

Reactions of $M[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NR}_2$ in THF, Et_2O and toluene ($M = \text{Li}$ and K ; $R = \text{Me}$, Et , ^iPr and Ph)

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Treatment of $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with $\text{ClSiMe}_2\text{NR}_2$ ($R = \text{Me}$, Et , ^iPr , Ph) in THF afforded $\text{Cp}^*(\text{CO})_2\text{-Fe}(\text{CH}_2)_4\text{OSiMe}_2\text{NR}_2$ accompanied with ring-opening and incorporation of a THF molecule between iron and silicon atoms. On the other hand, reactions between $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ and $\text{ClSiMe}_2\text{NR}_2$ in diethyl ether (for $R = \text{Me}$, Et), or in toluene in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA) (for $R = ^i\text{Pr}$, Ph) afforded the corresponding $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NR}_2$ ($R = \text{Me}$, Et , ^iPr , Ph), where the anionic complex was freshly prepared by treatment of $\text{Cp}^*(\text{CO})_2\text{FeH}$ with $n\text{-BuLi}$. In the case of the reaction of $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NPh}_2$, although the formation of the diphenylamino derivative $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NPh}_2$ was confirmed by NMR spectroscopy, purification of the product was unsuccessful. Subsequently, the exclusive formation of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NPh}_2$ was achieved by means of irradiation of $\text{Cp}^*(\text{CO})_2\text{FeMe}$ and $\text{HSiMe}_2\text{NPh}_2$ in toluene.

Introduction

It has been established that the terminal silyl group of a coordinatively unsaturated disilanyl complex can undergo a 1,2-migration to generate the corresponding silyl(silylene) complex.^{1,2} This transient silyl(silylene) complex can be stabilized by coordination of either an internal or external base to the silylene ligand. A typical example of this reaction is the irradiation of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{SiMe}_2\text{OMe}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), which causes the dissociation of CO to yield a methoxy-stabilized bis(silylene) complex, $\text{Cp}^*(\text{CO})\text{Fe}(\text{SiMe}_2 \cdots \text{O-Me} \cdots \text{SiMe}_2)$.³ Comparable base-stabilized bis(silylene) complexes have been synthesized for Ta, Cr, Mo, W, Mn, Fe, Ru, Os and Ir.⁴

Our recent interest has focused on the syntheses and reactivities of $\text{L}_m\text{MSiMe}_2\text{ER}_n$ compounds, in which the heteroatom (E) at the β -position possesses a lone pair of electrons.⁵ Our investigations on the synthesis of aminosilyl complexes, $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NR}_2$ ($R = \text{Me}$, Et , ^iPr and Ph), have led to the observation that treatment of $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NR}_2$ in THF resulted in the ring-opening and incorporation of a THF molecule between the iron and silicon atoms to produce $\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{OSiMe}_2\text{NR}_2$. Herein, we report the characterization and a possible formation mechanism of these products. Furthermore, we also describe our successful synthesis of the desired (aminosilyl)iron complexes through a similar salt-elimination reaction in diethyl ether (for $R = \text{Me}$, Et) or in toluene in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA) (for $R = ^i\text{Pr}$), or alternately, through photoreaction of $\text{Cp}^*(\text{CO})_2\text{FeMe}$ with $\text{HSiMe}_2\text{NPh}_2$.

Experimental

General procedures

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade diethyl ether, hexane, THF and toluene were distilled from sodium-benzophenone ketyl immediately before use. Benzene- d_6 was dried over a potassium mirror, and transferred into an NMR tube under vacuum. $\text{Cp}^*_2\text{Fe}_2(\text{CO})_4$,⁶ $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$,⁷ $\text{Cp}^*(\text{CO})_2\text{FeH}$,⁸ $\text{Cp}^*(\text{CO})_2\text{FeMe}$,⁶ $\text{ClSiMe}_2\text{NR}_2$ ($R = \text{Me}$, Et , ^iPr and Ph)¹⁰ and $\text{HSiMe}_2\text{NPh}_2$ ¹⁰ were prepared according to methods described in the literature. Other chemicals were purchased and used as received. All NMR data were recorded on a Bruker ARX-300 spectrometer. ²⁹Si NMR spectra were obtained by DEPT pulse

sequence. IR spectra were recorded on a Horiba FT-730 spectrometer.

Reaction of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ and LiNEt_2

To a stirred solution of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ (165 mg, 0.484 mmol) in THF (3 mL), cooled to -45°C , was added with stirring a solution of LiNEt_2 , which was freshly prepared by treatment of HNEt_2 (35 mg, 0.48 mmol) with $n\text{-BuLi}$ (1.4 M hexane solution, 0.35 mL, 0.49 mmol) in THF (5 mL). The reaction mixture was allowed to warm to room temperature, and stirred for 1 h at room temperature and for 2 h at 70°C . Volatiles were removed under reduced pressure. However, NMR spectroscopic data of the residue indicated that the reaction did not occur.

Reaction of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ and HNEt_2 in the presence of NEt_3

To a stirred solution of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ (100 mg, 0.294 mmol) and HNEt_2 (23 mg, 0.31 mmol) in THF (5 mL) was added NEt_3 (32 mg, 0.32 mmol) *via* a syringe. The mixture was stirred for 1 h at room temperature and for 2 h at 70°C . Volatiles were removed under reduced pressure. However, NMR spectroscopic data indicated that the reaction did not occur.

Reaction of $\text{K}[\text{Cp}^*(\text{CO})_2\text{Fe}]$ with $\text{ClSiMe}_2\text{NMe}_2$ in THF

Neat $\text{ClSiMe}_2\text{NMe}_2$ (710 mg, 5.16 mmol) was added *via* a syringe to a stirred solution of $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ in THF at -45°C , which was freshly prepared by reduction of $\text{Cp}^*_2\text{Fe}_2(\text{CO})_4$ (1.15 g, 2.33 mmol) with Na/K alloy [Na (73 mg, 3.2 mmol) and K (364 mg, 9.31 mmol)]. The reaction mixture was stirred for 30 min at -45°C , and was allowed to warm to room temperature with stirring for 1 h. Volatiles were removed under reduced pressure, and the residue was extracted with hexane (2×20 mL) to remove $\text{Cp}^*(\text{CO})_2\text{FeCl}$ and $[\text{Cp}^*(\text{CO})_2\text{Fe}]_2$. The combined extracts were filtered through a Celite pad, and the filtrate was concentrated *in vacuo* to dryness. The residue, which was shown by NMR spectroscopic data as a 5 : 1 mixture of $\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{OSiMe}_2\text{NMe}_2$ (**1-Me**) and $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NMe}_2$ (**2-Me**), was extracted with pentane (3×2 mL), and the combined extracts were filtered through a Celite pad. Concentration of the filtrate (to *ca.* 2 mL), and subsequent cooling to -75°C afforded orange crystals, which were washed with pentane and dried under vacuum to yield

1-Me (323 mg, 16%). Anal. Calc. for $C_{20}H_{35}FeNO_3Si$: C, 57.00; H, 8.37; N, 3.32. Found: C, 56.21; H, 8.25; N, 2.70%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.15 (s, 6H, SiMe₂), 1.15 (m, 2H, C _{α} H₂), 1.40 (s, 15H, Cp*), 1.86 (m, 4H, C _{β} H₂ and C _{γ} H₂), 2.50 (s, 6H, NMe₂), 3.70 (m, 2H, C _{δ} H₂). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): -3.0 (SiMe₂), 9.1 (C₅Me₅), 14.2 (C _{α}), 34.6 (C _{β}), 37.7 (NMe₂), 39.5 (C _{γ}), 62.1 (C _{δ}), 94.8 (C₅Me₅), 220.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): -2.1. IR (benzene- d_6 , cm⁻¹): 1981, 1923 (vs, ν_{CO}), 1090 (w), 642 (w), 598 (w), 571 (w). MS (EI, m/z): 421 (1, M⁺), 393 (3, M⁺ - CO), 365 (12, M⁺ - 2CO), 309 (74), 229 (100%, M⁺ - Cp* - 2CO - H).

Reaction of K[Cp*(CO)₂Fe] with ClSiMe₂NEt₂ in THF

Neat ClSiMe₂NEt₂ (1.36 g, 8.21 mmol) was added to a stirred solution of K[Cp*Fe(CO)₂] in THF (30 mL) at -45 °C, which was freshly prepared by reduction of Cp*₂Fe₂(CO)₄ (982 mg, 1.99 mmol) with Na/K alloy [Na (75 mg, 3.3 mmol) and K (409 mg, 10.5 mmol)]. The reaction mixture was similarly treated as described for K[Cp*Fe(CO)₂] with ClSiMe₂NMe₂. The NMR spectrum of the residue showed the selective formation of Cp*(CO)₂Fe(CH₂)₄OSiMe₂NEt₂ (**1-Et**). Molecular distillation of the residue at 90 °C at 4.0 × 10⁻⁴ Torr afforded **1-Et** as an orange oil (904 mg, 51%). Anal. Calc. for C₂₂H₃₉FeNO₃Si: C, 58.79; H, 8.75; N, 3.12. Found: C, 58.03; H, 8.65; N, 2.90%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.21 (s, 6H, SiMe₂), 1.01 (t, $^3J_{HH} = 7.0$ Hz, 6H, NCH₂CH₃), 1.20 (m, 2H, C _{α} H₂), 1.39 (s, 15H, Cp*), 1.94 (m, 4H, C _{β} H₂ and C _{γ} H₂), 2.86 (q, $^3J_{HH} = 7.0$ Hz, 4H, NCH₂CH₃), 3.77 (m, 2H, C _{δ} H₂). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): -2.2 (SiMe₂), 9.1 (C₅Me₅), 14.2 (C _{α}), 16.0 (NCH₂CH₃), 34.7 (C _{β}), 39.5 (C _{γ}), 39.7 (NCH₂CH₃), 62.1 (C _{δ}), 94.8 (C₅Me₅), 220.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): -3.6. IR (benzene- d_6 , cm⁻¹): 1981, 1923 (vs, ν_{CO}), 1092 (w), 1028 (w), 598 (w). MS (EI, m/z): 449 (4, M⁺), 421 (4, M⁺ - CO), 393 (12, M⁺ - 2CO), 337 (79), 257 (100%, M⁺ - Cp* - 2CO - H).

Reaction of K[Cp*(CO)₂Fe] with ClSiMe₂N^{*i*}Pr₂ in THF

Neat ClSiMe₂N^{*i*}Pr₂ (994 mg, 5.13 mmol) was added to a stirred solution of K[Cp*Fe(CO)₂] in THF (30 mL) at -45 °C, which was freshly prepared by reduction of Cp*₂Fe₂(CO)₄ (1.03 g, 2.08 mmol) with Na/K alloy [Na (67 mg, 2.9 mmol) and K (346 mg, 8.85 mmol)]. The reaction mixture was similarly treated as described for K[Cp*Fe(CO)₂] with ClSiMe₂NMe₂. According to the NMR spectrum of the resulting residue, Cp*(CO)₂Fe(CH₂)₄OSiMe₂N^{*i*}Pr₂ (**1-*i*Pr**) was formed selectively. Recrystallization of the residue from hexane at -75 °C afforded yellow crystals, which were subsequently washed with pentane (3 × 2 mL), and dried under vacuum to give pure **1-*i*Pr** (694 mg, 35%). Anal. Calc. for C₂₄H₄₃FeNO₃Si: C, 60.36; H, 9.08; N, 2.93. Found: C, 59.80; H, 9.01; N, 2.87%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.26 (s, 6H, SiMe₂), 1.12 (d, $^3J_{HH} = 6.7$ Hz, 12H, NCH(CH₃)₂), 1.19 (m, 2H, C _{α} H₂), 1.40 (s, 15H, Cp*), 1.92 (m, 4H, C _{β} H₂ and C _{γ} H₂), 3.25 (septet, $^3J_{HH} = 6.7$ Hz, 2H, NCH(CH₃)₂), 3.77 (m, 2H, C _{δ} H₂). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): 0.8 (SiMe₂), 9.1 (C₅Me₅), 14.2 (C _{α}), 24.6 (NCH(CH₃)₂), 34.7 (C _{β}), 39.6 (C _{γ}), 44.7 (NCH(CH₃)₂), 62.1 (C _{δ}), 94.8 (C₅Me₅), 220.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): -5.6. IR (KBr pellet, cm⁻¹): 1969, 1911 (vs, ν_{CO}), 1484 (m), 1263 (m), 966 (m), 930 (w), 756 (w). MS (EI, m/z): 477 (1, M⁺), 449 (2, M⁺ - CO), 421 (18, M⁺ - 2CO), 365 (79), 285 (79, M⁺ - Cp* - 2CO - H), 266 (100%).

Reaction of K[Cp*(CO)₂Fe] with ClSiMe₂NPh₂ in THF

A solution of ClSiMe₂NPh₂ (820 mg, 3.13 mmol) in THF (30 mL) was added to a stirred solution of K[Cp*Fe(CO)₂] in THF (30 mL) at -45 °C, which was freshly prepared by reduction of Cp*₂Fe₂(CO)₄ (843 mg, 1.71 mmol) with Na/K alloy [Na (61 mg, 2.7 mmol) and K (300 mg, 7.67 mmol)]. The

reaction mixture was treated similarly as described for K[Cp*Fe(CO)₂] with ClSiMe₂NMe₂. NMR analysis indicated that Cp*(CO)₂Fe(CH₂)₄OSiMe₂Ph₂ (**1-Ph**) was formed selectively. Recrystallization of the residue from diethyl ether-hexane at -30 °C afforded yellow crystals, which were subsequently washed with pentane (3 × 2 mL), and dried under vacuum to give pure **1-Ph** (456 mg, 27%). Anal. Calc. for C₃₀H₃₉FeNO₃Si: C, 66.05; H, 7.21; N, 2.57. Found: C, 65.89; H, 7.14; N, 2.43%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.21 (s, 6H, SiMe₂), 1.17 (m, 2H, C _{α} H₂), 1.38 (s, 15H, Cp*), 1.94 (m, 4H, C _{β} H₂ and C _{γ} H₂), 3.87 (m, 2H, C _{δ} H₂), 6.89 (t, $^3J_{HH} = 7.5$ Hz, 2H, *p*-Ph), 7.06-7.18 (m, 8H, *o*, *m*-Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): -1.1 (SiMe₂), 9.1 (C₅Me₅), 14.0 (C _{α}), 34.5 (C _{β}), 39.1 (C _{γ}), 62.6 (C _{δ}), 94.8 (C₅Me₅), 122.8 (*p*-Ph), 125.1 (*m*-Ph), 129.4 (*o*-Ph), 148.6 (*ipso*-Ph), 220.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): -3.3. IR (KBr pellet, cm⁻¹): 1979, 1917 (vs, ν_{CO}), 1250 (m), 1180 (m), 1084 (m), 984 (m), 879 (w). MS (EI, m/z): 545 (1, M⁺), 517 (2, M⁺ - CO), 489 (19, M⁺ - 2CO), 433 (21), 353 (100%, M⁺ - Cp* - 2CO - H).

Synthesis of Cp*(CO)₂FeSiMe₂NMe₂ (2-Me)

Neat ClSiMe₂NMe₂ (1.04 g, 7.55 mmol) was added to a stirred solution of Li[Cp*Fe(CO)₂] at -45 °C, which was freshly prepared by treatment of Cp*(CO)₂FeH (1.08 g, 4.35 mmol) with *n*-BuLi (1.44 M hexane solution, 3.1 mL, 4.5 mmol) in diethyl ether (70 mL).⁷ After the addition was completed, the reaction mixture was stirred at -45 °C for 30 min, and then was allowed to warm to room temperature and stirred overnight. Volatiles were removed under reduced pressure, and the residue was extracted with hexane (3 × 5 mL), followed by filtration through a Celite pad. Concentration of the filtrate (to ca. 7 mL), and subsequent cooling to -75 °C gave yellow crystals, which were washed with pentane and dried under vacuum to yield **2-Me** (943 mg, 62%). Anal. Calc. for C₁₆H₂₇FeNO₂Si: C, 55.01; H, 7.79; N, 4.01. Found: C, 54.71; H, 7.79; N, 3.71%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.64 (s, 6H, SiMe₂), 1.51 (s, 15H, Cp*), 2.62 (s, 6H, NMe₂). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): 6.7 (SiMe₂), 9.7 (C₅Me₅), 40.0 (NMe₂), 95.0 (C₅Me₅), 218.7 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): 52.6. IR (KBr pellet, cm⁻¹): 1971, 1911 (vs, ν_{CO}), 1375 (w), 1238 (w), 978 (m), 823 (w), 802 (m), 663 (m), 596 (m). MS (EI, m/z): 349 (10, M⁺), 102 (100%, SiMe₂NMe₂⁺).

Synthesis of Cp*(CO)₂FeSiMe₂NEt₂ (2-Et)

Neat ClSiMe₂NEt₂ (1.51 g, 9.11 mmol) was added to a stirred solution of Li[Cp*Fe(CO)₂] at -45 °C, which was freshly prepared by treatment of Cp*(CO)₂FeH (1.20 g, 4.84 mmol) with *n*-BuLi (1.50 M hexane solution, 3.3 mL, 5.0 mmol) in diethyl ether (70 mL).⁷ The reaction mixture was treated similarly as described in the synthesis of **2-Me**. Molecular distillation of the residue at 80 °C at 1.0 × 10⁻³ Torr yielded **2-Et** (851 mg, 46%) as an orange oil. Anal. Calc. for C₁₈H₃₁FeNO₂Si: C, 57.29; H, 8.28; N, 3.71. Found: C, 57.01; H, 8.25; N, 3.65%. 1H NMR (300 MHz, benzene- d_6 , δ): 0.69 (s, 6H, SiMe₂), 1.12 (t, $^3J_{HH} = 7.0$ Hz, 6H, NCH₂CH₃), 1.52 (s, 15H, Cp*), 3.03 (q, $^3J_{HH} = 7.0$ Hz, 4H, NCH₂CH₃). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene- d_6 , δ): 8.5 (SiMe₂), 9.7 (C₅Me₅), 15.9 (NCH₂CH₃), 41.9 (NCH₂CH₃), 94.8 (C₅Me₅), 219.0 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, benzene- d_6 , δ): 50.4. IR (benzene- d_6 , cm⁻¹): 1969, 1913 (vs, ν_{CO}), 1617 (m), 1452 (m), 1387 (m), 600 (m). MS (EI, m/z): 377 (16, M⁺), 130 (100%, SiMe₂NEt₂⁺).

Synthesis of Cp*(CO)₂FeSiMe₂N^{*i*}Pr₂ (2-*i*Pr)

To a stirred solution of Li[Cp*Fe(CO)₂], which was freshly prepared by treatment of Cp*(CO)₂FeH (725 mg, 2.92 mmol) with *n*-BuLi (1.60 M hexane solution, 1.9 mL, 3.0 mmol) in toluene (50 mL),⁷ was added TMEDA (354 mg, 3.05 mmol), followed by ClSiMe₂N^{*i*}Pr₂ (1.25 g, 6.45 mmol) at -45 °C. Upon

Table 1 Crystallographic data of **1-Ph** and **2-Ph**

Complex	1-Ph	2-Ph
Formula	C ₃₀ H ₃₉ FeNO ₃ Si	C ₂₆ H ₃₁ FeNO ₂ Si
Crystal size/mm	0.35 × 0.30 × 0.10	0.20 × 0.20 × 0.10
<i>M_w</i>	545.58	473.47
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.4866(8)	12.6585(5)
<i>b</i> /Å	9.4172(5)	12.8308(5)
<i>c</i> /Å	17.867(2)	15.2030(7)
<i>a</i> /°	96.519(5)	90
<i>β</i> /°	97.382(3)	101.665(2)
<i>γ</i> /°	93.474(1)	90
<i>V</i> /Å ³	1402.9(2)	2418.3(2)
<i>Z</i>	2	4
<i>D_s</i> /g cm ⁻³	1.291	1.300
<i>F</i> ₀₀₀	580.00	1000.00
<i>μ</i> (Mo-Kα)/cm ⁻¹	6.11	6.95
Transmission factor range	0.93–0.84	0.91–0.86
<i>T</i> /K	150	150
2θ _{max} /°	55	55
No. of reflns. collected	11070	21562
No. of unique reflns. (<i>R</i> _{int})	5470 (0.032)	5518 (0.043)
No. variables	325	280
<i>R^a</i> , <i>R_w^b</i>	0.071, 0.180	0.079, 0.166
<i>R</i> 1 ^c	0.046	0.053
No. of reflns. to calc <i>R</i> 1	4806	4599
GOF	1.63	1.29
<i>Δ</i> /e Å ⁻³	0.28, -0.61	0.49, -0.47
Max. shift/error in final cycle	0.001	0.0004

$$^a R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2. \quad ^b R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}. \quad ^c R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| \text{ for } I > 2.0\sigma(I).$$

addition, the reaction mixture was stirred at -45 °C for 30 min, then warmed to 80 °C, and stirred overnight. After removal of the volatiles under reduced pressure, the residue was extracted with pentane (2 × 10 mL), and the combined extracts were filtered through a Celite pad. Concentration of the filtrate (to ca. 5 mL), and cooling to -75 °C yielded pale brown crystals, which were subsequently washed with pentane and dried under vacuum to give **2-Pr** (469 mg, 40%). Anal. Calc. for C₂₀H₃₅FeNO₂Si: C, 59.25; H, 8.70; N, 3.45. Found: C, 59.66; H, 8.82; N, 3.36. ¹H NMR (300 MHz, benzene-*d*₆, δ): 0.80 (s, 6H, SiMe₂), 1.27 (d, ³*J*_{HH} = 6.8 Hz, 12H, NCH(CH₃)₂), 1.54 (s, 15H, Cp*), 3.56 (septet, ³*J*_{HH} = 6.8 Hz, 2H, NCH(CH₃)₂). ¹³C{¹H} NMR (75.5 MHz, benzene-*d*₆, δ): 9.8 (C₅Me₅), 11.9 (SiMe₂), 25.3 (NCH(CH₃)₂), 47.6 (NCH(CH₃)₂), 94.7 (C₅Me₅), 219.5 (CO). ²⁹Si{¹H} NMR (59.6 MHz, benzene-*d*₆, δ): 48.6. IR (KBr, cm⁻¹): 1970, 1928 (vs, ν_{CO}), 1359 (w), 1236 (w), 1166 (m), 954 (m), 863 (w), 737 (w), 655 (m), 595 (m). MS (EI, *m/z*): 405 (6, M⁺), 158 (100, SiMe₂N⁺Pr₂⁺).

Synthesis of Cp*(CO)₂FeSiMe₂NPh₂ (**2-Ph**)

(A) Reaction of Li[Cp*(CO)₂Fe] with ClSiMe₂NPh₂ in diethyl ether. To a stirred solution of Li[Cp*Fe(CO)₂], which was freshly prepared by treatment of Cp*(CO)₂FeH (670 mg, 2.70 mmol) with *n*-BuLi (1.36 M hexane solution, 2.0 mL, 2.7 mmol) in toluene (30 mL),⁷ was added TMEDA (385 mg, 3.31 mmol), followed by a solution of ClSiMe₂NPh₂ (620 mg, 2.37 mmol) in toluene (30 mL) at -45 °C. The reaction mixture was treated similarly as described for the synthesis of **2-Pr**. Although the NMR spectrum of the residue clearly exhibited the formation of **2-Ph**, the separation of **2-Ph** from impurities was not successful.

(B) Photolysis of Cp*(CO)₂FeMe in the presence of HSiMe₂NPh₂. A Pyrex NMR tube (10 mm o.d.) was charged with Cp*(CO)₂FeMe (100 mg, 0.382 mmol) and HSiMe₂NPh₂ (90 mg, 0.40 mmol), and was connected to a vacuum line. After introducing toluene (10 mL) into this tube under high vacuum using the trap-to-trap transfer technique, the tube was flame-

sealed. Following the irradiation of the sample for 20 min, the tube was opened in a glove-box, and the solution was transferred into a Schlenk tube. Volatiles were removed under reduced pressure, and the residue was dissolved in hexane (3 mL), and cooled to -75 °C. After removing the supernatant liquid using a syringe, the resulting yellow precipitate was washed with pentane (3 × 1 mL), and dried under vacuum to yield **2-Ph** (87 mg, 48%). Anal. Calc. for C₂₆H₃₁FeNO₂Si: C, 65.96; H, 6.60; N, 2.96. Found: C, 65.81; H, 6.82; N, 2.94%. ¹H NMR (300 MHz, benzene-*d*₆, δ): 0.69 (s, 6H, SiMe₂), 1.39 (s, 15H, Cp*), 6.91 (t, ³*J*_{HH} = 7.5 Hz, 2H, *p*-Ph), 7.18 (t, ³*J*_{HH} = 7.5 Hz, 4H, *m*-Ph), 7.29 (d, ³*J*_{HH} = 7.5 Hz, 4H, *o*-Ph). ¹³C{¹H} NMR (75.5 MHz, benzene-*d*₆, δ): 9.4 (C₅Me₅), 10.0 (SiMe₂), 95.3 (C₅Me₅), 122.5 (*p*-Ph), 127.5 (*m*-Ph), 129.0 (*o*-Ph), 151.7 (*ipso*-Ph), 218.8 (CO). ²⁹Si{¹H} NMR (59.6 MHz, benzene-*d*₆, δ): 47.3. IR (KBr, cm⁻¹): 1973, 1917 (vs, ν_{CO}), 1201 (m), 949 (m), 874 (m), 798 (m), 756 (m), 602 (m), 530 (m). MS (EI, *m/z*): 473 (10, M⁺), 226 (100%, SiMe₂NPh₂⁺).

X-Ray crystal structure determination of **1-Ph** and **2-Ph**

A single crystal of **1-Ph** or **2-Ph** was mounted on a glass fiber. Intensity data were collected on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-Kα radiation at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 0.70 min for **1-Ph** and 1.00 min for **2-Ph** per degree. Readout was performed in the 0.100-mm pixel mode. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied. Crystallographic data of **1-Ph** and **2-Ph** are listed in Table 1. Structures were solved by heavy-atom Patterson methods, and expanded using Fourier transform techniques. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included but not refined. Data reduction and refinement were performed using *teXsan* software packages. Selected interatomic distances and bond angles for **1-Ph** and **2-Ph** are listed in Tables 2 and 3, respectively.

CCDC reference numbers 200912 and 200913.

Table 2 Selected bond distances (Å) and angles (°) for **1-Ph**

Fe–C1	2.068(3)	Fe–C19	1.757(3)
Fe–C20	1.747(3)	Si–O1	1.655(2)
Si–N	1.755(2)	Si–C5	1.851(3)
Si–C6	1.845(3)	O1–C4	1.444(3)
O2–C19	1.149(4)	O3–C20	1.159(4)
N–C7	1.439(3)	N–C13	1.414(4)
C1–C2	1.528(4)	C2–C3	1.523(4)
C3–C4	1.517(4)		
C1–Fe–C19	89.3(1)	C1–Fe–C20	90.4(1)
O1–Si–N	109.5(1)	O1–Si–C5	109.9(1)
O1–Si–C6	105.7(1)	N–Si–C5	107.4(1)
N–Si–C6	113.2(1)	C5–Si–C6	111.1(1)
Si–O1–C4	118.7(2)	Si–N–C7	119.4(2)
Si–N–C13	124.4(2)	C7–N–C13	115.7(2)

Table 3 Selected bond distances and angles for **2-Ph**

Fe–Si	2.3355(7)	Fe–C15	1.741(3)
Fe–C16	1.741(3)	Si–N	1.787(2)
Si–C1	1.886(3)	Si–C2	1.884(3)
O1–C15	1.159(3)	O2–C16	1.151(4)
N–C3	1.418(3)	N–C9	1.436(3)
Si–Fe–C15	89.89(9)	Si–Fe–C16	81.83(9)
C15–Fe–C16	94.1(1)	Fe–Si–N	118.07(8)
Fe–Si–C1	112.52(10)	Fe–Si–C2	110.89(9)
N–Si–C1	106.7(1)	N–Si–C2	104.6(1)
C1–Si–C2	102.7(1)	Si–N–C3	124.6(2)
Si–N–C9	119.9(2)	C3–N–C9	113.2(2)

See <http://www.rsc.org/suppdata/dt/b3/b300261f/> for crystallographic data in CIF or other electronic format.

Results and discussion

Reaction of Cp*(CO)₂FeSiMe₂Cl with LiNEt₂

It has been reported that Cp(CO)₂FeSiMe₂NMe₂ can be synthesized through the reaction of Cp(CO)₂FeSiMe₂Cl with LiNMe₂ *via* salt elimination.¹¹ By applying this method, we attempted the synthesis of a related complex, Cp*(CO)₂FeSiMe₂NEt₂, in which the bulky and electron-donating Cp* ligand was introduced to stabilize the complex and its derivatives. However, even after heating the reaction mixture at 70 °C, the desired product was not formed, and the starting complex was recovered. This observation can be explained, not only by the steric effects of the Cp* ligand, but also by the electronic effects of the electron-donating Cp* ligand that enhances the back-donation from iron to silicon to counter the electron deficiency at the silyl silicon atom.

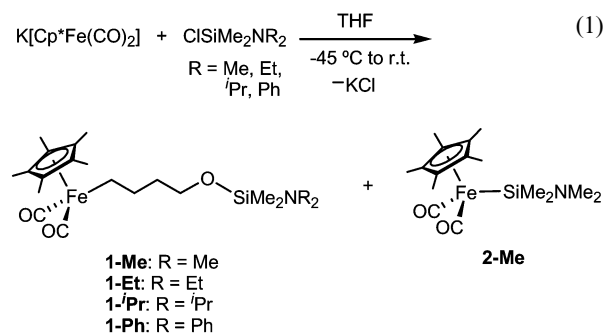
Reaction of Cp*(CO)₂FeSiMe₂Cl with HNEt₂

Höfler *et al.* have reported that the reaction of Cp(CO)₂FeSiCl₃ with HNRR' produced a complex mixture of FpSiCl_{3–n}(NRR')_n (*n* = 1–3), where *n* depended on the basicity and steric requirements of the amine.¹² However, the reaction of Cp*(CO)₂FeSiMe₂Cl with HNEt₂ in the presence of NEt₃ did not proceed, even at 70 °C, and the starting silyl complex was recovered. This observation can be similarly explained, as mentioned above, by the steric and electronic effects of the Cp* ligand.

Reactions of K[Cp*Fe(CO)₂] with ClSiMe₂NR₂ (R = Me, Et, ⁱPr and Ph) in THF

Although silyl–iron complexes of the Cp*(CO)₂FeSiR₃ type have been synthesized through the reactions of M[Cp*Fe(CO)₂] (M = K, Na) with chlorosilanes in moderate yields,^{3a,13} reactions of K[Cp*Fe(CO)₂] with ClSiMe₂NR₂ (R = Me, Et, ⁱPr, and Ph) did not afford pure aminosilyl complexes Cp*(CO)₂FeSiMe₂

NR₂ (eqn. (1)). Treatment of K[Cp*Fe(CO)₂] with ClSiMe₂NMe₂ in THF resulted in a mixture of Cp*(CO)₂Fe(CH₂)₄OSiMe₂NMe₂ (**1-Me**), Cp*(CO)₂FeSiMe₂NMe₂ (**2-Me**), Cp*(CO)₂FeCl, and [Cp*(CO)₂Fe]₂. To remove Cp*(CO)₂FeCl and [Cp*(CO)₂Fe]₂, the desired products were extracted from the reaction mixture using hexane, followed by removal of the solvent *in vacuo*. ¹H NMR spectrum of the resulting residue indicated a mixture of **1-Me** and **2-Me** with a ratio of 5 : 1. Recrystallization of the residue from pentane at –75 °C yielded **1-Me** as orange crystals in 16% yield. In the reaction between K[Cp*Fe(CO)₂] and ClSiMe₂NR₂ (R = Et, ⁱPr and Ph), the formation of Cp*(CO)₂FeSiMe₂NR₂ (**2**) was not observed. Isolated yields of **1-Et**, **1-ⁱPr**, and **1-Ph** were 51, 35 and 27%, respectively (eqn. (1)).



Elemental analysis and mass spectral data were consistent with the molecular formula of **1**.

As shown in the ¹H NMR spectrum of **1-Ph** (Fig. 1), the four methylene protons appear as three multiplets at 1.17 (2H), 1.94 (4H) and 3.87 (2H) ppm. The most upfield signal was assigned to the methylene fragment (C_aH₂) that is directly connected to the iron center, whereas the most downfield signal was assigned to the methylene fragment (C_δH₂) that is connected to the OSiMe₂NPh₂ moiety. The signal at 1.94 ppm consists of two overlapping methylene signals (C_βH₂ and C_γH₂). The peak assignments were confirmed by ¹H–¹H COSY NMR experiments. On the base of ¹³C–¹H COSY experiments, the four signals of the ¹³C{¹H} NMR spectrum of **1-Ph** were assigned to the methylene carbons at 14.0 (C_a), 34.5 (C_β), 39.1 (C_γ) and 62.6 ppm (C_δ). The ²⁹Si{¹H} NMR spectrum of **1-Ph** shows a signal at –3.3 ppm, which is consistent with the structure of **1-Ph** without iron–silicon bonds. The spectroscopic features of **1-Me**, **1-Et** and **1-ⁱPr** are comparable to those of **1-Ph**.

Structure of **1-Ph**

Single crystals of **1-Ph** that were suitable for the X-ray crystal structure analysis were obtained by cooling the diethyl ether–hexane solution to –30 °C. Selected bond distances and angles are listed in Table 2. As shown in the ORTEP drawing of **1-Ph** (Fig. 2), the iron fragment is bonded to the carbon end, whereas the aminosilyl group is bonded to the oxygen end of the ring-opened THF molecule. Although the interatomic distances of Fe–C1 (2.068(3) Å) and Si–O1 (1.655(2) Å) are within normal ranges for iron–carbon (2.07–2.10 Å)¹⁴ and silicon–oxygen (1.60–1.67 Å) single bonds,¹⁵ the distances are significantly greater than those for iron–oxygen (1.81–1.83 Å)¹⁴ and silicon–carbon (1.87–1.91 Å) single bonds.¹⁵ This result clearly rules out the formation of **1-Ph'**, in which the iron and silicon atoms are bonded to the oxygen and the carbon ends, respectively (Fig. 3). The sum of 359.5° for the bond angles around the nitrogen indicates that the atom is nearly planar. The planarity of the tricoordinate nitrogen atom with the bonded silicon atom is attributed to the π-interactions between the nitrogen 2p orbital and the silicon 3d or σ* orbitals.¹⁵

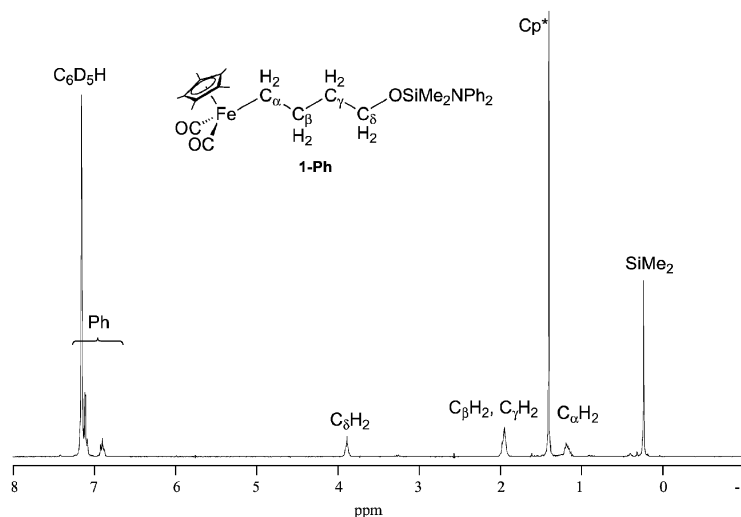


Fig. 1 ^1H NMR spectrum of **1-Ph**.

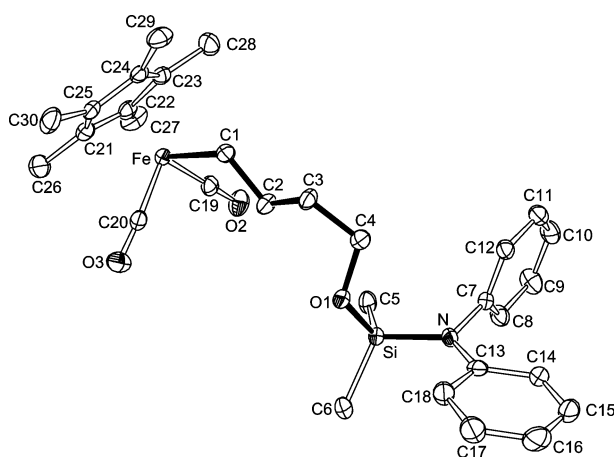
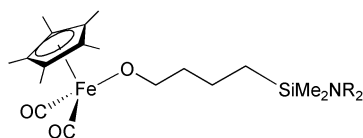


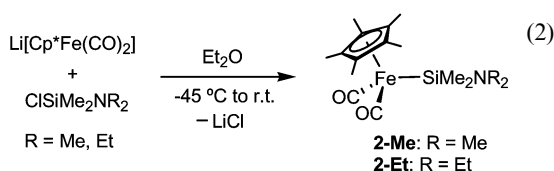
Fig. 2 ORTEP drawing of **1-Ph**.



1-Ph'
Fig. 3

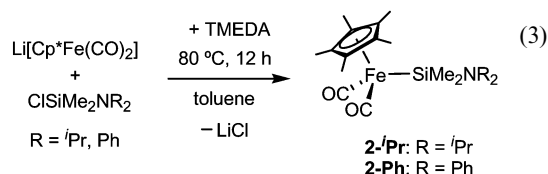
Reactions of $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NR}_2$ in diethyl ether ($\text{R} = \text{Me}, \text{Et}$) or in toluene ($\text{R} = \text{iPr}, \text{Ph}$) in the presence of TMEDA

To avoid the insertion of a THF molecule between the iron–silicon bond, diethyl ether or toluene was used as the solvent. Treatment of $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$, which was freshly prepared by the reaction of $\text{Cp}^*(\text{CO})_2\text{FeH}$ with $n\text{-BuLi}$ in diethyl ether,⁷ with $\text{ClSiMe}_2\text{NR}_2$ ($\text{R} = \text{Me}, \text{Et}$) gave $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NR}_2$ [**2-Me** ($\text{R} = \text{Me}$, 62%), **2-Et** ($\text{R} = \text{Et}$, 46%), respectively] (eqn. (2)).

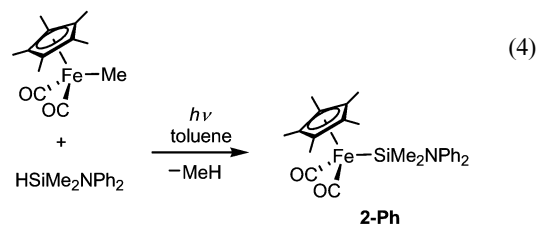


Since the reactions of $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NR}_2$ ($\text{R} = \text{iPr}, \text{Ph}$) required stronger conditions for the completion of the reaction, toluene was used as a solvent to increase the

temperature to 80°C , and TMEDA (1 equiv.) was added to activate $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ (eqn. (3)).



Recrystallization of the residue from pentane afforded **2-iPr** as pale brown crystals in 40% isolated yield. However, isolation of **2-Ph** from the reaction mixture was not achieved due to inseparable by-products. Subsequently, complex **2-Ph** was successfully synthesized and isolated in 48% yield by irradiation of $\text{Cp}^*(\text{CO})_2\text{FeMe}$ and $\text{HSiMe}_2\text{NPh}_2$ (eqn. (4)).



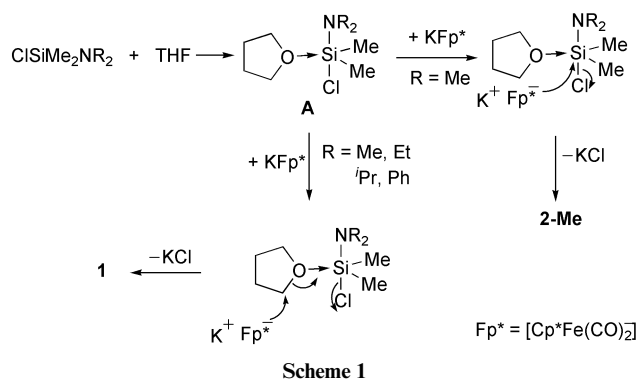
It is reasonable to consider that this reaction proceeded through successive CO ligand dissociation, Si–H oxidative addition, methane elimination and CO recombination. Elemental analysis and mass spectral data of **2** supported the formation of aminosilyliron complexes. The ^{29}Si NMR signals of **2** appeared in the region of 47–53 ppm, indicating the existence of iron–silicon bonds.

Formation mechanism of **1**

It may be considered that the formation mechanism of **1** involves the initial formation of **2**, followed by a nucleophilic attack on the silyl silicon atom by the THF oxygen atom. Brinkman and Gladysz have reported on the reaction of silylmanganese complex $(\text{OC})_3\text{MnSiMe}_3$ with THF in the presence of CO to afford acyl complex $(\text{OC})_3\text{MnCO}(\text{CH}_2)_4\text{OSiMe}_3$.¹⁶ The authors explained the reaction as a nucleophilic attack of THF oxygen on the silicon to generate $(\text{CO})_3\text{Mn}(\text{CH}_2)_4\text{OSiMe}_3$, which causes insertion of CO to give the acyl complex. It has been reported that the reaction of $\text{MgCl}[\text{Rh}(\text{dppe})_2]$ with Me_3SiCl in THF afforded $\text{HRh}(\text{dppe})_2$ and $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{OSiMe}_3$,¹⁷ and to account for this reaction, Bogdanovic *et al.* proposed

a sequence of steps involving the transient formation of $\text{Me}_3\text{SiRh}(\text{dppe})_2$, nucleophilic attack of THF against silicon and subsequent β -hydrogen elimination. However, this type of mechanism is not applicable to our reaction, because aminosilyl complexes **2** are stable in THF.

In an alternative mechanism, as illustrated in Scheme 1, the silicon center in $\text{ClSiMe}_2\text{NR}_2$ interacts with THF to generate pentacoordinate silicon species **A**.¹⁸ Subsequently, a nucleophilic attack by the $[\text{Cp}^*(\text{CO})_2\text{Fe}]^-$ ion on the α -carbon of THF results in the ring-opening of THF to give **1**. In the case of sterically less-hindered $\text{ClSiMe}_2\text{NMe}_2$, the nucleophilic attack on the silicon atom competes with the above reaction to afford **2-Me** as a minor product. Nicholson and Simpson proposed a similar reaction mechanism for the ring-opening of THF induced by a transition-metal anion.¹⁹ Accordingly, treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with $\text{Me}_n\text{SiCl}_{4-n}$ ($n = 1, 2, 3$) in THF afforded $(\text{CO})_4\text{Co}(\text{CH}_2)_4\text{OSiMe}_n\text{Cl}_{3-n}$. At the initial stage of this reaction, chlorosilanes are likely to exist as adducts with THF molecules. A subsequent nucleophilic attack by the cobalt anion on the α -carbon of the THF ligand results in the formation of $(\text{CO})_4\text{Co}(\text{CH}_2)_4\text{OSiMe}_n\text{Cl}_{3-n}$. A similar mechanism has also been postulated by Seebald *et al.* for the reaction of $\text{Li}[\text{Cp}_2\text{MoSnPh}_3]$ with ClSiMe_3 in THF to give $\text{Cp}_2\text{Mo}(\text{SnPh}_3)(\text{CH}_2)_4\text{OSiMe}_3$.²⁰



In contrast with our reactions in eqn. (1), $\text{Cp}^*(\text{CO})_2\text{FeSiR}_3$ ($\text{R} = \text{alkyl, aryl}$) were formed in moderate yields in the reactions of $\text{M}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ ($\text{M} = \text{Na, K}$) with R_3SiCl ($\text{R} = \text{alkyl, aryl}$) in THF.^{3a,13} The difference of the products was attributable to the electronegative nitrogen atom on the silicon in $\text{ClSiMe}_2\text{NR}_2$, which can strengthen the interactions between silicon and THF.¹⁸

In comparison with THF, diethyl ether has a smaller donor number (diethyl ether = 19.2, THF = 20.0) and dipole moment (diethyl ether = 1.15, THF = 1.75 D), with a more sterically hindered oxygen atom. These factors hinder the formation of pentacoordinate species $(\text{Et}_2\text{O})\text{SiClMe}_2(\text{NR}_2)$, as compared to the THF analog, and as a result, the nucleophilic attack of $[\text{Cp}^*\text{Fe}(\text{CO})_2]^-$ in diethyl ether can be considered to exclusively occur on the silicon of tetracoordinate $\text{ClSiMe}_2(\text{NR}_2)$ to afford **2**.

Structure of 2-Ph

As shown in the ORTEP drawing in Fig. 4, **2-Ph** adopts a normal piano-stool geometry; the iron center has a pentamethylcyclopentadienyl ligand in η^5 -fashion, two terminal CO ligands and an aminosilyl ligand. Selected bond distances and angles of **2-Ph** are listed in Table 3. The Fe–Si distance (2.3355(7) Å) is shorter than typical Fe–Si bond lengths in $\text{L}_n\text{Fe–SiR}_3$ ($\text{R} = \text{alkyl, aryl}$), but is comparable to those of silyl–iron complexes with electron-withdrawing groups on the silicon.²¹ The Si–N bond (1.787(2) Å) is significantly longer than the normal Si–N bonds in aminosilanes (1.70–1.76 Å).¹⁵ The elongation is attributable to the back-donation of the π -orbital from the HOMO of the $\text{Cp}^*\text{Fe}(\text{CO})_2$ fragment to the σ^* -orbital of the Si–N

bond.²² As illustrated in Fig. 5, this hypothesis is further supported by the conformation of **2-Ph** around the Fe–Si bond, which allows the nearly maximum overlap between the orbitals.²³

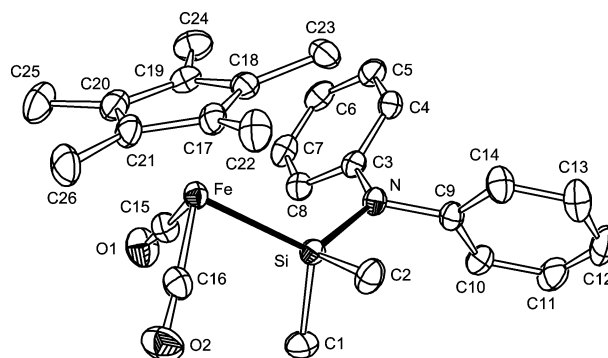


Fig. 4 ORTEP drawing of **2-Ph**.

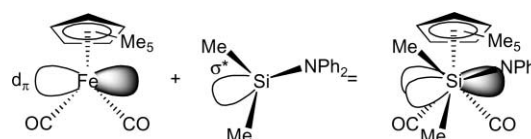


Fig. 5

Conclusion

Reactions of $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with several aminosilanes $\text{ClSiMe}_2\text{NR}_2$ ($\text{R} = \text{Me, Et, }^i\text{Pr, and Ph}$) in THF afforded THF-incorporated products $\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{OSiMe}_2\text{NR}_2$ (**1**) exclusively (for $\text{R} = \text{Et, }^i\text{Pr, and Ph}$), or as a main product (for $\text{R} = \text{Me}$). In contrast, reactions of $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ with $\text{ClSiMe}_2\text{NR}_2$ ($\text{R} = \text{Me, Et}$) in diethyl ether, or with $\text{ClSiMe}_2\text{NR}_2$ ($\text{R} = ^i\text{Pr, Ph}$) in toluene in the presence of TMEDA at 80 °C, afforded aminosilyl complexes $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NR}_2$ (**2**). Since **2** is stable in THF, it cannot possibly function as an intermediate for the formation of **1**. A plausible intermediate is pentacoordinate silicon species $(\text{THF})\text{SiMe}_2\text{Cl}(\text{NR}_2)$, and a nucleophilic attack of $\text{K}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ on the α -carbon of the THF molecule to afford **1**. In diethyl ether and in toluene–TMEDA, $\text{Li}[\text{Cp}^*\text{Fe}(\text{CO})_2]$ attacked the tetracoordinate silicon of $\text{ClSiMe}_2\text{NR}_2$ to yield **2**. For the preparation of sterically hindered $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{NPh}_2$ (**2-Ph**), irradiation of $\text{Cp}^*(\text{CO})_2\text{FeMe}$ and HSiMe_2Ph was found to be more effective than the above-mentioned salt elimination method.

Acknowledgements

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