adducts. For example, the Fe^{IV} polyhydride complex $FeH_4[P(CH_2CH_3)(C_6H_5)_2]_3$ has recently been proposed to be a dihydrogen–dihydride Fe^{II} complex on the basis of T_1 data and a reinterpretation of the published infrared data.[25] Unfortunately, measurements of T_1 for $Cp^*(PMe_3)FeH_3$ prepared from analytically pure $Cp^*(PMe_3)(C_2H_4)FeH$ have not been reproducible. As T_1 measurements are very sensitive to even trace amounts of paramagnetic impurities,[26] such a result is not

---

(15) (a) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1159. (b) Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Ibid.* **1970**, *9*, 447.

(16) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

(17) Aresta, M.; Gioannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *51*, 115.

(18) A decomposition product, $Cp^*(PMe_3)_2FeH$, was observed as a minor product (ν(FeH) = 1780 cm^{-1}).

(19) Observation of $^2J_{H-D}$ contrasts with the behavior of the crystallographically characterized dihydrogen adduct *trans*-$[Fe(\eta^2\text{-}H_2)(H)(DPPE)_2]^+BF_4^-$, also formally an Fe(IV) species, in which only line broadening is observed due to the presence of a second fluxional process: Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

(20) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

(21) For a recent comprehensive review with leading references, see: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

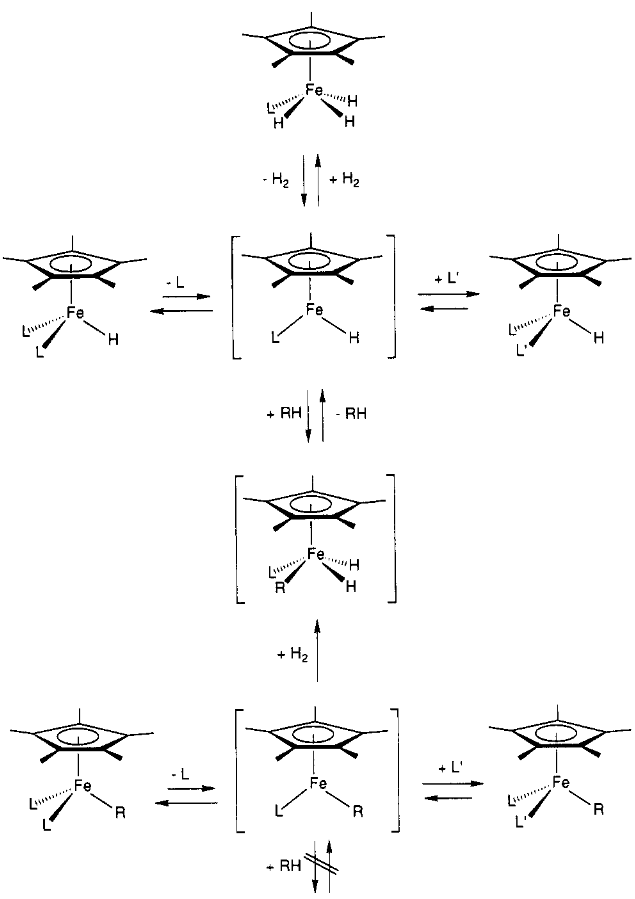
(22) (a) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C.R. Acad. Sci., Ser. 2* **1987**, *305*, 1523. (b) Antinolo, A.; Arliguie, T.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalon, F. A.; Otero, A.; Poilblanc, R. Submitted for publication. (c) Paciello, R. A.; Bercaw, J. E. *Abstracts of Papers*, 191st National Meeting of No. 82 American Chemical Society, New York City, April 13–18, 1986; American Chemical Society: Washington, DC, 1986; INOR 82.

(23) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303.

(24) (a) Jones, D. H.; Labinger, J. A.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1989**, *11*, 3087. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088.

(25) (a) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

Scheme II



unexpected. Another criterion has been the observation of a peak in the infrared spectrum attributable to bound dihydrogen between 2400 and 3100 cm^{-1}. Although such a peak is not observed for Cp*(PMe_3)FeH_3, the generally low intensities of these absorptions often make them difficult to observe, so their absence does not rule out a dihydrogen adduct.

One mechanism by which an intermediate coupling constant could be produced is a fluxional process such as that shown in Scheme I. A simple weighted average (with values of $^1J_{H-H}$ = 200 Hz and $^2J_{H-H}$ = 10 Hz) indicates about 10% of the dihydrogen–hydride complex. Variable-temperature ^{1}H NMR studies reveal that, if the complex is indeed fluxional, it remains so even at 400 MHz and −80 °C. Such a fluxional process has been proposed to account for the scrambling of a terminal hydride site with an η^2-H_2 site in the iridium complexes [$IrH(H_2)(PR_3)_2(C_{13}H_8N)$]$^+$.[27] The η^2-H_2 and terminal hydride ligands in *trans*-[$Fe(\eta^2$-$H_2)(H)(DPPE)_2$]BF_4 and in *trans*-[$M(\eta^2$-$H_2)(H)(DEPE)_2$]BF_4 (M = Fe, Os; DEPE = $Et_2PCH_2CH_2PEt_2$) also have been shown to exchange. The mechanism for this rearrangement could be intramolecular and could involve a transient *tri*hydrogen species.[28] Equilibrium mixtures of an η^2-H_2 adduct and the corresponding dihydride have recently been reported[29] for the cationic ruthenium complex [$CpRu(DMPE)H_2$]$^+$ and for $W(CO)_3(PR_3)_2H_2$; in the latter case ca. 15–30% dihydride is observed directly.[30]

The reactivity of the three- and four-legged piano stool complexes of iron are mostly readily accommodated according to Scheme II. The essential features are (1) the decreased reactivity of the DMPE species as compared with that of the bis(trimethylphosphine) derivatives, (2) catalytic H–D exchange of the hydrides with benzene-d_6, (3) the accessibility of the unsaturated species [Cp*(PMe_3)FeR] from the ethylene–hydride complex via β-H migration, and (4) ligand substitution reactions, analogous to those observed for the corresponding ruthenium compounds.[5b]

In summary, convenient one-pot syntheses of compounds with the general formula Cp*L_2FeX have been developed. The key intermediate, Cp*LFe(acac), can be isolated or used in situ. The reactivity of the acetylacetonate complex with Grignard reagents affords either the iron alkyl or the iron halide complex. The novel Fe^{IV} complex Cp*(PMe_3)FeH_3 appears to have two nearly equally stable structures: a classical trihydride form and a nonclassical dihydrogen–hydride form, in rapid equilibrium with each other. The reaction chemistry of these iron complexes is proposed to occur via coordinatively unsaturated and highly reactive [Cp*(PMe_3)FeX] species.

Experimental Section

General Considerations. All syntheses and chemical manipulations were carried out by standard high-vacuum and Schlenk techniques.[31] Hydrogen, nitrogen, and argon were purified by passage through MnO on vermiculite followed by activated 4-Å sieves.[32] Benzene, pentane, THF, diethyl ether, and toluene were purified by distillation from sodium/benzophenone ketyl solutions under argon or by vacuum transfer from the same drying and degassing medium or from "titanocene".[33] Benzene, toluene, and pentane required the addition of tetraglyme (Aldrich) to effect dissolution of the sodium. Methylene chloride was vacuum transferred from calcium hydride. Methanol was dried by stirring over $NaOCH_3$ and vacuum transferred. Deuterated solvents were purified and maintained in the same manner as the protonic isotopomers. $HBF_4 \cdot Et_2O$ was degassed and used as supplied from Aldrich. Hydrogen, carbon monoxide, and ethylene (freeze–pump–thawed three times) otherwise were used as obtained from Matheson. Grignard reagents were used as received from Aldrich. [$Fe(acac)_2$]$_x$ was obtained from Sharpe Chemicals Co. The solid was heated at 100 °C under vacuum to remove all base and H_2O and then sublimed at 160 °C through glass wool plugs.

IR spectra were recorded as Nujol mulls on KBr plates on a Beckman IR 4230 spectrophotometer. Routine ^{1}H and ^{31}P spectra for characterization were obtained in benzene-d_6 or THF-d_8, with $SiMe_4$ or H_3PO_4 as standard references, on JEOL Model FX-90Q or JEOL GX-400 spectrometers. T_1 measurements were obtained by using standard programs and data analysis packages on the JEOL GX-400 spectrometer. Elemental analyses were obtained from the California Institute of Technology analytical service.

Cp*(PMe_3)Fe(acac). To a mixture of [$Fe(acac)_2$]$_x$ (5 g, 19.7 mmol) and LiCp* (2.80 g, 19.7 mmol) was added 50 mL of THF and 2.2 mL of PMe_3 (21.7 mmol) at −78 °C. The solution was warmed to room temperature and stirred for 10 min. Volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with petroleum ether until the residue appeared pink. The volume of the filtrate was reduced

---

(26) Becker, E. D. *High Resolution NMR*; Academic Press: New York, 1980.

(27) (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794. (b) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(28) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

(29) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

(30) (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, R. I.; Fukishima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(31) Burger, B. J.; Bercaw, J. E. In *New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds*; Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(32) Brown, T. L.; Dickerhoff, D. W.; Bafus, D. A.; Morgan, G. L. *Rev. Sci. Instrum.* **1962**, *33*, 491.

(33) Marvich, R. H.; Britzinger, H. H. *J. Am. Chem. Soc.* **1972**, *93*, 2046.

to ca. 20 mL and cooled slowly. Dark red crystals were filtered off on a cold frit and dried under vacuum; yield 5.09 g, 70.7%. Anal. Calcd for $C_{18}H_{30}O_2PFe$: C, 59.02; H, 8.53. Found: C, 59.30; H, 8.45.

$Cp^*(PMe_3)_2FeCl$. To a mixture of $[Fe(acac)_2]_x$ (3.5 g, 13.8 mmol) and LiCp* (1.957 g, 13.8 mmol) was added 50 mL of THF and PMe_3 (3.0 ml, 29.5 mmol) at −78 °C. The solution was warmed to room temperature with stirring and then cooled again to −78 °C and $ClSiMe_3$ (3.48 mL, 27.6 mmol) added. The solution was warmed to room temperature and stirred 0.5 h. The volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with toluene until almost white. The filtrate was pulled down to an oil and petroleum ether added. The dark blue crystals were filtered on a cold frit and dried under vacuum; yield 3.028 g, 58%. Anal. Calcd for $C_{16}H_{33}P_2ClFe$: C, 50.75; H, 8.72. Found: C, 51.00; H, 8.65. ^1H NMR (benzene-d_6): δ 1.43 s (η^5-C_5Me_5) 1.26 m (PMe_3). ^{31}P NMR (benzene-d_6): δ 21.9.

Cp*(DMPE)FeCl. To a mixture of $[Fe(acac)_2]_x$ (3 g, 11.8 mmol) and LiCp* (1.677 g, 11.8 mmol) was added 50 mL of THF and 1.17 mL of DMPE (11.9 mmol) at −78 °C. The solution was warmed to ca. 0 °C and then cooled to −78 °C again, and $ClSiMe_3$ (3.13 mL, 24.8 mmol) was added. The solution was warmed to room temperature and stirred for 0.5 h. The volatiles were removed under vacuum thoroughly. The residue was extracted with 10 mL of petroleum ether to remove soluble products. The residue was then extracted with toluene, and the volatiles were removed from the supernatant to give a blue-gray residue. This residue was then extracted with Et_2O and the filtrate cooled slowly to give light blue crystals, which were filtered off on a cold frit and dried under vacuum; yield 887 mg, 20%. Anal. Calcd for $C_{16}H_{31}P_2ClFe$: C, 51.02; H, 8.30. Found: C, 51.14; H, 8.14. ^1H NMR (benzene-d_6): δ 1.58 s (η^5-C_5Me_5) 1.00 m ($Me_2PCH_2CH_2PMe_2$), 1.54 m ($Me_2PCH_2CH_2PMe_2$). ^{31}P NMR (benzene-d_6): δ 70.6.

$Cp^*(PMe_3)_2FeCH_3$. To a mixture of $[Fe(acac)_2]_x$ (1.583 g, 6.2 mmol) and LiCp* (885 mg, 6.2 mmol) was added 10 mL of THF and 1.3 mL of PMe_3 (12.8 mmol) at −78 °C. The mixture was warmed to room temperature with stirring and then cooled to −78 °C again, and CH_3MgCl (2.4 mL, 2.9 M in THF, 6.96 mmol) was added. The solution was warmed to room temperature with stirring. The volatiles were removed under vacuum, and the residue was dried thoroughly under vacuum. The residue was extracted with petroleum ether, and the volume of the filtrate was reduced to ca. 5 mL and cooled to −78 °C for 12 h. Dark red crystals were filtered off with use of a cold frit and dried under vacuum; yield 1.218 g, 54.6%. Anal. Calcd for $C_{17}H_{36}P_2Fe$: C, 56.98; H, 10.00. Found: C, 57.06; H, 9.72. ^1H NMR (benzene-d_6): δ 1.57 s (η^5-C_5Me_5), 1.05 m (PMe_3), −0.10 t ($^3J_{P-H}$ = 7.6 Hz, $FeCH_3$). ^{31}P NMR (benzene-d_6): δ 34.7.

$Cp^*(PMe_3)_2FeH$. To a mixture of $[Fe(acac)_2]_x$ (1.5 g, 5.9 mmol) and LiCp* (839 mg, 5.9 mmol) was added 15 mL of THF and 1.2 mL of PMe_3 (11.8 mmol) at −78 °C. The solution was warmed to room temperature with stirring and cooled again to −78 °C, CH_3MgCl was added (2.2 mL, 2.9 M in THF, 6.5 mmol), and the solution was warmed to room temperature with stirring. The volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with benzene and the filtrate transferred to a glass bomb and heated at 80 °C for 1 h under 3 atm of H_2. The volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with petroleum ether, the filtrate was reduced in volume to ca. 5 mL, and crystals were grown at −78 °C. The light orange crystals were filtered off with use of a cold frit and dried under vacuum; yield 1.5 g, 74%. Anal. Calcd for $C_{16}H_{34}P_2Fe$: C, 55.84; H, 9.60. Found: C, 55.74; H, 9.45. Infrared (Nujol mull): (FeH) 1780 cm^{-1} (s). ^1H NMR (benzene-d_6): δ 1.85 s (η^5-C_5Me_5) 1.20 m (PMe_3), −17.50 t ($^2J_{P-H}$ = 75.1 Hz, FeH). ^{31}P NMR (benzene-d_6): δ 32.6.

$Cp^*(PMe_3)_2FeBr$. To a mixture of $[Fe(acac)_2]_x$ (500 mg, 2.0 mmol) and LiCp* (280 mg, 2.0 mmol) was added 10 mL THF of and PMe_3 (0.2 mL, 2.0 mmol) at −78 °C. The solution was warmed to room temperature with stirring and cooled again to −78 °C and C_3H_5MgBr (2.95 mL, 1 M in Et_2O, 2.95 mmol) added. The solution was warmed to room temperature and stirred for 15 min. The volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with petroleum ether and the filtrate reduced in volume to ca. 2–3 mL. Crystals were obtained by cooling to −78 °C. The violet crystals were filtered off with use of a cold frit and dried under vacuum; yield 290 mg, 39%. Anal. Calcd for $C_{16}H_{33}P_2BrFe$: C, 45.42; H, 7.86. Found: C, 45.81; H, 7.79. ^1H NMR (benzene-d_6): δ 1.48 s (η^5-C_5Me_5), 1.30 m (PMe_3). ^{31}P NMR (benzene-d_6): δ 20.7.

$Cp^*(PMe_3)(C_2H_4)FeH$. To a mixture of $[Fe(acac)_2]_x$ (1 g, 3.9 mmol) and LiCp* (559 mg, 3.9 mmol) was added 10 mL of THF and exactly 1 equiv of PMe_3 (0.4 mL, 3.9 mmol) at −78 °C. The solution was warmed to room temperature and cooled again to −78 °C and CH_3CH_2MgCl (1.98 mL, 2 M in THF, 4.0 mmol) added. The solution was warmed to room temperature, the volatiles were removed under vacuum, and the thoroughly dried residue was extracted with petroleum ether. The filtrate was reduced to an oil, frozen, and then broken up by vigorous stirring under petroleum ether at −78 °C. The resultant yellow powder was filtered off with use of a cold frit, dried under vacuum, and recrystallized from petroleum ether to give off white crystals, yield 535 mg, 45.9%. Infrared (Nujol mull): 1860 cm^{-1} (m). All NMR data were found to be identical with previously published results.[7,9]

$Cp^*(PMe_3)Fe(\eta^3\text{-}C_3H_5)$. To a solution of $Cp^*(PMe_3)_2FeCl$ (496 mg, 1.3 mmol) in 15 mL of THF was added C_3H_5MgBr (1.74 mL, 1 M in Et_2O, 1.74 mmol) at −78 °C, and the solution was warmed to room temperature and stirred 15 min. The volatiles were removed under vacuum, and the residue was dried thoroughly. The residue was extracted with petroleum ether and the filtrate reduced to ca. 2–3 mL and cooled to −78 °C. The orange crystals that formed were filtered off with use of a cold frit and dried under vacuum; yield 305 mg, 76%. Anal. Calcd for $C_{16}H_{29}PFe$: C, 62.35; H, 9.48. Found: C, 62.09; H, 9.26. ^1H NMR (THF-d_8, −20 °C); δ 1.56 s (η^5-C_5Me_5), 0.84 d ($^2J_{P-H}$ = 6.6 Hz, PMe_3), 3.03 m, 1.55 d ($^3J_{H-H}$ = 6.0 Hz), −0.5 qt (J_{H-H} = 10.2 Hz, J_{H-H} = 1.2 Hz, C_3H_5). ^{31}P NMR (benzene-d_6): δ 32.8.

$Cp^*(PMe_3)_2FeCH_2C_6H_5$. To a mixture of $[Fe(acac)_2]_x$ (775 mg, 3.1 mmol) and LiCp* (433 mg, 3.1 mmol) was added 40 mL of THF and PMe_3 (0.62 mL, 6.1 mmol) at −78 °C. The solution was warmed to room temperature and cooled to −78 °C again, and $C_6H_5CH_2MgCl$ (1.6 mL, 2 M in THF, 3.2 mmol) was added. The solution was warmed to room temperature, the volatiles were removed under vacuum, and the residue was extracted with petroleum ether. The product was identified as $Cp^*(PMe_3)_2FeCl$ by ^1H NMR spectroscopy. The product was dissolved in 10 mL of THF and another 1 equiv of $C_6H_5CH_2MgCl$ added at −78 °C. The solution was warmed, the volatiles were removed, the residue was extracted, and crystals were grown at −78 °C. The crystals proved to contain bibenzyl (^1H NMR spectroscopy). The product was recrystallized from petroleum ether, and dark red crystals deposited at 0 °C, followed by white crystals at −78 °C. The red crystals were isolated and dried under vacuum; yield 332 mg, 25%. Anal. Calcd for $C_{23}H_{40}P_2Fe$: C, 63.59; H, 9.22. Found: C, 63.94; H, 9.31. ^1H NMR (benzene-d_6): δ 1.48 (η^5-C_5Me_5) 1.05 m (PMe_3) 1.93 t ($^2J_{P-H}$ = 5.9, $CH_2C_6H_5$), 7.25, 7.09, 6.99 ($CH_2C_6H_5$). ^{31}P NMR (benzene-d_6): δ 28.7.

$Cp^*(DMPE)FeCH_3$. To a solution of Cp*(DMPE)FeCl (200 mg, 0.6 mmol) in 10 mL of THF was added CH_3MgCl (0.2 mL, 2.9 M in THF, 0.6 mmol) at −78 °C. The solution was warmed to room temperature, the volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with petroleum ether, the volume of the filtrate was reduced to ca. 5 mL, and crystals were grown at −78 °C. The orange crystals were filtered off with use of a cold frit and dried under vacuum; yield 105 mg, 55.6%. Anal. Calcd for $C_{17}H_{34}P_2Fe$: C, 57.31; H, 9.62. Found: C, 57.53; H, 9.57. ^1H NMR (benzene-d_6): δ 1.67 s (η^5-C_5Me_5) 1.07 m ($Me_2PCH_2CH_2PMe_2$), −1.09 t ($^3J_{P-H}$ = 6.9 Hz, $FeCH_3$). ^{31}P NMR (benzene-d_6): δ 80.5.

Cp*(DMPE)FeH. To a solution of Cp*(DMPE)Fe (200 mg, 0.6 mmol) in 10 mL of THF was added Me_3CMgCl (0.3 mL, 2 M in et_2O, 0.6 mmol) at −78 °C. The solution was warmed to room temperature, the volatiles were removed under vacuum, and the residue was thoroughly dried. The residue was extracted with petroleum ether, the filtrate was reduced in volume to ca. 5 mL, and crystals were grown at −78 °C. The yellow crystals were filtered off with use of a cold frit and dried under vacuum; yield 94 mg, 52%. Anal. Calcd for $C_{16}H_{32}P_2Fe$: C, 56.15; H, 9.43. Found: C, 56.04; H, 9.33. Infrared (Nujol mull): 1815 cm^{-1} (m). ^1H NMR (benzene-d_6): δ 1.95 s (η^5-C_5Me_5), 1.29 m ($Me_2PCH_2CH_2PM_2$), 1.13 m ($Me_2PCH_2CH_2PMe_2$), −18.19 t ($^2J_{P-H}$

= 71.5 Hz, Fe*H*). ^{31}P NMR (benzene-d_6): δ 74.0.

[Cp*$(PMe_3)_3$Fe]$^+$$PF_6^-$. To a solution of Cp*$(PMe_3)_2$FeCl (108 mg, 0.29 mmol) and $K^+PF_6^-$ (53 mg, 0.29 mmol) in 10 mL of methanol at −78 °C was added 2 equiv of PMe_3 (0.05 mL). The solution was warmed to room temperature and stirred 15 min. The volatiles were removed under vacuum, and the residue was extracted with CH_2Cl_2. The filtrate was reduced to an oil and Et_2O added. The resultant red-orange precipitate was filtered at low temperature and dried; yield and 100 mg, 62%. Anal. Calcd for $C_{19}H_{42}P_4F_6Fe$: C, 40.44; H, 7.50. Found: C, 40.34; H, 7.11. ^{1}H NMR (THF-d_8): δ 1.62 s (η^5-C_5Me_5), 1.44 broad s (PMe_3). ^{31}P NMR (THF-d_8): δ 19.2, −144.5 h ($^1H_{P-F}$ = 710.4 Hz).

[Cp*$(PMe_3)_2$Fe(CO)]$^+$$PF_6^-$. A solution of Cp*$(PMe_3)_2$FeCl (123 mg, 0.33 mmol) and $K^+PF_6^-$ (70 mg, 0.38 mmol) in 10 mL of methanol at −78 °C was warmed to room temperature under 1 atm of CO and stirred for 0.5 h. The volatiles were removed under vacuum, and the residue was extracted with CH_2Cl_2. The filtrate was reduced to an oil and Et_2O added. The resultant yellow precipitate was filtered off at low temperature and dried; yield 129 mg, 77%. Anal. Calcd for $C_{17}H_{31}OP_2Fe$: C, 39.56; H, 6.44. Found: C, 39.13; H, 6.36. Infrared (Nujol mull): 1935 cm^{-1} (s). ^{1}H NMR (THF-d_8): δ 1.80 s (η^5-C_5Me_5) 1.50 m (PM_3). ^{31}P NMR (THF-d_8): δ 22.0, −144.6 h ($^1J_{P-F}$ = 710.4 Hz).

Cp*$(PMe_3)FeH_3$. In a typical preparation, 15 mg of Cp*$(PMe_3)(C_2H_4)$FeH was dissolved in 0.3 mL of benzene, benzene-d_6, or tetrahydrofuran and sealed in an NMR tube under 3 atm of H_2. The solution was agitated at room temperature and monitored by ^{1}H NMR spectroscopy; the reaction was complete in ca. 1.5 h. In benzene-d_6, deuterium could be observed to exchange into the hydride positions. Complete exchange into all hydrogen positions of the complex occurred in ca. 24 h at room temperature. The complex was generated in pentane, the solvent blown off with H_2 at room temperature, and an infrared spectrum obtained of the resultant oil (ν(FeH) 1905 cm^{-1} (s)). A solution infrared spectrum in tetrahydrofuran was obtained by generation of the trihydride and subsequent cannulation into a CsCl liquid cell under H_2.

Acknowledgment. We thank Professor Sunney Chan for helpful discussions and Dr. Emilio Bunel for disclosure of unpublished results. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and the Shell Companies Foundation.