Synthesis, Structure, and Fluxional Behavior of Donor-Stabilized Bis(silylene)tungsten Complexes

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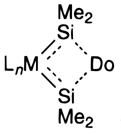
Donor-stabilized bis(silylene)tungsten complexes $\mathrm{CpW(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}}$ ($\mathrm{Cp} = \eta\text{-}\mathrm{C_5H_5}$; $\mathrm{Do} = \mathrm{NEt_2}$ (**1**), OMe (**2**)) were synthesized by photolysis of a $\mathrm{C_6D_6}$ solution containing $\mathrm{CpW(CO)_3Me}$ and $\mathrm{HSiMe_2SiMe_2Do}$. The X-ray crystal structures of **1** and **2** revealed that the W−Si bonds (2.502(2) and 2.501(2) Å for **1**; 2.490(3) Å for **2**) are significantly shorter than those of structurally similar silyltungsten complexes, while the Si−N bonds (1.930(6) and 1.920(7) Å) in **1** and the Si−O bonds (1.792(7) Å) in **2** are much longer than usual Si−N and Si−O single bonds. These structural data indicate that the W−Si bonds bear partial double bond character, whereas the Si−N and Si−O bonds are regarded as a hybrid of covalent bonding and dative bonding. The unsaturated nature of the tungsten−silicon bonds is also indicated by the significant downfield shift of the ^{29}Si NMR signals as well as large coupling constants between ^{29}Si and ^{183}W (**1** $\delta = 62.1$ ppm, $^1J_{\mathrm{W-Si}} = 91.5$ Hz; **2** $\delta = 99.3$ ppm, $^1J_{\mathrm{W-Si}} = 99.3$ Hz) compared to those of structurally similar silyltungsten complexes. The tungsten complexes **1** and **2** showed fluxional behavior due to silylene−methyl group exchange and, in the case of **1**, N−Et group exchange. A mechanism containing the generation of a base-free silyl(silylene)tungsten complex as the key intermediate is proposed for the fluxional process.

Introduction

We have synthesized donor-bridged bis(silylene) complexes **A** containing iron, ruthenium, manganese, and iridium as central metals, which can be regarded as intramolecular donor-stabilized silyl(silylene) complexes.[1] Germylene analogs, alkoxy-bridged bis(germylene)- and germylene(silylene)iron complexes, were also synthesized by our group.[2] The germylene complexes show a fluxional behavior due to the rotation of the germylene ligand around the iron−germylene bond, which has been proposed to proceed via generation of a base-free germyleneiron intermediate $\mathrm{Cp^*(OC)Fe({=}GeMe_2)EMe_2OR}$ ($\mathrm{Cp^*} = \eta\text{-}\mathrm{C_5Me_5}$; E = Si, Ge; R = Me, Bu^t). However, no silylene rotation has been observed in alkoxy-bridged bis(silylene)- and germylene(silylene)iron complexes. These results are consistent with the greater stability of $\mathrm{Fe{=}GeR_2}$ compared to $\mathrm{Fe{=}SiR_2}$ and also reflect the stronger Si−O bonding compared to Ge−O bonding.[2]



A

$\mathrm{L}_n\mathrm{M}$ = CpFe(CO), $\mathrm{CpRu(PR_3)}$, $\mathrm{Mn(CO)_4}$, $\mathrm{IrH\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)}$

Do = OMe, OBu^t, $\mathrm{NEt_2}$

Here, we report the synthesis and crystal structures of donor-bridged bis(silylene)tungsten complexes, $\mathrm{CpW(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}}$ ($\mathrm{Cp} = \eta\text{-}\mathrm{C_5H_5}$; $\mathrm{Do} = \mathrm{NEt_2}$ (**1**), OMe (**2**)). These are the first fully characterized tungsten complexes with silylene ligands.[3] Complexes **1** and **2** show fluxional behavior (vide infra).

Experimental Section

All manipulations were performed using either standard Schlenk tube techniques under a nitrogen atmosphere, vacuum line techniques, or a drybox under a nitrogen atmosphere. Tetrahydrofuran, benzene, hexane, and diethyl ether were dried and deoxygenated by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere. Diethylamine was dried over $\mathrm{CaH_2}$ and distilled under a nitrogen atmosphere before use. Lithium aluminum hydride was purchased from Wako Pure Chemical Industries, Ltd., and used as received. $\mathrm{CpW(CO)_3Me}$ was prepared according to the literature method.[4] Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer. Infrared (IR) spectra were obtained on a HORIBA FT-200 spectrometer. Mass and high-resolution mass spectra were recorded on a JEOL HX-110 spectrometer at the Instrumental Analysis Center for Chemistry, Tohoku University. Elemental analyses were also performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Synthesis of $\mathrm{HSiMe_2SiMe_2NEt_2}$.[5] $\mathrm{HNEt_2}$ (15.0 mL, 145 mmol) was added dropwise to a pentane solution (200 mL) of $\mathrm{ClSiMe_2SiMe_2Cl}$ (13.2 g, 70.4 mmol) at 0 °C with vigorous

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(1) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *100*, 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) Ueno, K.; Ito, S.; Endo, K.; Tobita, H.; Inomata, S.; Ogino, H. *Organometallics* **1994**, *13*, 3309. (e) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545. (f) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1997**, 437.

(2) (a) Koe, J. R.; Tobita, H.; Suzuki, T.; Ogino, H. *Organometallics* **1992**, *11*, 150. (b) Koe, J. R.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479.

(3) Zybill *et al.* reported the synthesis of a base-stabilized silylene-tungsten complex, see: Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C. *Organometallics* **1992**, *11*, 514.

(4) Fischer, E. O. *Inorg. Synth.* **1963**, *7*, 136.

(5) There is a closely related report on aminolysis of a trichlorodisilane, see: Yoshida, M.; Sakamoto, K.; Sakurai, H. The 65th Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, 1993; Abstract 3F332.

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Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	2
empirical formula	$C_{15}H_{27}NO_2Si_2W$	$C_{12}H_{20}O_3Si_2W$
fw	493.41	452.30
temp	293(2) K	293(2) K
wavelength	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	orthorhombic
space group	$P2_1/a$	*Pbma*
unit cell dimens	$a = 16.5690(14)$ Å	$a = 12.771(6)$ Å
	$b = 8.7952(9)$ Å	$b = 14.478(6)$ Å
	$c = 12.953(2)$ Å	$c = 8.755(4)$ Å
	$\beta = 94.430(12)°$	
vol	1882.0(4) Å^3	1618.8(12) Å^3
Z	4	4
density (calcd)	1.741 g/cm^3	1.856 g/cm^3
abs coeff	6.269 mm^{-1}	7.282 mm^{-1}
F(000)	968	872
cryst size	0.33 × 0.28 × 0.15 mm	0.45 × 0.36 × 0.42 mm
θ range for data collection	1.58−32.50°	2.33−30.00°
index ranges	$-24 \le h \le 24$	$0 \le h \le 17$
	$0 \le k \le 13$	$0 \le k \le 20$
	$0 \le l \le 19$	$0 \le l \le 12$
no. of reflns colld	6225	2212
no. of indep reflns	5888 [*R*(int) = 0.0218]	2212 [*R*(int) = 0.0000]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5888/0/196	2212/0/91
goodness-of-fit on F^2	0.998	1.030
final *R* indices [$I > 2s(I)$]	R1 = 0.0526, wR2 = 0.1176[a]	R1 = 0.0618, wR2 = 0.1350[b]
R indices (all data)	R1 = 0.0765, wR2 = 0.1246[a]	R1 = 0.0854, wR2 = 0.1448[b]
largest diff. peak and hole	2.479 and −4.258 e Å^{-3}	3.629 and −3.674 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$, calcd $w = 1/[\sigma^2(F_o^2) + (0.0713P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$; calcd $w = 1/[\sigma^2(F_o^2) + (0.0870P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

stirring. After the reaction mixture was stirred for 18 h at room temperature, the reaction mixture was filtered through a Celite pad. Volatiles were removed from the filtrate under reduced pressure, and the residue was dissolved in 10 mL of ether. The mixture was added dropwise with vigorous stirring to a suspension of $LiAlH_4$ (1.2 g) in ether (30 mL) at 0 °C and then stirred for 30 min. The mixture was filtered through a Celite pad, and the filtrate was concentrated under reduced pressure. The solution was filtered through a Celite pad and then distilled under reduced pressure (bp 70−72 °C/28 Torr). $HSiMe_2SiMe_2NEt_2$ was obtained as an extremely moisture-sensitive liquid (9.6 g, 51 mmol, 72%). ^1H NMR (300 MHz, C_6D_6): δ 3.97 (sept, 1H, $J = 4.6$ Hz, SiH), 2.76 (q, 4H, $J = 7.0$ Hz, NEt), 0.97 (t, 6H, $J = 7.0$ Hz, NEt), 0.20 (s, 6H, SiMe), 0.17 (d, 6H, $J = 4.6$ Hz, SiMe). ^{13}C NMR (75.5 MHz, C_6D_6): δ 41.3 (NEt), 16.2 (NEt), −0.4 (SiMe), −6.0 (SiMe). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT): δ −2.8, −42.4. MS (EI, 70 eV): *m/z* 189 (M^+, 24.9), 130 (100), 59 (9.9). Exact mass *m/z* calcd for $C_8H_{23}NSi_2$: 189.1369. Found: 189.1370.

Synthesis of $HSiMe_2SiMe_2OMe$. The synthesis of the hydromethoxydisilane $HSiMe_2SiMe_2OMe$ was recently reported by our group.[1e] However, the following procedure gave $HSiMe_2SiMe_2OMe$ in a better yield: To a benzene solution (10 mL) of $HSiMe_2SiMe_2NEt_2$ (8.4 g, 44 mmol) was added dropwise MeOH (4 mL, 99 mmol) at 0 °C with vigorous stirring. The mixture was stirred for 30 min at room temperature. Distillation (bp 90−100 °C) under atmospheric pressure gave the title compound as a moisture-sensitive liquid (5.0 g, 34 mmol, 74%).

Synthesis of $Cp(OC)_2W\{SiMe_2{\cdots}NEt_2{\cdots}SiMe_2\}$ (1). A Pyrex sample tube (10 mm o.d., 8 mm i.d.) with a ground-glass joint was charged with $CpW(CO)_3Me$ (0.80 g, 2.3 mmol) and $HSiMe_2SiMe_2NEt_2$ (0.45 g, 2.4 mmol) and connected to a vacuum line via a ground-glass joint. Toluene (about 5 mL) was transferred to the sample tube by conventional trap-to-trap distillation. The sample tube was then flame-sealed under vacuum. The solution was irradiated for 45 min externally with a medium-pressure Hg arc lamp (Ushio UV-450) placed in a water-cooled quartz jacket. The sample tube was immersed in ice-water during the irradiation. The distance from the light source to the sample was ca. 4 cm. After irradiation, the reaction mixture was transferred into a Schlenk tube, concentrated, and cooled to −18 °C in a refrigerator to give air- and moisture-sensitive yellow crystals of **1** (0.64 g, 1.3 mmol, 54%). ^1H NMR (300 MHz, C_6D_6, 295 K): δ 4.77 (s, 5H, Cp), 2.42 (br, 4H, $J = 7.1$ Hz, NEt), 0.75 (br, 6H, SiMe), 0.51 (t, 6H, $J = 7.1$ Hz, NEt), 0.39 (br, 6H, SiMe). ^{13}C NMR (75.5 MHz, C_6D_6, 295 K): δ 228.7 (CO, $^1J_{W-C} = 150.2$ Hz), 86.2 (Cp), 40.1 (br, NEt), 10.4 (NEt), 10.1 (br, SiMe), 6.3 (br, SiMe). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT, 295 K): δ 62.1 ($^1J_{W-Si} = 91.5$ Hz). IR (C_6D_6): ν_{CO} 1902, 1828 cm^{-1}. MS (EI, 70 eV): *m/z* 493 (M^+, 73.2), 422 (17.9), 392 (21.5), 130 (100). Anal. Calcd for $C_{15}H_{27}O_2NSi_2W$: C, 36.51; H, 5.27; N, 2.84. Found: C, 36.26; H, 5.27; N, 2.89.

Synthesis of $Cp(OC)_2W\{SiMe_2{\cdots}OMe{\cdots}SiMe_2\}$ (2). Complex **2** was synthesized by the photolysis of a mixture of $CpW(CO)_3Me$ and $HSiMe_2SiMe_2OMe$ and isolated (50% yield) in a similar manner to that of **1**. ^1H NMR (300 MHz, C_6D_6, 295 K): δ 4.71 (s, 5H, Cp), 2.58 (s, 3H, OMe), 0.68 (br, 6H, SiMe), 0.28 (br, 6H, SiMe). ^{13}C NMR (75.5 MHz, C_6D_6, 295 K): δ 228.1 (CO, $^1J_{W-C} = 146.2$ Hz), 86.4 (Cp), 51.8 (OMe), 9.1 (br, SiMe), 6.4 (br, SiMe). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT, 295 K): δ 99.3 ($^1J_{W-Si} = 99.3$ Hz). IR (C_6D_6): ν_{CO} 1911, 1842 cm^{-1}. MS (EI, 70 eV): *m/z* 452 (M^+, 100), 392 (45.6), 91 (70.8). Anal. Calcd for $C_{12}H_{20}O_3Si_2W$: C, 31.87; H, 4.46. Found: C, 32.16; H, 4.30.

X-ray Crystal Structure Determination of 1 and 2. A single crystal of **1** or **2** was sealed into a glass capillary under an atmosphere of dry nitrogen. The intensity data for X-ray crystal structure analysis were collected on a RIGAKU AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 293 K. The space group was determined based on the systematic absences and the subsequent least-squares refinement. Crystallographic data for **1** and **2** are summarized in Table 1. The structures were solved by Patterson and Fourier transform methods (SHELXS-86).[6] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections (SHELXL-93).[7] All hydrogen atoms were placed

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[6] Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

[7] Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993.

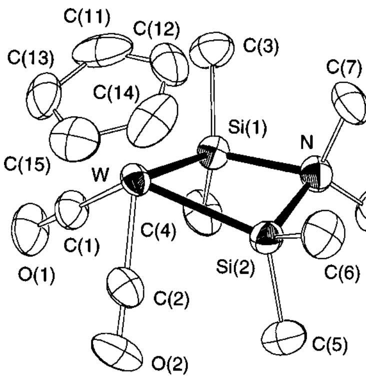
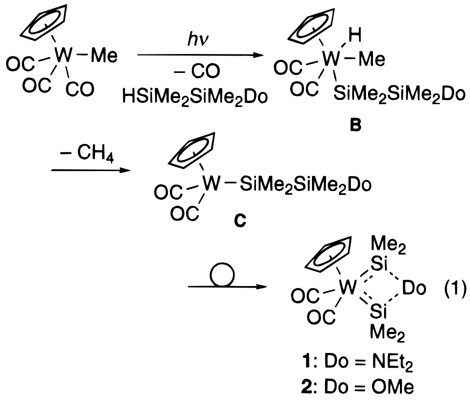


Figure 1. ORTEP drawing of **1** with thermal ellipsoids shown at the 50% probability level.

at their geometrically calculated positions (d_{CH} = 0.98 Å for methyl hydrogen atoms and 0.99 Å for methylene hydrogen atoms) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5\ U(C_{methyl})$ and $1.2\ U(C_{methylene})$). No absorption correction was applied. The final residue R1 and the weighted wR2 were 0.0526 and 0.1176, respectively for 4502 reflections with $I > 2\sigma(I)$ for **1** and 0.0618 and 0.1350, respectively, for 1640 reflections with $I > 2\sigma(I)$ for **2**, where $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. All calculations were performed on an Apple Macintosh computer.

Results and Discussion

Bis(silylene)tungsten complexes **1** and **2** were formed almost quantitatively by photolysis of a C_6D_6 solution containing $CpW(CO)_3Me$ and $HSiMe_2SiMe_2Do$ (eq 1).



These were isolated as pale yellow crystals and fully characterized by spectroscopic methods, elemental analysis, and X-ray crystallography. The isolated yields were 54% for **1** and 50% for **2**. The strategy used for the synthesis of the tungsten complexes **1** and **2** is a hybrid of the photochemical method[1a−d] and the thermal method[1e,f] which have been developed in our laboratory. Therefore, formation of the bis(silylene)tungsten complexes by the photolysis of a solution of $CpW(CO)_3Me$ and $HSiMe_2SiMe_2Do$ can be explained by the following mechanism: (i) Photochemical elimination of a carbonyl group followed by oxidative addition of a Si−H bond of $HSiMe_2SiMe_2Do$ to give an 18-electron intermediate **B**, (ii) reductive elimination of CH_4 affording a 16-electron disilanyltungsten complex $CpW(CO)_2SiMe_2SiMe_2Do$ (**C**), and (iii) 1,2-silyl group migration and cyclization to give the bis(silylene)tungsten complex.

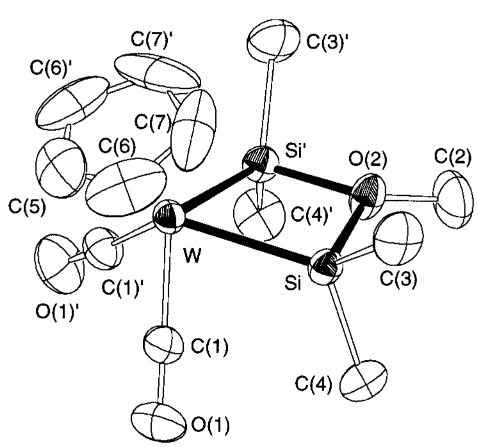


Figure 2. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) of 1

W−Si(1)	2.502(2)	W−Si(2)	2.501(2)
Si(1)−N	1.930(6)	Si(2)−N	1.920(7)
Si(1)−C(3)	1.879(8)	Si(1)-C(4)	1.900(7)
Si(2)−C(6)	1.881(8)	Si(2)−C(5)	1.889(8)
W−C(1)	1.941(7)	W−C(2)	1.932(8)
O(1)−C(1)	1.169(9)	O(2)−C(2)	1.172(10)
Si(2)−W−Si(1)	62.63(6)	C(2)−W−C(1)	81.5(3)
C(1)−W−Si(1)	74.1(2)	C(2)−W−Si(2)	72.6(2)
C(1)−W−Si(2)	111.9(2)	C(2)−W−Si(1)	114.2(2)
N−Si(1)−W	101.9(2)	N−Si(2)−W	102.3(2)
C(3)−Si(1)−C(4)	103.9(4)	C(3)−Si(1)−W	116.4(3)
C(4)−Si(1)−W	121.4(3)	C(6)−Si(2)−C(5)	103.9(4)
C(6)−Si(2)−W	115.2(3)	C(5)−Si(2)−W	122.5(3)
Si(2)−N−Si(1)	85.0(2)		

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) of 2[a]

W−Si	2.490(3)	Si−O(2)	1.792(7)
Si−C(3)	1.883(12)	Si−C(4)	1.886(12)
O(2)−C(2)	1.47(2)	W−C(1)	1.934(11)
C(1)−O(1)	1.175(13)		
Si#1−W−Si	64.05(13)	C(1)−W−C(1)#1	78.8(7)
C(1)−W−Si	75.0(3)	C(1)−W−Si#1	114.4(3)
C(1)#1−W−Si	114.4(3)	C(1)#1−W−Si#1	75.0(3)
O(2)−Si−W	99.2(3)	C(3)−Si−C(4)	105.4(6)
C(3)−Si−W	119.0(4)	C(4)−Si−W	124.4(4)
Si−O(2)−Si#1	94.9(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z$.

The X-ray crystal structures of **1** (Figure 1 and Table 2) and **2** (Figure 2 and Table 3) revealed that the W−Si bonds (2.502(2) and 2.501(2) Å for **1**; 2.490(3) Å for **2**) are significantly shorter than those of structurally similar silyltungsten complexes (2.53−2.63 Å).[8] The Si−N bonds (1.930(6) and 1.920(7) Å) in **1** and the Si−O bonds (1.792(7) Å) in **2** are much longer than the usual Si−N single bonds (1.70−1.76 Å) and Si−O single bonds (1.63−1.65 Å),[9] respectively, and comparable to those of the donor-stabilized bis(silylene)iron, manganese, and ruthenium complexes (1.93−1.96 Å for Si−N; 1.78−1.86 Å for Si−O).[1a−d] These structural data indicate that the W−Si bonds bear partial double bond character, whereas the Si−N and Si−O bonds are regarded as a hybrid of covalent bonding and dative bonding. The unsaturated

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(8) (a) Schmitzer, S.; Weis, U.; Käb, H.; Buchner, W.; Malisch, W.; Polzer, T.; Posset, U.; Kiefer, W. *Inorg. Chem.* **1993**, *32*, 303. (b) Sharma, S.; Kapoor, R. N.; Cervantes-Lee, F.; Pannell, K. H. *Polyhedron* **1991**, *10*, 1177.

(9) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 2, Chapter 3.

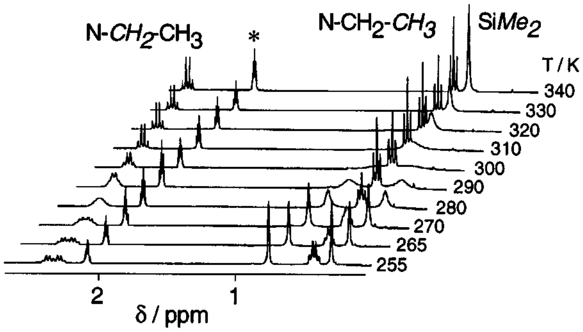


Figure 3. Variable-temperature ^{1}H NMR (300 MHz) spectra of **1** measured in toluene-d_8. The asterisk indicates $C_6D_5CD_2H$.

nature of the tungsten−silicon bonds are also indicated by the significant downfield shift of the ^{29}Si NMR signals as well as large coupling constants between ^{29}Si and ^{183}W (**1** $\delta = 62.1$ ppm, $^1J_{W-Si} = 91.5$ Hz; **2** $\delta = 99.3$ ppm, $^1J_{W-Si} = 99.3$ Hz) compared to those of structurally similar silyltungsten complexes ($\delta = -43.9$−58.3 ppm and $^1J_{W-Si} = 41.8$−64.1 Hz).[8]

The bis(silylene)tungsten complexes show fluxional behavior in solution. Figure 3 shows the variable-temperature ^{1}H NMR (VT ^{1}H NMR) spectra of **1**. At 255 K, complex **1** affords two singlet signals for the $SiMe_2$ groups and two quartet and two triplet signals for the NEt_2 group, which is consistent with the crystal structure shown in Figure 1. When the temperature is raised, these signals gradually broaden, coalesce, and finally become a singlet for the $SiMe_2$ group and a set of a quartet and a triplet for the NEt_2 group. The complex **2** also showed a similar spectral change for the Si−Me signals. The activation parameters, $\Delta H^‡$/(kJ mol^{-1}) and $\Delta S^‡$/(J mol^{-1} K^{-1}), were determined by line-shape analysis of the VT ^{1}H NMR spectra of the $SiMe_2$ signals and the methylene signals of the NEt_2 group for **1** and of the $SiMe_2$ signals for **2** (Table 4).[10] The activation parameters for **1** were also determined from VT ^{13}C{^{1}H} NMR spectra (Table 4), which agree reasonably with those obtained by VT ^{1}H NMR spectra.[10]

We propose the following mechanism for the fluxional process (Scheme 1): (i) Cleavage of a Si···Do bond, (ii) rotation of the resulting W=Si double bond and, in the case of **1**, rotation of the Si−N bond concomitant with inversion of amino group, and (iii) recombination of Do to the silylene ligand. This mechanism is essentially the same as that proposed previously for the fluxional behavior of Cp*Fe(CO){$(GeMe_2)$···OR···(EMe_2)} (E = Ge, Si).[2]

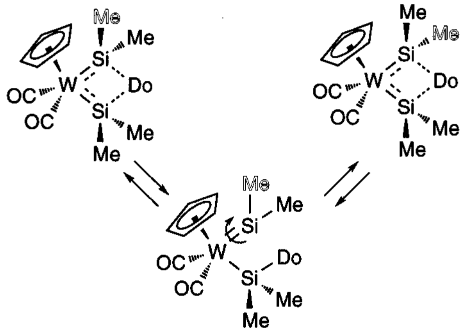
We previously reported that the HOMO of the bis(silylene)iron complex is made up of the π back-bonding interaction between the metal fragment and the SiR_2···Do···SiR_2 fragment and has an antibonding character on Si···Do bonding.[11] The electron-rich tungsten fragment weakens the Si···Do bond by the enhanced back-

Table 4. Activation Parameters for the SiMe and the NEt Exchange of 1 and the SiMe Exchange of 2

complex	probing signal	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}
1[a]	SiMe	72.8 (3.3)	49.0 (10.5)
	methylene of NEt	63.4 (3.9)	10.6 (13.5)
1[b]	SiMe	67.6 (1.5)	30.4 (5.1)
	methylene of NEt	67.7 (2.1)	24.9 (6.9)
2[a]	SiMe	70.2 (2.1)	39.9 (7.5)

[a] Determined from VT ^{1}H NMR spectra. [b] Determined from VT ^{13}C{^{1}H} NMR spectra.

Scheme 1



donation.[12] This facilitates formation of the base-free silyl(silylene) intermediate which leads to the $SiMe_2$ and NEt_2 group exchange. In addition to the electronic factor, the steric factor may also be important for the methyl group exchange. The donor-stabilized bis(silylene)iron complexes contain only one carbonyl ligand, while the tungsten complexes contain two carbonyl ligands. The interatomic distances between C(1)···C(4) (3.125(7) Å) and C(2)···C(5) (3.129(8) Å) in **1** and C(1)···C(4) (3.171(17) Å) in **2** are much smaller than the sum of the van der Waals radii of the methyl group and carbon atom (3.7 Å). The four-membered ring defined by W, two Si, and the bridging atom in **1** and **2** is significantly bent to make the bridging atom and the Cp ring close: Dihedral angles between the Si(1)−W−Si(2) plane and the Si(1)−N−Si(2) plane in **1** and that between the Si−W−Si′ plane and the Si−O(2)−Si′ plane in **2** are 152.6° and 163.7°, respectively. The corresponding dihedral angle in the diethylamino- and the methoxy-stabilized bis(silylene)iron complexes is 203.9° and 201.2°, respectively.[1a,b,d] Thus, the steric crowding in **1** and **2** is more serious than that of the donor-stabilized bis(silylene)iron complexes.

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Supporting Information Available: Tables of crystal data and structural refinement, atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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