J. Am. Chem. Soc. **1990**, *112*, 3415–3420 3415

Photolysis of Alkoxy-Substituted Disilanyliron Complexes: Preparation of Donor-Stabilized Bis(silylene)iron Complexes and the Crystal Structure of $(\mathrm{Me_2Si})\overset{..}{=}[(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Fe(CO)}]\overset{..}{=}[\mathrm{SiMe(OMe)}]\text{- -}\mathrm{OMe}$

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Abstract: Photolysis of $\mathrm{Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2}$ (**2b**) ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5Me_5}$) afforded the novel donor-stabilized bis(silylene)iron complexes $(\mathrm{Me_2Si})\overset{..}{=}[\mathrm{Cp'Fe(CO)}]\overset{..}{=}[\mathrm{SiMe(OMe)}]\text{- -}\mathrm{OMe}$, **3b** and **3b′**, as a pair of geometrical isomers in ca. 2:1 ratio. The X-ray crystal structure of **3b** shows very short Fe–Si bonds (2.21 and 2.22 Å), fairly long Si–O(trivalent) bonds (1.79 and 1.80 Å), and an almost planar configuration of the iron atom and terminal methoxy or methyl groups at each silicon. The sp^2 character of the silicon atoms is further supported by the remarkable low-field chemical shifts of the ^{29}Si NMR signals of **3b** and **3b′** (δ 127.4, 121.1, 98.9, and 93.9 ppm). These structural and spectroscopic data indicate that the Fe–Si bonds take on partial double-bond character ["bis(silylene)iron" structure], while the Si–O(trivalent) bonds contain covalent and dative contributions. Photolysis of several other alkoxy-substituted disilanyliron complexes also afforded bis(silylene)iron complexes.

Silylene complexes have been proposed as reactive intermediates in a number of reactions,[1] but there is no report of the isolation of a genuine donor-free monomeric silylene complex. With regard to donor-stabilized silylene complexes, Schmid and Welz reported the first synthesis and spectroscopic characterization of this type of complex.[2] After that, in 1987, two groups reported the syntheses and crystal structures of donor-stabilized silylene complexes: $[(\mathrm{OC})_4\mathrm{Fe{=}Si(OBu^t)_2{\cdot}HMPA}]$[3] and $[\mathrm{Cp'(Me_3P)_2Ru{=}SiPh_2{\cdot}NCMe}](\mathrm{BPh_4})$.[4] Since then some additional donor-stabilized silylene complexes have been prepared.[4b,5]

Recently, we[6] reported the photochemical conversion of $\mathrm{CpFe(CO)_2SiR_2SiR_3}$ (R = alkyl) to $\mathrm{CpFe(CO)_2SiR_3}$, independently to Pannell,[7] who studied the photochemical conversion of $\mathrm{CpFe(CO)_2SiMe_2SiPh_3}$. The reaction was considered to proceed through silyl(silylene)iron intermediates. We therefore sought silicon atom substituents to stabilize them and finally found alkoxy substituents to be effective. This paper describes the photolysis of alkoxy-substituted disilanyliron complexes and an X-ray crystal structure of one of the products. A brief report on the photolysis of $\mathrm{Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2}$ has been published.[8]

Experimental Section

All manipulations were carried out under nitrogen or under vacuum. Reagent-grade tetrahydrofuran (THF), hexane, diethyl ether, and benzene were distilled under a nitrogen atmosphere from sodium-benzophenone ketyl immediately before use. Pentane, benzene-d_6, toluene, and toluene-d_8 were dried over a potassium mirror and transferred to reaction vessels under vacuum before use. Methanol was purified by distillation over $\mathrm{Mg(OMe)_2}$. Pyridine, 2-methyl-2-propanol (*tert*-butyl alcohol), sodium, and potassium were used as received. Potassium *tert*-butoxide,[9] 1,2-dichlorotetramethyldisilane,[10] 1,1,2-trichlorotrimethyldisilane,[11] 1,1-dichlorotetramethyldisilane,[12] $\mathrm{Na[CpFe(CO)_2]}$,[13] $\mathrm{K[Cp'Fe(CO)_2]}$,[14] and $\mathrm{Na[Cp'Fe(CO)_2]}$[14] were prepared according to standard procedures. IR spectra were recorded on a Jasco IR-810 spectrophotometer. Solution samples were analyzed by use of 0.1 mm path length solution cells with sodium chloride windows, and neat samples with sodium chloride plates. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-90Q and Varian XL-200 Fourier transform spectrometers at 25 °C. ^{29}Si NMR spectra were obtained on the JEOL FX-90Q spectrometer. Mass spectra and high-resolution mass spectra were recorded with a JEOL JMS-D300 mass spectrometer.

Preparations. $\mathrm{Cp'Fe(CO)_2SiMe_2SiMe_2Cl}$ (1a). A solution of $\mathrm{K[Cp'Fe(CO)_2]}$ (12 mmol) in 30 mL of THF was slowly added to a solution of $\mathrm{ClMe_2SiSiMe_2Cl}$ (10 mmol) in 30 mL of THF with vigorous stirring at room temperature. The reaction mixture was stirred for 18 h. The volatile materials in the mixture were removed under reduced pressure. The solid brown-purple residue was extracted with three 15-mL portions of hexane. The extracts were combined, filtered through a Celite pad, and evaporated to dryness under vacuum. The resulting red-purple powders were purified by molecular distillation under high vacuum [120 °C (0.01 mmHg)]. Final distillation under high vacuum gave orange crystals of **1a**: yield 2.4 g (51%); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.47 (s, 15 H, Cp′), 0.68 (s, 6 H, Me), 0.64 (s, 6 H, Me); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 217.4 (CO), 95.3 ($\mathit{C}_5\mathrm{Me_5}$), 10.0 ($\mathrm{C_5(\mathit{C}H_3)_5}$), 4.3 (Me), 2.4 (Me); ^{29}Si NMR ($\mathrm{C_6D_6}$) δ 29.8, 15.6. Anal. Calcd for $\mathrm{C_{16}H_{27}ClFeO_2Si_2}$: C, 48.18; H, 6.82. Found: C, 48.28; H, 6.92.

$\mathrm{Cp'Fe(CO)_2SiMe_2SiMeCl_2}$ (1b). The preparative procedure of **1b** was similar to that of **1a** except in the following: (i) $\mathrm{Na[Cp'Fe(CO)_2]}$ was used instead of $\mathrm{K[Cp'Fe(CO)_2]}$, (ii) $\mathrm{Cl_2MeSiSiMe_2Cl}$ containing a small amount of $\mathrm{ClMe_2SiSiMe_2Cl}$ as an impurity was used instead of $\mathrm{ClMe_2SiSiMe_2Cl}$. A mixture (3.2 g) of **1b** (main product), **1a**, and $\mathrm{Cp'Fe(CO)_2SiMe(Cl)SiMe_2Cl}$ was obtained by the reaction between $\mathrm{Na[Cp'Fe(CO)_2]}$ (12 mmol) and the impure $\mathrm{Cl_2MeSiSiMe_2Cl}$ (2.6 g). The mixture was purified by molecular distillation. The content of **1b** in the mixture was found to be ~64% on the basis of its ^{1}H NMR spectrum. This mixture was used for the preparation of **2b** without further purification. Spectral data for **1b** are as follows: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.45 (s, 15 H, Cp′), 0.94 (s, 3 H, Me), 0.66 (s, 6 H, Me); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 216.6 (CO), 95.7 ($\mathit{C}_5\mathrm{Me_5}$), 10.0 ($\mathrm{C_5(\mathit{C}H_3)_5}$), 9.1 (Me), 2.5 (Me); ^{29}Si NMR ($\mathrm{C_6D_6}$) δ 39.9, 22.0. Anal. Calcd for $\mathrm{C_{15}H_{24}Cl_2FeO_2Si_2}$: C, 42.97; H, 5.77. Found for the mixture: C, 42.88; H, 5.88.

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(1) (a) Ojima, I.; Inaba, S.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7. (b) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (c) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Ibid.* **1977**, *99*, 3879. (d) Nakadaira, Y.; Kobayashi, T.; Sakurai, H. *J. Organomet. Chem.* **1979**, *165*, 399. (e) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Ibid.* **1980**, *184*, 13. (f) Thum, G.; Malisch, W. *Ibid.* **1984**, *264*, C5. (g) Kang, H.; Jacobson, D. B.; Shin, S. K.; Beauchamp, J. L.; Bowere, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 5668.

(2) Schmid, G.; Welz, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 785.

(3) (a) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (b) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368.

(4) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872.

(5) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203.

(6) (a) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (b) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797.

(7) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056.

(8) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092.

(9) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons, Inc.: New York, 1967; Vol. 1, p 686.

(10) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493.

(11) Sakurai, H.; Watanabe, T.; Kumada, M. *J. Organomet. Chem.* **1967**, *7*, 15.

(12) Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. *J. Organomet. Chem.* **1972**, *43*, 293.

(13) King, R. B.; Pannell, K. H.; Bannett, C. R.; Ishaq, M. *J. Organomet. Chem.* **1969**, *19*, 327.

(14) Cathelin, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

0002-7863/90/1512-3415\$02.50/0

$CpFe(CO)_2SiMe_2SiMe_2Cl$ (1c). A solution of $Na[CpFe(CO)_2]$ (32 mmol) in 100 mL of THF was added dropwise to a solution of 1,2-dichlorotetramethyldisilane (6.1 g, 32 mmol) in 200 mL of THF with vigorous stirring at room temperature. After stirring for an additional 15 h, the volatile materials were removed from the reaction mixture under vacuum. The brown residue was extracted with three 15-mL portions of hexane. The combined extracts were filtered through a Celite pad and concentrated under reduced pressure. The residue was purified by molecular distillation [75 °C (0.02 mmHg)] to give orange crystals of **1c**: yield 7.54 g (72%); ^1H NMR (C_6D_6) δ 4.17 (s, 5 H, Cp), 0.52 (s, 6 H, Me), 0.49 (s, 6 H, Me); ^{13}C NMR (C_6D_6) δ 215.0 (CO), 83.3 (Cp), 3.5 (Me), 2.9 (Me); ^{29}Si NMR (C_6D_6) δ 28.8, 17.3. Anal. Calcd for $C_{11}H_{17}ClFeSi_2O_2$: C, 40.19; H, 5.21. Found: C, 40.55; H, 5.31.

$CpFe(CO)_2SiMe_2SiMeCl_2$ (1d). The complex **1d** was prepared by the reaction between 32 mmol of $Na[CpFe(CO)_2]$ and 31 mmol of $ClMe_2SiSiMeCl_2$ in THF. The purification procedure was the same as that of **1c**. **1d**: yield 6.31 g (57%); ^1H NMR (C_6D_6) δ 4.17 (s, 5 H, Cp), 0.76 (s, 3 H, Me), 0.55 (s, 6 H, Me); ^{13}C NMR (C_6D_6) δ 214.2 (CO), 83.6 (Cp), 7.9 (Me), 2.7 (Me); ^{29}Si NMR (C_6D_6) δ 37.8, 22.6.

$CpFe(CO)_2Si(Cl)MeSiMe_3$ (1f). This complex was prepared by the reaction between 16 mmol of $Na[CpFe(CO)_2]$ and 15 mmol of $Cl_2MeSiSiMe_3$ in THF. After the same purification procedure as that of **1c**, orange crystals of **1f** was obtained in 57% yield: ^1H NMR (C_6D_6) δ 4.13 (s, 5 H, Cp), 0.96 (s, 3 H, Me), 0.25 (s, 9 H, Me); ^{13}C NMR (C_6D_6) δ 214.3 (CO), 213.8 (CO), 84.2 (Cp), 9.3 (Me), −1.3 (Me); ^{29}Si NMR (C_6D_6) δ 80.6, −9.1. Anal. Calcd for $C_{11}H_{17}ClFeO_2Si_2$: C, 40.19; H, 5.21. Found: C, 38.69; H, 5.12.

$Cp'Fe(CO)_2SiMe_2SiMe_2OMe$ (2a). To 30 mL of methanol containing 0.4 mL of pyridine was added 0.60 g of solid **1a** with vigorous stirring. After additional stirring for 45 min, volatile materials were evaporated under reduced pressure. The residue was extracted with two 10-mL portions of benzene and then with 20 mL of hexane. The extracts were combined and filtered through a Celite pad and the solvent was removed from the filtrate under vacuum. Molecular distillation of the orange residue [90 °C (0.01 mmHg)] gave orange crystals of **2a**. Yield 0.43 g (73%). The spectral data are listed in Table I. Anal. Calcd for $C_{17}H_{30}FeO_3Si_2$: C, 51.77; H, 7.67. Found: C, 52.34; H, 7.62.

$Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2$ (2b). To a methanol solution of a mixture (1.0 g) of **1b**, **1a**, and $Cp'Fe(CO)_2SiMe(Cl)SiMe_2Cl$ (see the preparation of **1b**) was added 3 equiv of pyridine dropwise with vigorous stirring. After stirring for 30 min, the solvent was evaporated under reduced pressure. The orange-brown residue was extracted with two 20-mL portions of hexane. The combined extracts were filtered through a Celite pad and evaporated to dryness under reduced pressure. Molecular distillation of the residue yielded orange crystals of a mixture of **2b**, **2a**, and $Cp'Fe(CO)_2SiMe(OMe)SiMe_2(OMe)$. Pure **2b** was obtained after chromatography through a column of silica gel (40 g). Benzene eluted **2b** as the first yellow band. Yield 0.50 g (51%). The spectral data of **2b** are listed in Table I. Anal. Calcd for $C_{17}H_{30}FeO_4Si_2$: C, 49.75; H, 7.37. Found: C, 49.74; H, 7.35.

$Cp'Fe(CO)_2SiMe_2SiMe_2OBu^t$ (2c). To a THF solution (40 mL) of $KOBu^t$ (3 mmol) were added orange crystals of **1a** (0.82 g, 2.1 mmol). After vigorous stirring for 20 h at room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with two 20-mL portions of hexane. The combined extracts were filtered through a pad of Celite and alumina (3:1) mixture, and the solvent was removed from the filtrate in vacuo. Orange crystals of **2c** were obtained by molecular distillation [100 °C (0.02 mmHg)] of the residue. Yield 0.44 g (48%). Anal. Calcd for $C_{20}H_{36}FeO_3Si_2$: C, 55.03; H, 8.31. Found: C, 55.18; H, 8.50. The spectral data are listed in Table I.

$CpFe(CO)_2SiMe_2SiMe_2OBu^t$ (2d). The preparative procedure of **2d** was almost identical with that of **2c** except for the use of **1c** instead of **1a**. Orange crystals of **2d** were obtained from the reaction between **1c** (9.7 mmol) and $KOBu^t$ (32 mmol). Yield 1.8 g (51%). Anal. Calcd for $C_{15}H_{26}FeO_3Si_2$: C, 49.17; H, 7.15. Found: C, 49.43; H, 7.17. The spectral data are listed in Table I.

$CpFe(CO)_2SiMe_2SiMe(OBu^t)_2$ (2e). **2e** was obtained as an orange liquid according to a preparative procedure similar to that for **2c** by using 17 mmol of $KOBu^t$ and 2.35 g (6.73 mmol) of **1d**. Yield 1.6 g (55%). Anal. Calcd for $C_{18}H32FeO_4Si_2$: C, 50.93; H, 7.60. Found: C, 50.72; H, 7.88. The spectral data are listed in Table I.

$CpFe(CO)_2Si(OMe)MeSiMe_3$ (2f). The preparative procedure for **2f** was similar to that for **2a**. **2f** was obtained as an orange liquid from **1f**, MeOH, and pyridine in 51% yield. Anal. Calcd for $C_{12}H_{20}FeO_3Si_2$: C, 44.44; H, 6.21. Found: C, 43.94; H, 5.93. The spectral data are listed in Table I.

Photolytic Procedure. Unless otherwise stated, photolysis of the alkoxy-substituted disilanyliron complexes were carried out as follows: An alkoxy-substituted disilanyliron complex, **2a**, **2b**, **2c**, **2d**, **2e**, or **2f**, was placed in a Pyrex NMR sample tube (5-mm o.d., 3-mm i.d.), and the tube was connected to a vacuum line via a ground-glass joint. The complex was dissolved in C_6D_6, transferred by the conventional trap-to-trap method. The sample tube was then flame-sealed under vacuum. Irradiation was carried out externally at room temperature with a 450-W medium-pressure Hg arc lamp (Ushio UV-450) placed in a water-cooled quartz jacket. The sample tube was immersed in water during the irradiation. The distance from the lamp to the sample tube was ~4 cm.

Determination of CO Generated during Photolysis of 2d. Evolution of a gas was observed during photolysis of all the alkoxy-substituted disilanyliron complexes. Identification and determination of the gas were carried out for the photolysis of **2d**. The gas was identified as carbon monoxide by its IR spectrum. The quantity of the generated gas was measured with a Toepler pump connected to a vacuum line. The decrease in concentration of **2d** during photolysis was monitored by use of ^1H NMR spectroscopy. The molar ratio of the generated CO to the consumed **2d** was 1.1:1.0.

Photolysis of 2a and Isolation of Its Product 3a. A Pyrex tube (10-mm o.d.) with a Teflon vacuum stopcock was charged with 0.1 g of **2a** and 5 mL of pentane. The solution was degassed on a vacuum line and then irradiated for 30 min. The volume of the solution was reduced to 1 mL. Cooling (−20 °C) the concentrated solution gave yellow plates of **3a**: mass spectrum (relative intensity) (10 eV) *m/e* 366 (12.2, M^+), 327 (23.6), 326 (100), 248 (10.3), 163 (12.0), 137 (10.7), 136 (93.9), 135 (33.8), 134 (47.9); exact mass calcd for $C_{16}H_{30}FeO_2Si_2$ (M^+) 366.1134, found 366.1136.

Photolysis of 2b and Isolation of Its Product 3b. Photolysis of a solution of **2b** gave a mixture of **3b** and its geometric isomer **3b′**. One of these products, **3b**, was isolated as yellow crystals as follows: A Pyrex tube (10-mm o.d.) with a Teflon vacuum stopcock was charged with 0.2 g of **2b** and 4 mL of toluene. The solution was subjected to three freeze–pump–thaw cycles and irradiated for 20 min. The solvent was evaporated under high vacuum. Cooling (−20 °C) the resultant dark-brown oil afforded yellow crystals of **3b**. Some of these crystals were used for the X-ray crystal structure analysis (see below): mass spectrum (20 eV) *m/e* (relative intensity) 382 (100, M^+), 354 (34.7), 326 (29.1), 264 (91.5), 190 (71.2), 105 (45.7); exact mass calcd for $C_{16}H_{30}FeO_3Si_2$ (M^+) 382.1083, found 382.1086.

X-ray Crystal Structure Determination of 3b. Crystals of **3b** suitable for X-ray structure analysis were obtained by cooling (−20 °C) the concentrated reaction mixture of **3b** in toluene. The crystals were mounted in thin glass capillaries in a glovebox under nitrogen, and the capillaries were flame sealed.

Intensity data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 15 °C. Crystallographic parameters are listed in Table II. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method using individual anisotropic thermal parameters. None of the hydrogen atoms was found. Determination of the absolute configuration was carried out by refinement with anomalous dispersion parameters. As a result of the refinement, the structure drawn in Figure 2 was slightly more favored (R = 0.0753) than that with inverse chirality (R = 0.0754). The final R value was 0.076 and the weighted R_w was 0.114.

All the calculations were performed on a Nippon Electric Co. ACOS-2020 computer system at the computer center of Tohoku University, using the local version of the Universal Crystallographic Computation Program (UNICS III).

Results and Discussion

Photolysis of 2b. Irradiation of a C_6D_6 solution of $Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2$ (**2b**) resulted in the formation of extremely air- and moisture-sensitive products with CO evolution. A ^{29}Si NMR spectrum for the reaction mixture shows four signals at remarkably low field (δ 127.4, 121.1, 98.9, and 93.9 ppm)[15] with ca. 1:2:2:1 intensity (Figure 1). This finding, as well as ^1H NMR, ^{13}C NMR, and MS data, suggests that there are two products in the ratio of about 2:1, and that they are a pair of geometrical isomers, **3b** and **3b′** (eq 1). **3b** was further characterized by an X-ray crystal structure analysis. The following observation was also made: X-ray measurements upon crystals obtained from the mixture of **3b** and **3b′** revealed that the crystals were all composed of pure **3b**, i.e., resolution occurs upon crystallization. The crystals were then dissolved in C_6D_6 and the ^1H NMR spectrum of the solution was measured. The spectrum was

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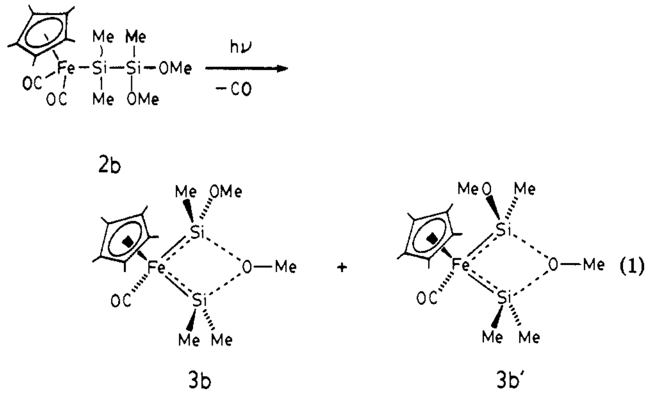
[15] A typographical error appears in our previous paper,[8] p 4093, column 1, line 39. The ^{29}Si NMR datum of the complex, 101.9 ppm, should read 98.9 ppm.



the same as that obtained after the photolysis of a C_6D_6 solution of **2b**. This observation indicates that, when **3b** is dissolved in C_6D_6, a rapid equilibration between **3b** and **3b′** is attained.

When a toluene solution of a reaction mixture containng **3b** and **3b′** was concentrated and cooled to −20 °C, yellow crystals of **3b** suitable for X-ray crystal structure analysis were obtained. Interatomic distances and angles are listed in Tables III and IV, respectively. Figure 2 shows an ORTEP view and the numbering scheme of **3b**. The Fe–Si bond lengths [2.207 (3) and 2.222 (3) Å] are very short among the known Fe–Si bond distances, the former being the shortest yet observed.[16] In contrast, the bond lengths between each silicon and the trivalent oxygen O(2) [1.793 (9) and 1.799 (8) Å] are much longer than normal Si–O single bonds, e.g., Si(2)–O(3) [1.632 (9) Å], and are even longer than those of dative Si–O(HMPA) bonds in the donor-stabilized silylene transition-metal complexes, $[(OC)_4Fe{=}Si(OBu^t)_2{\cdot}HMPA]$ [1.730 (3) Å],[3] $[(OC)_4Fe{=}SiMe_2{\cdot}HMPA]$ [1.731 (4) and 1.736 (4) Å for two crystallographically independent molecules],[5] and $[(OC)_5Cr{=}Si(OBu^t)_2{\cdot}HMPA]$ [1.736 (2) Å].[3] The geometries of each silicon atom and the three atoms attached directly to the silicon atom except O(2) are almost coplanar: Si(1) and Si(2) lie only 0.32 and 0.30 Å above the planes defined by Fe, C(5), and C(6) and Fe, O(3), and C(4), respectively. The arrangement of O(2), Si(1), Si(2), and C(2) is also planar: O(2) lies 0.14 Å above the plane defined by Si(1), Si(2), and C(2). The Fe–Si(1)–O(2)–Si(2) frame is not planar but significantly bent: dihedral angles between the planes defined by Si(1), Fe, and Si(2) and Si(1), O(2), and Si(2) and the planes defined by Fe, Si(1), and O(2) and Fe, Si(2), and O(2) are 158.8 and 156.9°, respectively.

From these structural features, we propose bonding model A in Chart I for **3b**. This bonding model A shows that the two Fe–Si bonds take on partial double-bond character, while each Si–O(trivalent) bond is a mixture of dative and covalent bonding. By use of classical bonding description, model A could be described as a combination of two resonance forms B and C. The sp^2 character of the silicon atoms is further supported by the ^{29}Si NMR data (Figure 1): the chemical shifts for **3b** (δ 121.1 and 98.9 ppm) and **3b′** (δ 127.4 and 93.9 ppm) are comparable to those for the species containing sp^2 silicon atoms, e.g., silenes (Si=C) and disilenes (Si=Si).[17]

The ^{1}H NMR signals assigned to the bridging methoxy groups for **3b** and **3b′** appear at significantly high field (δ 2.89 and 2.82 ppm, respectively) compared to those of the terminal methoxy groups for **3b** and **3b′** (δ 3.70 and 3.37 ppm, respectively) and that for the starting material **2b** (δ 3.50 ppm). This observation suggests the existence of high electron density on the bridged methoxy group. However, charge separation over the whole molecule appears slight since **3b** and **3b′** are very soluble in typical nonpolar organic solvents.

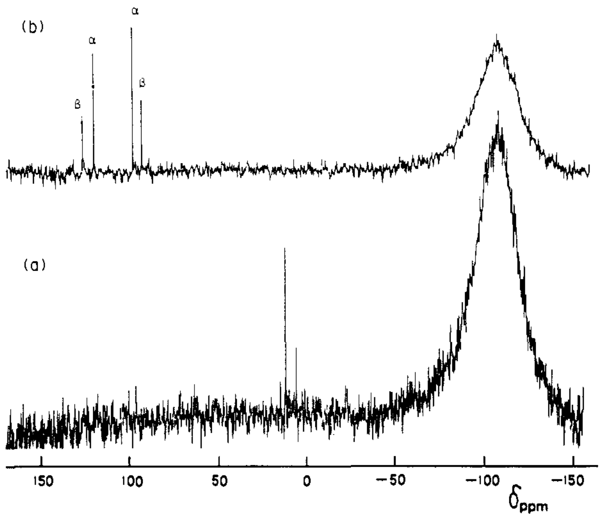


Figure 1. ^{29}Si NMR spectral change upon photolysis of **2b** in C_6D_6: (a) before irradiation; (b) after 30-min irradiation. The signals with α and β are assigned to **3b** and **3b′**, respectively. The broad signal at ∼−100 ppm is attributable to the Pyrex glass of the NMR sample tube.

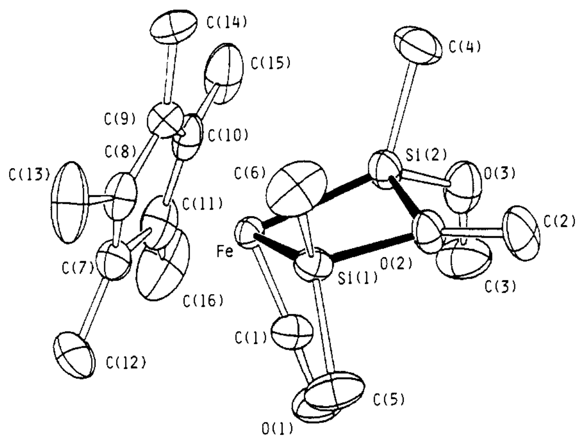
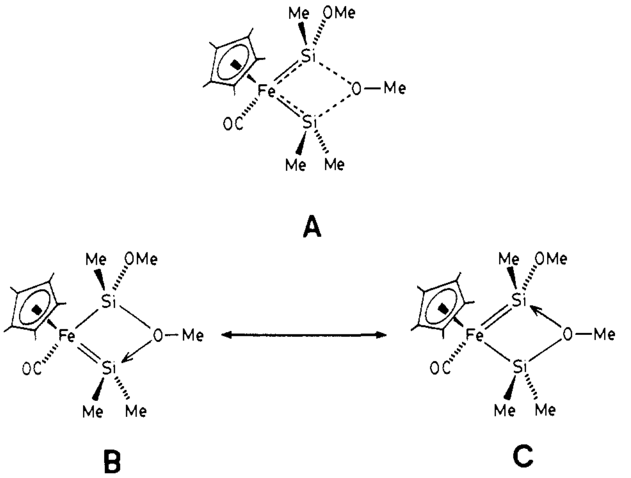


Figure 2. ORTEP view and numbering scheme of **3b**.

Chart I



The CO stretching frequency for the terminal carbonyl ligand of **3b** (and also **3b′**) (1875 cm^{-1}) is appreciably lower than those of the starting material **2b** (1920 and 1972 cm^{-1}) and that of a structurally similar complex $CpFeH(CO)(SiCl_3)_2$ (2025 cm^{-1}).[18] This finding indicates a strong back-donation from iron to the carbonyl ligand. The strong back-donation is also reflected in the short Fe–C(1) bond (1.68 Å) and the long C(1)–O(1) bond (1.20 Å) compared to those of $CpFeH(CO)(SiCl_3)_2$ (1.75 and 1.13 Å, respectively).[19]

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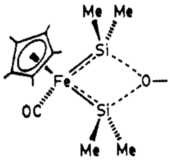
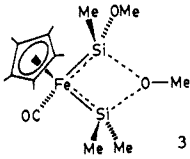
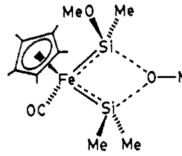
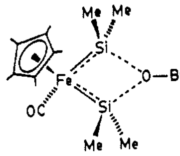
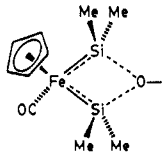
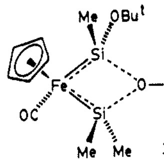
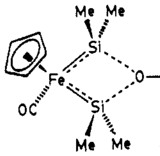
(16) To our knowledge, the previous shortest Fe–Si distance ever determined is 2.22 Å for $(Et_4N)[Fe(SiCl_3)(CO)_4]$: Jansen, P. R.; Oskam, A.; Olie, K. *Cryst. Struct. Commun.* **1975**, *4*, 667. Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1.

(17) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(18) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

Table I. The ^1H, ^{13}C, ^{29}Si NMR and IR Data of Alkoxy-Substituted Disilanyliron Complexes and Their Photolysis Products

compound	^1H NMR (C_6D_6), δ/ppm	^{13}C NMR (C_6D_6), δ/ppm	^{29}Si NMR (C_6D_6), δ/ppm	IR (C_6D_6), ν_{CO}/cm^{-1}
$Cp'Fe(CO)_2SiMe_2SiMe_2OMe$ (**2a**)	3.33 (s, 3 H, OMe), 1.61 (s, 15 H, Cp′), 0.63 (s, 6 H, Me), 0.41 (s, 6 H, Me)	217.9 (CO), 95.2 (C_5Me$_5$), 50.1 (OMe), 9.9 (C$_5$*Me*$_5$), 3.1 (Me), −0.4 (Me)	21.2, 12.3	1970, 1918
$Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2$ (**2b**)	3.50 (s, 6 H, OMe), 1.62 (s, 15 H, Cp′), 0.72 (s, 6 H, Me), 0.41 (s, 3 H, Me)	217.8 (CO), 95.2 (C_5Me$_5$), 50.1 (OMe), 9.8 (Me), 3.5 (Me), −2.2 (Me)	10.7, 4.6	1972, 1920
$Cp'Fe(CO)_2SiMe_2SiMe_2OBu^t$ (**2c**)	1.64 (s, 15 H, Cp′), 1.27 (s, 9 H, Bu^t), 0.63 (s, 6 H, Me), 0.52 (s, 6 H, Me)	218.1 (CO), 95.0 (C_5Me$_5$), 73.5 (*C*Me$_3$), 32.4 (C*Me*$_3$), 10.2 (Me), 4.0 (Me), 3.1 (Me)	13.0, 10.2	1975, 1920
$CpFe(CO)_2SiMe_2SiMe_2OBu^t$ (**2d**)	4.41 (s, 5 H, Cp), 1.17 (s, 9 H, Bu^t), 0.57 (s, 6 H, Me), 0.39 (s, 6 H, Me)	215.8 (CO), 83.4 (Cp), 73.6 (*C*Me$_3$), 32.5 (C*Me*$_3$), 3.4 (Me), 2.9 (Me)	14.1, 7.8	1990, 1938
$CpFe(CO)_2SiMe_2SiMe(OBu^t)_2$ (**2e**)	4.50 (s, 5 H, Cp), 1.30 (s, 18 H, Bu^t), 0.64 (s, 6 H, Me), 0.44 (s, 3 H, Me)	216.3 (CO), 83.5 (Cp), 73.2 (*C*Me$_3$), 32.5 (C*Me*$_3$), 5.2 (Me), 3.5 (Me)	11.2, −15.7	1988, 1930
$CpFe(CO)_2Si(OMe)MeSiMe_3$ (**2f**)	4.23 (s, 5 H, Cp), 3.37 (s, 3 H, OMe), 0.79 (s, 3 H, Me), 0.26 (s, 9 H, Me)	216.0 (CO), 215.1 (CO), 83.4 (Cp), 51.9 (OMe), 5.3 (Me), −0.3 (Me)	68.7, −14.3	1990, 1935
 3a	2.67 (s, 3 H, OMe), 1.83 (s, 15 H, Cp′), 0.54 (s, 6 H, Me), 0.42 (s, 6 H, Me)	220.4 (CO), 89.6 (C_5Me$_5$), 50.9 (OMe), 11.6 (Me), 7.2 (Me), 5.4 (Me)	125.2	1870
 3b +  3b′	3.70 (s, 3 H, OMe, **3b**), 3.37 (s, 3 H, OMe, **3b′**), 2.89 (s, 3 H, OMe, **3b**), 2.82 (s, 3 H, OMe, **3b′**), 1.90 (s, 15 H, Cp′, **3b′**), 1.82 (s, 15 H, Cp′, **3b**), 0.57 (s, 3 H, Me, **3b**), 0.57 (s, 3 H, Me, **3b′**), 0.55 (s, 3 H, Me, **3b′**), 0.47 (s, 3 H, Me, **3b′**), 0.43 (s, 3 H, Me, **3b**), 0.38 (s, 3 H, Me, **3b**)	221.0 (CO, **3b**), 220.0 (CO, **3b′**), 90.0 (C_5Me$_5$, **3b′**), 89.8 (C_5Me$_5$, **3b**), 51.9 (OMe), 51.8 (OMe), 51.0 (OMe), 11.6 (Me), 9.9 (Me), 7.3 (Me), 6.5 (Me), 5.8 (Me), 5.2 (Me), 3.3 (Me)	127.4 (**3b′**), 121.1 (**3b**), 98.9 (**3b**), 93.9 (**3b′**)	1875
 3c	1.85 (s, 15 H, Cp′), 1.07 (s, 9 H, Bu^t), 0.82 (s, 6 H, Me), 0.68 (s, 6 H, Me)	219.9 (CO), 89.4 (C_5Me$_5$), 87.7 (*C*Me$_3$), 30.6 (C*Me*$_3$), 12.0 (Me), 11.5 (Me), 9.5 (Me)	126.2	1870
 3d	4.24 (s, 5 H, Cp), 0.99 (s, 9 H, Bu^t), 0.89 (s, 6 H, Me), 0.53 (s, 6 H, Me)	218.3 (CO), 88.8 (*C*Me$_3$), 77.9 (Cp), 30.6 (C*Me*$_3$), 12.0 (Me), 11.7 (Me)	122.3	1882
 3e	4.23 (s, 5 H, Cp), 1.46 (s, 9 H, Bu^t), 1.28 (s, 9 H, Bu^t), 0.97 (s, 3 H, Me), 0.58 (s, 3 H, Me), 0.54 (s, 3 H, Me)	218.2 (CO), 89.7 (*C*Me$_3$), 78.3 (Cp), 73.2 (*C*Me$_3$), 32.4 (C*Me*$_3$), 30.4 (C*Me*$_3$), 15.2 (Me), 11.3 (Me), 11.2 (Me)	121.6, 89.6	1884
 3f	4.22 (s, 5 H, Cp), 2.66 (s, 3 H, OMe), 0.60 (s, 6 H, Me), 0.31 (s, 6 H, Me)	218.7 (CO), 77.7 (Cp), 51.8 (OMe), 7.4 (Me), 6.7 (Me)	123.7	1882

The photoinduced formation of **3b** and **3b′** from **2b** may be explained by three successive reactions (Scheme I). The mechanism is essentially the same as that proposed previously for the photochemical conversion reaction of disilanyliron complexes to monosilyl complexes[6,7] except for the final step, namely: (i) photochemically induced loss of CO to generate a coordinatively unsaturated complex D; (ii) 1,2-shift of the terminal dimethoxymethylsilyl group to the Fe atom to form a silyl(silyene)iron intermediate E; and (iii) coordination of one of the methoxy oxygens to the silylene ligand, which leads to the formation of the donor-stabilized bis(silylene)iron complexes, **3b** and **3b′**. The last cyclization step (iii) seems to be reversible since **3b** readily isomerizes to **3b′** at room temperature.

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(19) Manojlovic-Muir, L.; Muir, K.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 447.

Table II. Crystal Data for **3b**

formula	$C_{16}H_{30}FeO_3Si_2$
fw	382.43
cryst system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
syst absence	$(h00)$: $h = 2n$ $(0k0)$: $k = 2n$ $(00l)$: $l = 2n$
a/Å	10.547 (2)
b/Å	21.932 (4)
c/Å	8.742 (3)
V/Å^3	2022.2 (8)
Z	4
d_{calcd}/g cm^{-3}	1.26
μ/cm^{-1}	8.69
cryst size/mm	0.5 × 0.3 × 0.2
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
temp/°C	15
reflcn measd	$-h,+k,+l$
2θ range/deg	3–60
scan mode	ω–2θ
ω scan width/deg	$1.0 + 0.35 \tan\theta$
bkgd (count time)/s	7.0
ω scan rate/deg mm^{-1}	4.0
max scan times	3
no. of unique data	3488
no. of data used with $\|F_o\| > 3\sigma(\|F_o\|)$	1900
no. of params refined	200
R^a	0.076
$R_w{}^b$	0.114
quality of fit indicator^c	0.82
largest shift/esd, final cycle	0.09
max resid electron dens/e Å^{-3}	0.84 (0.85 Å from Fe atom)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sum^2(|F_o|) + aF_o{}^2]^{-1}$, where $a = 0.015$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameter})]^{1/2}$.

Table III. Interatomic Distances (Å) for **3b**

Fe–Si(1)	2.222 (3)	Fe–Si(2)	2.207 (3)
Fe–C(1)	1.676 (11)	C(1)–O(1)	1.198 (14)
Si(1)–O(2)	1.793 (9)	Si(2)–O(2)	1.799 (8)
Si(1)–C(5)	1.88 (2)	Si(2)–O(3)	1.632 (9)
Si(1)–C(6)	1.88 (2)	Si(2)–C(4)	1.94 (2)
O(2)–C(2)	1.45 (2)	O(3)–C(3)	1.41 (2)
Fe–C(7)	2.108 (13)	Fe–C(8)	2.082 (11)
Fe–C(9)	2.079 (12)	Fe–C(10)	2.094 (12)
Fe–C(11)	2.073 (11)		
C(7)–C(8)	1.38 (2)	C(8)–C(9)	1.39 (2)
C(9)–C(10)	1.42 (2)	C(10)–C(11)	1.40 (2)
C(11)–C(7)	1.47 (2)	C(7)–C(12)	1.52 (2)
C(8)–C(13)	1.50 (2)	C(9)–C(14)	1.53 (2)
C(10)–C(15)	1.50 (2)	C(11)–C(16)	1.52 (2)
Fe···O(2)	2.962 (7)	Si(1)···Si(2)	2.622 (4)
O(1)···C(3)	3.33 (2)	C(4)···C(14)	3.59 (2)
C(6)···C(13)	3.54 (2)		

Table IV. Bond Angles (deg) for **3b**

Si(1)–Fe–Si(2)	72.60 (11)	Si(1)–Fe–C(1)	84.9 (4)
Si(2)–Fe–C(1)	91.7 (4)		
Fe–Si(1)–O(2)	94.5 (3)	Fe–Si(1)–C(5)	123.1 (5)
Fe–Si(1)–C(6)	123.6 (6)	O(2)–Si(1)–C(5)	101.5 (6)
O(2)–Si(1)–C(6)	102.2 (6)	C(5)–Si(1)–C(6)	105.8 (7)
Fe–Si(2)–O(2)	94.8 (3)	Fe–Si(2)–O(3)	126.9 (4)
Fe–Si(2)–C(4)	127.2 (5)	O(2)–Si(2)–O(3)	103.1 (4)
O(2)–Si(2)–C(4)	100.0 (5)	O(3)–Si(2)–C(4)	98.5 (6)
Si(1)–O(2)–Si(2)	93.8 (4)	Si(1)–O(2)–C(2)	131.6 (7)
Si(2)–O(2)–C(2)	132.4 (8)		
Fe–C(1)–O(1)	177 (1)		
C(11)–C(7)–C(8)	107 (1)	C(7)–C(8)–C(9)	110 (1)
C(8)–C(9)–C(10)	109 (1)	C(9)–C(10)–C(11)	108 (1)
C(10)–C(11)–C(7)	107 (1)		
C(8)–C(7)–C(12)	128 (1)	C(11)–C(7)–C(12)	125 (1)
C(7)–C(8)–C(13)	124 (1)	C(9)–C(8)–C(13)	126 (1)
C(8)–C(9)–C(14)	125 (1)	C(10)–C(9)–C(14)	126 (1)
C(9)–C(10)–C(15)	127 (1)	C(11)–C(10)–C(15)	125 (1)
C(10)–C(11)–C(16)	127 (1)	C(7)–C(11)–C(16)	125 (1)

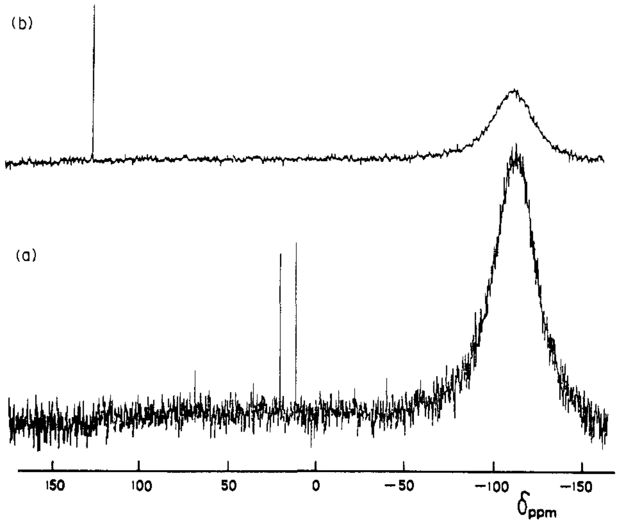
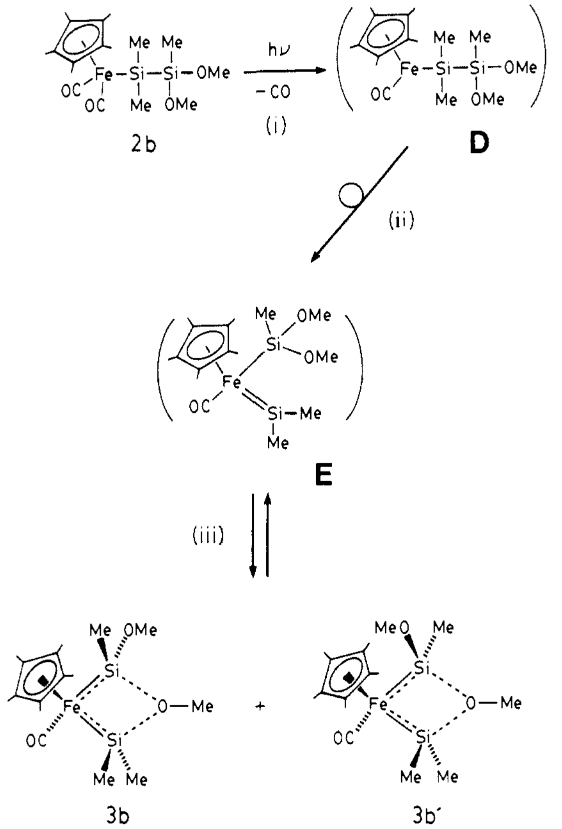


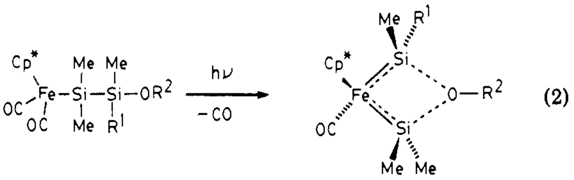
Figure 3. ^{29}Si NMR spectral change upon photolysis of **2a** in C_6D_6: (a) before irradiation; (b) after 30-min irradiation. The sharp signal is assigned to **3a**. The broad signal at ∼−100 ppm is attributable to the Pyrex glass of the NMR sample tube.

Scheme I

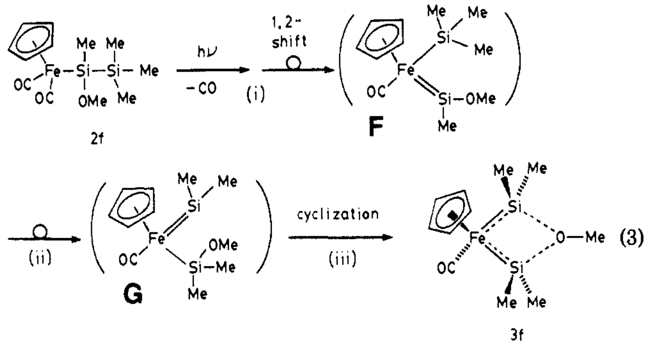


The ratio of **3b** to **3b′** is likely to depend upon the difference between the steric interactions between the bulky Cp′ ring and the substituents on the asymmetric silicon atom. It is apparent that the methoxy group is bulkier than the methyl groups. This leads to the formation of **3b** in preference to **3b′**. This steric interaction is large even in the less hindered product **3b**: The C(4)···C(14) and C(6)···C(13) distances (3.59 and 3.54 Å, respectively) are considerably smaller than the sum of the van der Waals radii of two methyl groups (4.0 Å). The nonplanarity of the Fe–Si(1)–O(2)–Si(2) core may also be attributed to this steric repulsion.

Photolyses of 2a, 2c, 2d, 2e, and 2f. Photolysis of an alkoxy-substituted disilanyliron complex, **2a**, **2c**, **2d**, **2e**, or **2f**, resulted in the formation of a bis(silylene)iron complex, **3a**, **3c**, **3d**, **3e**, or **3f**, respectively, with generation of CO (eqs 2 and 3). Interestingly, only one product **3e** was obtained from the photolysis of (di-*tert*-butoxydisilanyl)iron complex **2e**, in contrast to the formation of two geometric isomers, **3b** and **3b′**, from the photolysis of **2b**. The structure of **3e** is assignable to the less sterically hindered isomer shown in eq 2.



2a, 3a: Cp* = Cp′; R^1 = R^2 = Me
2c, 3c: Cp* = Cp′; R^1 = Me; R^2 = Bu^t
2d, 3d: Cp* = Cp; R^1 = Me; R^2 = Bu^t
2e, 3e: Cp* = Cp; R^1 = OBu^t; R^2 = Bu^t



The mechanism for the photoreactions of **2a**, **2c**, **2d**, and **2e** is considered to be similar to that of **2b** (Scheme I). However, for the formation of **3f** from **2f**, migration of a methyl group from one silicon atom to another is required to yield two $SiMe_2$ moieties. Such migration of substituents on silicon atoms has already been noted in the photochemical conversion of $CpFe(CO)_2SiR_2SiR_3$ (R = alkyl, aryl) to $CpFe(CO)_2SiR_3$ and it has been proposed that such migration occurs in silyl(silyene)iron intermediates.[6,7] Thus, **3f** is formed from **2f** via methyl group migration in the silyl(silylene)iron intermediate (eq 3) in the following manner: (i) formation of a silyl(methoxysilylene)iron intermediate F; (ii) methyl group migration from the silyl group to the silylene ligand; formation of a methoxysilyl(silylene)iron intermediate G; and (iii) cyclization to form **3f**.

The bis(silylene)iron complexes, **3a**, **3c**, **3d**, **3e**, and **3f**, as well as **3b** and **3b′**, show ^{29}Si NMR signals at very low field (90–125 ppm; see Table I). Particularly, each of the photolytic products, **3a**, **3c**, **3d**, and **3f**, which were derived from (monoalkoxydisilanyl)iron complexes, gives only one signal at low field, exemplified by the spectrum of **3a** in Figure 3. The result indicates that the two silicon atoms in each starting complex become equivalent in the corresponding product and is consistent with the structure of the alkoxy-stabilized bis(silylene)iron complex.

There are some other characteristic spectral differences between the starting materials and the products (Table I). As stated above for **2b**, **3b**, and **3b′**, the ^{1}H NMR signals assigned to the bridged alkoxy groups in the bis(silylene)iron complexes appear at appreciably high field compared to those for the terminal alkoxyl groups of the starting materials. The chemical shift difference amounts to approximately 0.8 ppm for the methoxy-bridged complexes, **3a** and **3f**, and 0.2 ppm for the *tert*-butoxy-bridged complexes, **3c**, **3d**, and **3e**. The IR spectrum of each of the bis(silylene)iron complexes shows only one terminal ν_{CO} band below 1900 cm^{-1} consistent with the structure with a single CO ligand.

Acknowledgment. This work has been supported by Nippon Sheet Glass Foundation for Material Science and Grants-in-Aid for Special Project Research No. 63740329 and Scientific Research No. 01740348 from the Ministry of Education, Science and Culture. We thank Toray Silicone Co., Ltd., for a gift of silicon compounds.

Note Added in Proof. After this paper was submitted for publication, there appeared a paper by K. H. Pannell et al. (*J. Am. Chem. Soc.* **1989**, *111*, 4482) that is closely related to the work of refs 6 and 7.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters for **3b** (2 pages); observed and calculated structure factors for **3b** (9 pages). Ordering information is given on any current masthead page.

Effects of Redox Potential, Steric Configuration, Solvent, and Alkali Metal Cations on the Binding of Carbon Dioxide to Cobalt(I) and Nickel(I) Macrocycles

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Abstract: The binding of CO_2 to metal macrocycles has been determined electrochemically by using cyclic voltammetry or differential pulse polarography. The CO_2 binding constants, K_{CO_2}, for a series of Co(I) tetraazamacrocycle complexes in $(CH_3)_2SO$ showed a strong correlation with the Co(II/I) redox potential. Although meso and *d,l* stereoisomers of $[Co^I(Me_6[14]4,11\text{-diene})]^+$ had identical redox potentials, K_{CO_2} differed by a factor of 10^2 for these stereoisomers, suggesting a large steric effect on CO_2 binding. Binding of CO_2 to Ni(I) tetraazamacrocycles in $(CH_3)_2SO$ yielded a redox potential dependence similar to that of Co(I) macrocycles. A weak correlation between K_{CO_2} and the solvent dielectric constant was found for *d,l*-$[Co(Me_6[14]4,11\text{-diene})]^+$. In tetrahydrofuran (THF), *d,l*-$[Co(Me_6[14]4,11\text{-diene})]^+$ was found to bind CO_2 more strongly in the presence of 0.1 M Li^+ than in the presence of 0.1 M tetrabutylammonium (TBA^+). Electrochemically determined K_{CO_2}'s for Co(salen)$^-$ and Co(Me_2salen)$^-$ in THF indicated a strong dependence on redox potential and electrolyte cation.

Much recent work has been focussed on the catalytic activation of CO_2,[1,2] including many electrocatalytic schemes involving macrocyclic complexes of cobalt and nickel.[3,4] Although several mechanistic studies have been performed on thermal CO_2 acti-

0002-7863/90/1512-3420$02.50/0