Synthesis and Properties of Intramolecularly Base-Stabilized (Disilanyl−silylene)ruthenium and -iron Complexes[†]

Hiromi Tobita,* Hitoe Kurita, and Hiroshi Ogino*
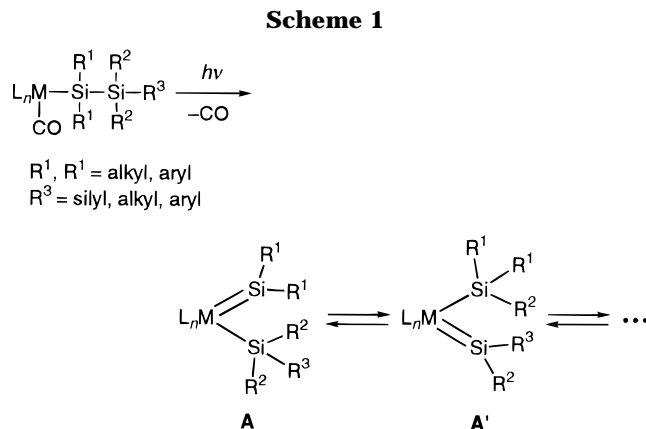
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received March 5, 1998

Photolysis of the 3-methoxytrisilanyl complex $CpM(CO)_2SiMe_2SiMe_2SiMe_2OMe$ (**1a**, M = Ru; **1b**, M = Fe) afforded the intramolecularly methoxy-stabilized disilanyl−silylene complex $Cp(OC)M\{=SiMe_2 \leftarrow O(Me)SiMe_2SiMe_2\}$ (**2a**, M = Ru; **2b**, M = Fe) as a primary product. Prolonged irradiation of the solution resulted in the decay of **2a,b** with release of a dimethylsilylene moiety to give the methoxy-bridged bis(silylene) complex $Cp(OC)M\{SiMe_2 \cdots O(Me) \cdots SiMe_2\}$ (**3a**, M = Ru; **3b**, M = Fe). The X-ray crystal structure analysis of **2a** revealed that **2a** has a five-membered chelate ring and the Ru−Si(silylene) bond (2.291-(2) Å) is much shorter than the other Ru−Si bond (2.350(1) Å). It can be concluded from the bond lengths that the former possesses a partial double-bond character while the latter is a normal Ru−Si single bond. Photolysis of diisopropyl derivatives $CpM(CO)_2SiMe_2Si^iPr_2SiMe_2OMe$ (**4a**, M = Ru; **4b**, M = Fe) gave $Cp(OC)M\{=SiMe_2 \leftarrow O(Me)SiMe_2Si^iPr_2\}$ (**5a**, M = Ru; **5b**, M = Fe) exclusively, in which the positions of substituents on silicon atoms in **5a** and **5b** were determined by $^{29}Si-^1H$ COLOC and NOESY NMR spectra. A mechanism involving 1,2-migration of the methoxydisilanyl group to the metal center was suggested. Irradiation of the tetrasilanyl complex $CpFe(CO)_2SiMe_2SiMe_2SiMe_2SiMe_2OMe$ (**6**) caused a complicated reaction, giving at least five products having methoxy groups coordinated to silylene ligands.

Introduction

Extensive investigation on the photolysis of polysilanylcarbonylmetal complexes by Pannell et al. and us revealed that the scrambling of substituents and rearrangement of the polysilanyl ligands occur efficiently under irradiation even at room temperature.[1] For these reactions, a 1,2-silyl shift followed by the 1,3-shift of substituents on the resultant silyl−silylene complexes **A** have been proposed to occur as key steps of the mechanism (Scheme 1).[1,2] Isolation and structure determination of several base-stabilized bis(silylene)metal complexes formed by the rearrangement of disilanylmetal complexes gave firm evidence of the 1,2-silyl shift

Scheme 1

R^1, R^1 = alkyl, aryl
R^3 = silyl, alkyl, aryl

in disilanyl complexes.[3] With regard to the 1,3-shift of substituents, we have recently offered spectroscopic evidence of an HMPA-stabilized (silyl−silylene)iron complex using dynamic NMR spectroscopy.[4] Now many transformation reactions of various transition-metal complexes containing W,[5] Fe,[6] Rh,[7] Ir,[7] Ni,[8] Pd,[9] and Pt[9] have been reported to proceed through the 1,3-shift mechanism.

[†] Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.
(1) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Tobita, H.; Ogino, H. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 530.
(2) (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (b) Pannell, K. H.; Rozell, J. M.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (c) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954. (d) Jones K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (e) Zhang, Z.; Sanchez, R.; Pannell, K. H. *Organometallics* **1995**, *14*, 2605. (f) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (g) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797. (h) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (i) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959. (j) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435. (k) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459.
(3) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835. (d) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545. (e) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023.

(4) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459.
(5) (a) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173. (b) Figge, L. K.; Carroll, P. J.; Berry, D. H. *Organometallics* **1996**, *15*, 209.
(6) (a) Bodensieck, U.; Braunstein, P.; Deck, W.; Faure, T.; Knorr, M.; Stern, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2440. (b) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315.

In contrast to the case for disilanyl complexes, the photoreactions of complexes having trisilanyl or longer polysilanyl ligands have scarcely been investigated. Pannell et al. extensively studied the photochemical rearrangement of linear polysilanyl complexes to branched ones,[10] but isolation or stabilization of the proposed intermediates, i.e., polysilanyl—silylene complexes, has never been accomplished. We report herein the photolysis of (methoxytrisilanyl)ruthenium and -iron complexes giving intramolecularly base-stabilized (disilanyl—silylene)ruthenium and -iron complexes, and the X-ray crystal structure of one of them.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere by standard Schlenk or high-vacuum-line techniques. Ether, THF, hexane, and toluene were distilled from sodium benzophenone ketyl and chloroform was distilled from calcium hydride under a nitrogen atmosphere before use. Methanol was distilled from $Mg(OMe)_2$ and then dried over molecular sieves 3A. Pyridine was dried by distillation from CaH_2. Methylcyclohexane (spectrophotometric grade) was used after distillation from sodium. Benzene-d_6 was dried over molecular sieves 4A. Benzene-d_6, hexane, and toluene for sealed-tube preparation were dried with a potassium mirror and degassed under high vacuum. $Cp_2Ru_2(CO)_4$,[11] $Cp_2Fe_2(CO)_4$,[12] $ClMe_2SiSiMe_2SiMe_2Cl$,[13] $PhMe_2SiCl$,[14] $^iPr_2SiCl_2$,[15] and $ClMe_2Si(SiMe_2)_2SiMe_2Cl$[16] were prepared according to published procedures. Other chemicals were used as received from commercial sources.

Photolyses were performed with an Ushio UM-452 450 W medium-pressure Hg lamp placed in a water-cooled quartz jacket. Samples for photolysis were placed in a Pyrex glass tube or Pyrex NMR tube.

NMR measurements were performed on a Bruker ARX-300 NMR spectrometer. IR spectra were obtained on Horiba FT-200 and Bruker IFS66v spectrophotometers. Electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer. Mass spectra were taken on Hitachi M-2500S and JEOL JMS-HX110 mass spectrometers. Liquid chromatography was done on a Yamazen YFLC-540 instrument.

Preparation of $CpRu(CO)_2SiMe_2SiMe_2SiMe_2OMe$ (1a). To the Na–K alloy prepared from Na (16 mg, 0.696 mmol) and K (92 mg, 2.35 mmol) was added $Cp_2Ru_2(CO)_4$ (433 mg, 0.974 mmol) in THF (30 mL), and the mixture was sonicated at 0 °C for 1 h and then stirred at room temperature for 2 h.

The remaining Na–K alloy was removed by filtration of the reaction mixture through a Schlenk filter with a Celite pad, and the resulting solution of $M[CpRu(CO)_2]$ (M = Na, K) was added to $ClMe_2SiSiMe_2SiMe_2Cl$ (477 mg, 1.94 mmol) in THF (10 mL) cooled with a chloroform—liquid N_2 bath. The mixture was stirred for 1 h and then warmed to room temperature and stirred for an additional 2 h. After removal of the solvent in vacuo, the brown oily residue was extracted with three 20 mL portions of hexane and the combined extract was filtered through a Schlenk filter with a Celite pad. The filtrate was evaporated to dryness; to the residue were added MeOH (30 mL) and pyridine (0.4 mL), and the mixture was stirred at room temperature for 1 h. After removal of volatiles, the orange oily residue was separated by liquid chromatography (silica gel; eluent hexane/dichloromethane, 4/1) to give **1a** (469 mg, 1.10 mmol, 56%) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): δ 0.29 (s, 6H, SiMe), 0.31 (s, 6H, SiMe), 0.71 (s, 6H, SiMe), 3.29 (s, 3H, OMe), 4.71 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ −4.3 (SiMe), −0.3 (SiMe), 5.0 (SiMe), 50.6 (OMe), 86.9 (Cp), 202.3 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −40.9, 6.0, 19.8. IR (hexane solution): 2013, 1957 cm^{-1} (ν_{CO}). MS (EI, 70 eV): m/z 413 (0.7, M$^+$ − Me), 397 (0.9, M$^+$ − OMe), 311 (4, M$^+$ − CO − SiMe$_2$OMe), 281 (26, M$^+$ − SiMe$_2$SiMe$_2$OMe), 253 (14, M$^+$ − CO − SiMe$_2$SiMe$_2$OMe), 205 (100, M$^+$ − CpRu(CO)$_2$). Anal. Calcd for $C_{14}H_{26}O_3RuSi_3$: C, 39.32; H, 6.13. Found: C, 39.37; H, 5.84.

Preparation of $CpFe(CO)_2SiMe_2SiMe_2SiMe_2OMe$ (1b). To the Na–K alloy prepared from Na (72 mg, 3.13 mmol) and K (342 mg, 8.75 mmol) was added $Cp_2Fe_2(CO)_4$ (998 mg, 2.82 mmol) in THF (30 mL), and the mixture was stirred at room temperature for 2.5 h. The remaining Na–K alloy was removed by filtration of the reaction mixture through a Schlenk filter with a Celite pad, and the resulting solution of $M[CpFe(CO)_2]$ (M = Na, K) was added to $ClMe_2SiSiMe_2SiMe_2$-Cl (1.62 g, 6.61 mmol) in THF (10 mL) cooled with a chloroform—liquid-N$_2$ bath. The mixture was stirred for 1 h and then warmed to room temperature and stirred for an additional 18 h. After removal of the solvent in vacuo, the brown oily residue was extracted with three 20 mL portions of hexane and the combined extract was filtered through a Schlenk filter with a Celite pad. The filtrate was evaporated to dryness, and molecular distillation of the residue gave CpFe-(CO)$_2$SiMe$_2$SiMe$_2$SiMe$_2$Cl (1.28 g, 3.31 mmol, 59%) as a brown oil.

CpFe(CO)$_2$SiMe$_2$SiMe$_2$SiMe$_2$Cl (2.09 g, 5.41 mmol) was placed in a 30 mL two-necked flask; and MeOH (50 mL) and pyridine (0.8 mL) were added to it, and the mixture was stirred at room temperature for 1 h. After removal of volatiles, the orange oily residue was separated by silica gel flash chromatography (eluent toluene/hexane, 1/1) to give **1b** (793 mg, 2.08 mmol, 38%) as a brown oil. ^{1}H NMR (300 MHz, C_6D_6): δ 0.30 (s, 6H, SiMe), 0.31 (s, 6H, SiMe), 0.65 (s, 6H, SiMe), 3.28 (s, 3H, OMe), 4.24 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ −4.2 (SiMe), −0.4 (SiMe), 4.7 (SiMe), 50.5 (OMe), 83.3 (Cp), 215.9 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −39.7, 19.7, 20.8. IR (hexane solution): 1997, 1945 cm^{-1} (ν_{CO}). MS (EI, 70 eV): m/z 382 (0.2, M$^+$), 367 (1.3, M$^+$ − Me), 354 (4.5, M$^+$ − CO), 326 (2.6, M$^+$ − 2CO), 235 (7.8, M$^+$ − SiMe$_2$SiMe$_2$OMe), 205 (100, M$^+$ − CpFe(CO)$_2$). Anal. Calcd for $C_{14}H_{26}FeO_3Si_3$: C, 43.97; H, 6.85. Found: C, 43.67; H, 6.69.

Preparation of $PhMe_2SiSi^iPr_2SiMe_2Ph$. A solution of PhMe$_2$SiCl (16.8 g, 98.2 mmol) in THF (80 mL) was added dropwise to a finely cut lithium wire (4.3 g, 0.62 mol) with stirring, and further stirring for 2 h at room temperature gave a deep purple solution of PhMe$_2$SiLi. This solution was transferred into an addition funnel through glass wool to remove excess lithium and was added to a solution of i-Pr$_2$-SiCl$_2$ (8.12 g, 43.8 mmol) in THF (50 mL) at room temperature within 1 h. The orange-red reaction mixture was stirred at room temperature for 12 h and then hydrolyzed. The aqueous layer was extracted with ether, and the extracts were com-

(7) (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (b) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477.
(8) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861.
(9) (a) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (b) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530. (c) Yamashita, H.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403. (d) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043.
(10) (a) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (b) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (c) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075.
(11) Gibson, D. H.; Hsu, W.-L.; Steinmetz, A. L. *J. Organomet. Chem.* **1981**, *208*, 89.
(12) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.
(13) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.
(14) (a) Chatt, J.; Williams, A. A. *J. Chem. Soc.* **1956**, 688. (b) Maienthal, M.; Hellmann, M.; Haber, C. P.; Hymo, L. A.; Carpenter, S.; Carr, A. J. *J. Am. Chem. Soc.* **1954**, *76*, 6392.
(15) (a) Metras, F.; Valade, J. *Bull. Soc. Chim. Fr.* **1965**, 1423. (b) Gilman, H.; Miles, D. H.; Moore, L. O.; Gerow, C. W. *J. Org. Chem.* **1959**, *24*, 219.
(16) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

bined with the organic layer. After removal of volatiles, the residue was distilled under reduced pressure (147 °C/0.15 mmHg) to give PhMe$_2$SiSi^{i}Pr$_2$SiMe$_2$Ph (8.25 g, 21.5 mmol, 49%) as a colorless oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.42 (s, 12H, SiMe), 1.01 (d, J = 7.8 Hz, 12H, CHMe_2), 1.22 (septet, J = 7.8 Hz, 2H, CHMe$_2$), 7.13−7.17 (m, 6H, Ph), 7.46−7.63 (m, 4H, Ph). ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ 0.1 (SiMe), 13.0 (SiCHMe$_2$), 21.1 (SiCHMe_2), 128.1 (Ph), 128.7 (Ph), 134.5 (Ph). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −27.7 (Si^{i}Pr$_2$), 19.1 (SiMe$_2$).

Preparation of ClMe$_2$SiSi^{i}Pr$_2$SiMe$_2$Cl. PhMe$_2$SiSi^{i}Pr$_2$-SiMe$_2$Ph (7.86 g, 20.4 mmol) and AlCl$_3$ (ca. 0.5 g, 4 mmol) were dissolved in benzene (60 mL), and the solution was cooled to 0 °C. Hydrogen chloride gas was slowly bubbled through the solution, and the reaction was monitored by gas chromatography. After all the starting trisilane was consumed, acetone (5 mL) was added to deactivate AlCl$_3$. Removal of volatiles followed by distillation under reduced pressure (115 °C, 2 mmHg) afforded ClMe$_2$SiSi^{i}Pr$_2$SiMe$_2$Cl (5.32 g, 17.7 mmol, 87%) as a colorless paste. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.52 (s, 12H, SiMe), 1.01 (d, J = 6.9 Hz, 12H, CHMe_2), 1.27 (m, 2H, CHMe$_2$). ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ 5.8 (SiMe), 12.1 (SiCHMe$_2$), 20.7 (SiCHMe_2). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$, DEPT for SiMe): δ 25.2 (SiMe$_2$).

Preparation of CpRu(CO)$_2$SiMe$_2$Si^{i}Pr$_2$SiMe$_2$OMe (4a). Complex **4a** was prepared in a manner similar to that for **1a**. Metalation of Cp$_2$Ru$_2$(CO)$_4$ (478 mg, 1.08 mmol), reaction with ClMe$_2$SiSi^{i}Pr$_2$SiMe$_2$Cl (688 mg, 2.28 mmol), and subsequent treatment with MeOH and pyridine afforded **4a** (576 mg, 1.19 mmol, 55%) as a colorless oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.39 (s, 6H, SiMe), 0.87 (s, 6H, SiMe), 1.28 (d, J = 7.0 Hz, 6H, CHMe_2), 1.29 (d, J = 7.0 Hz, 6H, CHMe_2), 1.38 (septet, J = 7.0 Hz, 2H, CHMe$_2$), 3.20 (s, 3H, OMe), 4.80 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ 2.9 (SiMe), 8.4 (SiMe), 13.5 (SiCHMe$_2$), 21.3 (SiCHMe_2), 21.5 (SiCHMe_2), 49.5 (OMe), 87.4 (Cp), 202.8 (CO). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −21.3 (Si^{i}Pr$_2$), 4.8 (SiMe$_2$), 20.5 (SiMe$_2$). IR (hexane solution): 2013, 1957 cm^{-1} (ν_{CO}). MS (EI, 70 eV): m/z 484 (0.2, M$^+$), 469 (0.6, M$^+$ − Me), 288 (69, M$^+$ − Si^{i}Pr$_2$SiMe$_2$OMe), 261 (100, M$^+$ − CpRu-(CO)$_2$). Anal. Calcd for C$_{18}$H$_{34}$O$_3$RuSi$_3$: C, 44.69; H, 7.08. Found: C, 44.68; H, 6.80.

Preparation of CpFe(CO)$_2$SiMe$_2$Si^{i}Pr$_2$SiMe$_2$OMe (4b). Complex **4b** was prepared in a manner similar to that of **1b**. Metalation of Cp$_2$Fe$_2$(CO)$_4$ (511 mg, 1.44 mmol), reaction with ClMe$_2$SiSi^{i}Pr$_2$SiMe$_2$Cl (509 mg, 1.69 mmol), and subsequent treatment with MeOH and pyridine afforded **4b** (432 mg, 0.985 mmol, 58%) as a brown oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.38 (s, 6H, SiMe), 0.81 (s, 6H, SiMe), 1.28 (d, J = 7.0 Hz, 6H, CHMe_2), 1.29 (d, J = 7.0 Hz, 6H, CHMe_2), 1.39 (septet, J = 7.0 Hz, 2H, CHMe$_2$), 3.19 (s, 3H, OMe), 4.33 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ 2.8 (SiMe), 8.0 (SiMe), 13.6 (SiCHMe$_2$), 21.3 (SiCHMe_2), 21.6 (SiCHMe_2), 49.5 (OMe), 83.7 (Cp), 216.4 (CO). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −19.6, 20.4, 20.8. IR (hexane solution): 1996, 1945 cm^{-1} (ν_{CO}). MS (EI, 70 eV): m/z 423 (0.8, M$^+$ − Me), 410 (0.3, M$^+$ − CO), 261 (100, M$^+$ − CpFe(CO)$_2$). Anal. Calcd for C$_{18}$H$_{34}$FeO$_3$Si$_3$: C, 49.30; H, 7.81. Found: C, 49.60; H, 7.81.

Preparation of CpFe(CO)$_2$SiMe$_2$SiMe$_2$SiMe$_2$SiMe$_2$OMe (6). Complex **6** was prepared in a manner similar to that of **1b**. Metalation of Cp$_2$Fe$_2$(CO)$_4$ (332 mg, 0.932 mmol), reaction with ClMe$_2$Si(SiMe$_2$)$_2$SiMe$_2$Cl (950 mg, 3.13 mmol), and subsequent treatment with MeOH and pyridine afforded **6** (693 mg, 1.57 mmol, 84%) as an orange solid. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.31 (s, 6H, SiMe), 0.34 (s, 6H, SiMe), 0.38 (s, 6H, SiMe), 0.65 (s, 6H, SiMe), 3.28 (s, 3H, OMe), 4.23 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ −5.0 (SiMe), −3.2 (SiMe), −0.1 (SiMe), 5.3 (SiMe), 50.6 (OMe), 83.1 (Cp), 215.9 (CO). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ −45.2, −33.4, 19.9, 22.9. IR (hexane solution): 1995, 1946 cm^{-1} (ν_{CO}). MS (EI, 70 eV): m/z 425 (0.8, M$^+$ − Me), 412 (0.2, M$^+$ − CO), 263 (38, M$^+$ − CpFe-(CO)$_2$), 205 (100, M$^+$ − CpFe(CO)$_2$ − SiMe$_2$). Anal. Calcd for C$_{16}$H$_{32}$FeO$_3$Si$_4$: C, 43.62; H, 7.32. Found: C, 43.92; H, 7.53.

Photolysis in an NMR Tube. Unless otherwise stated, photolyses of complexes **1a**, **1b**, **4a**, **4b**, and **6** were performed as follows. A thick-walled Pyrex NMR tube (5 mm o.d., 3 mm i.d.) was charged with a complex (1.9−40 mg) and connected to a vacuum line via a ground-glass joint. Benzene-d_6 (ca. 0.5 mL) was introduced into the sample tube by the trap-to-trap-transfer technique, and the tube was flame-sealed under vacuum. Irradiation was carried out externally with a medium-pressure Hg lamp placed in a water-cooled quartz jacket. The NMR tube and the jacket were immersed in a water bath kept at 2 °C during irradiation. The distance from the light source to the sample was ca. 4 cm.

Photolysis of 1a, 1b, 4a, and 4b and Isolation of the Products Cp(OC)M{=SiMe$_2$←O(Me)SiMe$_2$SiR$_2$} (2a, M = Ru, R = Me; 2b, M = Fe, R = Me; 5a, M = Ru, R = ^{i}Pr; 5b, M = Fe, R = ^{i}Pr). A typical experimental procedure is described for the photolysis of **1a**. A Pyrex sample tube (10 mm o.d., 8 mm i.d.) with a greaseless vacuum valve and a ground-glass joint was charged with **1a** (0.1 g) and connected to a vacuum line. Dry and degassed hexane (ca. 5 mL) was transferred to the sample tube by the trap-to-trap-transfer technique, and the solution was irradiated at 2 °C for 20 min. After irradiation, the solution was concentrated to ca. 1 mL under reduced pressure, and the tube was flame-sealed. Storing the sealed tube in a refrigerator at −30 °C led the precipitation of extremely air- and moisture-sensitive pale yellow crystals of **2a**. In a similar manner, **2b**, **5a**, and **5b** were obtained. **2a**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ −0.07 (s, 3H, SiMe), 0.14 (s, 3H, SiMe), 0.35 (s, 3H, SiMe), 0.55 (s, 3H, SiMe), 0.68 (s, 3H, SiMe), 0.77 (s, 3H, SiMe), 2.79 (s, 3H, OMe), 4.81 (s, 5H, Cp); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ −1.8 (SiMe), −1.1 (SiMe), 3.7 (SiMe), 4.0 (SiMe), 11.1 (SiMe), 11.2 (SiMe), 52.6 (OMe), 83.2 (Cp), 206.0 (CO); ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ −1.2, 48.5, 137.1 (Ru=Si); IR (C$_6$D$_6$ solution) 1898 cm^{-1} (ν_{CO}); MS (EI, 70 eV) m/z 400 (7, M$^+$), 385 (6, M$^+$ − Me), 342 (100, M$^+$ − SiMe$_2$). Anal. Calcd for C$_{13}$H$_{26}$O$_2$RuSi$_3$: C, 39.07; H, 6.56. Found: C, 38.96; H, 6.16. **2b**: yellow crystals; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ −0.03 (s, 3H, SiMe), 0.20 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), 0.49 (s, 3H, SiMe), 0.67 (s, 3H, SiMe), 0.68 (s, 3H, SiMe), 2.84 (s, 3H, OMe), 4.19 (s, 5H, Cp); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ −1.4 (SiMe), −0.6 (SiMe), 3.0 (SiMe), 3.6 (SiMe), 9.1 (SiMe), 10.8 (SiMe), 53.1 (OMe), 78.5 (Cp), 216.7 (CO); ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ 14.3, 50.8, 157.3 (Fe=Si); IR (C$_6$D$_6$ solution) 1866 cm^{-1} (ν_{CO}); MS (EI, 70 eV) m/z 354 (4, M$^+$), 296 (88, M$^+$ − SiMe$_2$), 268 (100, M$^+$ − SiMe$_2$ − CO), 205 (99, M$^+$ − CpFe(CO)); exact mass calcd for C$_{13}$H$_{26}$FeO$_2$Si$_3$ 354.0590, found 354.0601. **5a**: pale yellow crystals; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.08 (s, 3H, SiMe), 0.30 (s, 3H, SiMe), 0.41 (s, 3H, SiMe), 0.74 (s, 3H, SiMe), 1.08 (d, J = 3 Hz, 3H, CHMe_2), 1.11 (d, J = 3 Hz, 3H, CHMe_2), 1.30 (d, J = 7 Hz, 3H, CHMe_2), 1.37 (d, J = 7 Hz, 3H, CHMe_2), 1.45 (septet, J = 3 Hz, 1H, CHMe$_2$), 1.46 (septet, J = 7 Hz, 1H, CHMe$_2$), 2.81 (s, 3H, OMe), 4.91 (s, 5H, Cp); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 0.9 (SiMe), 1.5 (SiMe), 11.0 (SiMe), 12.1 (SiMe), 17.0 (SiCHMe$_2$), 18.0 (SiCHMe$_2$), 21.9 (SiCHMe_2), 22.2 (SiCHMe_2), 22.5 (SiCHMe_2), 22.9 (SiCHMe_2), 52.3 (OMe), 82.4 (Cp), 206.6 (CO); ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ 31.3 (Si^{i}Pr$_2$), 51.9 (SiMe$_2$OMe), 135.8 (Ru=Si); IR (C$_6$D$_6$ solution) 1880 cm^{-1} (ν_{CO}); MS (EI, 70 eV) m/z 456 (50, M$^+$), 441 (5, M$^+$ − Me), 428 (19, M$^+$ − CO), 413 (100, M$^+$ − Me − CO). Anal. Calcd for C$_{17}$H$_{34}$O$_2$RuSi$_3$: C, 44.80; H, 7.52. Found: C, 44.91; H, 7.51. **5b**: yellow crystals; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.09 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), 0.40 (s, 3H, SiMe), 0.72 (s, 3H, SiMe), 1.11 (d, J = 7 Hz, 3H, CHMe_2), 1.16 (d, J = 7 Hz, 3H, CHMe_2), 1.33 (d, J = 7 Hz, 3H, CHMe_2), 1.39 (d, J = 7 Hz, 3H, CHMe_2), 1.43 (septet, J = 7 Hz, 1H, CHMe$_2$), 1.60 (septet, J = 7 Hz, 1H, CHMe$_2$), 2.85 (s, 3H, OMe), 4.35 (s, 5H, Cp); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 1.3 (SiMe), 1.4 (SiMe), 9.4 (SiMe), 11.2 (SiMe), 17.2 (SiCHMe$_2$), 19.2 (SiCHMe$_2$), 22.0 (SiCHMe_2), 22.4 (SiCHMe_2), 22.9 (SiCHMe_2), 23.1 (SiCHMe_2), 52.8 (OMe), 77.8 (Cp), 217.9 (CO); ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ 42.5 (Si^{i}Pr$_2$),

**Table 1. Crystallographic Data for
Cp(OC)Ru{=SiMe₂←O(Me)SiMe₂SiMe₂} (2a)**

sample	Cp(OC)Ru{=SiMe₂← O(Me)SiMe₂SiMe₂}
formula	C₁₃H₂₆O₂RuSi₃
fw	399.68
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a/Å	9.454(1)
b/Å	13.148(1)
c/Å	8.239(1)
α/deg	94.11(3)
β/deg	110.59(1)
γ/deg	81.29(2)
V/Å³	947.5(2)
Z	2
d_{calcd}/g cm⁻³	1.40
μ(Mo Kα)/cm⁻¹	9.85
cryst size/mm	0.50 × 0.40 × 0.40
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite
temp/°C	20
reflcns measd	±h, ±k, l
2θ range/deg	3−60
scan mode	$\omega - 2\theta$
ω-scan width/deg	1.6 + 0.35 tan θ
bkgd (count time)/s	7.0
ω-scan rate/deg min⁻¹	4.0
no. of unique data	8932
no. of data used with $|F_o| > 3\sigma\,(F_o)$	4439
no. of params refined	230
R^a	0.049
$R_w{}^b$	0.070
quality of fit indicator^c	1.45
largest shift/esd, final cycle	0.34
max resid electron dens/e Å⁻³	1.36

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o^2]^{-1}$, where $a = 0.001$. ^{c} $[\sum w(||F_o| - |F_c||)^2/(N_{observns} - N_{params})]^{1/2}$.

52.9 (SiMe₂OMe), 154.9 (Fe=Si); IR (C₆D₆ solution) 1868 cm⁻¹ (ν_{CO}); MS (EI, 70 eV) m/z 410 (100, M⁺), 382 (26, M⁺ − CO), 367 (55, M⁺ − Me − CO). Anal. Calcd for C₁₇H₃₄FeO₂Si₃: C, 49.73; H, 8.35. Found: C, 49.25; H, 8.20.

X-ray Crystal Structure Determination of 2a. A single crystal of **2a** was cut to the size of 0.50 × 0.40 × 0.40 mm and was sealed in a 0.5 mm i.d. thin-walled glass capillary under a nitrogen atmosphere. The intensity data were collected on a Rigaku AFC-6A automated four-circle diffractometer using graphite-monochromated Mo Kα radiation at 20 °C. Crystallographic parameters are listed in Table 1. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method with individual anisotropic thermal parameters for non-hydrogen atoms. None of the hydrogen atoms were found from difference Fourier synthesis maps, so that the positions of hydrogen atoms of the cyclopentadienyl ligand were calculated and fixed.

The calculations were performed on a Nippon Electric Co. ACOS-3900 computer system at the Computer Center of Tohoku University using the Universal Crystallographic Computation Program System UNICS III.[17]

Results and Discussion

Photolysis of CpM(CO)₂SiMe₂SiMe₂SiMe₂OMe (1a, M = Ru, 1b, M = Fe). Photolysis of the 3-methoxytrisilanyl complexes **1a** and **1b** in C₆D₆ with a medium-pressure Hg lamp afforded intramolecularly methoxy-stabilized disilanyl−silylene complexes **2a** and **2b**, respectively, as the primary products. Prolonged
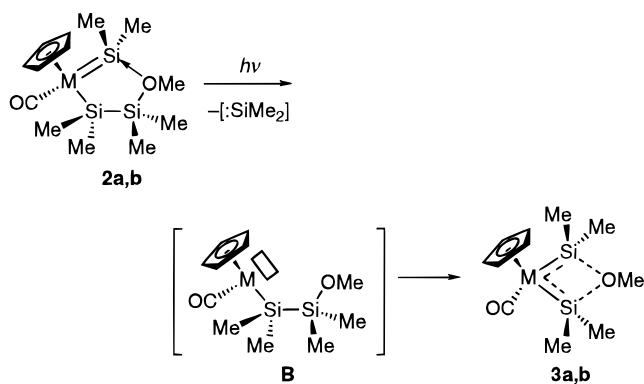
(17) Sakurai, T.; Kobayashi, M. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

Scheme 2

irradiation of the solution resulted in the decay of **2a,b** with release of a dimethylsilylene moiety to give the methoxy-bridged bis(silylene) complexes **3a,b** (eq 1).[18]
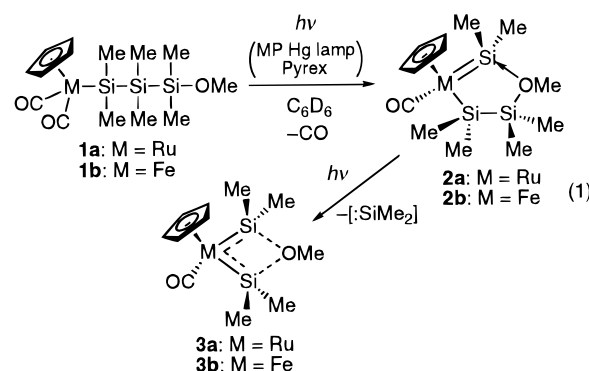
The ¹H, ¹³C, and ²⁹Si NMR spectra of **2a,b** show that the three silicon atoms and the six methyl groups on these silicon atoms are all nonequivalent at room temperature. The ²⁹Si NMR signals of **2a** appear at 137.2, 48.5, and −1.2 ppm and those of **2b** at 157.3, 50.8, and 14.3 ppm. The large downfield shift of the lowest field signal for each complex indicates that **2a,b** each have a silylene ligand. Moreover, the lowest field signals of **2a** and **2b** appear more than 30 ppm lower than the signals of methoxy-bridged bis(silylene) complexes **3a** (104.2 ppm) and **3b** (124.2 ppm), respectively. This is apparently due to the localized metal−silicon unsaturated bonds in **2a,b**, which are in contrast with the ones in **3a,b** that are delocalized to two bonds. Another characteristic feature of intramolecularly methoxy-coordinated silylene complexes is the upfield shift of the methoxy signal in the ¹H NMR spectrum.[3,19] The methoxy protons of **2a** and **2b** appear at 2.84 and 2.79 ppm, respectively. These are higher in field than the usual Si−OMe signals such as **1a** (3.28 ppm) and **1b** (3.29 ppm), but are not as high as those of **3a** (2.63 ppm) and **3b** (2.62 ppm).[12] This phenomenon may be attributable to the fact that the trivalent oxygen of **3** has two Si−O dative bonds, while that of **2** has one Si−O dative bond and one Si−O covalent bond.

The conversion of iron complex **1b** to **2b** is much faster than the following conversion of **2b** to **3b**, whereas

(18) Complexes **3a,b** were prepared by photolysis of CpM(CO)₂SiMe₂-SiMe₂OMe (M = Ru, Fe) and fully characterized in: Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2844.

(19) (a) Koe, J. R.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479. (b) Ueno, K.; Ito, S.; Endo, K.; Tobita, H.; Inomata, S.; Ogino, H. *Organometallics* **1994**, *13*, 3309.
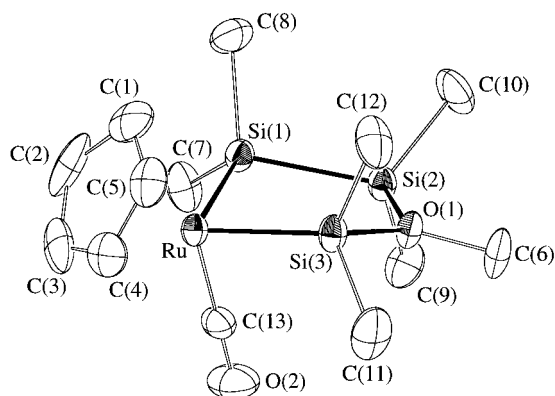
Figure 1. ORTEP drawing of Cp(OC)Ru{=SiMe₂←O(Me)-SiMe₂SiMe₂} (**2a**).

the rate of the corresponding conversion of ruthenium complex **1a** to **2a** is comparable to that of **2a** to **3a**. Thus, the NMR yields of **2b** and **3b** after 95% consumption of **1b** were 84 and 3%, respectively, while those of **2a** and **3a** after 91% consumption of **1a** were 54 and 28%, respectively. This is mainly because the conversion of ruthenium complex **1a** to **2a** is much slower than that of iron complex **1b** to **2b** under irradiation with a medium-pressure Hg lamp through Pyrex glass. This can be explained by the difference of the efficiency of light absorption: under the irradiation conditions, the most important emissions for photolysis of the complexes are the lines at 313 and 365 nm, and apparently the colorless ruthenium complex **1a** absorbs the light less than yellow iron complex **1b**.[20]

A plausible mechanism for the silylene expulsion from **2a,b** to give **3a,b** may involve the initial photochemical loss of the coordinated silylene to give coordinatively unsaturated intermediate **B**, which then immediately rearranges to **3a,b** (Scheme 2). Photochemically induced loss of coordinated silylenes has been reported for base-stabilized silylene complexes of iron and chromium.[21]

X-ray Structure Determination of 2a. The ORTEP drawing of **2a** is shown in Figure 1. Bond distances and angles are summarized in Table 2. The Ru−Si(1)−Si(2)−O(1)−Si(3) five-membered ring takes an envelope geometry in which the ruthenium atom deviates from the plane toward the CO ligand (dihedral angle between the planes defined by Ru−Si(1)−Si(3) and Si(1)−Si(2)−O(1)−Si(3) 24.9°). This is apparently due to the steric repulsion between a Cp ring and the methyl groups on Si(1) and Si(3). The Ru−Si(1) and Ru−Si(3) bond lengths are 2.350(1) and 2.291(2) Å, respectively. The former is in the range of normal Ru−Si single-bond

(20) For CpM(CO)₂Me, the absorption maxima were reported to be 235 and 280 nm for M = Ru and 275 and 345 nm for M = Fe: Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. For CpM(CO)₂SiMe₂SiMe₃, the absorption maxima have been measured to be 270 nm (ε 2700) for M = Ru and 284 (ε 5000) and 330 sh nm (ε 1900) for M = Fe.

(21) (a) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (b) Leis, C.; Zybill, C.; Lachmann, J.; Müller, G. *Polyhedron* **1991**, *10*, 1163. (c) Corriu, R. J. P.; Chauhan, B. P. S.; Lanneau, G. F. *Organometallics* **1995**, *14*, 1646. (d) Chauhan, B. P. S.; Corriu, R. J. P.; Lanneau, G. F.; Priou, C.; Auner, M.; Handwerker, H.; Herdtweck, E. *Organometallics* **1995**, *14*, 1657.

(22) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245, 309.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Cp(OC)Ru{=SiMe₂←O(Me)SiMe₂SiMe₂} (2a)

Bond Distances			
Ru−Si(1)	2.350(1)	Ru−Si(3)	2.291(2)
Ru−C(13)	1.811(6)	O(2)−C(13)	1.164(8)
Si(1)−Si(2)	2.332(2)	Si(2)−O(1)	1.752(4)
Si(3)−O(1)	1.849(3)	O(1)−C(6)	1.475(7)
Si(1)−C(7)	1.916(9)	Si(1)−C(8)	1.915(7)
Si(2)−C(9)	1.863(7)	Si(2)−C(10)	1.883(7)
Si(3)−C(11)	1.917(7)	Si(3)−C(12)	1.883(10)
C(1)−C(2)	1.504(15)	C(2)−C(3)	1.396(13)
C(3)−C(4)	1.383(13)	C(4)−C(5)	1.355(12)
C(5)−C(1)	1.386(12)		

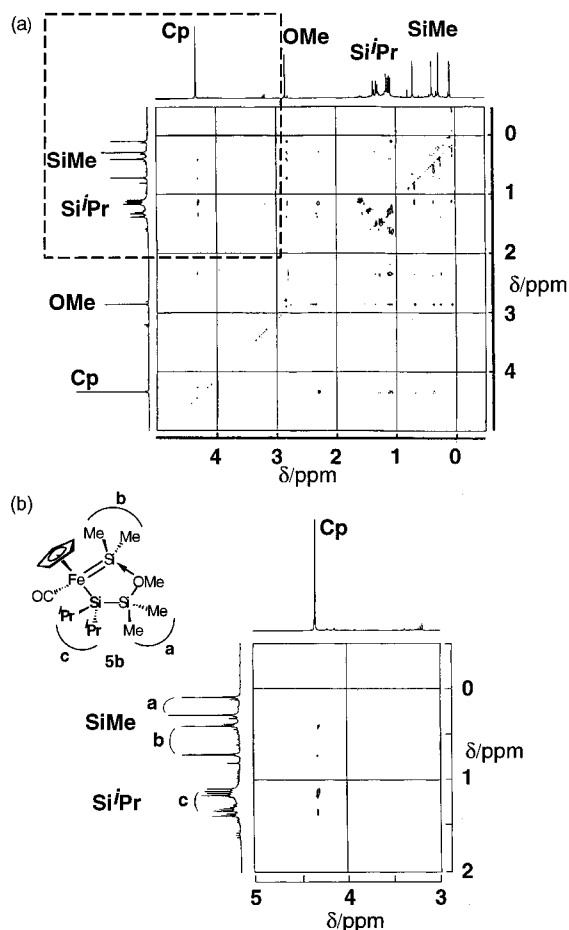| Bond Angles			
Si(1)−Ru−Si(3)	87.67(5)	Si(1)−Ru−C(13)	85.5(2)
Si(3)−Ru−C(13)	86.4(2)	Ru−Si(1)−Si(2)	108.51(6)
Ru−Si(1)−C(7)	114.4(3)	Ru−Si(1)−C(8)	105.4(2)
Si(2)−Si(1)−C(7)	105.3(3)	Si(2)−Si(1)−C(8)	105.4(2)
C(7)−Si(1)−C(8)	105.9(3)	Ru−Si(3)−O(1)	114.0(1)
Ru−Si(3)−C(11)	117.1(2)	Ru−Si(3)−C(12)	117.8(3)
O(1)−Si(3)−C(11)	98.9(2)	O(1)−Si(3)−C(12)	98.5(3)
C(11)−Si(3)−C(12)	107.5(4)	Si(1)−Si(2)−O(1)	100.9(1)
Si(1)−Si(2)−C(9)	115.4(2)	Si(1)−Si(2)−C(10)	117.3(2)
O(1)−Si(2)−C(9)	105.0(3)	O(1)−Si(2)−C(10)	104.3(3)
C(9)−Si(2)−C(10)	111.8(3)	Si(2)−O(1)−Si(3)	120.5(2)
Si(2)−O(1)−C(6)	118.9(3)	Si(3)−O(1)−C(6)	119.9(3)
Ru−C(13)−O(2)	178.5(5)		
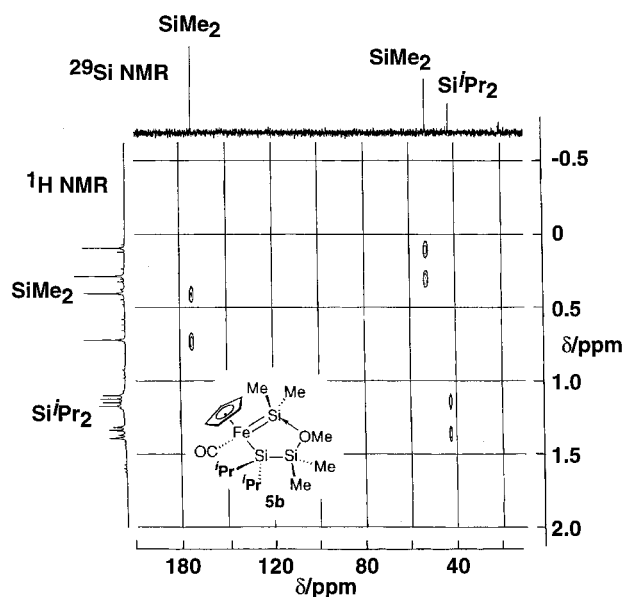
Figure 2. ²⁹Si−¹H COLOC spectrum of **5b** (300 MHz for ¹H NMR, C₆D₆).

lengths (2.34−2.51 Å),[22] while the latter is even shorter than the Ru−Si bond lengths of bis(silylene)ruthenium complex **3a** (2.316(3), 2.311(3) Å),[18] indicating the enhanced double-bond character of the bond in **2a**. The two Si−O distances are also significantly different, and the longer bond (Si(3)−O(1) = 1.849(3) Å) can be regarded as a dative bond and the shorter bond (Si(2)−O(1) = 1.752(4) Å) as a covalent bond, even though the latter is much longer than a normal Si−O (divalent) bond (1.63 Å). These observations are entirely consistent with the conclusions obtained from the NMR data.

The sum of the bond angles around trivalent oxygen O(1) is 359.3°. This clearly indicates that O(1) adopts an almost planar geometry with sp² hybridization. The sum of the three bond angles around Si(3) in **2a**, *i.e.*, C(11)−Si(3)−C(12), Ru−Si(3)−C(11), and Ru−Si(3)−C(12), is 342.5°. This value is between the sum of three

Figure 3. ^{1}H NOESY spectrum of **5b** (300 MHz, C$_6$D$_6$): (a) the whole spectrum; (b) the expansion of the area inside the dotted line and assignment of signals.

valence angles around an ideal sp^2-hybridized atom (360°) and and sp^3-hybridized atom (328.5°) but is significantly smaller than the corresponding values for bis(silylene)ruthenium complex **3a** (350.7 and 350.8°).[18] This is attributable to the difference in ring sizes between **2a** and **3a**: the Ru−Si(3)−O(1) angle inside the five-membered ring of **2a** (114.0(1)°) is larger than the corresponding Ru−Si−O angle inside the four-membered ring of **3a** (96.5(2)° (average)). However, the methyl groups on Si(3) in **2a** cannot come closer to the methyl group on O(1) accompanying this ring expansion because of the steric repulsion between them. This repulsion is clearly reflected in the C(6)···C(11) distance (3.123(10) Å) which is shorter than the sum of effective

van der Waals radii of two methyl groups (4.0 Å)). These steric effects result in greater pyramidalization of Si(3) in **2a**.

Photolysis of CpM(CO)$_2$SiMe$_2$Si^{i}Pr$_2$SiMe$_2$OMe (4a, M = Ru; 4b, M = Fe). Photolysis of 2,2-diisopropyltrisilanyl complexes **4a** and **4b** led to the exclusive formation of **5a** and **5b**, respectively, where the two isopropyl groups are located on the α-silicon atom of the disilanyl group (eq 2). The NMR yields for **5a** and **5b**
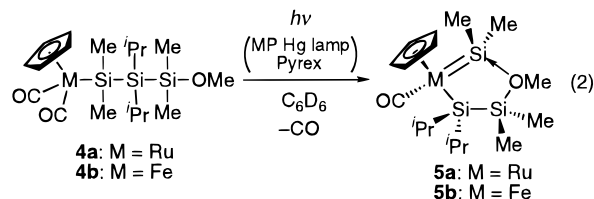

are 64 and 65%, respectively. In these cases, in contrast to **2a** and **2b**, prolonged irradiation caused the decay of **5a** and **5b** but did not give bis(silylene) complexes corresponding to **3a,b**.

The ^{29}Si NMR signals of three silicon atoms and the ^{13}C and ^{1}H NMR signals of four Si−Me groups in **5** appear nonequivalently, respectively. The methyl groups in each isopropyl group are diastereotopic, so that **5** shows four doublets for them. The positions of methyl and isopropyl groups on silicon atoms in **5a** and **5b** were determined by the combination of ^{29}Si−^{1}H COLOC and ^{1}H NOESY spectra (Figures 2 and 3 for **5b**): the ^{29}Si NMR signal of the silylene ligand of **5b** (154.9 ppm) shows a long-range coupling with two Si−Me signals at lower field in the COLOC spectrum, indicating that the substituents on the silylene ligand are methyl groups. Moreover, in the NOESY spectrum, the Cp protons show cross-peaks with the methyl protons of isopropyl groups and the Si−Me's of the silylene ligand but do not show these peaks with the other two Si−Me signals. These observations are consistent with the structure of **5b** shown in eq 2. Almost identical spectra were also obtained for **5a**.

Two possible mechanisms for the formation of disilanyl−silylene complexes are given in Scheme 3: (1) 1,2-migration of the methoxydisilanyl group to the metal center via the α−Si−Si bond cleavage (mechanism A) and (2) 1,3-migration of the methoxysilyl group to the metal center via β-Si−Si bond cleavage (mechanism B). Only **5** forms via mechanism A, while **5** and **5′** form via mechanism B, where both SiMe$_2$ and Si^{i}Pr$_2$ groups in the disilene ligand are attacked by the methoxyl group.

Scheme 3
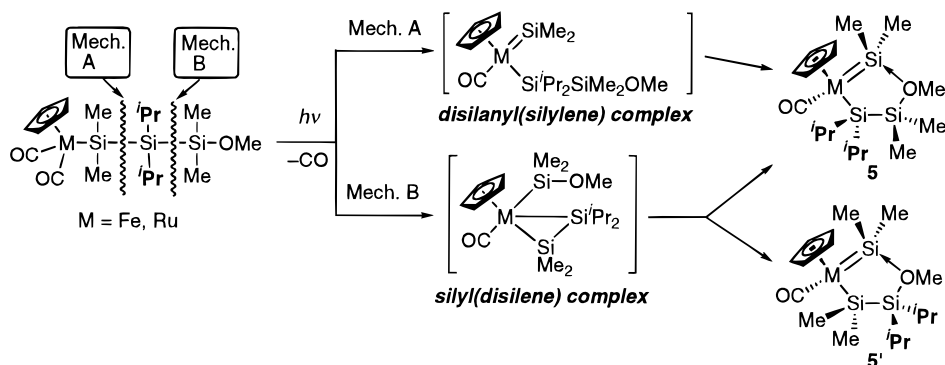
From the experimental result demonstrating the exclusive formation of **5**, mechanism A seems more favorable, although mechanism B cannot be ruled out. Pannell et al. reported the photochemical rearrangement of linear polysilanyl groups in $CpFe(CO)_2(SiMe_2)_nMe$ ($n \geq 3$) into branched ones.[10] They explained the results reasonably by 1,3-migration of substituents on (polysilanyl—silylene)iron intermediates formed via a mechanism analogous to mechanism A. In our systems, scrambling of substituents on **5a** or **5b** was not observed at room temperature, probably because of the strong coordination of the intramolecular alkoxyl group to the silylene ligand which retards the 1,3-migration of substituents.[23]

Photolysis of $CpFe(CO)_2SiMe_2SiMe_2SiMe_2SiMe_2$-OMe (6). In contrast to the methoxydisilanyl-[3] and methoxytrisilanyliron complexes, the photoreaction of methoxytetrasilanyl complex **6** was complicated and gave at least five products. All of them showed ^{1}H NMR signals for the methoxy groups at fields higher than 3 ppm, which indicates that all of them have methoxy groups coordinated to silylene ligands. Isolation of the products was unsuccessful because they were extremely sensitive to air. However, if we take into account the photolysis of $CpFe(CO)_2SiMe_2SiMe_2SiMe_2SiMe_3$ leading to rearrangement into $CpFe(CO)_2Si(SiMe_3)_3$, reported by Pannell et al.,[10a] the result implies that the photolysis of **6** yielded several intramolecularly methoxy-stabilized silylene complexes accompanied by the extensive scrambling of substituents.

Supporting Information Available: Tables of final atomic parameters and temperature factors of non-hydrogen atoms, calculated hydrogen parameters, mean-square displacement tensors for non-hydrogen atoms, interatomic distances and angles, and least-squares planes and atomic deviations for **2a** (8 pages). Ordering information is given on any current masthead page.

OM9801655

(23) We recently observed the thermal rearrangement of the (disilanyl—silylene)iron fragment in **2b** and **5b** into a methoxy-stabilized (silylene—silylsilylene)iron fragment. These results will be reported elsewhere.