The Strong Acidity and the Process for Deprotonation of (η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$

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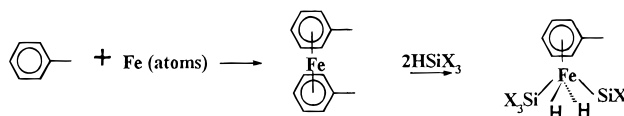
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The acidity and the process for deprotonation of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ in acetonitrile were studied with pyridine derivatives. (η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is a very strong acid and deprotonates in acetonitrile. The formation of hydrogen-bonded complexes M−H···N prior to deprotonation is observed when pyridine, 2,6-lutidine, and 2,2′-bipyridine are used. With 1 equiv of bipyridine, the hydrogen-bonded species is quite stable, two hydrides are deprotonated, and [bpyH$_2$]$^{2+}$ is formed. The small ^{57}Fe−hydride coupling constant (3.6 Hz) for (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is consistent with strong acidity of the compound. The 10.8 Hz coupling between ^{57}Fe and the hydride in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ and (η^6-toluene)Fe(H)(py)(SiCl$_3$) is similar to those observed in other Fe(II) hydrido compounds. The observation of the coupling only between *p*-H and the hydride in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ and (η^6-toluene)Fe(H)(py)(SiCl$_3$) indicates that the configuration with the hydride *trans* to *p*-H is dominant in solution and the rotation of the toluene is not fast at room temperature.

Introduction

Transition metal hydrides are of critical importance in organometallic chemistry, either as stoichiometric reagents for both organic and organometallic syntheses or as intermediates in catalytic processes.[1] The acidities of transition metal carbonyl hydrides have been studied in water, methanol, and acetonitrile.[2−4] A wide range of pK_a values (over 20 pK_a units) have been found.[2] Acetonitrile has been found to be an excellent solvent to study the acidity of transition metal hydrides.[4] Both thermodynamic acidity (equilibrium extent of deprotonation) and kinetic acidity (the rate at which a proton is removed from its M−H bond) of transition metal hydrides in acetonitrile were systematically investigated by Norton and co-workers.[4] Slow proton transfer was observed in transition metal hydrides, and it was attributed to steric hindrance, structural and electronic rearrangements accompanying proton transfer.[3−5] The anionic ligands SiCl$_3^-$, SiPh$_3^-$, and GePh$_3^-$ show a significant acid-strengthening influence.[6] For example, the complex HFe(Cp)(CO)(SiCl$_3$)$_2$ has a pK_a of 2.6 in CH$_3$CN,[7] comparing to 8.3 for HCo(CO)$_3$[4c] and 7.3 for H$_2$SO$_4$ in CH$_3$CN.[8]

Recently we reported the synthesis and characterization of a new class of π-arene Fe(IV) complexes, (η^6-arene)Fe(H)$_2$(SiX$_3$)$_2$ (X$_3$ = Cl$_3$,[9] F$_3$,[10] HCl$_2$,[11] MeCl$_2$[11]), prepared by reacting HSiX$_3$ (X$_3$ = Cl$_3$,[9] F$_3$,[10] HCl$_2$,[11] MeCl$_2$[11]) with arene-solvated iron atoms.

The acidity and the process for deprotonation of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ were studied by using pyridine derivatives with different steric requirements. Herein we report the results of our study.

Experimental Section

General Procedures. All reactions and manipulations were performed either on a high-vacuum line or in a glovebox under an atmosphere of dry argon. The iron chips, trichlorosilane, 2,6-lutidine, 2,2′-bipyridine, and 2,6-di-*tert*-butylpyridine were purchased from Aldrich and used as received. Methods for the synthesis of the Fe(IV) compounds are given in the preceding papers.[9−11] Pyridine was distilled over CaH$_2$ under an atmosphere of nitrogen before use. Deuterated solvents in ampules were purchased from Aldrich and Cambridge Isotopes and used as received. NMR spectra were obtained on a 400 MHz Bruker spectrometer equipped with a Sun workstation. Reported chemical shifts refer to room-temperature conditions (27 °C) unless specified otherwise. ^{1}H NMR chemical shifts were measured relative to tetramethylsilane when available or partially deuterated solvent peaks but are reported relative to tetramethylsilane. For variable-temperature ^{1}H NMR experiments, the compounds were dissolved in CD$_3$CN, and a delay of at least 10 min was allowed whenever temperature was changed. In a typical experiment, 5−6 mg of the complex was dissolved in CD$_3$CN, and the ^{1}H NMR spectrum was recorded. A microliter syringe was used to add liquid bases or CD$_3$CN solutions of solid bases to the NMR tube, and the solution was mixed throughly before ^{1}H NMR spectra were recorded. The ^{1}H NMR data for the toluene-coordinated complexes are given in Table 1.

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Table 1. ^{1}H NMR Data (δ) for Toluene-Coordinated Complexes Prepared

complex	o-H, m-H, p-H of arene	methyl H; hydride
(η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$[a]	6.32 (t of d), 6.36 (t of t), 6.15 (t of t), $^3J_{H-H} = 6.0$ Hz, $^3J_{H-H} = 1.4$ Hz	2.41 (s); -17.11 (s), $^2J_{Si-H} = 14.8$ Hz, $^1J_{Fe-H} = 3.6$ Hz
(η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$[b]	5.09 (d), 5.19 (t), 4.71 (t), $^3J_{H-H} = 6.0$ Hz	1.46 (s); -17.13 (s), $^2J_{Si-H} = 14.8$ Hz
[(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ [a]	5.29 (d), 5.24 (t), 5.43 (d of t), $^3J_{H-H} = 5.6$ Hz, $^3J_{H-H} = 1.0$ Hz	2.25 (s); -15.54 (s), $^2J_{Si-H} = 57.6$ Hz, $^1J_{Fe-H} = 10.8$ Hz
(η^6-toluene)Fe(H)(py)(SiCl$_3$)[a,c]	5.48 (d), 5.54 (t), 5.66 (d of t), $^3J_{H-H} = 5.6$ Hz, $^3J_{H-H} = 1.0$ Hz	2.33 (s); -15.83 (s), $^2J_{Si-H} = 51.6$ Hz, $^1J_{Fe-H} = 10.8$ Hz

[a] In CD$_3$CN. [b] In C$_6$D$_6$. [c] Coordinated py (CD$_3$CN): 9.27 (d, 2H), $^3J_{H-H} = 5.6$ Hz; 8.36 (t, 1H), $^3J_{H-H} = 7.6$ Hz; 7.89 (t, 2H), $^3J_{H-H} = 6.8$ Hz.
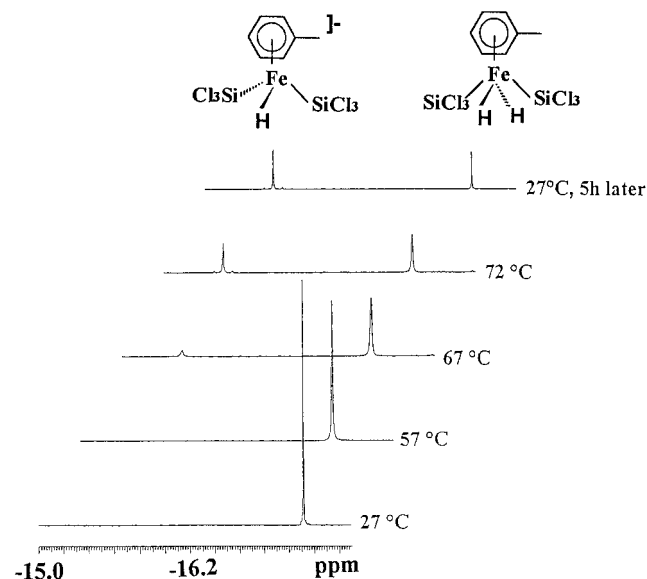
**Figure 1.** Hydride region of variable-temperature ^{1}H NMR spectra of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ in CD$_3$CN.

Reactions of (η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with 2,3-Dimethyl-2-butene. Two microliters of 2,3-dimethyl-2-butene (about 1 equiv) was added to a CD$_3$CN solution of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$, and ^{1}H NMR spectra were recorded. Signals of 2,3-dimethyl-2-chlorobutane were observed to appear and increase in 2 days. ^{1}H NMR data, δ(CD$_3$CN): 1.90 (heptet, 1H), $^3J_{H-H} = 6.8$ Hz; 1.53 (singlet, 6H); 1.01 (doublet, 6H), $^3J_{H-H} = 6.8$ Hz. Lit.[12] ^{1}H NMR δ(CD$_3$CN): 1.89 (heptet, $J = 6.8$ Hz, 1H, CH-3), 1.54 (s, 6H, 2 x CH$_3$—), 1.02 (d, $J = 6.8$ Hz, 6H, 2 x CH$_3$—). The signals for (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ were observed to decrease and signals for free toluene to increase. When excess 2,3-dimethyl-2-butene was used, the reaction ceased when (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ was consumed.

Reactions of (η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with 2,3-Dimethyl-1-butene. Three microliters of 2,3-dimethyl-1-butene (slightly more than 1 equiv) was added to a CD$_3$CN solution of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$, and ^{1}H NMR spectra were recorded every 10–12 h. The signals of 2,3-dimethyl-2-chlorobutane and 2,3-dimethyl-2-butene (singlet, 1.62 ppm) were observed to appear and increase. The signals for 2,3-dimethyl-1-butene and (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ were observed to decrease. The reaction ceased when (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ was consumed.

Results and Discussion

The variable-temperature ^{1}H NMR spectra of (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ in CD$_3$CN are given in Figure 1. At room temperature, no deprotonation was observed. At 67 °C, signals for [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ were observed and increased with time. When the temperature was lowered back to room temperature, the intensities of the hydride signals for (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ and [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ were about the same. However, no attempt was made to measure

Scheme 1

$$S = CD_3CN$$
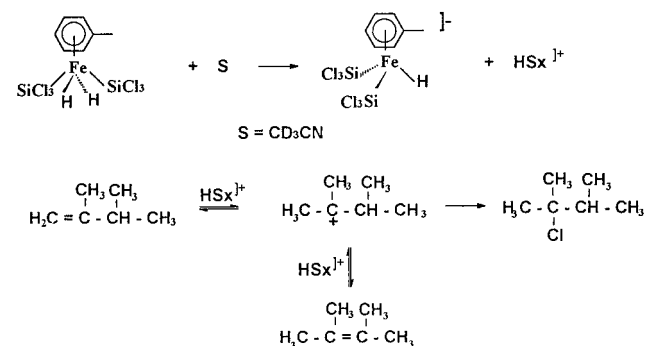
the pK_a, as toluene was substituted too, evidenced by appearance of free toluene during the experiment. This behavior suggests that the pK_a should be comparable to that of HFe(Cp)(CO)(S-iCl$_3$)$_2$, which deprotonates in acetonitrile with a pK_a of 2.6.[7]

The strong acidity of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ was also probed by reactions with substituted butenes. Both 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene react with (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ at room temperature to generate 2,3-dimethyl-2-chlorobutane. However, 2,3-dimethyl-2-butene is also generated when 2,3-dimethyl-1-butene is used. Both 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene take up a proton released by (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ to form a tertiary carbocation, and there is an equilibrium between them. 2,3-Dimethyl-2-butene is more stable than 2,3-dimethyl-1-butene, so the isomerization does proceed through the carbocation from 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene, but does not do so reversibly. The very reactive carbocation also abstracts a Cl from SiCl$_3$ groups to form the stable compound 2,3-dimethyl-2-chlorobutane (Scheme 1).

Proton- and electron-transfer reactions are the most fundamental reactions in chemistry and biology. Recently, considerable attention was focused on the deprotonation of transition metal hydrides.[4,5] Both experimental[13] and theoretical[14] studies show a substantial negative charge on the hydride of HCo(CO)$_4$, although HCo(CO)$_4$ is a strong acid in water and has a pK_a in acetonitrile about equal to that of HCl. It has been suggested that the proton transfer proceeds through hydrogen-bonded intermediates.[15] The need to repolarize the H—M bond was used to explain the large kinetic barriers in the deprotonation process.

$$M^{\delta+}-H^{\delta-} + B \leftrightarrow M^{\delta-}-H^{\delta+}\cdots B \leftrightarrow M^- + H-B^+$$
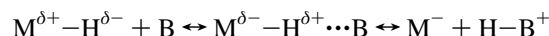
Norton and co-workers searched for hydrogen bonding between HCo(CO)$_4$ and oxygen and nitrogen bases in acetoni-

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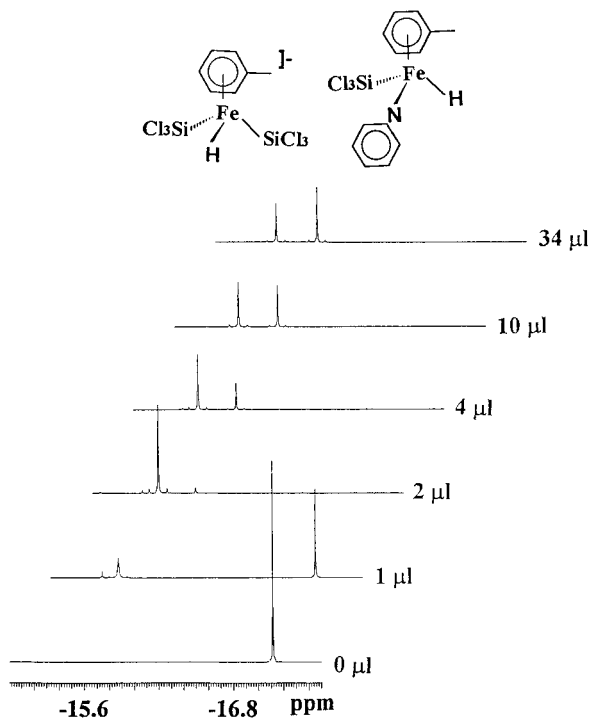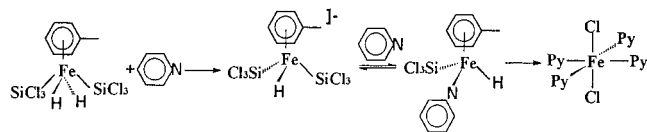
Figure 2. Hydride region of ^{1}H NMR spectra of (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ in CD$_3$CN with different amounts of pyridine.

Scheme 2

trile and matrices using IR and Raman spectroscopy but were unsuccessful.[15] Epstein and co-workers could not detect hydrogen bonding between nitrogen bases and [Cp*$_2$OsH]PF$_6$, but when phosphine oxides were used, hydrogen bonding was observed.[16]

In our laboratory the deprotonation of (η^6-toluene)Fe(H)$_2$-(SiCl$_3$)$_2$ in CD$_3$CN at room temperature was studied by using pyridine derivatives with different steric requirements. The ^{1}H NMR spectra of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with various amounts of pyridine are shown in Figure 2. Pyridine deprotonates (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ immediately to generate the anion [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$. Excess pyridine substitutes one SiCl$_3$ group to give (η^6-toluene)Fe(H)(py)(SiCl$_3$) (Scheme 2). However, only crystals of *trans*-Fe(py)$_4$Cl$_2$ could be isolated from the solution, even with 1 equiv of pyridine.[17]

The chemical shifts of the arene hydrogens of toluene show different patterns in these complexes. They are shown in Figure 3 together with those for free toluene. (η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$ has the same pattern as free toluene: *p*-H, highest field; *m*-H, lowest field; *o*-H, midfield. The couplings between the arene hydrogens and the two hydrides were observed to be 1.4 Hz, similar to those observed in Cp$_2$FeH$^+$ (1.3 Hz)[18] and Cp$_2$ReH
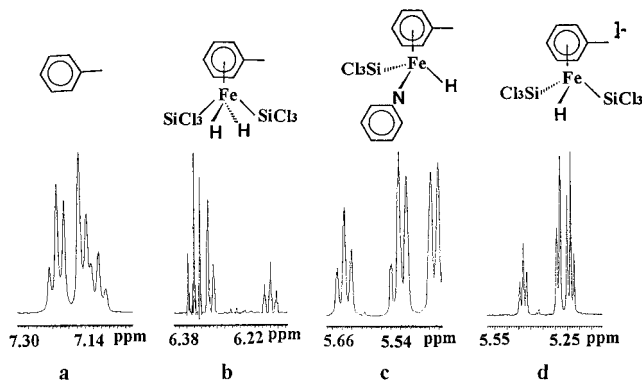

Figure 3. ^{1}H NMR arene regions in CD$_3$CN: (a) free toluene; (b) (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$; (c) (η^6-toluene)Fe(H)(py)(SiCl$_3$); (d) [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$.

(1.0 Hz).[19] This suggests that the rotation of the toluene in (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is very fast at room temperature and the influence of other ligands on the toluene is about the same for *p*-, *m*-, and *o*-H. However, in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ the pattern is different, with *p*-H lowest field, *m*-H highest field, and *o*-H midfield. Only the coupling between *p*-H and the hydride was observed (1.0 Hz). Apparently *p*-, *m*-, and *o*-H are influenced differently by the "legs" of "the piano stool". It may be that the rotation of the toluene in [(η^6-toluene)-Fe(H)(SiCl$_3$)$_2$]$^-$ is not very fast, and the configuration with the hydride *trans* to *p*-H is dominant in solution, which exerts different influences on *p*-, *m*-, and *o*-H of the toluene. In (η^6-toluene)Fe(H)(py)(SiCl$_3$) the pattern is also different, with *p*-H lowest field, *o*-H highest field, and *m*-H midfield. Again, only the coupling between the hydride and *p*-H (1.0 Hz) was observed. The steric repulsions between the methyl group of the toluene and the pyridine and between the methyl group and the SiCl$_3$ group cause the configuration with the hydride to be eclipsed and the methyl group to be the most stable configuration. The hydride is thus *trans* to the *p*-H, which generates large coupling between them.

Iron-57 NMR techniques have developed rapidly in the last two decades.[20] However, the one-bond coupling between ^{57}Fe and a hydride has been observed only in a few hydrido iron complexes with indirect two-dimensional NMR spectroscopy.[21,22] It was found that, for Cp'Fe(H)L$_2$ (L = phosphine, diphosphine, ethylene), the $^1J_{Fe-H}$ values (9 Hz) do not vary significantly upon substitution of other ligands on the iron.[21,22]

The hydride regions of NMR spectra for our complexes are given in Figure 4. Two sets of satellites were observed. The nuclei of spin $^1/_2$ to which the hydrides might couple are ^{13}C (1.11% natural abundance), ^{29}Si (4.70%), and ^{57}Fe (2.25%). In (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$, the 14.8 Hz coupling is taken as the two-bond coupling between the ^{29}Si and the hydride and the 3.6 Hz coupling as the one-bond coupling between ^{57}Fe and the hydride. In [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$, $^2J_{Si-H}$ is 57.6 Hz and $^1J_{Fe-H}$ is 10.8 Hz. In (η^6-toluene)Fe(H)(py)(SiCl$_3$), $^2J_{Si-H}$ is 51.6 Hz and $^1J_{Fe-H}$ is 10.8 Hz. The $^1J_{Fe-H}$ values (10.8 Hz) in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ and (η^6-toluene)Fe(H)(py)(SiCl$_3$) are very close to those values (9 Hz) observed in other Fe(II) complexes.[21,22] The small coupling (3.6 Hz) between the ^{57}Fe and the hydrides in (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is consistent with the strong acidity of the compound. Jetz and Graham observed

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(17) Crystal data: yellow single crystals of *trans*-Fe(py)$_4$Cl$_2$ at −160 °C are tetragonal, of space group *P*4$_3$2$_1$2 (No. 96) with *a* = 15.818(2) Å, *c* = 17.029(3) Å, and *V* = 4261(1) Å^3. It also crystallizes in space group *I*4$_1$/*acd* (No. 142) with *a* = 15.945(2) Å and *c* = 17.287(6) Å at room temperature (see: Long, G. J.; Clarke, P. J. *Inorg. Chem.* **1978**, *17*, 1394).

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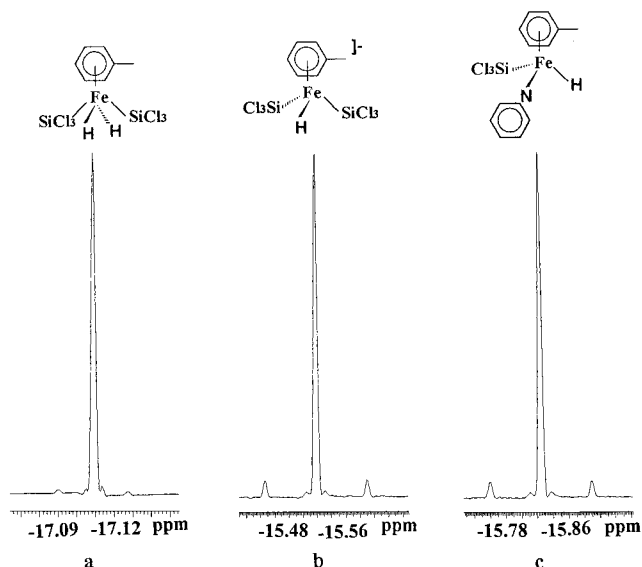(22) Benn, R.; Brevard, C. *J. Am. Chem. Soc.* **1986**, *108*, 5622.

Figure 4. ^{1}H NMR hydride regions in CD_3CN: (a) (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$; (b) [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$; (c) (η^6-toluene)Fe-(H)(py)(SiCl$_3$).
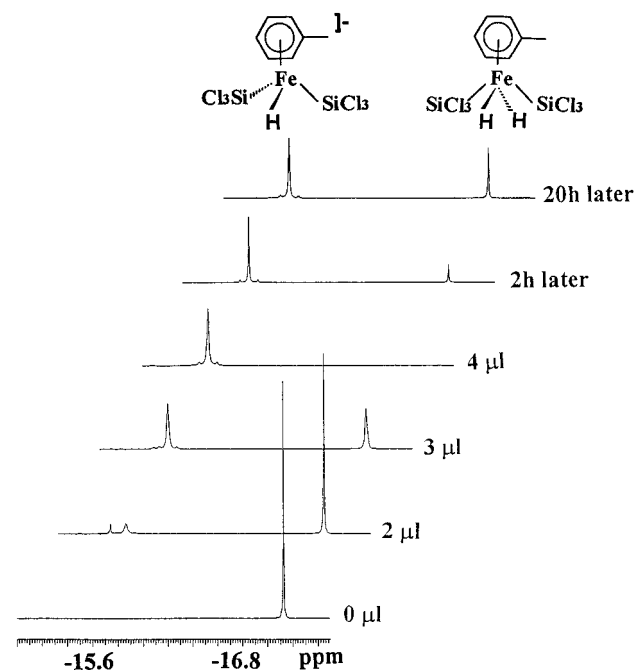
Figure 5. Hydride region of ^{1}H NMR spectra of (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ in CD_3CN with 2,6-lutidine under different conditions.

two sets of satellites flanking the hydride resonance (δ −11.64 ppm) in HFe(Cp)(CO)(SiCl$_3$)$_2$.[7] The 20 Hz coupling was assigned as $^2J_{Si-H}$ and the 14.5 Hz coupling as $^1J_{Fe-H}$.[7] However, the 14.5 Hz coupling may be due to the coupling between the hydride and [13]CO, as the average hydride−[13]CO coupling constant is 14.1 Hz for Cp(H)W(CO)$_3$.[23]

Returning again to the present study, the ^{1}H NMR spectra of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with 2,6-lutidine under different conditions are shown in Figure 5. 2,6-Lutidine is more sterically demanding than pyridine. It deprotonated (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ at room temperature to give [(η^6-toluene)-Fe(H)(SiCl$_3$)$_2$]$^-$. Excess lutidine caused the substitution of one SiCl$_3$ group to generate (η^6-toluene)Fe(H)(lutidine)(SiCl$_3$) (not observed), which is apparently not stable. This intermediate species then appeared to react with [py·HSiCl$_3$] to give back
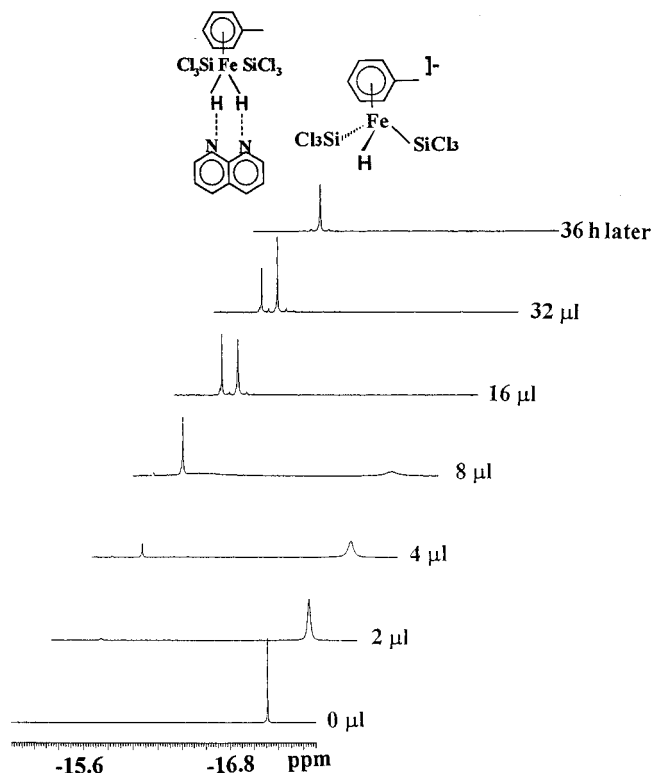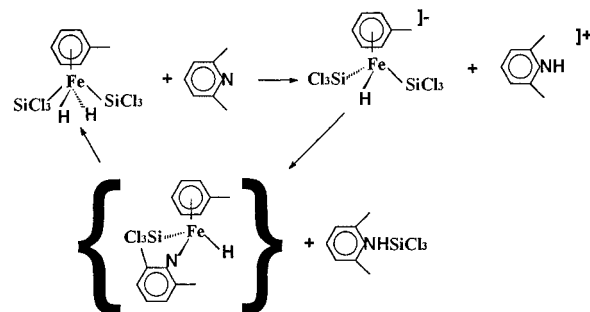
(23) Faller, J. W.; Anderson, A. S.; Chen, C. *Chem. Commun.* **1969**, 719.

Figure 6. Hydride region of ^{1}H NMR spectra of (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ in CD_3CN with different amounts of 2,2′-bipyridine.

Scheme 3

the starting material, (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$. An equilibrium was then established between (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ and [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ (Scheme 3).
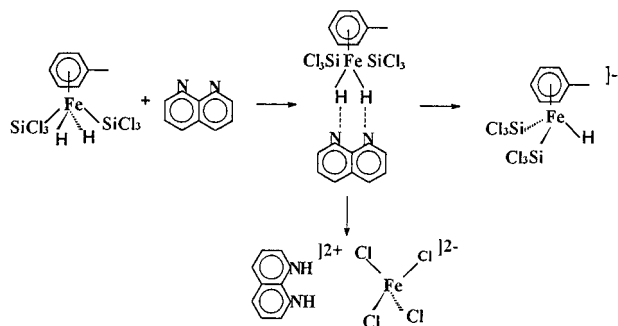
The distance between the two hydrides in (η^6-toluene)-Fe(H)$_2$(SiCl$_3$)$_2$ is about 2.2 Å,[9] and the distance between the N atoms of the planar 2,2′-bipyridine (bpy) in (η^6-toluene)Fe(bpy) is about 2.5 Å.[24] Perhaps two hydrogen bonds between the two hydrides and bpy would be able to stabilize the intermediate two-hydrogen-bonded species. The ^{1}H NMR spectra of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with bpy are given in Figure 6. A new hydride peak at −15.41 ppm appeared first, which was also observed in the pyridine and lutidine reactions but quickly disappeared in those cases. The significant downfield shift of the hydride signal suggests formation of hydrogen bonds between (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ and bpy.[25] When excess bpy was used, it deprotonated (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ to generate [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$, which did not react further (Scheme 4). However, when 1 equiv bpy was used, red crystals[26] of [bpyH$_2$][FeCl$_4$] were obtained in a few hours,

(24) Radonovich, L. J.; Eyring, M. W.; Groshens, T. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2816.
(25) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233.

Scheme 4

and a colorless solution remained. If Scheme 4 is correct, and a bpy·(H)$_2$(SiCl$_3$)$_2$Fe(toluene) adduct is formed, the interaction is not sufficiently strong to allow a stable entity, and decomposition to [bpyH$_2$][FeCl$_4$] occurs. The formation of hydrogen-bonded species prior to deprotonation is also supported by the observation that even excess 2,6-di-*tert*-butylpyridine does not

(26) Crystal data: red single crystals of [bpyH$_2$][FeCl$_4$] at −160 °C are monoclinic, of space group $P2_1/c$ (No. 14) with $a = 7.129(1)$ Å, $b = 13.662(2)$ Å, $c = 14.245(2)$ Å, $\beta = 100.22(3)°$, $V = 1365.4(7)$ Å^3, and $Z = 4$ ($d_{calcd} = 1.731$ g/cm^3, μ(Cu Kα) = 136.27 cm^{-1}). A total of 1802 unique reflections ($2\theta_{max} = 109.8°$) were collected using $\omega-2\theta$ scans with graphite-monochromated Cu Kα radiation. The structure parameters were refined to convergence: $R = 0.057$, $R_W = 0.057$ (based on F) for reflections with $I > 0.01\sigma(I)$.

deprotonate (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$, as the two bulky *tert*-butyl groups prevent the approach of the N atom to the hydride.

Conclusions

(η^6-Toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is a very strong acid and deprotonates in acetonitrile. The formation of hydrogen-bonded complexes M−H···N prior to deprotonation is observed when pyridine, 2,6-lutidine, and 2,2′-bipyridine are used. With 1 equiv of bipyridine, both hydrides are deprotonated, and [bpyH$_2$]$^{2+}$ is formed. The small coupling (3.6 Hz) between ^{57}Fe and the hydride in (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ is consistent with strong acidity of the compound. The 10.8 Hz coupling between ^{57}Fe and the hydride in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ and (η^6-toluene)Fe(H)(py)(SiCl$_3$) is similar to those observed in other Fe(II) hydrido compounds. The observation of coupling only between p-H and the hydride in [(η^6-toluene)Fe(H)(SiCl$_3$)$_2$]$^-$ and (η^6-toluene)Fe(H)(py)(SiCl$_3$) indicates that the configuration with the hydride *trans* to p-H is dominant in solution, and the rotation of the toluene is not fast at room temperature.

2,3-Dimethyl-2-butene and 2,3-dimethyl-1-butene react with (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ to form a tertiary carbocation, which abstracts a Cl from SiCl$_3$ groups to form 2,3-dimethyl-2-chlorobutane. The isomerization from 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene is also observed.