Synthesis, Structure, and Reactivity of a Bis(silylene)carbonylruthenium Complex and a Novel Addition Reaction of Photochemically Generated Dimethylsilylene to Bis(silylene) Complexes $Cp(OC)M\{SiMe_2{\cdots}O(Me){\cdots}SiMe_2\}$ (M = Ru, Fe)

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Photolysis of $CpRu(CO)_2SiMe_2SiMe_3$ (**1a**) with a low- or medium-pressure Hg lamp for a long time caused the loss of a $SiMe_2$ moiety to give $CpRu(CO)_2SiMe_3$ (**2**), perhaps through the photochemical dissociation of a CO ligand. This mechanism was supported by the quantitative formation of the bis(silylene)ruthenium complex $Cp(OC)Ru\{SiMe_2{\cdots}O(Me){\cdots}SiMe_2\}$ (**3a**) by photolysis of the (methoxydisilanyl)ruthenium complex $CpRu(CO)_2SiMe_2SiMe_2OMe$ (**1b**). The X-ray crystal structure analysis of **3a** revealed that **3a** has an almost planar Ru−Si−O−Si four-membered chelate ring with short Ru−Si bonds (2.316(3) and 2.311(3) Å) and long Si···O bonds (1.801(7) and 1.793(7) Å). **3a** reacts with MeOH instantaneously to give $Cp(OC)Ru(H)(SiMe_2OMe)_2$ (**4**) quantitatively. Photolysis of $CpM(CO)_2SiMe_2SiMe_2OMe$ (**1b**, M = Ru; **1c**, M = Fe) or $Cp(OC)M\{SiMe_2{\cdots}O(Me){\cdots}SiMe_2\}$ (**3a**, M = Ru; **3b**, M = Fe) with the photochemical silylene precursor $(SiMe_2)_6$ by means of a low-pressure Hg lamp afforded a mixture of **3a** or **3b**, disilanyl−silylene complexes $Cp(OC)M\{{=}SiMe_2{\leftarrow}O(Me)SiMe_2SiMe_2\}$ (**5a**, M = Ru; **5b**, M = Fe), and $(SiMe_2)_5$. Two possible mechanisms for the addition of dimethylsilylene to **3** to give **5** were proposed.

Introduction

Photoreactions of disilanyl- and polysilanylcarbonylmetal complexes have been extensively investigated for various iron complexes of the type $CpFe(CO)_2Si_nR_{2n+1}$[1−4] and for the manganese complex $(OC)_5MnSiMe_2SiMe_2OMe$.[5] The mechanism for this reaction involving 1,2-silyl migration to form silyl−silylene complexes has been established by the isolation and structure determination of some donor-stabilized bis(silylene) complexes.[3−7] For the heavier congeners of iron and manganese complexes, photolyses of some disilanylcarbonylruthenium and -rhenium complexes have been investigated previously by Pannell et al., but they were reported to be photochemically inert.[8] It has been implied that the Ru and Re complexes are more resistant to CO expulsion than the related iron complexes. We report here the photoreactions of $CpRu(CO)_2SiMe_2SiMe_2R$ (R = Me, OMe) that proceed under more forced conditions and the formation, structure, and reactivity of a methoxy-stabilized bis(silylene)ruthenium complex in the case of R = OMe. We also report a novel addition reaction of photochemically generated dimethylsilylene to methoxy-stabilized bis(silylene)ruthenium and -iron complexes giving disilanyl−silylene complexes.

Experimental Section

General Considerations. All manipulations were performed 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 dichloromethane from calcium hydride under a nitrogen atmosphere before use. Methanol was distilled from $Mg(OMe)_2$ and then dried over molecular sieves 3A. Methylcyclohexane (spectrophotometric grade) was used after distillation from sodium. Benzene-d_6 was dried over molecular sieves 4A. Benzene-d_6 and hexane for sealed-tube preparation were dried with a potassium mirror and degassed under high vacuum.

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[1] (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.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (d) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954. (e) Jones K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (f) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (g) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075. (h) Zhang, Z.; Sanchez, R.; Pannell, K. H. *Organometallics* **1995**, *14*, 2605. (i) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315.

[2] (a) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (b) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2979. (c) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (d) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959. (e) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435. (f) 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.

[4] Ueno, K.; Ito, S.; Endo, K.; Tobita, H.; Inomata, S.; Ogino, H. *Organometallics* **1994**, *13*, 3309.

[5] Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835.

[6] Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545.

[7] Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023.

[8] Pannell, K. H.; Rozell, J. M.; Tsai, W.-M. *Organometallics* **1987**, *6*, 2085.

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$Cp_2Ru_2(CO)_4$,[9] $Cp_2Fe_2(CO)_4$,[10] $CpRu(CO)_2SiMe_2SiMe_3$ (**1a**),[8] and $CpRu(CO)_2SiMe_3$ (**2**)[8] were prepared according to published procedures. Other chemicals were used as received from commercial sources.

Photolyses were performed either with an Ushio UM-452 450 W medium-pressure Hg lamp placed in a water-cooled quartz jacket or with a Sen-Tokushukougen 125 W spiral low-pressure Hg lamp.

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.

Preparation of $CpRu(CO)_2SiMe_2SiMe_2OMe$ (1b). To a Na/K alloy prepared from sodium (0.048 g, 2.1 mmol) and potassium (0.215 g, 5.50 mmol) was added $Cp_2Ru_2(CO)_4$ (0.367 g, 0.826 mmol) in THF (30 mL), and the mixture was stirred at room temperature for 4 h. The reaction mixture was filtered through a Schlenk filter with a Celite pad to remove the rest of the Na/K alloy, and the brown filtrate was added dropwise to a THF (10 mL) solution of $ClMe_2SiSiMe_2Cl$ (0.443 g, 2.37 mmol) cooled with a chloroform−liquid N_2 bath. The reaction mixture was stirred for 1 h; then the cooling bath was removed and the mixture was stirred at room temperature for 14 h. After removal of volatiles, the residue was stirred with hexane (50 mL) and the mixture was filtered through a Celite pad. Removal of hexane under reduced pressure gave an orange oil. Methanol (20 mL) and pyridine (0.4 mL) were added to this, and the mixture was stirred for 45 min. After removal of volatiles, purification of the residue by medium-pressure liquid chromatography on silica gel (eluent hexane/ether, 5/1) afforded **1b** (0.170 g, 0.460 mmol, 28%) as a colorless oil. ^1H NMR (300 MHz, C_6D_6): δ 0.28 (s, 6H, SiMe), 0.61 (s, 6H, SiMe), 3.27 (s, 3H, OMe), 4.76 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ −0.9 (SiMe), 3.5 (SiMe), 50.2 (OMe), 86.9 (Cp), 202.4 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −0.6, 18.7. IR (C_6D_6): ν_{CO} 2013, 1957 cm^{-1}. Mass (EI, 70 eV): m/z 370 (0.5, M^+), 342 (93, $M^+ - CO$), 327 (36, $M^+ - CO - Me$), 314 (13, $M^+ - 2CO$), 281 (100, $M^+ - SiMe_2OMe$), 253 (87, $M^+ - CO - SiMe_2OMe$). Anal. Calcd for $C_{12}H_{20}O_3RuSi_2$: C, 38.92; H, 5.45. Found: C, 39.18; H, 5.26.

Preparation of $CpFe(CO)_2SiMe_2SiMe_2OMe$ (1c). In a manner analogous to the preparation of **1b**, except for using $Cp_2Fe_2(CO)_4$ instead of $Cp_2Ru_2(CO)_4$ and purifying the final product by molecular distillation (90 °C/ 0.1 mmHg), **1c** was obtained as a yellow-brown oil in 61% yield based on $Cp_2Fe_2(CO)_4$. ^1H NMR (300 MHz, C_6D_6): δ 0.30 (s, 6H, SiMe), 0.57 (s, 6H, SiMe), 3.26 (s, 3H, OMe), 4.28 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ −0.8 (SiMe), 3.1 (SiMe), 50.2 (OMe), 83.3 (Cp), 215.9 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 13.8, 19.7. IR (C_6D_6): ν_{CO} 1998, 1944 cm^{-1}. Mass (EI, 70 eV): m/z 324 (5, M^+), 296 (60, $M^+ - CO$), 268 (44, $M^+ - 2CO$), 147 (100, $M^+ - CpFe(CO)_2$). Anal. Calcd for $C_{12}H_{20}FeO_3Si_2$: C, 44.44; H, 6.22. Found: C, 44.23; H, 5.96.

Photolytic Procedure. Unless otherwise stated, photolysis of disilanylruthenium and -iron complexes was carried out as follows. A disilanyl complex (ca. 20 mg) was placed in a Pyrex or quartz NMR sample tube (5 mm o.d.), and the tube was attached to a vacuum line via a ground-glass joint. Benzene-d_6 (0.5 mL) was introduced into the NMR tube by the trap-to-trap-transfer technique, and the tube was flame-sealed under vacuum. Irradiation was carried out externally for the sample in a Pyrex tube with a medium-pressure Hg lamp at 2 °C and for the sample in a quartz tube with a low-pressure Hg lamp at room temperature. The reactions were monitored by ^1H NMR spectroscopy. For the photolysis of **1a** in a Pyrex tube, the yield of the product $CpRu(CO)_2SiMe_3$ (**2**) was determined by gas chromatography using n-tetradecane as an internal standard.

Table 1. Crystallographic Data for $Cp(OC)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (3a)

sample	$Cp(OC)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$
formula	$C_{11}H_{20}O_2RuSi_2$
fw	341.52
cryst syst	orthorhombic
space group	*Pbca* (No 61)
syst absence	$(h0l)$: $l = 2n + 1$ $(0kl)$: $k = 2n + 1$ $(hk0)$: $h = 2n + 1$ $(0k0)$: $k = 2n + 1$ $(h00)$: $h = 2n + 1$ $(00l)$: $l = 2n + 1$
a/Å	13.142(2)
b/Å	27.538(3)
c/Å	8.366(9)
V/Å^3	3028
Z	8
d_{calcd}/g cm^{-3}	1.50
μ(Mo Kα)/cm^{-1}	11.5
cryst size/mm	0.30 × 0.20 × 0.15
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
monochromator	graphite
temp/°C	20
reflns measd	h,k,l
2θ range/deg	3−50
scan mode	ω
ω-scan width/deg	$1.1 + 0.35 \tan\theta$
bkgd (count time)/s	7.0
ω-scan rate/deg min^{-1}	4.0
no. of unique data	2011
no. of data used with $\|F_o\| > 3\sigma(F_o)$	1739
no. of params refined	146
R^a	0.054
$R_w{}^b$	0.069
quality of fit indicator^c	1.35
largest shift/esd, final cycle	0.20
max resid electron dens/e Å^{-3}	1.35

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

Photolysis of 1b and Isolation of Its Product 3a. Complex **1b** (198 mg, 0.536 mmol) was placed in a Pyrex tube (10 mm o.d.) having a Teflon needle bulb at the top. The tube was attached to a vacuum line, and degassed hexane (5 mL) was trap-to-trap-transferred into it. After the Teflon bulb was closed, the tube was detached from the vacuum line and irradiated with a medium-pressure Hg lamp at 2 °C for 1 h. The tube was attached to the vacuum line again, and the reaction mixture was concentrated to ca. 1 mL. The tube was flame-sealed and stored at 2 °C to give pale yellow crystals of $Cp(OC)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**3a**). ^1H NMR (300 MHz, C_6D_6): δ 0.32 (s, 6H, SiMe), 0.60 (s, 6H, SiMe), 2.62 (s, 3H, OMe), 4.83 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ 6.9 (SiMe), 9.0 (SiMe), 51.8 (OMe), 83.1 (Cp), 207.0 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 104.2. IR (C_6D_6): ν_{CO} 1957 cm^{-1}. Mass (EI, 70 eV): m/z 342 (27, M^+), 327 (24, $M^+ - Me$), 314 (10, $M^+ - CO$), 283 (70, $M^+ - CO - OMe$). Anal. Calcd for $C_{11}H_{20}O_2RuSi_2$: C, 38.69; H, 5.90. Found: C, 39.09; H, 5.93.

X-ray Crystal Structure Determination of 3a. A single crystal of **3a** was cut with a blade to the size suitable for X-ray structure analysis (0.30 × 0.20 × 0.15 mm) in a glovebox, the crystal was mounted in a thin glass capillary, and the capillary was flame-sealed. The intensity data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. Crystallographic parameters are listed in Table 1. The structure was solved by direct methods (RANTAN81)[11] and refined anisotropically

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[9] Gibson, D. H.; Hsu, W.-L.; Steinmetz, A. L. *J. Organomet. Chem.* **1981**, *208*, 89.

[10] King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.

[11] (a) Jia-Xing, Y. *Acta Crystallogr., Sect. A* **1981**, *37*, 642. (b) Jia-Xing, Y. *Acta Crystallogr., Sect. A* **1983**, *39*, 35.

for non-hydrogen atoms. None of the hydrogen atoms were found by difference Fourier synthesis; therefore, the hydrogen atoms on the Cp ring were located by calculation. The final *R* value was 0.054, and the weighted R_w was 0.069.

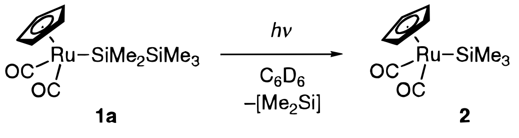
All the calculations were performed on a Nippon Electric Co. ACOS-3900 computer system at the computer center of Tohoku University, using the Universal Crystallographic Computation Program (Unics III).[12]

Reaction of 3a with MeOH. Complex **3a** (10 mg, 2.9×10^{-5} mol) was placed in a thick-walled Pyrex NMR tube, and the tube was attached to a vacuum line through a ground-glass joint. Benzene-d_6 (ca. 0.1 mL) and MeOH (1.3 mL, 3.22×10^{-5} mol) were transferred into the NMR tube by the trap-to-trap technique, and the tube was warmed to room temperature. After a few minutes, volatiles were removed by the trap-to-trap-transfer technique to give crude Cp(OC)Ru(H)-$(SiMe_2OMe)_2$ (**4**) as a colorless oil. The ^{1}H NMR spectrum of the crude product in benzene-d_6 indicated that the reaction is almost quantitative. Attempts of crystallization of **4** were unsuccessful because it decomposed in solution, even under a nitrogen atmosphere. ^{1}H NMR (300 MHz, C_6D_6): δ −10.9 (s, 1H, RuH), 0.62 (s, 6H, SiMe), 0.67 (s, 6H, SiMe), 3.35 (s, 6H, OMe), 4.72 (s, 5H, Cp). ^{13}C NMR (75.5 MHz, C_6D_6): δ 10.5 (SiMe), 10.6 (SiMe), 50.5 (OMe), 88.2 (Cp), 201.6 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 50.6. IR (hexane): ν_{CO} 1948 cm^{-1}. Mass (EI, 70 eV): *m/z* 374 (6, M$^+$), 359 (6, M$^+$ − Me), 284 (100, M$^+$ − SiMe$_2$OMe − H). Exact mass calcd for $C_{12}H_{24}O_3RuSi_2$ 374.0308, found 374.0305.

Photolysis of 1b, 1c, 3a, or Cp(OC)Fe{SiMe$_2$···O-(Me)···SiMe$_2$} (3b) in the Presence of (SiMe$_2$)$_6$. A typical procedure is as follows: Complex **1b** (6.3 mg, 1.71×10^{-5} mol) and $(SiMe_2)_6$ (6.9 mg, 1.96×10^{-5} mol) were placed in a quartz NMR tube, and the tube was attached to a vacuum line through a ground-glass joint. Benzene-d_6 (ca. 0.5 mL) was transferred into the NMR tube by the trap-to-trap technique, and the tube was flame-sealed. The tube was then irradiated at room temperature with a low-pressure Hg lamp, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The products, **3a**, Cp(OC)Ru{=SiMe$_2$←O(Me)SiMe$_2$SiMe$_2$} (**5a**),[13] and $(SiMe_2)_5$, were characterized by comparing the ^{1}H and ^{29}Si NMR spectra of the reaction mixture with those of the authentic samples.

Results and Discussion

Photolysis of CpRu(CO)$_2$SiMe$_2$SiMe$_3$ (1a). Pannell et al. previously reported that, in contrast to the case for the iron analogue, irradiation of **1a** with a 500 W Hanovia lamp gave no deoligomerization (<1%) after 48 h. We found that the deoligomerization reaction proceeded slowly on irradiation through a quartz jacket with a strong 125 W spiral low-pressure Hg lamp (15% conversion after 30 min irradiation) (eq 1). The same reaction occurred also slowly with a 450 W medium-pressure Hg lamp through a Pyrex jacket (33% conversion after 15 min irradiation).



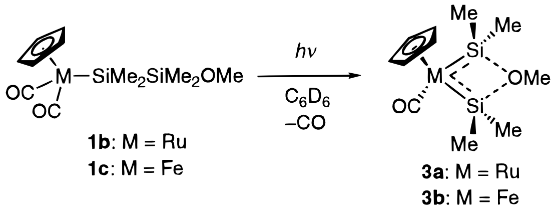
(1)

The product was characterized as **2** by comparing the ^{1}H NMR (δ 0.51, 4.49 ppm) and other spectroscopic data with those of an authentic sample.[8] The conversion yield of **2** steeply decreased with the increase of conversion (50% yield after 3% conversion and 15% yield after 33% conversion). This is in contrast to the photolysis of the iron analogue CpFe(CO)$_2$SiMe$_2$SiMe$_3$, which gives CpFe(CO)$_2$SiMe$_3$ in 64% yield after 80% conversion.[1a,2a] This indicates that **2** is more photosensitive than the iron analogue CpFe(CO)$_2$SiMe$_3$.

Kazlauskas and Wrighton reported a somewhat lower quantum efficiency (ca. 0.40) for the photosubstitution of CpRu(CO)$_2$CH$_3$ at 313 nm compared to that of CpFe(CO)$_2$CH$_3$ (≥0.7) at 366 nm.[14] Moreover, since the absorption maxima in the electronic spectrum of CpRu-(CO)$_2$CH$_3$ (280, 235 nm) appear at much shorter wavelength compared to those of CpFe(CO)$_2$CH$_3$ (345, 275 nm), we can expect much slower photoreaction for the ruthenium complex if a light from a medium-pressure Hg lamp through a Pyrex filter is used for the photolysis.

In the case of **1a**, the absorption maximum with the lowest energy appears at 270 nm (ϵ 2700 M^{-1} cm^{-1}) in methylcyclohexane, which is much shorter in wavelength than the corresponding maximum of CpFe-(CO)$_2$SiMe$_2$SiMe$_3$ (330 (sh) nm (1900 M^{-1} cm^{-1})). This apparently causes a much slower reaction for **1a** compared to that for the iron analogue, especially when a 450 W medium-pressure Hg lamp is used. Another possible factor which retards the formation of **2** may be the inertness of a silylene ligand toward substitution by CO in a possible intermediate CpRu(CO)(=SiMe$_2$)-SiMe$_3$. To confirm the existence of the (silyl−silylene)-ruthenium intermediate, the following reaction was carried out.

Photolysis of CpM(CO)$_2$SiMe$_2$SiMe$_2$OMe (1b, M = Ru; 1c, M = Fe). Photolysis of the (methoxydisilanyl)ruthenium complex **1b** in C_6D_6 in a Pyrex NMR tube with a medium-pressure Hg lamp resulted in a clean conversion to **3a** after 60 min (NMR yield 95%) (eq 2).



(2)

In a similar manner, photolysis of the iron analogue **1c** afforded the known complex **3b** quantitatively.[3b] Complex **3a** was isolated as pale yellow crystals by a large-scale photolysis followed by crystallization from hexane.

Complex **3a** shows a downfield shifted ^{29}Si NMR signal at δ 104.2 ppm, an upfield-shifted ^{1}H NMR signal of the bridging methoxyl group at δ 2.62 ppm, and a CO stretching band at 1957 cm^{-1} in the IR spectrum. These spectroscopic data are all consistent with the structure of **3a** shown in eq 2. The structure of **3a** was further confirmed by the X-ray crystal structure analysis (vide infra). The ^{29}Si NMR chemical shift of **3a** is almost the same as that of the triphenylphosphine derivative Cp(Ph$_3$P)Ru{SiMe$_2$···O(Me)···SiMe$_2$} (δ 108.7

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[12] Sakurai, T.; Kobayashi, M. *Rikagaku Kenkyuusho Houkoku* **1979**, *55*, 69.

[13] Complexes **5a** and **5b** were synthesized by photolysis of CpM-(CO)$_2$SiMe$_2$SiMe$_2$SiMe$_2$OMe (M = Ru, Fe) and are fully characterized in: Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1988**, *17*, 2850.

[14] Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602.

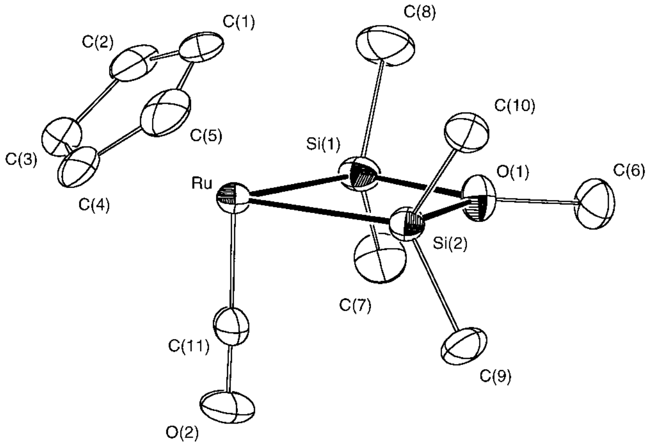
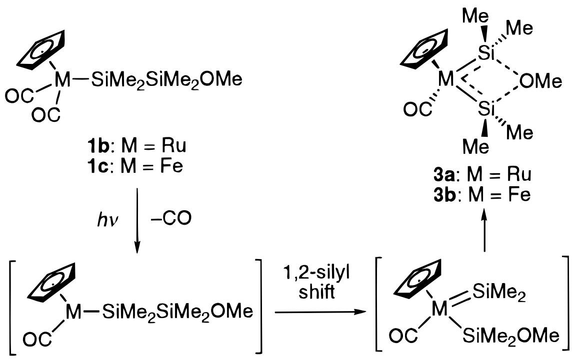


Figure 1. ORTEP drawing of Cp(OC)Ru{$SiMe_2$···O(Me)···$SiMe_2$} (**3a**).

Scheme 1



ppm)[6] but is fairly upfield shifted compared to the iron analogues Cp(OC)Fe{$SiMe_2$···O(Me)···$SiMe_2$} (δ 123.7 ppm)[3b] and Cp*(OC)Fe{$SiMe_2$···O(Me)···$SiMe_2$} (Cp* = η^5-C_5Me_5; δ 125.2 ppm).[3] This phenomenon can be rationalized by the smaller paramagnetic shielding effect originating from the larger p and d orbital radii of ruthenium compared to those of iron.[15]

As has already been suggested for the formation of several other alkoxy-stabilized bis(silylene) complexes, the mechanism for the formation of **3** is considered to involve the initial photoinduced dissociation of a CO ligand followed by a 1,2-shift of the terminal silyl group and final cyclization (Scheme 1).

X-ray Structure Determination of 3a. The ORTEP drawing of **3a** is shown in Figure 1. Selected bond distances and angles are summarized in Table 2. The Ru−Si bonds (2.316(3) and 2.311(3) Å) are shorter than normal Ru−Si single bonds (2.34−2.51 Å),[16] close to those of the donor-stabilized silyleneruthenium complexes [Cp*($(Me_3P)_2$Ru=$SiPh_2$·NCMe]BPh_4 (2.328(2) Å)[17] and Cp(Ph_3P)Ru{$SiMe_2$···O(Me)···$SiMe_2$} (average 2.326 Å)[6] and longer than that of the donor-free silyleneruthenium complex [Cp*$(Me_3P)_2$Ru=$SiMe_2$]$B(C_6F_5)_4$ (2.238(2) Å).[18] The Si−O bonds in **3a** (1.801(7) and 1.793(7) Å) are much longer than a normal Si−O single bond (1.63 Å) but is somewhat shorter than the corresponding bonds in Cp(Ph_3P)Ru{$SiMe_2$···O(Me)···$SiMe_2$} (average 1.84 Å).[6] The latter fact is attributable to the weaker back-donation from the Ru center to the σ^* orbital of the Si−O bonds in **3a** compared to that in the latter complex containing an electron-donating phosphine ligand. These bond length data are consistent with the bonding scheme of **3a** having unsaturated Ru−Si bonds and dative O−Si bonds.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Cp(OC)Ru{$SiMe_2$···O(Me)···$SiMe_2$} (3a)

	Bond Distances		
Ru−Si(1)	2.316(3)	Ru−Si(2)	2.311(3)
Ru−C(11)	1.830(10)	O(2)−C(11)	1.152(12)
Si(1)−O(1)	1.801(7)	Si(2)−O(1)	1.793(7)
Si(1)−C(7)	1.910(10)	Si(1)−C(8)	1.905(13)
Si(2)−C(9)	1.883(10)	Si(2)−C(10)	1.903(10)
O(1)−C(6)	1.464(13)		
C(1)−C(2)	1.460(17)	C(2)−C(3)	1.391(16)
C(3)−C(4)	1.447(16)	C(4)−C(5)	1.419(17)
C(5)−C(1)	1.444(19)		
	Bond Angles		
Si(1)−Ru−Si(2)	70.68(9)	Si(1)−Ru−C(11)	88.0(3)
Si(2)−Ru−C(11)	87.5(3)		
Ru−Si(1)−O(1)	96.3(2)	Ru−Si(1)−C(7)	125.0(3)
Ru−Si(1)−C(8)	119.1(4)	O(1)−Si(1)−C(7)	102.2(4)
O(1)−Si(1)−C(8)	102.6(5)	C(7)−Si(1)-C(8)	106.6(5)
Ru−Si(2)−O(1)	96.7(2)	Ru−Si(2)−C(9)	124.8(3)
Ru−Si(2)−C(10)	118.8(3)	O(1)−Si(2)−C(9)	101.7(4)
O(1)−Si(2)−C(10)	102.7(4)	C(9)−Si(2)−C(10)	107.2(5)
Si(1)−O(1)−Si(2)	96.3(3)	Si(1)−O(1)−C(6)	132.9(6)
Si(2)−O(1)−C(6)	130.6(6)		
Ru−C(11)−O(2)	178.5(8)		

The sum of the bond angles around trivalent oxygen O(1) is 359.8°. This indicates that the oxygen adopts a planar geometry with sp^2 hybridization. The sums of the bond angles between the three bonds around each of the Si(1) and Si(2) atoms except the O(1)−Si dative bond are 350.7 and 350.8°, respectively. This implies that there is significant contribution of the π interaction between the sp^2-hybridized Si atoms and the ruthenium center.

The Ru−Si−O−Si four-membered chelate ring is almost planar: dihedral angles between the planes defined by Ru−Si(1)−Si(2) and Si(1)−Si(2)−O(1) and the planes defined by Ru−Si(1)−O(1) and Ru−Si(2)−O(1) are 178.9 and 178.8°, respectively. This is in contrast to most of the structurally determined, donor-bridged bis(silylene) complexes which have nonplanar four-membered chelate rings.[3,4,6,7] The only exception is the manganese complex $(OC)_4$Mn{$SiMe_2$···O(Me)···$SiMe_2$}, which has a planar four-membered chelate ring, because this complex has the same environment on both sides of the ring.[5] Complex **3a** has different ligands on the top and the bottom of the four-membered chelate ring and still has an almost planar chelate ring. This result implies that the four-membered chelate ring of the donor-bridged bis(silylene) complex is essentially planar, and this geometry is preferred when the in-

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[15] (a) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699. (b) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714. (c) Mason, J. *Multinuclear NMR*; Plenum Press: New York, 1987.

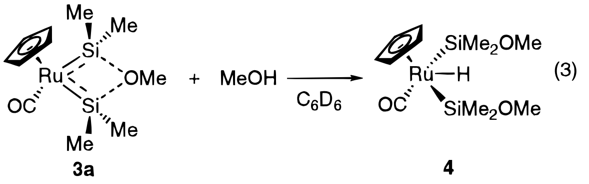
[16] (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245, 309.

[17] (a) Straus, D. L.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D. L.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

[18] Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495.

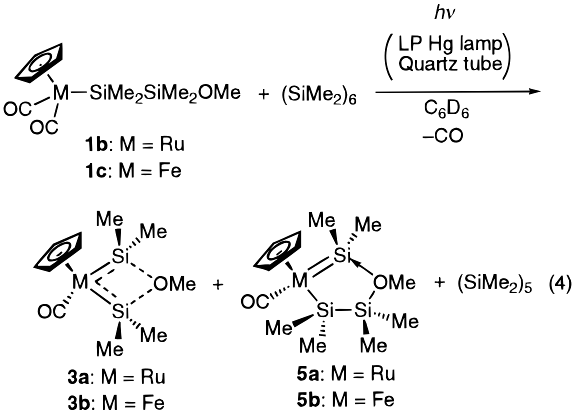
tramolecular steric repulsion is small as in the case of **3a**, whereas large intramolecular steric repulsion causes the distortion of the chelate ring.

Reaction of 3a with MeOH. Like other methoxy-stabilized bis(silylene)iron[19] and -ruthenium[20] complexes, complex **3a** reacts with MeOH instantaneously to give the addition product $Cp(OC)Ru(H)(SiMe_2OMe)_2$ (**4**) cleanly (eq 3).



Complex **4** shows only one ^{29}Si NMR signal at δ 50.6 ppm for two silyl ligands. This indicates that **4** takes a *trans* geometry. The ^{1}H NMR signals for Si−Me split into two singlets because two methyl groups on the same silicon atom are mutually diastereotopic. The formation of **4** can be explained by the initial nucleophilic attack of MeOH at the silylene ligand of **3a** followed by proton migration from the coordinated MeOH to the ruthenium center. This reaction confirms that the Ru−Si bonds in **3a** are highly polarized in $Ru^{\delta-}-Si^{\delta+}$ fashion and the silylene ligand is strongly electrophilic.[17,21]

Photolysis of 1b, 1c, or $Cp(OC)M\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (3a, M = Ru; 3b, M = Fe) with $(SiMe_2)_6$. Photolysis of a mixture of the methoxy−disilanyl complex **1b** or **1c** and the photochemical silylene precursor $(SiMe_2)_6$ with a low-pressure Hg lamp afforded a mixture of bis(silylene) complex **3a** or **3b**, disilanyl−silylene complex **5a** or **5b**, and $(SiMe_2)_5$ (eq 4). Complexes **5a** and **5b** showed their ^{1}H and ^{29}Si NMR signals at exactly the same positions as those of the authentic samples prepared by the photolysis of $CpM(CO)_2SiMe_2SiMe_2SiMe_2OMe$ (M = Ru, Fe).[13]



The ratio of **5** to **3** reached a maximum and then slowly decreased in the presence of the silylene precursor $(SiMe_2)_6$, but **3** never disappeared. The maximum ratio of **5** to **3** depends on the relative amount of $(SiMe_2)_6$ to **1**, and the larger the relative amount of $(SiMe_2)_6$, the higher the ratio of **5** to **3** (Tables 3 and 4).

Table 3. Time Course of the Molar Ratio of 1b and 5a to 3a on the Photolysis of 1b[a]

irradiation time/min	initial molar ratio of **1b** to $(SiMe_2)_6$			
	1:1		1:9	
	1b	**5a**	**1b**	**5a**
0.5	6.5	0.5		
5	1.6	0.8	4.5	1.5
15	0.5	1.1	1.6	3.9
20	0.3	1.1	1.2	4.0
30	0	1.3	0.5	3.8
50	0	1.0	0	3.3
70	0	0.8	0	3.3

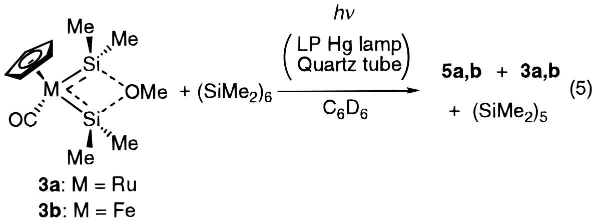
[a] The ratio was determined on the basis of the relative intensity of ^{1}H NMR signals of the methoxy groups of **1b** and **5a** compared to that of **3a**.

Table 4. Time Course of the Molar Ratio of 1c and 5b to 3b on the Photolysis of 1c[a]

irradiation time/min	initial molar ratio of **1c**:$(SiMe_2)_6$			
	2:1		1:2	
	1c	**5b**	**1c**	**5b**
2	2.5	0.2	2.2	0.4
5	0.7	0.3	1.0	0.8
10	0.3	0.5	0.5	1.1
15	0	0.5	0	1.4
20	0	0.6	0	1.3
30	0	0.6	0	1.4
40	0	0.4	0	1.3

[a] The ratio was determined on the basis of the relative intensity of ^{1}H NMR signals of the methoxy groups of **1c** and **5b** compared to that of **3b**.

This reaction probably proceeds through the initial formation of **3** from **1** followed by the addition of free dimethylsilylene photochemically generated from $(SiMe_2)_6$. Accumulation of **3** in the early stage of this photolysis supports this mechanism. Another possible mechanism involves the addition of dimethylsilylene to the 16e species $CpM(CO)SiMe_2SiMe_2OMe$ formed by decarbonylation from **1** followed by cyclization. However, the lifetime of the 16e species is estimated to be as short as that of $CpFe(CO)SiMe_3$ (ca. 10 ns),[22] so that the possibility of the collision of two short-lived species, i.e., $CpM(CO)SiMe_2SiMe_2OMe$ and dimethylsilylene, is expected to be very low. The former reaction mechanism was further supported by the fact that photolysis of **3a,b** with the photochemical silylene precursor $(SiMe_2)_6$ also gave a mixture of **3a,b**, **5a,b**, and $(SiMe_2)_5$ (eq 5).



Two routes to **5** shown in Scheme 2 are conceivable according to the position on **3** where dimethylsilylene

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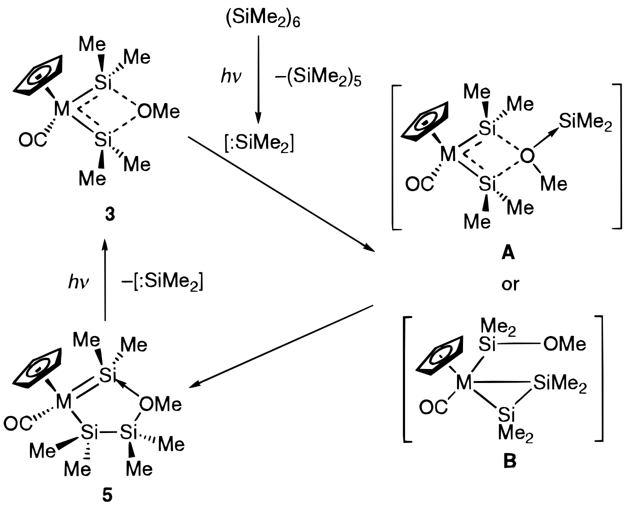
(19) Ueno, K.; Tobita, H.; Seki, S.; Ogino, H. *Chem. Lett.* **1993**, 1723.

(20) Wada, H.; Tobita, H.; Ogino, H. *Organometallics* **1997**, *16*, 2200.

(21) (a) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (b) Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C. *Organometallics* **1992**, *11*, 514. (c) Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* **1983**, *258*, C1. (d) Cundari, T. R.; Gordon, M. S. *J. Phys. Chem.* **1992**, *96*, 631. (e) Márquez, A.; Sanz, F. *J. Am. Chem. Soc.* **1992**, *114*, 2903. (f) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. (g) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775.

(22) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Borg, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113*, 2011.

Scheme 2



attacks: (1) Dimethylsilylene attacks the trivalent oxygen to form an adduct **A**, in which the silylene moiety then inserts into the Si···O dative bond, or (2) dimethylsilylene adds to the M═Si unsaturated bond to give a η^2-disilene complex **B**, which then rearranges. The insertion of silylene into an Si–O bond is well-known,[23] and the reactions in low-temperature matrixes confirmed that the first step of this reaction was the coordination of silylene onto the oxygen.[24] Addition of silylene to an unsaturated bond such as C═C, C≡C, C═O, etc. is also well established,[23] though the addition to a metal–(main group element) multiple bond is rare.[25] So far we have no experimental result which prefers one route to the other.

Photolysis of purely isolated **5** has unequivocally demonstrated that **5** photochemically liberates a dimethylsilylene unit to give **3**.[13] Thus, the simultaneous operation of these two processes, namely the addition of dimethylsilylene to **3** and the liberation of dimethylsilylene from **5**, perhaps causes the attainment of the photostationary state between **3** and **5** in the presence of a photochemical silylene source.

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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 **3a** (8 pages). Ordering information is given on any current masthead page.

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[23] Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, pp 229–277.

[24] Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487.

[25] Reisacher, H.-U.; Duesler, E. N.; Paine, R. T. *J. Organomet. Chem.* **1997**, *539*, 37.