Nonphotochemical Synthesis of a Base-free Silyl(silylene)iron Complex and Its Reaction with CO: Another Direct Evidence for Reversible 1,2- and 1,3-Group Migrations

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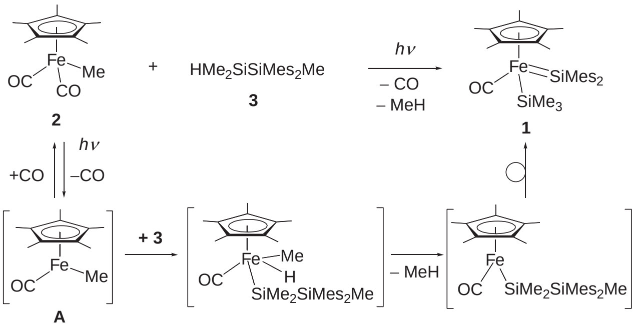
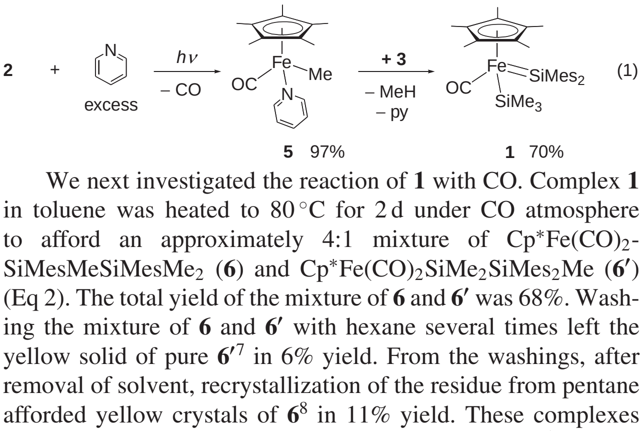
A base-free silyl(silylene)iron complex **1**, which had been originally synthesized by a photochemical method, was prepared in higher yield by a newly developed thermal method. Reaction of this silyl(silylene)iron complex **1** with CO at 80 °C cleanly produced a mixture of two isomeric disilanyliron complexes **6** and **6′** via 1,3-group migrations followed by 1,2-silyl migration. Oppositely, each of disilanyl complexes **6** and **6′** reproduced the silyl(silylene)iron complex **1** with a release of CO almost quantitatively at room temperature by irradiation with a fluorescent lamp.

During the past two decades, the chemistry of transition-metal silylene complexes have been extensively studied and the important role of these species in transition-metal-catalyzed reactions were often suggested.[1,2] Especially, silyl(silylene) complexes have been postulated to be key intermediates for the reactions involving group-migrations such as redistribution and oligomerization of hydrosilanes on the basis of several indirect evidences.[3] We have recently succeeded in the synthesis of the first base-free silyl(silylene)iron complex Cp*Fe(CO)(=$SiMes_2$)$SiMe_3$ (**1**) and provided the most straightforward evidence for facile 1,2- and 1,3-group-migration reactions in the silyl(silylene) complex systems by investigating the reaction of the isolated **1** with ^{t}BuNC.[4] Thus, irradiation of Cp*$Fe(CO)_2Me$ (**2**) in the presence of $HSiMe_2SiMes_2Me$ (**3**, Mes = mesityl (2,4,6-trimethyphenyl)) produced **1** in 60% NMR yield, which was isolated in 40% yield. Complex **1** reacted with ^{t}BuNC at 80 °C to yield Cp*Fe(CO)(CN^{t}Bu)SiMesMeSiMesMe$_2$ (**4**) via 1,2- and 1,3-group migrations. Here, we present the higher-yield nonphotochemical synthesis of **1** and another clear evidence for 1,2- and 1,3-group migrations on **1** using CO as a reactant.

In the photochemical synthesis of **1** shown in Scheme 1, the following problems have disturbed the improvement of the yield: (1) **1** decomposes slowly under irradiation, and this decomposition is enhanced in the presence of CO probably through its high reactivity toward coordinated or free silylene,[3b] and (2) prolonged irradiation accumulates the decomposition products such as Cp*$_2Fe_2(CO)_4$ etc., which make the purification of **1** more difficult. To overcome these problems, we attempted to replace one of CO ligands in **2** with pyridine, a labile ligand for an electron-rich metal center, which is expected to dissociate easily to generate **A** under mild conditions. Thus, Cp*Fe(CO)(py)Me (**5**) was successfully prepared in 97% yield by irradiation of **2** in toluene in the presence of excess pyridine. After removal of volatiles from the toluene solution, **5** was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectra.[6] To a toluene solution of **5** was added a hexane solution of **3**, and the mixture was stirred at room temperature overnight to produce **1** in 70% isolated yield based on **5** (Eq 1). This nonphotochemical synthetic method is superior to the previous one because photochemical decomposition of **1** is avoided and a large-scale synthesis of **1** from **5** is easier.

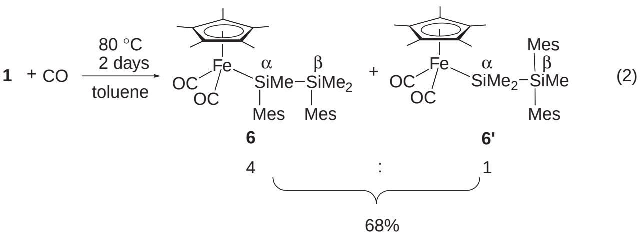


Scheme 1.



5 97% **1** 70%

We next investigated the reaction of **1** with CO. Complex **1** in toluene was heated to 80 °C for 2 d under CO atmosphere to afford an approximately 4:1 mixture of Cp*$Fe(CO)_2$-SiMesMeSiMesMe$_2$ (**6**) and Cp*$Fe(CO)_2SiMe_2SiMes_2Me$ (**6′**) (Eq 2). The total yield of the mixture of **6** and **6′** was 68%. Washing the mixture of **6** and **6′** with hexane several times left the yellow solid of pure **6′**[7] in 6% yield. From the washings, after removal of solvent, recrystallization of the residue from pentane afforded yellow crystals of **6**[8] in 11% yield. These complexes were fully characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, ^{1}H–^{29}Si COLOC NMR, IR, and Mass spectra.[7,8]



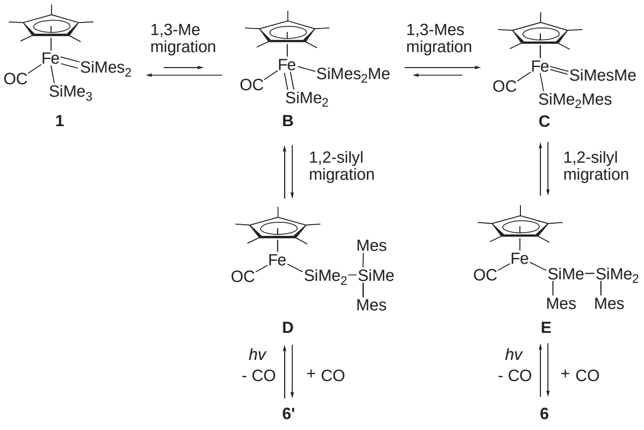
The existence of two carbonyl ligands in **6** was confirmed by observation of two signals for CO ligands, mutually diastereotopic, at 219.7 and 220.9 ppm in the ^{13}C NMR spectrum, and two ν(CO) bands at 1973 and 1919 cm^{-1} in the IR spectrum. The ^{29}Si NMR signals appear in the normal region of the disilanyl iron complexes (10.7 ppm for the α-Si atom and −11.4 ppm for the β-Si atom (Eq 2)). The methyl groups on the terminal β-Si atom show their signals inequivalently at 0.75 and 0.91 ppm in the ^{1}H NMR spectrum. This is because these two methyl groups are diastereotopic due to the chirality of the α-Si atom bound to the Fe atom. The signal of a methyl group on the α-Si atom appears at 1.00 ppm. The assignment of these signals is based on the ^{1}H–^{29}Si COLOC NMR spectrum. Other spectral data of **6** closely resemble those of **4**, whose structure has been determined by X-ray crystallography,[4] except the signals for the ^{t}BuNC ligand in **4**.

The structure of complex **6′** is more symmetric than that of **6**. In the ^{1}H NMR spectrum, a singlet signal for two methyl groups on the α-Si atom appears at 0.65 ppm and that for a methyl group on the β-Si atom at 1.20 ppm. Two mesityl groups on the β-Si atom are equivalent and exhibit only one set of three signals for the *o*-Me, *m*-H, and *p*-Me groups. The ^{13}C NMR spectrum shows a single signal for two carbonyl ligands at 219.6 ppm, while the IR spectrum displays two ν(CO) bands at 1975 and 1921 cm^{-1}, indicating the presence of two CO ligands. The ^{29}Si NMR signals appear at 18.5 ppm for the α-Si atom and -16.6 ppm for the β-Si atom. These assignments were also confirmed by the ^{1}H–^{29}Si COLOC NMR spectrum.

From the isolated **6** and **6′**, the reverse reaction forming **1** was observed under soft irradiation of light: When a C_6D_6 solution containing **6** or **6′** in a Pyrex NMR tube was irradiated at room temperature with a fluorescent lamp for 17–38 h, **1** was recovered almost quantitatively with a release of CO (Eq 3). Irradiation with a 450 W medium pressure Hg lamp also afforded **1** but in lower yield because of the decomposition of **1**.

$$\mathbf{6} \xrightarrow[-\mathrm{CO} \quad 88\%]{\text{fluorescent light, rt, 17 h}} \mathbf{1} \xleftarrow[95\% \quad -\mathrm{CO}]{\text{fluorescent light, rt, 38 h}} \mathbf{6'} \qquad (3)$$

A mechanism for the formation of **6** and **6′** from **1** (Scheme 2) is essentially the same as that previously reported for the formation of **4**.[4] The key steps consist of (1) a thermal equilibrium among three isomeric silyl(silylene) complexes (**1**, **B**, and **C**) via 1,3-methyl or mesityl migrations, (2) 1,2-silyl migrations from **B** and **C** to produce unsaturated disilanyl complexes **D** and **E**, and (3) coordination of CO to **D** and **E** to produce **6′** and **6**. The preferred formation of **6** compared to **6′** is attributable to the preferred formation of **C** compared to **B**, which is due to the instability of **B** compared to **C** caused by the steric repulsion among Cp* and two mesityl groups on the silyl ligand. The reverse reaction from **6′** or **6** to **1**, initiated by photodecarbonylation, can be reasonably explained by tracking back the same mechanism. Importantly, in this research, we proved that all the 1,2-silyl and 1,3-group-migration steps between **1** and **6** or **6′** are reversible under mild conditions.



Scheme 2.

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References and Notes

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5 UV–vis data of **3** (hexane): $\lambda_{\max} = 394$ nm (sh, $\varepsilon = 5.7 \times 10^2$ M^{-1} cm^{-1}), 426 nm ($\varepsilon = 4.3 \times 10^2$ M^{-1} cm^{-1}).

6 **5**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.33 (s, 3H, FeMe), 1.42 (s, 15H, C_5Me_5), 6.08 (m, 2H, *m*-H), 6.51 (tt, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, *p*-H), 8.28 (m, 2H, *o*-H). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6) δ -3.6 (FeMe), 9.3 ($C_5\mathit{Me}_5$), 89.1 (C_5Me_5), 123.2 ($N\mathit{C}_5H_5$), 134.1 ($N\mathit{C}_5H_5$), 156.9 ($N\mathit{C}_5H_5$), 224.6 (CO). IR (C_6D_6) ν_{CO} 1882 (s) cm^{-1}.

7 **6′**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.65 (s, 6H, $SiMe_2$), 1.20 (s, 3H, $SiMes_2\mathit{Me}$), 1.46 (s, 15H, C_5Me_5), 2.13 (s, 6H, *p*-Me), 2.52 (s, 12H, *o*-Me), 6.79 (s, 4H, *m*-H). For ^{13}C{^{1}H} NMR data, see Supporting Information. ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6) δ -16.6 ($SiMes_2Me$), 18.5 ($SiMe_2$). IR (C_6D_6) ν_{CO} 1975 (s), 1921 (s) cm^{-1}. MS (EI, 70 eV) 543 ($M^+ - CO - Me$, 4), 515 ($M^+ - 2CO - Me$, 7), 409 ($M^+ - SiMesMe_2$, 37), 339 ($SiMesMeSiMesMe_2$, 60), 309 (100). UV–vis (hexane) $\lambda_{\max} = 270$ nm (sh, $\varepsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}), 307 nm ($\varepsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $C_{33}H_{46}FeO_2Si_2$: C, 67.55; H, 7.90%. Found: C, 67.39; H, 8.00%.

8 **6**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.75 (s, 3H, $SiMes\mathit{Me}_2$), 0.91 (s, 3H, $SiMes\mathit{Me}_2$), 1.00 (s, 3H, $SiMes\mathit{Me}$), 1.31 (s, 15H, C_5Me_5), 2.09 (s, 3H, *p*-Me), 2.14 (s, 3H, *p*-Me), 2.39 (s, 6H, *o*-Me), 2.50 (s, 3H, *o*-Me), 2.57 (s, 3H, *o*-Me), 6.72 (s, 3H, *m*-H), 6.78 (s, 1H, *m*-H). For ^{13}C{^{1}H} NMR data, see Supporting Information. ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6) δ -11.4 ($SiMesMe_2$), 10.7 (SiMesMe). IR (C_6D_6) ν_{CO} 1973 (s), 1919 (s) cm^{-1}. MS (EI, 70 eV) 586 (M^+, 2), 571 ($M^+ - Me$, 1), 558 ($M^+ - CO$, 1), 543 ($M^+ - CO - Me$, 5), 515 ($M^+ - 2CO - Me$, 7), 485 ($M^+ - 2CO - 3Me$, 2), 409 ($M^+ - SiMesMe_2$, 72), 339 ($SiMesMeSiMesMe_2$, 100). UV–vis (hexane) $\lambda_{\max} = 259$ nm ($\varepsilon = 1.4 \times 10^4$ M^{-1} cm^{-1}), 320 nm ($\varepsilon = 7.7 \times 10^3$ M^{-1} cm^{-1}). Anal. Calcd for $C_{33}H_{46}FeO_2Si_2$: C, 67.55; H, 7.90%. Found: C, 67.16; H, 7.97%.

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