

# Unusual Iron(IV) Complexes: Metal Atom Syntheses and Studies of $(\eta^6\text{-arene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ (Arene = Benzene, Toluene, *p*-Xylene)

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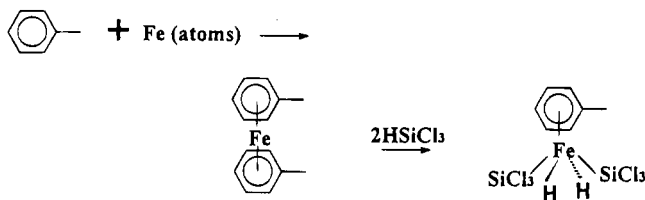
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Iron atoms codeposited with excess arene (benzene, toluene, or *p*-xylene) at  $-196$  or  $-78$  °C yielded a brown matrix containing arene-solvated iron atoms. Treatment of this matrix with a limited amount of  $\text{HSiCl}_3$  produced novel Fe(IV) arene compounds. We have obtained and structurally characterized the following substances: **1**,  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ , space group *Pnma*,  $a = 15.244(2)$  Å,  $b = 11.115(1)$  Å,  $c = 8.309(1)$  Å,  $Z = 4$ ,  $V = 1407.9(5)$  Å<sup>3</sup>; **2**,  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ , space group *P2<sub>1</sub>/a*,  $a = 12.232(2)$  Å,  $b = 8.591(1)$  Å,  $c = 13.873(2)$  Å,  $\beta = 92.66(2)^\circ$ ,  $Z = 4$ ,  $V = 1456.3(6)$  Å<sup>3</sup>; **3**,  $(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ , space group *P2<sub>1</sub>/a*,  $a = 8.323(1)$  Å,  $b = 24.302(2)$  Å,  $c = 8.627(1)$  Å,  $\beta = 116.541(9)^\circ$ ,  $Z = 4$ ,  $V = 1561.2(7)$  Å<sup>3</sup>. In the NMR, the  $^{29}\text{Si}-^1\text{H}$  coupling constants have been observed to be 15 Hz for all three compounds, dramatically lower than  $^1J_{\text{Si}-\text{H}} = 370$  Hz for  $\text{HSiCl}_3$ . The structural and NMR data show that the oxidative addition of  $\text{H}-\text{SiCl}_3$  to the Fe center is complete and these compounds are formally Fe(IV) dihydride derivatives. The interaction between arene and Fe is very strong; no arene exchange has been observed, even at elevated temperatures. Thermal decomposition appears to proceed by  $\text{HSiCl}_3$  reductive elimination. In addition, the first reaction of added ligands causes  $\text{HSiCl}_3$  elimination.

## Introduction

Recently we reported preliminary results of the synthesis and characterization of  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .<sup>1</sup> Iron atoms were codeposited with excess toluene at  $-196$  °C forming "toluene-solvated iron atoms",<sup>2</sup> which react with  $\text{HSiCl}_3$ , upon warming, to form  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .



The recent discovery of a greater number of complexes having  $\eta^2$ -silane ligands,<sup>3,4</sup>  $\eta^2\text{-H}_2$  ligands,<sup>3,5</sup> or agostic C–H bonds<sup>3,6</sup> and the great interest in Fe(IV) complexes,<sup>7</sup> coupled with the

fact that only a few Fe(IV) complexes<sup>8</sup> have been well characterized, prompted us to synthesize additional new derivatives.

Herein we report the syntheses, structures, and reactivity studies of three compounds:  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ ,  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ , and  $(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ . The evidence for formulating these species as Fe(IV) dihydrides is discussed.

## 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 and trichlorosilane were purchased from Aldrich and used as received. Toluene, benzene, *p*-xylene, and hexanes were distilled under an atmosphere of nitrogen before use from Na/K and benzophenone ketyl. Arene and trichlorosilane were degassed by two or three freeze–pump–thaw cycles prior to the metal atom syntheses. The solvated metal atom dispersion (SMAD) apparatus was described in detail elsewhere.<sup>9</sup> Infrared spectra were obtained using a Bio-Rad FTS-40 spectrometer. NMR spectra were obtained on a Varian XL-400, operating at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ . Reported chemical shifts refer to room-temperature conditions (27 °C) unless specified otherwise.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. For variable-temperature  $^1\text{H}$  NMR experiments, the compounds were dissolved in toluene-*d*<sub>8</sub>, and a delay of at least 10 min was allowed whenever the temperature was changed. Microanalyses were performed by Galbraith Laboratories, Inc.

**Preparation of  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (1).** Iron vapor (1.2 g) was codeposited with benzene (about 90 g) at  $-196$  °C.  $\text{HSiCl}_3$  (about

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10 mL) was distilled in and the matrix warmed to room temperature over 5–6 h. The solution was stirred overnight. The reaction mixture was filtered through Celite under argon. The volatiles were removed under reduced pressure, the resultant yellow solid was dissolved in benzene, and the solution was layered with hexanes at room temperature. Yellow prism crystals of **1** were formed on the wall of the Schlenk tube within 2 weeks (1–2% yield based on Fe vaporized).  $^1\text{H}$  NMR of **1**,  $\delta(\text{C}_6\text{D}_6)$ : 4.99 (s),  $-17.07$  ppm (s).  $^{13}\text{C}$  NMR: 98.16 ppm. IR (KBr):  $1944\text{ cm}^{-1}$  for Fe–H vibration. Anal. Calcd for  $\text{C}_6\text{H}_8\text{Cl}_6\text{FeSi}_2$ : C, 17.80; H, 2.00. Found: C, 18.66; H, 2.27.

**Preparation of  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (**2**).** Iron vapor (1.2 g) was codeposited with toluene (about 90 g) at  $-196\text{ }^\circ\text{C}$ .  $\text{HSiCl}_3$  (about 10 mL) was distilled in and the matrix warmed to  $-78\text{ }^\circ\text{C}$  and held there for about 2 h, followed by warming slowly to room temperature and stirring overnight. After workup, the resultant yellow solid was recrystallized from a mixture of toluene/hexanes at  $-3\text{ }^\circ\text{C}$  to yield yellow crystals of **2** in a few days. The best experiment gave a yield of 5% based on Fe vaporized.  $^1\text{H}$  NMR of **2**,  $\delta(\text{C}_6\text{D}_6)$ : 5.19 (t, 2H), 5.09 (d, 2H), 4.71 (t, 1H), 1.46 (s, 3H),  $-17.07$  ppm (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR: 112.25, 99.22, 98.63, 93.97, 19.55 ppm. IR (KBr):  $1930\text{ cm}^{-1}$  for Fe–H vibration. Anal. Calcd for  $\text{C}_7\text{H}_{10}\text{Cl}_6\text{FeSi}_2$ : C, 20.07; H, 2.41; Cl, 50.78; Fe, 13.33; Si, 13.41. Found: C, 19.47; H, 2.50; Cl, 49.66; Fe, 13.33; Si, 12.08.

**Preparation of  $(\eta^6\text{-}p\text{-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (**3**).** Iron vapor (1.2 g) was codeposited with *p*-xylene (about 90 g) at  $-78\text{ }^\circ\text{C}$  within a bath of 2-propanol/dry ice.  $\text{HSiCl}_3$  (about 10 mL) was distilled in and the matrix warmed to room temperature over 5–6 h. The solution was stirred overnight. After workup, the yellow precipitate was dissolved in benzene, and the solution was layered with hexanes at room temperature. Yellow crystals of **3** were obtained within 2 weeks (about 1% yield).  $^1\text{H}$  NMR of **3**,  $\delta(\text{C}_6\text{D}_6)$ : 5.21 (s), 1.47 (s),  $-17.20$  ppm (s). IR (KBr):  $1952\text{ cm}^{-1}$  for Fe–H vibration.

**X-ray Crystallography.** All measurements were made on a Rigaku AFC5R diffractometer with a graphite-monochromated Cu  $K\alpha$  radiation and a 12 kW rotating-anode generator. The data for all three structures were collected at  $-160\text{ }^\circ\text{C}$  using the  $\omega$ - $2\theta$  scan technique. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

**Crystal Structure of  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .** A yellow prism crystal of  $0.30 \times 0.20 \times 0.30$  mm was mounted on the tip of a glass fiber. Twenty-five well-centered reflections in the range of  $61.07 < 2\theta < 69.07^\circ$  were used to obtain the cell parameters and an orientation matrix for data collection. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant. An empirical absorption correction, using the program DIFABS, was applied, resulting in transmission factors ranging from 0.89 to 1.03. The data were corrected for Lorentz and polarization effects. The space group *Pnma* (No. 62) was determined on the basis of the systematic absences and the successful solution and refinement of the structure. The structure was solved by direct methods, and all atoms, including hydrogen atoms, were found and refined. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 935 observed reflections with  $I > 0.01\sigma(I)$  and 97 variable parameters, and it converged to  $R = 0.053$  and  $R_w = 0.074$ .

**Crystal Structure of  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .** A yellow prism crystal with dimensions of  $0.20 \times 0.20 \times 0.15$  mm was mounted on the tip of a glass fiber. A monoclinic cell was determined from the geometrical parameters of 25 well-centered reflections with  $2\theta$  values between  $60.0$  and  $69.2^\circ$ . Inspection of the systematic absences led to the inference that the correct space group would be *P2<sub>1</sub>/a* (No. 14). A set of three standard reflections, monitored after every 150 reflections, showed no decay during data collection. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located from the difference Fourier maps and refined isotropically. The final cycle of full-matrix least-squares refinement based on 1838 observed reflections and 185 variables converged and gave a final agreement at  $R = 0.056$  and  $R_w = 0.073$ .

**Crystal Structure of  $(\eta^6\text{-}p\text{-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .** A yellow prism crystal having dimensions of  $0.20 \times 0.20 \times 0.40$  mm was selected. Unit cell parameters were obtained by centering and indexing 25

**Table 1.** Crystallographic Data for  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ ,  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ , and  $(\eta^6\text{-}p\text{-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$

	$(\eta^6\text{-benzene})\text{-Fe}(\text{H})_2(\text{SiCl}_3)_2$	$(\eta^6\text{-toluene})\text{-Fe}(\text{H})_2(\text{SiCl}_3)_2$	$(\eta^6\text{-}p\text{-xylene})\text{-Fe}(\text{H})_2(\text{SiCl}_3)_2$
formula	$\text{FeCl}_6\text{Si}_2\text{C}_6\text{H}_8$	$\text{FeCl}_6\text{Si}_2\text{C}_7\text{H}_{10}$	$\text{FeCl}_6\text{Si}_2\text{C}_8\text{H}_{12}$
fw	404.87	418.89	432.92
space group	<i>Pnma</i> (No. 62)	<i>P2<sub>1</sub>/a</i> (No. 14)	<i>P2<sub>1</sub>/a</i> (No. 14)
<i>a</i> , Å	15.244(2)	12.232(2)	8.323(1)
<i>b</i> , Å	11.115(1)	8.591(1)	24.302(2)
<i>c</i> , Å	8.309(1)	13.873(2)	8.627(1)
$\beta$ , deg		92.66(2)	116.541(9)
<i>V</i> , Å <sup>3</sup>	1407.9(5)	1456.3(6)	1561.2(7)
<i>Z</i>	4	4	4
<i>d</i> <sub>calcd.</sub> , g/cm <sup>3</sup>	1.910	1.910	1.842
$\mu$ , cm <sup>-1</sup>	208.5	201.8	188.5
$\lambda$ , Å	1.541 84	1.541 84	1.541 84
<i>T</i> , °C	$-160(1)$	$-160(1)$	$-160(1)$
no. of data ( $I > 0.1\sigma(I)$ )	935	1838	1916
no. params refined	97	185	202
transm factor:	1.03, 0.89	1.20, 0.94	1.25, 0.81
max, min			
<i>R</i> <sup>a</sup>	0.053	0.056	0.047
<i>R</i> <sub>w</sub> <sup>b</sup>	0.074	0.073	0.064

$$^a R = \sum[|F_o| - |F_c|]/\sum|F_o|, \quad ^b R_w = \sum w^{1/2}[|F_o| - |F_c|]/\sum w^{1/2}|F_o|.$$

**Table 2.** Positional and Equivalent Isotropic Thermal Parameters for  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> , Å <sup>2</sup>
Fe	0.58845(8)	1/4	0.1384(1)	2.12(6)
Cl(1)	0.3915(1)	0.3946(2)	0.0064(2)	4.36(8)
Cl(2)	0.4925(2)	1/4	$-0.2710(3)$	7.8(2)
Cl(3)	0.7915(1)	0.1050(2)	0.0522(3)	5.1(1)
Cl(4)	0.7093(2)	1/4	$-0.2472(3)$	11.1(3)
Si(1)	0.4752(2)	1/4	$-0.0278(3)$	2.9(1)
Si(2)	0.7109(2)	1/4	$-0.0035(3)$	3.5(1)
C(1)	0.6737(7)	1/4	0.342(1)	4.0(5)
C(2)	0.6281(5)	0.3594(7)	0.3326(8)	4.3(3)
C(3)	0.5377(5)	0.3580(7)	0.3228(8)	4.1(3)
C(4)	0.4904(6)	1/4	0.321(1)	3.6(4)
H(0)	0.586(3)	0.152(6)	0.023(7)	3(1)
H(1)	0.733(7)	1/4	0.36(1)	4(2)
H(2)	0.664(6)	0.45(1)	0.33(1)	9(3)
H(3)	0.502(5)	0.429(7)	0.314(8)	5(2)
H(4)	0.421(5)	1/4	0.32(1)	2(2)

reflections found initially and refined by centering another 25 reflections in the range of  $61.87 < 2\theta < 69.57^\circ$ . From the systematic absences, the space group was uniquely assigned as *P2<sub>1</sub>/a* (No. 14). No decay was observed during data collection. Direct methods were used to solve the structure. Hydrogen atoms were found and refined. In the final cycle of full-matrix least-squares refinement, 202 variables were refined to convergence using 1916 observed reflections, leading to residuals of  $R = 0.047$  and  $R_w = 0.064$ , with all non-hydrogen atoms being refined anisotropically.

The figures of merit and some important crystallographic data for **1–3** are listed in Table 1. The fractional coordinates for all atoms of **1** are listed in Table 2, while the fractional coordinates for all atoms of **2** and **3** are listed in Tables 3 and 4, respectively.

## Results and Discussion

**Preparation.** "Arene-solvated iron atoms"<sup>2</sup> are stable only at low temperature (probably lower than  $-30\text{ }^\circ\text{C}$ ); upon warming, they react with  $\text{HSiCl}_3$  to give the novel Fe(IV) arene complexes. Toluene-solvated iron atoms in liquid toluene react with  $\text{HSiCl}_3$  even at  $-78\text{ }^\circ\text{C}$ . For benzene and *p*-xylene, the best results have been obtained when the matrixes are warmed slowly to room temperature. When metal vapor reactions were carried out at  $-196\text{ }^\circ\text{C}$  with *p*-xylene, this arene froze in the showhead of the reactor. Therefore, the reactions were carried out at  $-78\text{ }^\circ\text{C}$ .

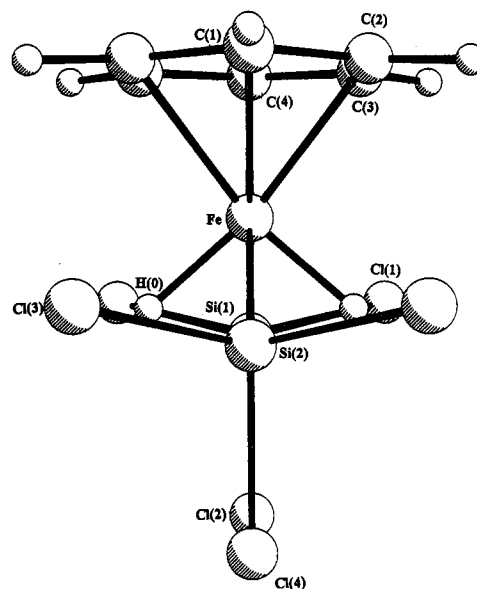
**Table 3.** Positional and Equivalent Isotropic Thermal Parameters for  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ 

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
Fe	0.84002(6)	0.3650(1)	0.25262(6)	2.03(4)
Cl(1)	0.8194(1)	0.2956(2)	-0.0024(1)	3.06(7)
Cl(2)	1.0636(1)	0.3183(2)	0.0942(1)	3.18(7)
Cl(3)	0.9210(1)	0.0084(2)	0.1207(1)	3.55(7)
Cl(4)	0.6565(1)	0.1686(2)	0.4053(1)	3.10(7)
Cl(5)	0.8964(1)	0.2499(2)	0.4995(1)	3.39(7)
Cl(6)	0.8655(1)	-0.0371(2)	0.3535(1)	4.09(8)
Si(1)	0.9070(1)	0.2467(2)	0.1258(1)	2.32(7)
Si(2)	0.8189(1)	0.1903(2)	0.3680(1)	2.42(7)
C(1)	0.9178(5)	0.5934(7)	0.2499(4)	2.6(3)
C(2)	0.8464(5)	0.5740(7)	0.1681(5)	2.6(3)
C(3)	0.7366(5)	0.5268(8)	0.1778(5)	2.9(3)
C(4)	0.6976(5)	0.4996(8)	0.2690(5)	2.9(3)
C(5)	0.7665(5)	0.5187(7)	0.3510(5)	2.5(3)
C(6)	0.8774(5)	0.5627(7)	0.3416(5)	2.8(3)
C(7)	1.0337(6)	0.6462(9)	0.2409(6)	3.1(3)
H(0)	0.778(5)	0.232(8)	0.206(4)	3(1)
H(1)	0.936(7)	0.22(1)	0.280(5)	5(2)
H(2)	0.871(5)	0.586(8)	0.098(5)	3(1)
H(3)	0.701(5)	0.495(7)	0.123(5)	2(1)
H(4)	0.629(5)	0.446(8)	0.272(4)	3(1)
H(5)	0.743(5)	0.503(7)	0.414(5)	2(1)
H(6)	0.920(6)	0.556(9)	0.400(5)	4(2)
H(7A)	1.050(9)	0.76(1)	0.238(7)	8(3)
H(7B)	1.083(8)	0.61(1)	0.281(6)	6(2)
H(7C)	1.055(7)	0.64(1)	0.164(6)	6(2)

**Table 4.** Positional and Equivalent Isotropic Thermal Parameters for  $(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ 

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
Fe	0.8047(1)	0.12062(3)	0.3718(1)	2.36(4)
Cl(1)	0.6700(2)	0.17043(6)	-0.0612(2)	3.75(6)
Cl(2)	0.7054(2)	0.03894(6)	-0.0080(2)	3.49(6)
Cl(3)	1.0560(2)	0.11259(8)	0.1059(2)	4.10(7)
Cl(4)	1.2020(2)	0.08133(6)	0.7543(2)	3.50(6)
Cl(5)	1.2748(2)	0.16393(8)	0.5023(2)	4.35(7)
Cl(6)	1.0825(2)	0.20876(6)	0.7250(2)	3.80(6)
Si(1)	0.8166(2)	0.11200(6)	0.1202(2)	2.67(6)
Si(2)	1.0780(2)	0.14269(7)	0.5724(2)	2.68(6)
C(1)	0.5520(8)	0.1617(2)	0.3072(8)	3.0(2)
C(2)	0.5239(8)	0.1094(3)	0.226(1)	3.0(2)
C(3)	0.6012(8)	0.0608(3)	0.3203(9)	3.1(2)
C(4)	0.7068(8)	0.0637(2)	0.5018(7)	2.7(2)
C(5)	0.7373(8)	0.1149(3)	0.5845(8)	2.9(2)
C(6)	0.6627(9)	0.1632(3)	0.4858(8)	3.1(3)
C(7)	0.467(1)	0.2128(3)	0.207(1)	3.8(3)
C(8)	0.781(1)	0.0113(3)	0.600(1)	3.6(3)
H(1A)	0.920(9)	0.080(3)	0.36(1)	4(2)
H(1B)	0.86(1)	0.162(3)	0.33(1)	6(2)
H(2)	0.457(7)	0.106(2)	0.125(7)	0(1)
H(3)	0.599(8)	0.022(3)	0.260(8)	3(1)
H(5)	0.807(8)	0.120(2)	0.702(9)	3(1)
H(6)	0.69(1)	0.189(3)	0.54(1)	5(2)
H(7A)	0.33(1)	0.216(3)	0.20(1)	5(2)
H(7B)	0.42(1)	0.204(3)	0.10(1)	5(2)
H(7C)	0.538(9)	0.245(3)	0.243(8)	4(1)
H(8A)	0.68(1)	-0.006(5)	0.62(1)	10(3)
H(8B)	0.85(1)	0.015(3)	0.70(1)	3(2)
H(8C)	0.82(1)	-0.008(4)	0.55(1)	7(3)

**Molecular Structures.**  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (**1**). A PLUTO drawing of the molecule is shown in Figure 1. The selected bond distances and angles are listed in Table 5 with estimated standard deviations given in parentheses. The molecule exists as a four-legged "piano stool" where the  $\text{SiCl}_3$  and H ligands serve as legs and benzene serves as the seat. The two  $\text{SiCl}_3$  groups are *trans* to each other, as are the two hydrides. The structure of **1** has  $C_{2v}$  symmetry, and the whole molecule sits on a mirror plane with Fe, Si(1), Si(2), Cl(2), Cl(4), C(1), C(4) on the plane. The distances between Fe and C atoms of benzene range from 2.095(6) to 2.14(1)  $\text{\AA}$ , with the distance

**Figure 1.** PLUTO drawing of  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ . The molecule sits on a mirror plane.**Table 5.** Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ 

Distances			
Fe-Si(1)	2.210(3)	Fe-Si(2)	2.207(3)
Fe-C(1)	2.14(1)	Fe-C(2)	2.109(6)
Fe-C(3)	2.095(6)	Fe-C(4)	2.128(9)
Fe-H(0)	1.45(7)	Cl(1)-Si(1)	2.072(2)
Cl(2)-Si(1)	2.038(4)	Cl(3)-Si(2)	2.079(2)
Cl(4)-Si(2)	2.026(4)	C(1)-C(2)	1.403(9)
C(2)-C(3)	1.38(1)	C(3)-C(4)	1.400(9)
Angles			
Si(1)-Fe-Si(2)	109.1(1)	Si(1)-Fe-C(1)	166.1(3)
Si(1)-Fe-C(2)	134.6(2)	Si(1)-Fe-C(3)	99.7(2)
Si(1)-Fe-C(4)	84.0(3)	Si(1)-Fe-H(0)	64(2)
Si(2)-Fe-C(1)	84.8(3)	Si(2)-Fe-C(2)	99.6(2)
Si(2)-Fe-C(3)	134.7(2)	Si(2)-Fe-C(4)	166.9(3)
Si(2)-Fe-H(0)	71(2)	C(1)-Fe-H(0)	123(2)
C(2)-Fe-H(0)	161(2)	C(2)-Fe-H(0)'	95(2)
C(3)-Fe-H(0)	155(2)	C(3)-Fe-H(0)'	93(2)
C(4)-Fe-H(0)	117(2)	H(0)-Fe-H(0)'	97(5)

from the Fe to the center of the ring equal to 1.608  $\text{\AA}$ . The ring carbon-Fe distances in a similar compound,  $\text{Cp}(\text{OC})\text{Fe}(\text{H})(\text{SiCl}_3)_2$ ,<sup>8c</sup> range from 2.084(7) to 2.106(11)  $\text{\AA}$ , the mean value being 2.093(4)  $\text{\AA}$ . In our compound, the Fe-H distance is 1.45(7)  $\text{\AA}$  and the Fe-Si distances are 2.210(3) and 2.207(3)  $\text{\AA}$ , which are shorter than the Fe-Si distances, 2.252(3)  $\text{\AA}$ , in  $\text{Cp}(\text{OC})\text{Fe}(\text{H})(\text{SiCl}_3)_2$ .<sup>8c</sup> The distance between the Si and H atoms in **1** is over 2.0  $\text{\AA}$ , as is the distance between the two hydrides. Thus, apparently there is no bonding interaction between the two H atoms or between the H and Si atoms. The oxidative addition of the Si-H bond to the Fe center is complete. The benzene molecule is flat with C atoms having a mean deviation of 0.0025  $\text{\AA}$  from the plane defined by C(1), C(2), C(3), and C(4).

$(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (**2**). Crystals of **2** conform to the space group  $P2_1/a$  with one independent molecule in the asymmetric unit. Figure 2 displays a PLUTO drawing of the molecule. The selected bond distances and angles are listed in Table 6. The bond distances between Fe and the arene C atoms range from 2.111(6) and 2.182(7)  $\text{\AA}$ , with the distance from Fe to the center of the ring equal to 1.609  $\text{\AA}$ . The Fe-Si distances are 2.222(2) and 2.226(2)  $\text{\AA}$ , the same as those in **1** within experimental error. The Fe-H distances lie between 1.50(6) and 1.72(9)  $\text{\AA}$ , and are less reliable due to the inherent

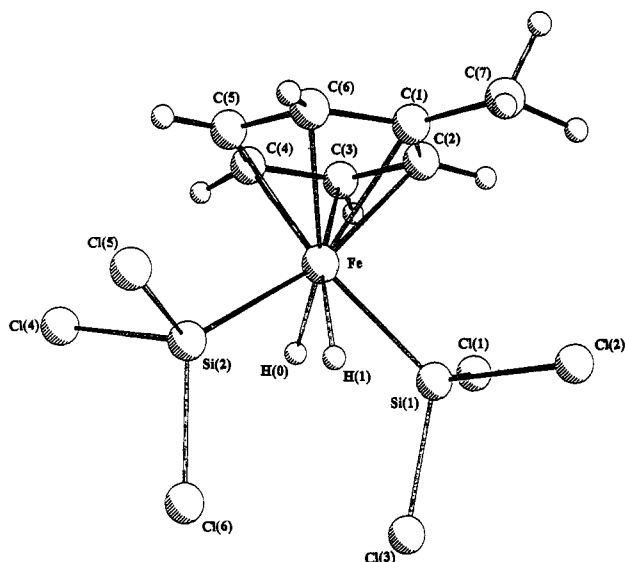


Figure 2. PLUTO drawing of  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .

Table 6. Selected Bond Distances (Å) and Angles (deg) for  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$

Distances			
Fe-Si(1)	2.222(2)	Fe-Si(2)	2.218(2)
Fe-C(1)	2.182(7)	Fe-C(2)	2.148(6)
Fe-C(3)	2.119(7)	Fe-C(4)	2.111(6)
Fe-C(5)	2.128(6)	Fe-C(6)	2.137(6)
Fe-H(0)	1.50(6)	Fe-H(1)	1.72(9)
Cl(1)-Si(1)	2.076(2)	Cl(2)-Si(1)	2.077(2)
Cl(3)-Si(1)	2.056(2)	Cl(4)-Si(2)	2.084(2)
Cl(5)-Si(2)	2.081(2)	Cl(6)-Si(2)	2.048(2)
C(1)-C(2)	1.410(9)	C(1)-C(6)	1.411(9)
C(1)-C(7)	1.498(9)	C(2)-C(3)	1.416(9)
C(3)-C(4)	1.392(9)	C(4)-C(5)	1.394(9)
C(5)-C(6)	1.419(9)		
Angles			
Si(1)-Fe-Si(2)	108.77(7)	Si(1)-Fe-C(1)	102.7(2)
Si(1)-Fe-C(2)	85.7(2)	Si(1)-Fe-C(3)	98.4(2)
Si(1)-Fe-C(4)	132.2(2)	Si(1)-Fe-C(5)	167.0(2)
Si(1)-Fe-C(6)	138.1(2)	Si(1)-Fe-H(0)	60(2)
Si(1)-Fe-H(1)	65(2)	Si(2)-Fe-C(1)	133.3(2)
Si(2)-Fe-C(2)	165.5(2)	Si(2)-Fe-C(3)	135.3(2)
Si(2)-Fe-C(4)	99.7(2)	Si(2)-Fe-C(5)	83.7(2)
Si(2)-Fe-C(6)	98.6(2)	Si(2)-Fe-H(0)	74(2)
Si(2)-Fe-H(1)	58(3)	C(1)-Fe-H(0)	153(2)
C(1)-Fe-H(1)	110(3)	C(2)-Fe-H(0)	115(2)
C(2)-Fe-H(1)	132(3)	C(3)-Fe-H(0)	90(2)
C(3)-Fe-H(1)	163(2)	C(4)-Fe-H(0)	93(2)
C(4)-Fe-H(1)	157(3)	C(5)-Fe-H(0)	122(2)
C(5)-Fe-H(1)	127(2)	C(6)-Fe-H(0)	161(2)
C(6)-Fe-H(1)	108(3)	H(0)-Fe-H(1)	84(4)

difficulties in X-ray diffraction. The plane defined by six arene C atoms has a mean deviation of 0.006 Å, while the methyl group, C(7), is bent up 0.04 Å from the plane.

$(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  (3). A PLUTO drawing of the molecule is shown in Figure 3. The selected bond distances and angles are listed in Table 7. The bond distances between Fe and the arene C atoms range from 2.116(7) to 2.164(6) Å. The orientation of the *p*-xylene is such that two methyl groups basically eclipse the two hydride ligands to avoid the steric repulsion from the bulky  $\text{SiCl}_3$  groups. The distance between Fe and the center of the arene is 1.608 Å. The plane defined by six arene carbons has a mean deviation of 0.010 Å with C(1), C(2), C(4), and C(5) slightly above the plane and C(3) and C(6) slightly below the plane. C(3) and C(6) atoms are bent about 1° from the plane; this distortion is very small compared with those of other  $(\eta^6\text{-arene})\text{MoL}_4$  complexes<sup>10</sup> (which have a deformation from the plane of 8–10°) and

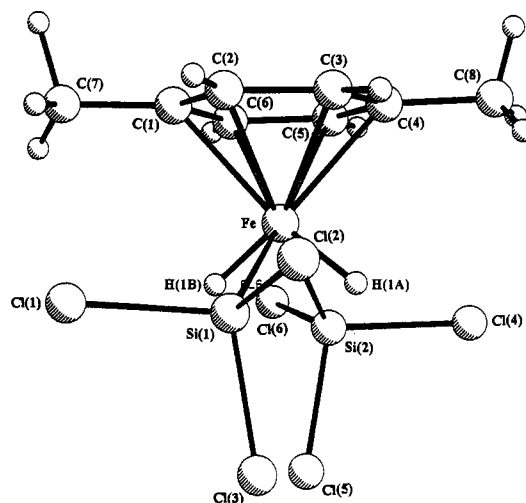


Figure 3. PLUTO drawing of  $(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ .

Table 7. Selected Bond Distances (Å) and Angles (deg) for  $(\eta^6\text{-p-xylene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$

Distances			
Fe-Si(1)	2.226(2)	Fe-Si(2)	2.222(2)
Fe-C(1)	2.164(6)	Fe-C(2)	2.119(6)
Fe-C(3)	2.124(6)	Fe-C(4)	2.158(6)
Fe-C(5)	2.150(7)	Fe-C(6)	2.116(7)
Fe-H(1A)	1.40(7)	Fe-H(1B)	1.24(8)
Cl(1)-Si(1)	2.061(2)	Cl(2)-Si(1)	2.078(2)
Cl(3)-Si(1)	2.051(2)	Cl(4)-Si(2)	2.075(2)
Cl(5)-Si(2)	2.050(2)	Cl(6)-Si(2)	2.066(2)
C(1)-C(2)	1.419(9)	C(1)-C(6)	1.399(9)
C(1)-C(7)	1.498(9)	C(2)-C(3)	1.416(9)
C(3)-C(4)	1.414(9)	C(4)-C(5)	1.401(9)
C(4)-C(8)	1.502(9)	C(5)-C(6)	1.420(9)
Angles			
Si(1)-Fe-Si(2)	107.84(7)	Si(1)-Fe-C(1)	104.7(2)
Si(1)-Fe-C(2)	85.8(2)	Si(1)-Fe-C(3)	96.3(2)
Si(1)-Fe-C(4)	129.7(2)	Si(1)-Fe-C(5)	165.5(2)
Si(1)-Fe-C(6)	141.0(2)	Si(1)-Fe-H(1A)	64(3)
Si(1)-Fe-H(1B)	65(4)	Si(2)-Fe-C(1)	128.9(2)
Si(2)-Fe-C(2)	165.2(2)	Si(2)-Fe-C(3)	140.5(2)
Si(2)-Fe-C(4)	104.0(2)	Si(2)-Fe-C(5)	85.3(2)
Si(2)-Fe-C(6)	96.3(2)	Si(2)-Fe-H(1A)	74(3)
Si(2)-Fe-H(1B)	71(4)	C(1)-Fe-H(1A)	157(3)
C(1)-Fe-H(1B)	89(3)	C(2)-Fe-H(1A)	119(3)
C(2)-Fe-H(1B)	112(3)	C(3)-Fe-H(1A)	90(3)
C(3)-Fe-H(1B)	149(4)	C(4)-Fe-H(1A)	90(3)
C(4)-Fe-H(1B)	164(4)	C(5)-Fe-H(1A)	116(3)
C(5)-Fe-H(1B)	127(4)	C(6)-Fe-H(1A)	155(3)
C(6)-Fe-H(1B)	96(3)	H(1A)-Fe-H(1B)	102(5)

predictions by extended Hückel calculations.<sup>11</sup> The two methyl groups, C(7) and C(8), are bent up 0.05 Å from the plane probably due to steric repulsions. The Fe-Si distances are 2.226(2) and 2.222(2) Å. The Fe-H distances lie between 1.40(7) and 1.24(8) Å.

<sup>1</sup>H NMR Spectra. The <sup>1</sup>H NMR spectrum of 1 in C<sub>6</sub>D<sub>6</sub>, together with two inserts, is shown in Figure 4. The free benzene signal is at 7.16 ppm with <sup>1</sup>J<sub>C-H</sub> = 159 Hz. The chemical shift for the bound benzene protons is 4.99 ppm with <sup>1</sup>J<sub>C-H</sub> = 182 Hz. The significant increase of the coupling constant between C and H from free benzene to the bound benzene may indicate a very strong interaction between the benzene and the iron. This coupling constant may serve as an

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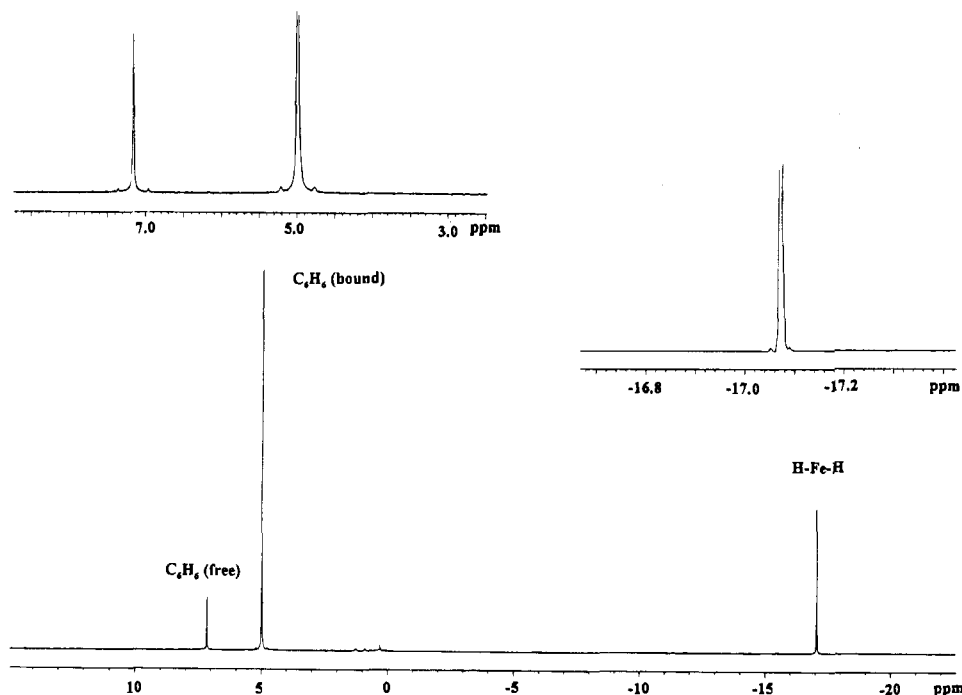


Figure 4.  $^1\text{H}$  NMR spectrum of  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  in  $\text{C}_6\text{D}_6$  at room temperature.

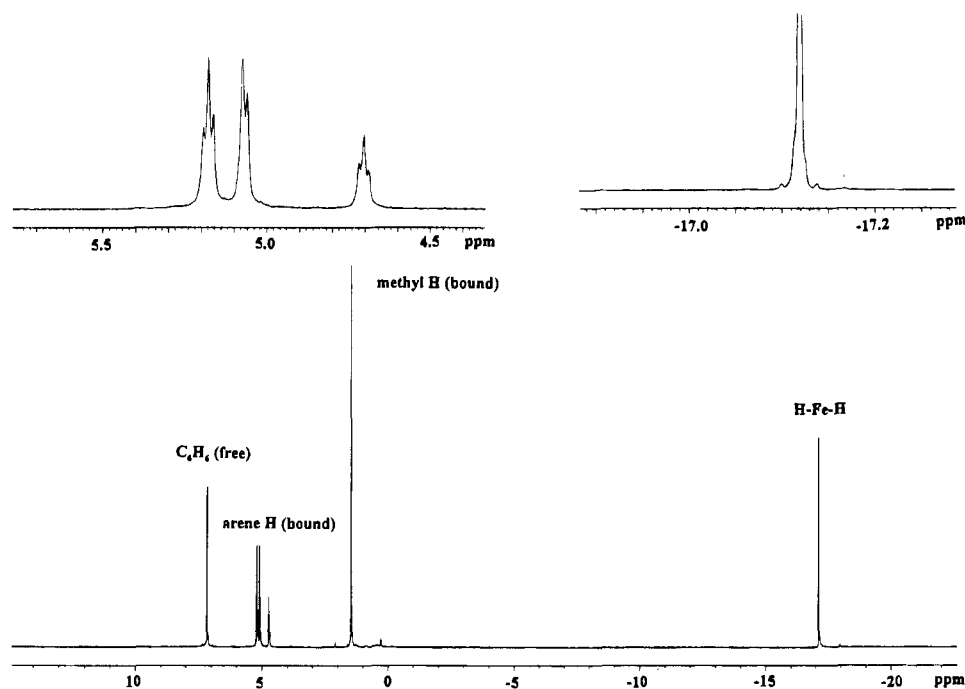


Figure 5.  $^1\text{H}$  NMR spectrum of  $(\eta^6\text{-toluene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  in  $\text{C}_6\text{D}_6$  at room temperature.

indicator of the bond distance and/or bond strength in  $\eta^6\text{-arene}$  complexes, and we are currently looking into this more systematically. The chemical shift for the hydride is  $-17.07$  ppm with  $^2J_{\text{Si-H}} = 15$  Hz. This weak coupling between  $^{29}\text{Si}$  and  $^1\text{H}$  is consistent with the relatively large distance between Si and H. Actually, the magnitude of the  $J_{\text{Si-H}}$  coupling constant is a reliable indicator for the bonding interaction between Si and H in transition metal complexes.<sup>4</sup> Considering the extremes, the upper limit is  $^1J_{\text{Si-H}}$ ; i.e., H is directly bonded to Si with a two-center, two-electron bond. The lower limit is  $^2J_{\text{Si-H}}$  in complexes with no Si-H interaction. The  $^1\text{H}$  NMR spectrum of  $\text{HSiCl}_3$  in  $\text{C}_6\text{D}_6$  was taken, and  $^1J_{\text{Si-H}}$  for  $\text{HSiCl}_3$  was found to be 370 Hz. Some examples with small or no Si-H interactions are  $^2J_{\text{Si-H}} = 20$  Hz in  $\text{Cp}(\text{OC})\text{Fe}(\text{H})(\text{SiCl}_3)_2$ ,<sup>12</sup> 7.9 Hz<sup>13</sup> in  $\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2$ , and 3.5 Hz in  $\text{Cp}_2\text{W}(\text{H})\text{Si}$

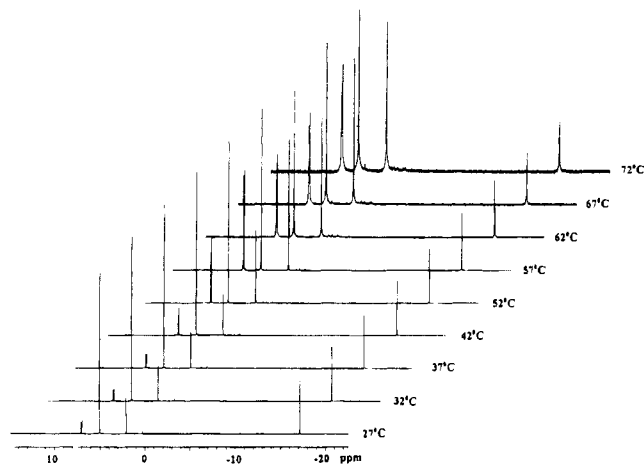
$(\text{SiMe}_3)_3$ .<sup>14</sup> In these complexes, any chemical bonding interaction between Si and H is considered to be negligible. However, where some bonding interaction is present (perhaps a three-centered  $\text{SiMH}$  moiety), the  $J_{\text{Si-H}}$  coupling constants are normally between 30 and 70 Hz.<sup>4a</sup>

The  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ , together with two inserts, is shown in Figure 5. There are three sets of signals for the phenyl protons: a triplet at 5.19, a doublet at 5.09, and a triplet at 4.71 ppm. Within the arene, the three-bond H-H coupling constant is 6 Hz. The peak for the methyl proton is

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**Figure 6.**  $^1\text{H}$  NMR spectra of  $(\eta^6\text{-benzene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$  in toluene- $d_8$  at elevated temperatures. The ratio of bound benzene to hydride did not change in the experiment. A small peak of  $\text{HSiCl}_3$  at 4.5 ppm was observed starting at 57 °C, and the peak increased as temperature increased.

a singlet at 1.46 ppm. The hydride peak is at  $-17.13$  ppm with  $^2J_{\text{Si-H}} = 15$  Hz.

**Variable-Temperature  $^1\text{H}$  NMR Study of Arene Exchange.** One of the driving forces for our studies of these Fe(IV) complexes is to ascertain the lability of the  $\pi$ -arene ligands and the possible catalytic activities of these new compounds. The  $\pi$ -arene ligands in Co(II) and Ni(II) analogs, i.e.  $(\pi\text{-arene})\text{Co}(\text{C}_6\text{F}_5)_2$ <sup>15</sup> and  $(\pi\text{-arene})\text{NiL}_2$  ( $\text{L} = \text{C}_6\text{F}_5$ ,  $\text{SiCl}_3$ ,  $\text{SiF}_3$ ),<sup>16</sup> are extremely labile. But no arene exchange was observed for complexes **1** and **2** when more electron-releasing arenes, including  $\text{C}_6\text{Me}_6$ , were present in solution at elevated temperatures. The  $^1\text{H}$  NMR spectra of **1** in toluene- $d_8$  at elevated temperatures are shown Figure 6. At high temperatures, the spectra became broader, as some decomposition occurred, and some gel was found at the interface of the solution within the NMR tube.

**Reactions with  $\text{D}_2$  and  $\text{HBF}_4$ .** It has been observed that some dihydrogen complexes undergo facile exchange of  $\text{H}_2$  with  $\text{D}_2$ .<sup>5</sup> When  $\text{D}_2$  gas was bubbled through a solution of **2** in toluene- $d_8$ , no exchange product was obtained, which further rules out the molecular form of  $\text{H}_2$  coordination to the Fe center. Complex **2** did not react with  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  to give a cation with  $\text{H}_2$  coordination, which has been an important way to make molecular  $\text{H}_2$  complexes.<sup>5</sup>

**Reactions with  $\text{PPh}_3$  and  $\text{CD}_3\text{CN}$ .** There was no reaction between  $\text{PPh}_3$  and **2** in  $\text{C}_6\text{D}_6$  at room temperature. Signals of free  $\text{HSiCl}_3$  were observed above 50 °C, indicating the substitution of  $\text{HSiCl}_3$  by  $\text{PPh}_3$ . An arrayed experiment with temperature was carried out with **2** in  $\text{CD}_3\text{CN}$ . No substitution was observed at room temperature. Free  $\text{HSiCl}_3$  was observed starting at 42 °C, and free toluene peaks were observed at 52 °C. These results show that  $\text{HSiCl}_3$  ligands are substituted first by  $\sigma$ -donor ligands in solution at elevated temperatures, and arene ligands can be substituted, too. When  $\sigma$ -donor ligands are not present in solution, heating leads to decomposition apparently by reductive elimination of  $\text{HSiCl}_3$ . Currently we are exploring more in-depth chemistry of the new family of Fe(IV) compounds.

## Conclusions

We have synthesized and characterized three novel  $\pi$ -arene Fe(IV) complexes,  $(\pi\text{-arene})\text{Fe}(\text{H})_2(\text{SiCl}_3)_2$ . From the structural and NMR data, we conclude that there is no chemical interaction between Si and H or between H and H in the complexes. The two-bond coupling between  $^{29}\text{Si}$  and  $^1\text{H}$ , 15 Hz, shows that the oxidative addition of the Si–H bond to the Fe center is complete. The significant increase of the coupling between  $^{13}\text{C}$  and  $^1\text{H}$  for the  $\eta^6$ -benzene ligand is interesting and may be a signature of a rather strongly bound, nonlabile arene.

The stability of these compounds apparently relies on the closed-shell 18-electron configuration and probably the synergistic push–pull of electron density by electron-rich arene and electron-demanding  $\text{SiCl}_3$  groups.

**Acknowledgment.** We are grateful for the financial support of the National Science Foundation. We thank Dr. Fusao Takusagawa for obtaining the crystal structures.

**Supporting Information Available:** Complete tables of bond distances, bond angles, anisotropic thermal parameters, and least-squares plane calculations for **1–3** (16 pages). Ordering information is given on any current masthead page.

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