Synthesis, Structure, and Photochemistry of Disilyl Derivatives of the Fp (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) System: $\text{FpMe}\underline{\text{Si(CH}_2)_4\text{Si}}\text{MeFp}$ and FpPhMeSiSiMePhFp

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The synthesis of $\text{FpMe}\underline{\text{Si(CH}_2)_4\text{Si}}\text{MeFp}$ (**1a**) is reported (Fp = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2)$, along with small amounts of $[\text{FpMe}\underline{\text{Si(CH}_2)_4\text{Si}}\text{Me}]_2\text{O}$ (**2**). Photolysis of **1a** with a medium-pressure Hg lamp for 8 h resulted in the formation of two different types of intermediate silylene-bridged complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-SiMeSi(CH}_2)_4)$ (**4**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}\underline{\text{Si(CH}_2)_4\text{Si}}\text{Me}_2)$ (**5**), each existing as a mixture of three equilibrating geometrical isomers, respectively; **4** slowly photoisomerized to the isomers **5** prior to expulsion of the second CO group. Prolonged irradiation of **5** gave a mixture of the cis and trans isomers of the bis(silylene)-bridged complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-SiMe}_2)(\mu\text{-Si(CH}_2)_4)$ (**6**). Similar photolysis of FpMePhSiSiPhMeFp (**3**) resulted in the sequential formation of the mono(silylene)-diiron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-SiMeSiMePh}_2)$ (**7**) and the bis(silylene)diiron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-SiPh}_2)(\mu\text{-SiMe}_2)$ (**8**). The molecular structures of **1a**, **5a**, and **6a** have been determined by X-ray diffraction analysis.

Introduction

The synthesis and study of silylene− (or silene−) transition-metal complexes is an intriguing area of organosilicon chemistry, since numerous metal-catalyzed processes proceed via their intermediacy.[1−5] Photochemical treatment of oligosilyl Fp complexes, $\text{FpSiR}_2\text{SiR}_3$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$), that contain direct iron−silicon bonds results in the formation of the silyl silylene intermediates $(\eta^5\text{-}C_5H_5)Fe(CO)(SiR_3)({=}SiR_2)$ via α-elimination reactions.[6,7] Such intermediates can eliminate silylenes or undergo rearrangement reactions involving 1,3-alkyl, -aryl, and -silyl migrations (eqs 1 and 2). The silylene can be trapped intramolecularly or intermolecularly.[6h−j,7b,f,g,8]

$$\text{Fp}{-}\text{SiMe}_2\text{SiMe}_3 \rightarrow \text{Fp}{-}\text{SiMe}_3 + [\text{SiMe}_2] \quad (1)$$

$$\text{Fp}{-}\text{SiMe}_2\text{SiMe}_2\text{SiMe}_2\text{SiMe}_3 \rightarrow \text{Fp}{-}\text{Si(SiMe}_3)_3 \quad (2)$$

The related bimetallic systems exhibit significantly different chemistry due to the capacity for metal−metal interactions.[9,10] For example, photochemical treatment of $\text{FpSiMe}_2\text{SiMe}_2\text{Fp}$ resulted in the sequential formation of mono(silylene)- and bis(silylene)-bridged diiron complexes (Scheme 1).[10b,c] Such reactions also proceed via equilibrating silyl silylene intermediates. To examine the potential of this chemistry in ring systems, we report the synthesis, characterization, and photochemistry of $\text{FpMe}\underline{\text{Si(CH}_2)_4\text{Si}}\text{MeFp}$. We also study the related diiron 1,2-diphenyl-1,2-dimethyldisilyl system FpMePhSiSiPhMeFp.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere or under high vacuum. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. The following reagents were used as received from

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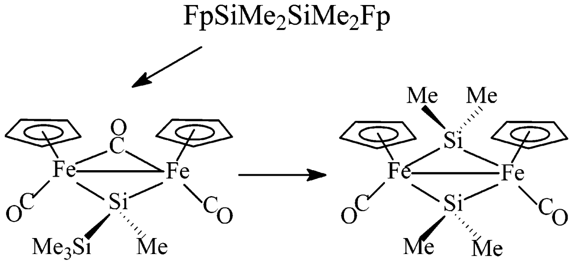
Scheme 1



the suppliers named: silica gel (grade 62, 60–200 mesh), anhydrous HCl, $Br(CH_2)_4Br$, Aldrich; CF_3SO_3H, Lancaster; $Ph_2MeSiCl$, Gelest. Other reagents were synthesized by literature procedures with some modifications: $Ph_2MeSiSiMePh_2$,[11] ClPhMeSiSiMePhCl,[9b] and 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane.[12] Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer. Infrared (IR) spectra were obtained using hexane or THF as solvent on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra were obtained from the Nebraska Center for Mass Spectrometry. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of 1 and 2. To 50 mL of a THF solution of $[Fp]^-Na^+$ (prepared from 2.00 g (5.60 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) was added 1.13 g (5.30 mmol) of 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane at 0 °C. The solution was stirred at low temperature and then warmed to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered, concentrated to 5 mL, and placed upon a 2.5 × 20 cm silica gel column. Elution with a hexane/benzene solvent mixture (90:10) developed a yellow band, which was collected and after solvent removal afforded a yellow solid product. The solid was further recrystallized from a mixture of hexane and methylene chloride solvents to yield 1.53 g (58%) of orange-yellow crystals. ^1H, ^{13}C, and ^{29}Si NMR spectra of the yellow crystals indicated a mixture of two compounds (**1** and **2**) in a ratio of 3:1. **1** and **2** could be separated by recrystallization from a mixture of CH_2Cl_2 and hexane.

1a: mp 132–134 °C; ^1H NMR (C_6D_6) δ 0.69 (s, 6H, CH_3), 1.15–1.20, 1.38–1.45, 1.68–1.77, 2.02–2.07 (br m, $(CH_2)_4$), 4.31 (s, 10H, Cp); ^{13}C NMR (C_6D_6) δ 4.08 (CH_3), 25.9, 28.5 ($(CH_2)_4$), 83.4 (Cp), 216.84, 216.77, 216.52, (CO); ^{29}Si NMR (C_6D_6) δ 30.9; IR (ν_{CO}, cm^{-1}) 1993 (s), 1944 (s), 1936 (sh, m). Anal. Calcd for $C_{20}H_{24}Fe_2O_4Si_2$: C, 48.40; H, 4.87; Found: C, 48.44; H, 4.96.

2: mp 140–142 °C; ^1H NMR (C_6D_6) δ 0.43, 0.61 (s, s, 6H, 6H, CH_3), 0.93–1.53, 2.03 (br m, 12H, 4H, $(CH_2)_4$), 4.30 (s, 10H, Cp); ^{13}C NMR (C_6D_6) δ 0.97, 1.46 (CH_3), 22.4, 22.6, 27.2, 27.7 ($(CH_2)_4$), 83.4 (Cp), 215.78, 215.83 (CO); ^{29}Si NMR (C_6D_6) δ 7.75 (SiOSi), 13.0 (Fp-Si); IR (ν_{CO}, cm^{-1}) 1996 (s), 1945 (s). Anal. Calcd for $C_{26}H_{38}Fe_2O_5Si_4$: C, 47.70; H, 5.85; Found: C, 47.72; H, 5.85.

Synthesis of FpPhMeSiSiMePhFp (3). To 50 mL of a THF solution of $[Fp]^-Na^+$ (prepared from 2.00 g (5.60 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) was added 1.31 g (4.20 mmol) of ClPhMeSiSiMePhCl at 0 °C. The solution was stirred at low temperature and then warmed to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered, concentrated to 5 mL, and placed upon a 2.5 × 20 cm silica gel column. Elution with a hexane/benzene solvent mixture (90:10) developed a yellow band, which was collected and after solvent removal afforded a yellow oily product. This oily product was dissolved in 20 mL of hexane. The solution was cooled to −5 °C, and the orange-yellow precipitate was collected via filtration. The solid was further recrystallized from a hexane/methylene chloride solvent mixture to yield 0.64 g (26%) of orange-yellow crystals of **3**. ^1H, ^{13}C, and ^{29}Si NMR spectra of **3** showed a mixture of two diastereomers (**3a** and **3b**) in the ratio of 5:1. **3a** (rac) and **3b** (meso) could be separated by recrystallization from a solvent mixture of CH_2Cl_2 and hexane.

3a: mp 158–160 °C; ^1H NMR (C_6D_6) δ 1.07 (s, 6H, CH_3), 4.02 (s, 10H, Cp), 7.18–7.28, 7.74–7.76 (m, 6H, 4H, Ph); ^{13}C NMR (C_6D_6) δ 4.09 (CH_3), 83.7 (Cp), 128.1, 128.2, 134.9, 147.8 (Ph), 216.2, 216.5 (CO); ^{29}Si NMR (C_6D_6) δ 19; IR (ν_{CO}, cm^{-1}) 2003 (s), 1994 (s), 1949 (s). Anal. Calcd for $C_{28}H_{26}Fe_2O_4Si_2$: C, 56.58; H, 4.41; Found: C, 56.51; H, 3.98.

3b: mp 258–260 °C; ^1H NMR (C_6D_6) δ 1.14 (s, 6H, CH_3), 3.98 (s, 10H, Cp), 7.26–7.28, 7.84–7.87 (m, 6H, 4H, Ph); ^{13}C NMR (C_6D_6) δ 5.62 (CH_3), 83.5 (Cp), 128.1, 128.2, 134.9, 147.7 (Ph), 216.2, 216.7 (CO); ^{29}Si NMR (C_6D_6) δ 19.9; IR (ν_{CO}, cm^{-1}) 2004 (s), 1995 (s), 1949 (s). Anal. Calcd for $C_{28}H_{26}Fe_2O_4Si_2$: C, 56.58; H, 4.41; Found: C, 56.47; H, 4.42.

Photolysis of 1a: Formation of 4 and 5. A 5 mm Pyrex NMR tube was charged with 0.10 g (0.20 mmol) of **1a** and 1 mL of C_6D_6 and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp at a 10 cm distance from the lamp. The progression of the reaction was monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The color of the solution changed from yellow to violet-red upon irradiation, and the ^{29}Si NMR spectrum obtained after 2 h of irradiation showed the formation of two different types of silylene-bridged complexes, **4** and **5**, each existing as a number of isomers. Prolonged irradiation for 15 h resulted in the complete disappearance of the starting material **1a** and slow conversion of complexes **4** to the more stable **5** as a mixture of three geometrical isomers. Further irradiation for 30 h led to an almost complete conversion of **4** to **5**. At this stage the irradiation was stopped. When the reaction mixture was stored at −5 °C for 10 days, red-violet crystals of **5a** were obtained exclusively. The crystals were collected and washed with hexane to give 63 mg of product (67%). We could not assign the ^{13}C and ^1H NMR data to each isomer of **4**, since there are a total of seven different complexes coexisting in the reaction mixture before the complete disappearance of **4**.

4: ^{29}Si NMR (C_6D_6) δ 8.13, 8.39, 9.41 ($Si(CH_3)$), 228.5, 237.1, 240.3 (μ-Si).

5: ^1H NMR (C_6D_6) δ 0.28, 0.41 (s, s, 3H, 3H, $Si(CH_3)_2$, **5c**), 0.31 (s, 6H, $Si(CH_3)_2$, **5b**), 0.46 (s, 6H, $Si(CH_3)_2$, **5a**), 1.15, 1.77, 2.04 (bd m, 2H, 2H, 4H, $(CH_2)_4$, **5a**), 1.03–1.11, 1.72–1.76, 1.88–2.01 (bd m $(CH_2)_4$, **5b** + **5c**), 4.12 (s, 10H, Cp, **5a**), 4.22 (s, 10H, Cp, **5b**), 4.30, 4.47 (s, s, 5H, 5H, Cp, **5c**); ^{13}C NMR (C_6D_6) δ −0.88, 0.09 (CH_3, **5c**), −0.79 (CH_3, **5a**), 0.24 (CH_3, **5b**), 21.02, 27.33, 27.91, 30.29 ($(CH_2)_4$, **5b**), 19.93, 27.21, 30.62, 31.06 ($(CH_2)_4$, **5a**), 20.32, 27.26, 30.04, 30.10 ($(CH_2)_4$, **5c**), 83.66 (Cp, **5b**), 84.26 (Cp, **5a**), 84.39, 84.96 (Cp, **5c**), 213.17 (CO, **5a**), 213.34 (CO, **5c**), 213.38 (CO, **5b**), 274.36 (μ-CO, **5b**), 275.03 (μ-CO, **5a**), 276.74 (μ-CO, **5c**); ^{29}Si NMR (C_6D_6) δ −7.64 ($Si(CH_3)_2$, **5a**), −6.38 ($Si(CH_3)_2$, **5c**), −5.14 ($Si(CH_3)_2$, **5a**), 236.02 (μ-Si, **5b**), 242.52 (μ-Si, **5a**), 245.65 (μ-Si, **5c**); IR (ν_{CO}, cm^{-1}) in THF 1992 (s), 1962 (s), 1929 (s), 1773 (s, μ-CO); HRMS (EI) calcd for $C_{19}H_{24}{}^{56}Fe_2O_3Si_2$ *m/z* 467.9962, found *m/z* 467.9958. LRMS (EI): 468.0 M^+, 16; 412.0 $[M - 2CO]^+$, 75; 291.0 $[M - 2CO - CpFe]^+$, 100; 186.0 Fc^+, 62; 120.9 $[CpFe]^+$, 66. Anal. Calcd for $C_{19}H_{24}Fe_2O_3Si_2$: C, 48.74; H, 5.17. Found: C, 48.49; H, 5.30.

Photolysis of 1a: Formation of 6. A 5 mm Pyrex NMR tube was charged with 0.10 g (0.20 mmol) of **1a** and 1 mL of C_6D_6 and sealed under vacuum. Irradiation was carried out as above for 110 h or until NMR monitoring showed the complete disappearance of **1a** and **5** and the formation of **6**, as a mixture of two isomers, **6a** (cis) and **6b** (trans). At this

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stage the irradiation was stopped. When the reaction mixture was stored at −5 °C for 1 week, red-violet crystals of **6a** were obtained exclusively. The crystals were collected and washed with hexane to give 45 mg of product (51%).

6: ^{1}H NMR (C_6D_6) δ 1.03, 1.27 (s, s, 3H, 3H, Si(CH_3)$_2$, **6a**), 1.15 (s, 6H, Si(CH_3)$_2$, **6b**), 1.36, 1.53−1.55, 1.77−1.82, 1.98−2.00 (br m, 8H, (CH_2)$_4$, **6a**), 1.52, 1.97 (br m, 8H, (CH_2)$_4$, **6b**), 3.91 (s, 10H, Cp, **6a**), 4.01 (s, 10H, Cp, **6b**); ^{13}C NMR (C_6D_6) δ 13.41, 15.58 (CH_3, **6a**), 15.83 (CH_3, **6b**), 23.5, 27.1, 28.9, 29.3 ((CH_2)$_4$, **6a**), 26.88, 28.86 ((CH_2)$_4$, **6b**) 80.7 (Cp, **6b**), 81.5 (Cp, **6a**), 213.9 (CO, **6a**), 214.9 (CO, **6b**); ^{29}Si NMR (C_6D_6) δ 235.9, 251.7 (**6a**), 244.5, 265.0 (**6b**); IR (ν_{CO}, cm^{-1}) in THF 1933 (s); HRMS (EI) calcd for $C_{18}H_{24}{}^{56}Fe_2O_2Si_2$ *m/z* 440.0014, found *m/z* 440.0004. LRMS (EI): 444 M$^+$, 26; 412 [M − CO]$^+$, 100; 382 [M − 2CO − H_2]$^+$, 43; 186.0 Fc$^+$, 35; 121 [CpFe]$^+$, 12. Anal. Calcd for $C_{18}H_{24}Fe_2O_2Si_2$: C, 49.11; H, 5.49; Found: C, 49.45; H, 5.45.

Photolysis of 3a: Formation of 7. A 5 mm Pyrex NMR tube was charged with 0.10 g (0.17 mmol) of **3a** and 1 mL of C_6D_6 and sealed under vacuum. Irradiation after 12 h indicated the complete disappearance of the starting material **3** and the formation of **7**, as a mixture of three main geometrical isomers (**7a**:**7b**:**7c** = 9:12:10). After the solvent was removed, the resulting violet-red solid was washed twice with the cold hexane and dried under vacuum to yield **7** (31 mg, 33%).

7: ^{1}H NMR (C_6D_6) δ 0.77, 0.79, 0.91 (SiCH_3Ph$_2$), 1.19, 1.35, 1.57 (SiCH_3SiCH$_3$Ph$_2$), 4.00 (Cp, **7a**), 4.19 (Cp, **7b**), 4.10, 4.39 (Cp, **7c**), 7.22−7.42, 7.82−7.84, 7.94−7.96 (m, Ph); ^{13}C NMR (C_6D_6) δ −0.31, 0.06, 0.94 (SiCH$_3$Ph$_2$), 11.56, 12.03, 13.11 (SiCH$_3$SiMePh$_2$), 84.23, 84.90 (Cp, cis), 84.97, 95.83 (Cp, trans), 128.49, 128.75, 129.20, 129.62, 135.75, 136.05, 139.83, 140.03 (Ph, cis), 128.45, 128.85, 129.31, 129.69, 135.26, 136.00, 138.77, 140.12 (Ph, trans), 213.47, 213.86 (CO, cis), 213.69, 213.76 (CO, trans), 273.81, 274.89, 276.21 (μ-CO); ^{29}Si NMR (C_6D_6) δ −10.97, −9.91, −9.57 (SiCH$_3$Ph$_2$), 221.46, 234.11, 235.96 (μ-Si); IR (ν_{CO}, cm^{-1}) 1993 (s), 1976 (sh, m), 1938 (s), 1781 (s, μ-CO); HRMS (FAB): calcd for $C_{27}H_{26}{}^{56}Fe_2O_3Si_2$ *m/z* 566.0119, found *m/z* 566.0116.

The ^{29}Si NMR spectrum of this photolysis mixture also exhibited four very weak resonances at δ −10.13, −9.96, 219.5 (μ-Si), and 223.9 (μ-Si), attributed to the formation of a small amount of 1,3-methyl migration products (μ-SiPhSiMe$_2$Ph), some resonances of which have been observed in ^{1}H and ^{13}C NMR spectra of the photolysis mixture. However, we could not unambiguously assign these comparatively weaker resonances and were unable to isolate the material.

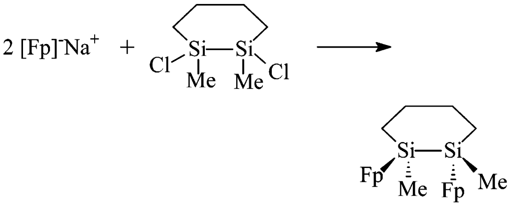
Photolysis of 3a: Formation of 8. In an experiment set up the same as that above, irradiation was continued for 70 h or until NMR monitoring showed the complete disappearance of both **3a** and **7** and the formation of **8**, as a mixture of cis (**8a**) and trans (**8b**) isomers. The solvent was evaporated, and the violet-red solid was washed twice with cold hexane and dried under vacuum to yield **8** (35 mg, 38%).

8: ^{1}H NMR (C_6D_6) δ 1.17, 1.45 (Si(CH_3)$_2$, **8a**), 1.43 (Si(CH_3)$_2$, **8b**), 4.11 (Cp, **8a**), 4.15 (Cp, **8b**), 7.25−7.96 (bd. m. Ph); ^{13}C NMR (C_6D_6) δ 14.63 (CH_3, **8b**), 15.40, 18.76 (CH_3, **8a**), 80.65, 81.54 (Cp), 127.5, 128.2, 128.3, 128.5, 128.9, 134.12, 134.4, 134.6, 149.9, 151.8, 153.5 (Ph), 215.1, 215.27 (CO); ^{29}Si NMR (C_6D_6) δ 219.5, 228.2, 234.7, 236.2;. IR (ν_{CO}, cm^{-1}) in THF 1908 (s); HRMS (EI) calcd for $C_{26}H_{26}{}^{56}Fe_2O_2Si_2$ *m/z* 538.0170, found *m/z* 538.0173. LRMS (EI): 538.0 M$^+$, 28; 510.0 [M − CO]$^+$, 100; 361.0 [CpFe═(SiPhMe)$_2$]$^+$, 33; 296.0 [Fe═(SiPhMe)$_2$]$^+$, 66; 186.0 Fc$^+$, 28; 120.9 [CpFe]$^+$, 25.

X-ray Diffraction Studies. Crystals (**1a**, **5a**, and **6a**) suitable for X-ray diffraction analysis were obtained from different solutions: CH_2Cl_2 and hexane (**1a**) and benzene-d_6 (**5a** and **6a**). Intensity data were collected on a Nicolet-Siemens R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit cell parameters and standard deviations were obtained by a least-squares fit of 25 reflections randomly distributed in reciprocal space in the 2θ range of 15−30°. The ω-scan technique was applied in the 2θ range (3.5° ≤ 2θ ≤ 45.0° (**1a**), 4.12° ≤ 2θ ≤ 45.08° (**5a**), 5.16° ≤ 2θ ≤ 45.10° (**6a**)) with variable scan speeds. For **6a**, data collection was performed at 198 K to improve the quality of the data. A semiempirical absorption correction was applied to the data set, giving a minimum/maximum transmission ratio of 0.295/0.368 for **1a**. No absorption correction was applied in the cases of **5a** and **6a**. All structures were solved by direct methods and refined using the PC version of the SHELEXTL PLUS crystallographic software by Siemens. Full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$ was carried out with anisotropic thermal parameters for non-hydrogen atoms. There is some unresolved disorder in the Cp rings in **5a** and at the C8 and C9 atoms in **6a**, respectively. The weighing scheme has the form $w^{-1} = \sigma^2(F) + gF^2$, and the final R factors have the forms $R = \sum w|F_o - F_c|/\sum F_o$ and $R_w = [w|F_o - F_c|^2/\sum wF_o{}^2]^{1/2}$. Crystallographic data are summarized in Table 1.

Results and Discussion

Synthesis and Spectroscopic Properties. The new complexes $\mathrm{FpMe\underline{Si(CH_2)_4Si}MeFp}$ (**1**) and FpMePhSiSiPhMeFp (**3**) were readily prepared in THF by the salt-elimination reactions between [Fp]$^-$Na$^+$ and the corresponding dichlorodisilanes in THF (eq 3). Analysis



1a

(3a)

$$2\,[\mathrm{Fp}]^-\mathrm{Na}^+ + \mathrm{ClMePhSiSiPhMeCl} \longrightarrow \underset{\mathbf{3}}{\mathrm{FpMePhSiSiPhMeFp}} \qquad (3b)$$

of the crude reaction products of **1** after column chromatography by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy showed that only the trans isomer (**1a**) was formed along with the disiloxane complex $\mathrm{[FpMe\underline{Si(CH_2)_4Si}Me]_2O}$ (**2**). **1a** and **2** could be separated by recrystallization from a mixture of methylene chloride and hexane. The formation of **2** possibly resulted from the hydrolysis of small amounts of $\mathrm{FpMe\underline{Si(CH_2)_4Si}MeCl}$ during the column chromatography. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3** showed a mixture of the two diastereomers **3a** (rac) and **3b** (meso), in the ratio of 5:1. **3a** and **3b** could also be separated by recrystallization from a mixture of hexane and CH_2Cl_2.

The new complexes exhibit spectroscopic data in total accord with the proposed structures. The ^{29}Si NMR spectrum of **1a** exhibits a signal at 30.9 ppm, which is comparable to that of the tetramethyldisilyl analogue FpSiMe$_2$SiMe$_2$Fp at 29.2 ppm. Compound **2** shows two ^{29}Si NMR signals at 12.96 and 7.75 ppm, which are assigned to Fp*Si*Si and Si*Si*O*Si*Si, respectively. Similar Fp*Si*Si resonances are observed in the related complexes FpSiMe$_2$SiMe$_2$OMe,[7b] FpSiMe$_2$SiMe$_2$Cl,[10b] and FpSiMe$_2$SiMe$_2$Fc.[10b] The infrared spectra of **1**−**3** exhibit either two broad stretching frequencies at ∼1995 and 1945 cm^{-1} (**2**) or four frequencies at ∼2003, 1995, 1945, and 1937 cm^{-1} (**1** and **3**) due to the presence of isomers in

Table 1. Crystallographic Data for 1a, 5a, and 6a

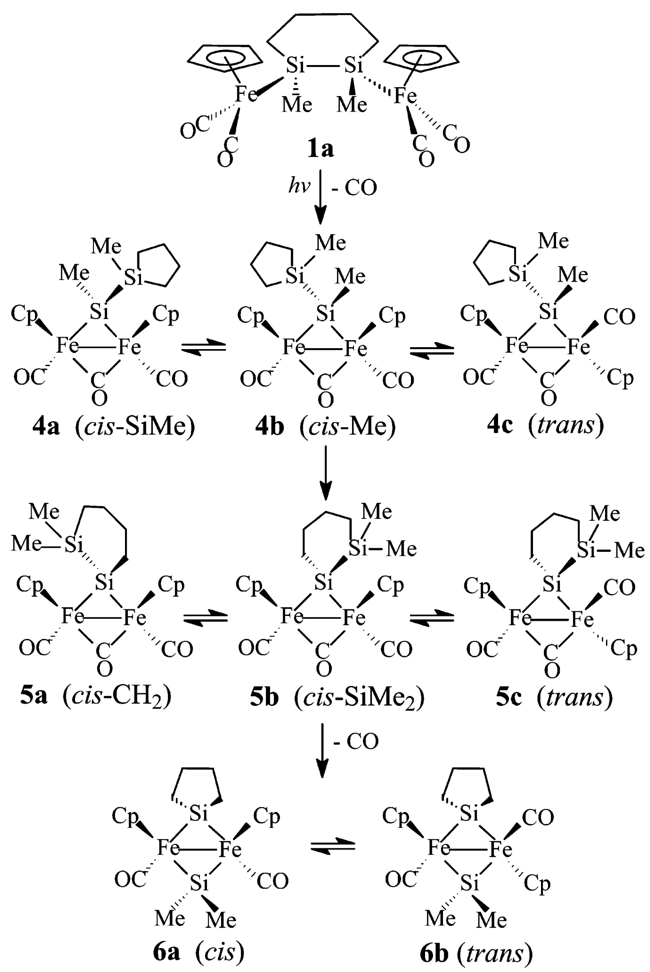
	1	5a	6a
empirical formula	$C_{20}H_{24}Fe_2O_4Si_2$	$C_{19}H_{24}Fe_2O_3Si_2$	$C_{18}H_{24}Fe_2O_2Si_2$
fw	496.3	468.26	440.25
cryst size (mm)	0.42 × 0.60 × 0.70	0.62 × 0.60 × 0.52	0.42 × 0.28 × 0.28
group syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
unit cell dimens			
a (Å)	7.984(3)	10.197(5)	8.735(3)
b (Å)	13.482(4)	12.773(9)	15.769(3)
c (Å)	20.937(8)	15.581(6)	13.772(3)
α, deg	90	90	90
β, deg	97.87(3)	90	96.11(2)
γ, deg	90	90	90
V (Å^3)	2232.4(14)	2029.4(19)	1886.2(8)
Z	4	4	4
d_{calcd} (g.cm^{-1})	1.477	1.533	1.550
μ, cm^{-1}	14.26	15.63	16.73
temp (K)	296	296	198
2θ range (deg)	3.5−45.0	4.12−45.08	5.16−45.10
index ranges			
h	0−8	−10 to 10	−5 to 10
k	−2 to 14	−13 to 13	−1 to 18
l	−22 to 22	−16 to 16	−16 to 16
no. of rflns collected	3805	3825	3827
no. of indep data	2927 ($R_{int} = 2.77\%$)	1543 ($R_{int} = 6.87\%$)	3313 ($R_{int} = 8.44\%$)
abs cor	semiempirical	N/A	N/A
final R indices (obsd data) (%)	$R = 3.08$, $R_w = 4.53$	$R = 10.59$, $R_w = 27.33$	$R = 7.15$, $R_w = 19.75$
goodness of fit	1.17	1.503	0.795

solution. The molecular structures of **1a** and **3b** have been determined by X-ray diffraction analysis.

Photochemistry of 1a. A C_6D_6 solution of **1a** in a flame-sealed Pyrex NMR tube was irradiated using a 450 W medium-pressure Hg lamp. Periodic monitoring by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy indicated that after 8 h of irradiation **1a** had partially transformed to the two new silylene-bridged complexes **4** and **5**, each existing as a mixture of three geometrical isomers, respectively (Scheme 2). Prolonged irradiation resulted in the gradual decrease of **1a** and **4** and increase of **5**. The spectra obtained after 15 h of irradiation showed the complete disappearance of the starting material **1a**. Further irradiation for 15 h led to the almost complete disappearance of **4** and formation of **5** along with trace amounts of the cis and trans isomers of **6**. These results are analogous to those obtained in the photochemistry of $FpSiMe_2SiMe_2Fp$, but the reaction is much slower (30 h vs 2 h), and the results are more complex. Continuous irradiation for 110 h resulted in the complete disappearance of **5** and formation of **6**.

The ^{29}Si NMR signals at 8.13, 8.39, and 9.41 ppm are assigned to the silacyclopentyl groups in three geometrical isomers of **4** in which the silacyclopentyl group is linked to the bridging silicon atom. These resonances are about 14−16 ppm more downfield than those of the related complexes **5** (−7.64, −6.38, and −5.14 ppm) and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$ (−6.72, −5.56, and −4.70 ppm) formed in the photolysis of $FpSiMe_2SiMe_2Fp$. These downfield shifts are expected for the related silacyclopentane derivatives ($\Delta\delta = 16.77$ ppm for silacyclopentane and $\Delta\delta = 16.5$ ppm for silacyclopentene).[13,14] A series of significantly downfield resonances are assigned to the bridging silylenes of **4** (228.5, 237.1, and 240.3 ppm) and **5** (236.0 (**5b**), 242.5 (**5a**), and 245.7 ppm (**5c**)). We could not unambiguously assign the ^{29}Si NMR data to each isomer of **4**, and prolonged irradiation of **4** led to its complete conversion to **5**. For complex **6**, four ^{29}Si resonances observed at 235.9 (**6a**),

Scheme 2



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[13] Williams, E. A. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 511−555.

[14] (a) Scholl, R. G.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376. (b) Filleux-Blanchard, M.-L.; An, N. D.; Manuel, G. *Org. Magn. Reson.* **1978**, *11*, 150.

244.5 (**6b**), 251.7 (**6a**), and 265.0 ppm (**6b**) are assigned to the distinct bridging silylene units in the cis and trans isomers. These resonances are comparable to those observed in [(η^5-C_5H_5)Fe(CO)]$_2$(μ-SiMe$_2$)$_2$, (229.5 and 243.8 ppm) and [(η^5-C_5H_5)Fe(CO)]$_2$(μ-SiMe$_2$)(μ-GeMe$_2$) (230.8 and 244.7 ppm). In the ^{13}C NMR spectrum of **6**, the bridging dimethylsilylene unit (μ-SiMe$_2$) exhibits three resonances. Two SiMe resonances of equal intensity observed at 13.4 and 15.6 ppm are assigned to the cis isomer with an approximate mirror about the center of the Fe−Fe bond, and the remaining resonance at 15.8 ppm is assigned to the trans isomer with a C_2 axis about the center of the Fe−Fe bond.

The formation of **4** and **5** is related to the observation by Malisch et al. for the compounds [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-SiMeX) (X = H, Cl)[10a] and the chemistry noted in Scheme 1 by ourselves and the Ogino group.[10b,c,15] On the basis of the Ogino analysis of these latter systems,[15] we have briefly studied the related isomerization of **5** by observing the ^{1}H NMR spectral change of a C_6D_6 solution of **5a** with time. When **5a** was dissolved in C_6D_6 in a sealed NMR tube and the ^{1}H NMR spectrum recorded within 20 min, a mixture of **5a** and trace amounts of **5b** and **5c** was observed. The isomers equilibrate over a 5 day time period at room temperature, and the ^{1}H NMR spectrum recorded after 5 days showed that the molar ratio of three geometrical isomers is **5a**:**5b**:**5c** = 27:54:19. The isomer distribution indicates that **5b** (*cis*-SiMe$_2$) is thermodynamically the most stable. This result indicates that there is a steric interaction between the bulky SiMe$_2$CH$_2$ group and the Cp rings in **5b** smaller than that between the less bulky CH$_2$ group and the Cp rings in **5a**. The anomaly can be understood if we compare the Si−Si and Si−C bond lengths (2.342 Å vs 1.858 Å) placing the "bulky" group further from the Cp rings and reducing the steric interaction. The isomerization of **5a** is much slower than that of its analogues [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-EMe-SiMe$_3$) (E = Si, Ge).[10c,d,15] For the final bis(silylene) photoproducts, pure **6a** was found to equilibrate to a molar ratio of **6a**:**6b** = 23:77 over a 5 day time period at room temperature, indicating that, as anticipated, the trans isomer **6b** is the more stable isomer.

Single-Crystal X-ray Diffraction Studies. The molecular structure of **1a** is illustrated in Figure 1, and selected bond distances and angles are provided in Table 2. The molecule can be regarded as the replacement of the two methyl groups of tetramethyl-1,2-disilacyclohexane by two Fp units. The Fp moieties are mutually trans to each other, and the disilacyclohexane ring adopts a twist-chair conformation. Both the Si−Si (2.362(1) Å) and Fe−Si bond lengths (2.342(1) and 2.351(1) Å) are in the normal range noted for related complexes containing the Fe−Si−Si fragment.[16] However, it is interesting that the Fe−Si bond lengths are much shorter than that (2.390 Å) in the parent analogue [(η^5-C_5H_5)Fe(CO)$_2$]$_2$Si$_2$Me$_4$,[16a] the longest bond of this type reported to date, possibly attributed to the ring effect. The dihedral angle between the two Cp rings is 104.5°. The silicon substituents take an almost staggered conformation about the silicon−silicon bond with torsion angles in the range of 34.1−45.0°.

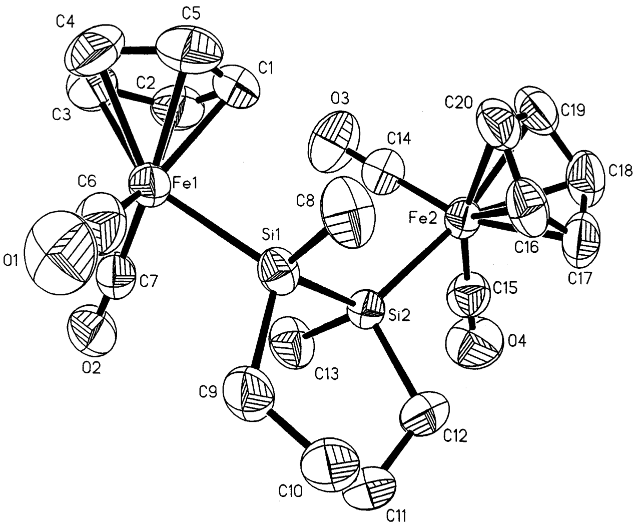

Figure 1. Molecular structure of **1a**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a

Fe(1)−Si(1)	2.342(1)	Fe(2)−Si(2)	2.351(1)
Si(1)−Si(2)	2.362(1)	Fe(1)−C(6)	1.731(4)
Fe(1)−C(7)	1.736(3)	Fe(2)−C(14)	1.736(3)
Fe(2)−C(15)	1.733(4)	O(1)−C(6)	1.156(5)
O(2)−C(7)	1.141(4)	O(3)−C(14)	1.152(4)
O(4)−C(15)	1.148(5)		
Fe(1)−Si(1)−Si(2)	117.8(1)	Fe(2)−Si(2)−Si(1)	122.0(1)
Si(2)−Si(1)−C(8)	112.2(1)	Si(2)−Si(1)−C(9)	100.0(1)
Si(1)−Si(2)−C(12)	102.4(1)	Si(1)−Si(2)−C(13)	105.7(1)
C(8)−Si(1)−C(9)	105.1(2)	C(2)−Si(1)−C(13)	105.5(2)
C(6)−Fe(1)−C(7)	93.7(2)	C(14)−Fe(2)−C(15)	94.3(2)

When the reaction solution containing **5** was stored in a sealed NMR tube at −5 °C, violet-red crystals of **5a** were exclusively obtained. Similar treatment of **6** yielded violet-red crystals of **6a**. The single-crystal structures of both **5a** and **6a** have been determined by X-ray diffraction analysis. The quality of the single-crystal structure of **5a** is poor, due to some unresolved disorder in the Cp rings, but it serves to confirm the geometrical configuration, and this is illustrated in Figure 2, with selected bond distances and angles listed in Table 3. The two Cp rings are mutually cis, and the Cp ring and the μ-SiCH$_2$ unit are also cis to each other with respect to the four-membered ring defined by Fe1, Si1, Fe2, and C11 atoms. This structure is one (cis-CH$_2$) of the two cis isomers, and the single-crystal structure of the other cis isomer (cis-SiMe$_3$) in the analogue [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-SiMeSiMe$_3$)] was previously reported by Ogino and co-workers.[10c] The Fe−Fe (2.622(3) Å) and the Fe−Si bond lengths (2.291(4) and 2.290(4) Å) are completely in line with those (2.622(1) Å for the Fe−Fe bond, 2.294(1) and 2.301(1) Å for the Fe−Si bonds) in [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-SiMeSiMe$_3$)].

The crystal structure of the bis(silylene)-bridged bis(cyclopentadienyl)diiron complex **6a** appears to be the first example of a bis(silylene)diiron compound, although the crystal structures of several mono(silylene)-bridged analogues are known.[10c,17] To get good-quality structural data, collection was performed at −75 °C. The molecular structure is illustrated in Figure 3, and

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(15) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435.

(16) (a) Pannell, K. H.; Cervantes, J.; Parkanyi, L.; Cervantes-Lee, F. *Organometallics* **1990**, *9*, 859. (b) Pannell, K. H.; Lin, H.-S.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

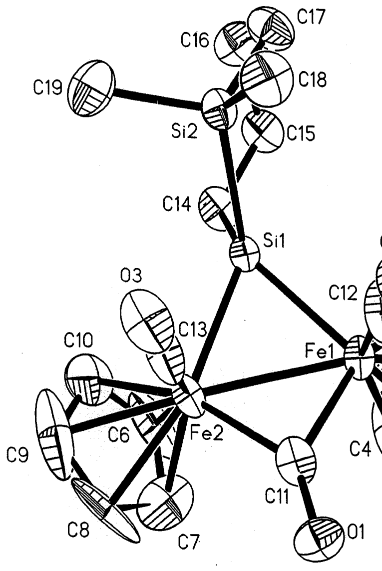


Figure 2. Molecular structure of **5a**.

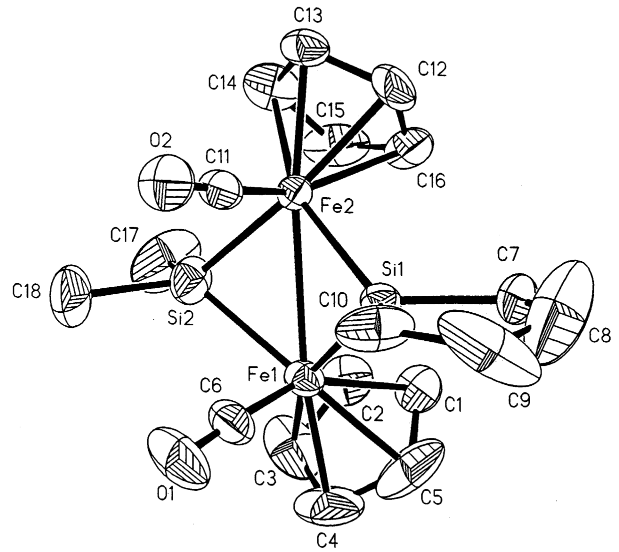


Figure 3. Molecular structure of **6a**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5a

Fe(1)−Si(1)	2.291(4)	Fe(2)−Si(1)	2.290(4)
Si(1)−Si(2)	2.342(5)	Fe(1)−C(11)	1.925(13)
Fe(1)−C(12)	1.761(13)	Fe(2)−C(11)	1.887(13)
Fe(2)−C(13)	1.715(13)	O(1)−C(11)	1.206(15)
O(2)−C(12)	1.097(16)	O(3)−C(13)	1.173(17)
Si(2)−C(17)	1.858(15)	Si(2)−C(9)	1.845(14)
Fe(1)−Si(1)−Fe(2)	69.83(11)	Fe(2)−C(11)−Fe(1)	86.9(6)
Fe(1)−Si(1)−Si(2)	127.28(16)	Fe(2)−Si(1)−Si(2)	126.24 (17)
C(11)−Fe(1)−Fe(2)	45.9(4)	C(11)−Fe(2)−Fe(1)	47.1(4)
Si(1)−Fe(2)−Fe(1)	55.10(9)	Si(1)−Fe(1)−Fe(2)	55.07(9)
C(11)−Fe(1)−Si(1)	98.8(4)	C(11)−Fe(2)−Si(1)	100.0(4)

selected bond distances and angles are listed in Table 4. The molecule of **6a** consists of two [(η^5-C_5H_5)Fe(CO)] moieties linked to each other by one Fe−Fe bond and two bridged silylene ligands. The two Cp rings are mutually cis to each other. The Fe−Fe bond length (2.7423(14) Å) is longer than those found in related mono(silylene)-bridged analogues reported to date, 2.614−2.633 Å.[17] The Fe−Si bond lengths (mean 2.269 Å) are longer than those of the cis-$SiMe_3$ isomer of $[CpFe(CO)]_2(\mu\text{-CO})(\mu\text{-SiMeSiMe}_3)]$[10c] but close to those

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6a

Fe(1)−Si(1)	2.272(4)	Fe(1)−Si(2)	2.268(2)
Fe(2)−Si(1)	2.261(4)	Fe(2)−Si(2)	2.274(2)
Fe(1)−Fe(2)	2.7423(14)	Fe(1)−C(6)	1.721(8)
Fe(2)−C(11)	1.723(7)	C(9)−C(10)	1.531(18)
O(1)−C(6)	1.167(10)	O(2)−C(11)	1.159(9)
Si(1)−C(7)	1.905(8)	Si(1)−C(10)	1.884(8)
Si(2)−C(17)	1.867(11)	Si(2)−C(18)	1.893(10)
C(7)−C(8)	1.403(16)[a]	C(8)−C(9)	1.39(2)[a]
Fe(2)−Si(1)−Fe(1)	74.46(6)	Fe(1)−Si(2)−Fe(2)	74.28(7)
Si(1)−Fe(2)−Fe(1)	52.95(6)	Si(2)−Fe(2)−Fe(1)	52.77(6)
Si(2)−Fe(1)−Fe(2)	52.95(6)	Si(1)−Fe(1)−Fe(2)	52.59(5)
Si(2)−Fe(1)−Si(1)	101.77(8)	Si(1)−Fe(2)−Si(2)	101.94(8)
C(7)−Si(1)−C(10)	92.1(5)	C(17)−Si(2)−C(18)	99.2(6)

[a] The disorder at the C8 and C9 atoms results in shorter C−C single-bond distances.

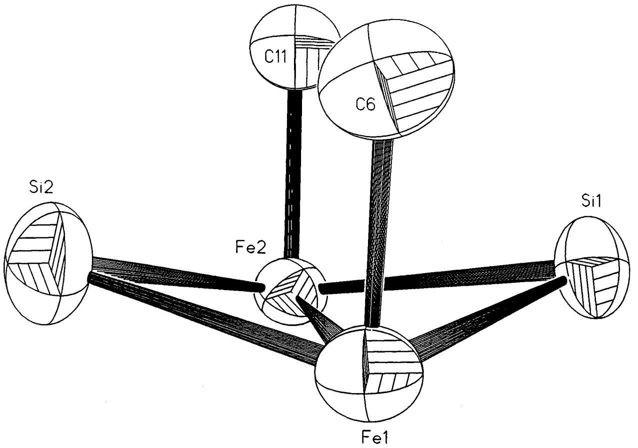
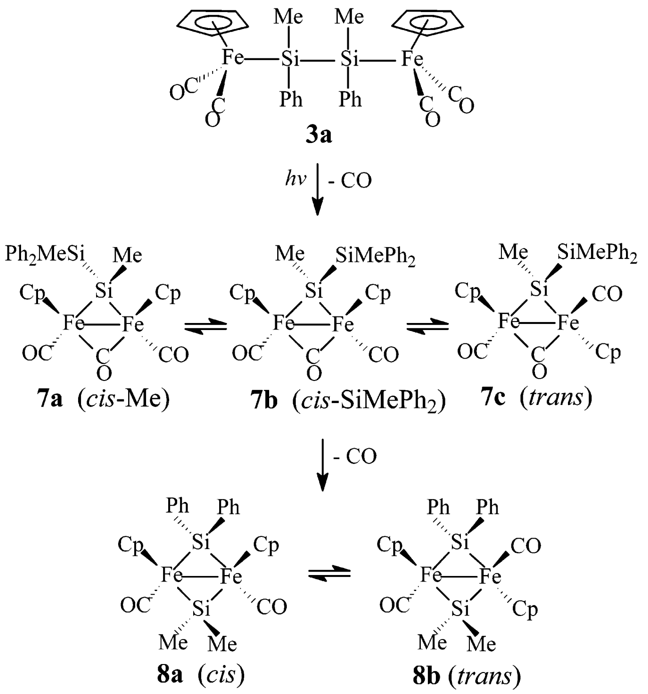


Figure 4. Butterfly structure of the bis(silylene)iron fragment of **6a**.

Scheme 3



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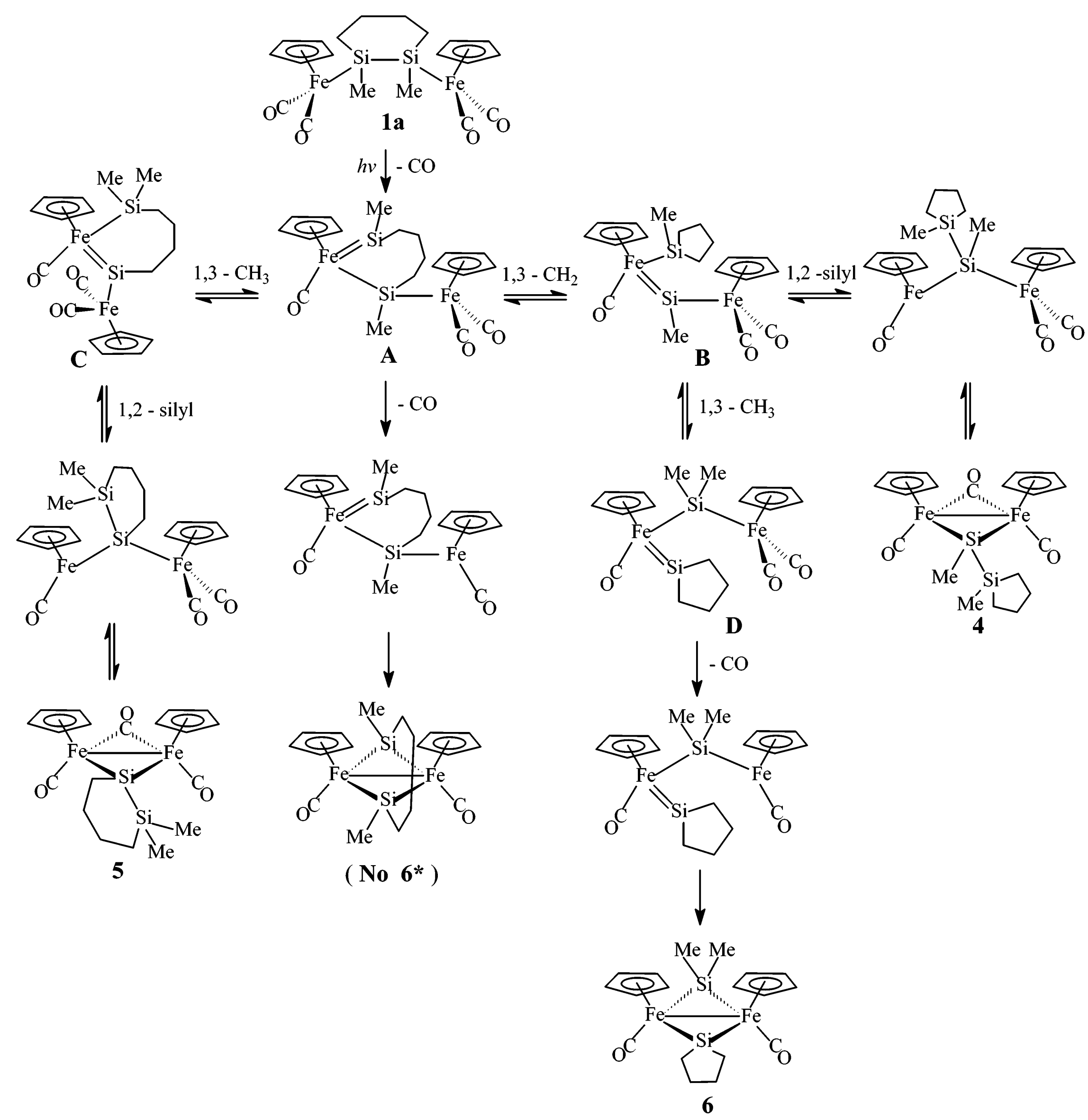
(17) (a) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843. (b) Tobita, H.; Kawano, Y.; Shimoi, M.; Ogino, H. *Chem. Lett.* **1987**, 2247. (c) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125. (d) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575.

Scheme 4



(2.270(1) and 2.272(1) Å) of the cis-H isomer of [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-SiHBu^t)].[17a] The Fe−Si−Fe angle (mean 74.37°) is the largest of this type (68.15−71.05°) reported to date.[10c,17] The two silylene ligands are arranged in a butterfly configuration with respect to the Fe−Fe bond (Figure 4), with a dihedral angle of 160°.

Photochemistry of FpMePhSiSiPhMeFp (3a and 3b). Separate irradiation of the two isomers **3a** and **3b** in sealed NMR tubes gave the same results, indicating that the photoreaction is not stereospecific. Irradiation of **3a** for 12 h led to the complete disappearance of **3a** and formation of **7** along with trace amounts of the cis and trans isomers of **8** (Scheme 3). The ^{29}Si NMR spectrum of the reaction mixture showed that **7** exists as a mixture of the three main isomers **7a**−**7c** formed via 1,3-phenyl migration and two minor isomers formed via 1,3-methyl migration. We could not unambiguously assign the ^{13}C and ^{1}H NMR data to the minor isomers. Prolonged irradiation resulted in the gradual decrease of **7** and increase of **8**. The spectra obtained after 70 h of irradiation showed the complete disappearance of **7** and the formation of **8**. These results are also analogous to those obtained in the photolysis of FpSiMe$_2$SiMe$_2$-Fp, but the phenyl replacement of methyl groups greatly slows down the photoreaction (12 h vs 2 h).

Both **7** and **8** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and high-resolution mass spectroscopy (HRMS). The ^{29}Si NMR resonances at −11.0, −9.91, −9.57, 221.5, 234.1, and 236.0 ppm are assigned to the three main geometrical isomers of **7**, in which the SiMePh$_2$ unit is attached to the bridging silicon atom. In the ^{1}H and ^{13}C NMR spectra of **7**, two completely different types of methyl resonances were observed, strongly suggesting that the three main isomers result from 1,3-phenyl migration (μ-SiMeSiMePh$_2$) rather than 1,3-methyl migration (μ-SiPhSiMe$_2$Ph). For complex **8**, four ^{29}Si resonances observed at 219.5, 228.2, 234.7, and 236.2 ppm are assigned to the different bridging silylene units in the cis and trans isomers. In the ^{13}C NMR spectrum of **8**, the bridging dimethylsilylene unit (μ-SiMe$_2$) exhibits three resonances. Two SiMe resonances of equal intensity observed at 15.4 and 18.8 ppm are assigned to the cis isomer (**8a**) with an approximate mirror about the center of the Fe−Fe bond, while the remaining resonance at 14.6 ppm is assigned to the trans isomer (**8b**) with a C_2 axis about the center of the Fe–Fe bond. A similar phenomenon was also observed in the ^{1}H NMR spectrum of **8**.

Mechanism. The results of the photochemistry of **1a** and **3** agree with the general mechanism we and the Ogino group have proposed with respect to the disilyldiiron system, $FpSiMe_2SiMe_2Fp$, and is illustrated in Scheme 4. However, since there are different silicon substituent groups in **1a** and **3**, different 1,3-migration products were observed. During the initial stage of photolysis of **1a** photoproducts **4** and **5** were formed simultaneously; i.e., no significant preference for 1,3-CH_2 or 1,3-CH_3 migration to form the intermediates C and B was noted. However, **4** did eventually photoisomerize to **5** prior to expulsion of the second CO group. We have not examined the relative amounts of **4** and **5** in the absence of irradiation and, since it has been noted that thermal equilibria and photostationary states of metal silylenes can be quite distinctive,[18] cannot determine the relative thermodynamic stabilities of these species. Since **6*** is a very strained molecule, only the isomer **6** was formed via both 1,3-CH_2 and 1,3-CH_3 migration (intermediate D).

In the photolysis of **3**, the predominant formation of the (μ-$SiMeSiMePh_2$) isomers strongly suggests that the aryl migration is much more favorable than the alkyl migration. Since the intermediate (η^5-C_5H_5)Fe(CO)(=$SiPh_2$)$SiMe_2$Fp (the equivalent of intermediate D in Scheme 4) where the $SiPh_2$ group replaces the (silacyclopentyl group) is more dominant than (η^5-C_5H_5)Fe(CO)(=SiPhMe)SiPhMeFp (equivalent of intermediate A), the isomer **8** was predominantly formed rather than **8***, the equivalent of **6***, where the phenyl groups replaces the CH_2 moiety in $(CH_2)_4$.[19]

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, TX.

Supporting Information Available: Listings of crystal data and data collection, solution, and refinement details, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **1a**, **5a**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030026+

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[18] Kawano, Y.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 499.

[19] For a more detailed discussion concerning the importance of the relative stabilities of the silylene intermediates, compared to their rate of trapping to form final products, see: Zhang, Y.; Pannell, K. H. *Organometallics* **2003**, *22*, 1766.