Synthesis, Crystal Structures, and Fluxional Behavior of Donor-Bridged Bis(silylene)molybdenum and -chromium Complexes

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Received March 22, 1999

Donor-bridged bis(silylene)molybdenum and -chromium complexes $CpM(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}$ ($Cp = \eta$-C_5H_5; M = Mo, Do = OMe (**1a**); M = Mo, Do = NEt_2 (**1b**); M = Cr, Do = OMe (**2**)) were synthesized by photolysis of a C_6D_6 solution containing $CpM(CO)_3Me$ and $HSiMe_2SiMe_2Do$. The X-ray crystal structures of **1a**, **1b**, and **2** revealed that the M−Si bonds (2.4795(9) and 2.4804(9) Å for **1a**, 2.4996(9) and 2.5008(9) Å for **1b**, and 2.355(2) Å for **2**) are significantly shorter than those of structurally similar silylmolybdenum and -chromium complexes, while the Si−O bonds in **1a** (1.782(2) and 1.788(3) Å) and **2** (1.788(3) Å) and the Si−N bonds in **1b** (1.933(2) and 1.923(3) Å) are much longer than usual Si−O and Si−N single bonds. These structural data indicate that the M−Si bonds bear partial double-bond character, whereas the Si−O and Si−N bonds are regarded as a hybrid of covalent bonding and dative bonding. The unsaturated nature of the metal−silicon bonds is also shown by the significant downfield shift of the ^{29}Si NMR signals (**1a**, δ = 117.6 ppm; **1b**, δ = 80.5 ppm; **2**, δ = 128.6 ppm) compared to those of structurally similar silylmolybdenum and -chromium complexes. Complexes **1a**, **1b**, and **2** showed fluxional behavior due to silylene−methyl group exchange and, in the case of **1b**, N−Et group exchange. A mechanism involving the generation of a base-free silyl(silylene) complex as the key intermediate is proposed to explain the fluxional process.

Introduction

Considerable attention has been focused on the synthesis and chemical behavior of silylene−transition metal complexes.[1−5] Silyl(silylene) transition metal complexes $L_nM(=SiR_2)SiR_3$ are attractive synthetic targets since such complexes have been assumed to be key intermediates in metal-catalyzed substituent scrambling and skeletal redistribution of organosilicon and organosilicon−transition metal compounds.[5−12] Pannell,[6,13] the present authors,[7,14] and Turner[15] reported convincing evidence for the formation of silyl(silylene)-iron intermediates during the degradation of oligosilanyliron complexes. Silyl(silylene) complexes have been isolated as intramolecular[14,16−19] or external[20] donor-stabilized silyl(silylene) complexes. A unique type of the intramolecular donor-stabilized complexes is the "donor-bridged bis(silylene) complex" **A** (Scheme 1), which is equivalent to a resonance hybrid of two canonical forms

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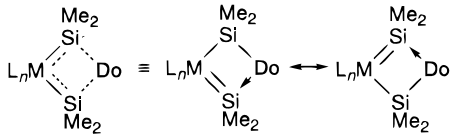
10.1021/om990201f CCC: $18.00
Publication on Web 06/15/1999

Scheme 1



A

of intramolecular donor-stabilized silyl(silylene) complexes and thus has two unsaturated silicon atoms in the molecule.[14,16−18] The first donor-free silyl(silylene) complex was recently synthesized by the reaction of thermally stable silylene with a platinum complex.[21]

In the previous paper, we reported the synthesis of donor-bridged bis(silylene)tungsten complexes, $CpW(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}$ ($Cp = \eta\text{-}C_5H_5$; Do = OMe (**3a**), NEt_2 (**3b**)), by photolysis of $CpW(CO)_3Me$ in the presence of a hydrodisilane $HSiMe_2SiMe_2Do$.[17] In this paper, we report the synthesis and crystal structures of the lighter congeners of the donor-bridged bis(silylene)tungsten complexes $CpM(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}$ (**1a**, M = Mo, Do = OMe; **1b**, M = Mo, Do = NEt_2; **2**, M = Cr, Do = OMe), which complete the series of bis(silylene) complexes of the group 6 metals. To our knowledge, there has been only one example of an isolated molybdenum complex with a silylene ligand,[22] and **1a** and **1b** are the first structurally determined silylenemolybdenum complexes. The bis(silylene)tungsten complexes showed fluxional behavior due to the rotation of the silylene ligand around the tungsten−silylene bond.[17] Similar fluxional behavior has been observed for germylene rotation in silylene(germylene) and bis(germylene)iron complexes[23] and, very recently, for silylene rotation in bis(silylene)ruthenium complexes.[18] The bis(silylene)molybdenum and -chromium complexes, **1a**, **1b**, and **2**, show fluxional behavior due to the rotation of the silylene ligand similar to that observed for the bis(silylene)tungsten complexes.

Experimental Section

All manipulations were performed either using standard Schlenk tube techniques under a nitrogen atmosphere, using vacuum line techniques, or in a drybox under a nitrogen atmosphere. Toluene was dried and deoxygenated by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere. Benzene-d_6 and toluene-d_8 were dried over a potassium mirror and distilled directly into the reaction vessel before use. $CpMo(CO)_3Me$[24] and $CpCr(CO)_3Me$[25] were prepared according to the literature methods. Syntheses of $HSiMe_2SiMe_2NEt_2$ and $HSiMe_2SiMe_2OMe$ were described in our previous paper.[17] 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 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 $Cp(OC)_2Mo\{(SiMe_2)\cdots OMe\cdots(SiMe_2)\}$ (1a). A Pyrex sample tube (10 mm o.d., 8 mm i.d.) with a ground-glass joint was charged with $CpMo(CO)_3Me$ (0.70 g, 2.7 mmol) and $HSiMe_2SiMe_2OMe$ (0.59 g, 4.0 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 90 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 **1a** (0.32 g, 0.88 mmol, 33%). ^{1}H NMR (300 MHz, C_6D_6, 295 K): δ 4.77 (s, 5H, C_5H_5), 2.62 (s, 3H, OCH_3), 0.47 (br, 6H, $SiCH_3$), 0.44 (br, 6H, $SiCH_3$). ^{13}C NMR (75.5 MHz, C_6D_6, 295 K): δ 237.0 (*C*O), 88.0 (C_5H_5), 51.9 (OCH_3), 9.2 (br, $SiCH_3$), 6.5 (br, $SiCH_3$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT, 295 K): δ 117.6. IR (C_6D_6): ν_{CO} 1915, 1848 cm^{-1}. MS (EI, 70 eV): *m*/*z* 366 (M^+, 100.0), 306 ($M^+ - 4CH_3$, 82.8). Anal. Calcd for $C_{12}H_{20}MoO_3Si_2$: C, 39.55; H, 5.53. Found: C, 39.79; H, 5.24.

Synthesis of $Cp(OC)_2Mo\{(SiMe_2)\cdots NEt_2\cdots(SiMe_2)\}$ (1b). Complex **1b** was synthesized and isolated in 44% yield in a manner similar to that of **1a** using $CpMo(CO)_3Me$ (0.42 g, 1.7 mmol) and $HSiMe_2SiMe_2NEt_2$ (0.77 g, 4.1 mmol). ^{1}H NMR (300 MHz, C_6D_6, 295 K): δ 4.84 (s, 5H, C_5H_5), 2.40 (br, 4H, J = 7.0 Hz, NCH_2CH_3), 0.67 (br, 6H, $SiCH_3$), 0.51 (t, 6H, J = 7.0 Hz, NCH_2CH_3), 0.35 (br, 6H, $SiCH_3$). ^{13}C NMR (75.5 MHz, C_6D_6, 295 K): δ 237.4 (*C*O), 88.0 (C_5H_5), 40.7 (br, NCH_2CH_3), 38.7 (br, NCH_2CH_3), 10.4 (NCH_2CH_3), 10.1 (br, $SiCH_3$), 6.3 (br, $SiCH_3$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT, 295 K): δ 80.5. IR (C_6D_6): ν_{CO} 1903, 1834 cm^{-1}. MS (EI, 70 eV): *m*/*z* 407 (M^+, 100.0), 347 ($M^+ - 4CH_3 - 2H$, 26.3), 130 (M^+ − CpMo(CO), 92.7). Anal. Calcd for $C_{15}H_{27}MoNO_2Si_2$: C, 44.43; H, 6.71; N, 3.45. Found: C, 44.69; H, 6.96; N, 3.52.

Synthesis of $Cp(OC)_2Cr\{(SiMe_2)\cdots OMe\cdots(SiMe_2)\}$ (2). Complex **2** was synthesized and isolated in a manner similar to that of **1a** by the photolysis of $CpCr(CO)_3Me$ (0.18 g, 0.80 mmol) and $HSiMe_2SiMe_2OMe$ (0.18 g, 1.2 mmol) for 15 min (12% yield). ^{1}H NMR (300 MHz, C_6D_6, 295 K): δ 4.21 (s, 5H, C_5H_5), 2.56 (s, 3H, OCH_3), 0.59 (br, 6H, $SiCH_3$), 0.19 (br, 6H, $SiCH_3$). ^{13}C NMR (75.5 MHz, C_6D_6, 295 K): δ 243.7 (*C*O), 84.0 (C_5H_5), 52.3 (OCH_3), 8.1 (br, $SiCH_3$), 6.4 (br, $SiCH_3$). ^{29}Si NMR (59.6 MHz, C_6D_6, DEPT, 295 K): δ 128.6. IR (C_6D_6): ν_{CO} 1900, 1838 cm^{-1}. MS (EI, 70 eV): *m*/*z* 320 (M^+, 100.0), 264 ($M^+ - 2CO$, 85.2). Anal. Calcd for $C_{12}H_{20}CrO_3Si_2$: C, 44.98; H, 6.29. Found: C, 44.81; H, 6.28.

X-ray Crystal Structure Determination of 1a, 1b, and 2. A single crystal of **1a**, **1b**, or **2** was sealed in a glass capillary under an atmosphere of dry nitrogen. Intensity data for X-ray crystal structure analysis were collected on a RIGAKU AFC-6S four-circle diffractometer with graphite-monochromated Mo Kα radiation at 293 K. No absorption correction was applied. Space group was determined based on the systematic absences and the subsequent least-squares refinement. For **2**, the centrosymmetric space group *Pnma* was adopted since the *E*-statistics supported the centrosymmetric space group and the solution by the acentrosymmetric alternative $Pn2_1a$ was found to be computationally unstable. Crystallographic data for **1a**, **1b**, and **2** are summarized in Table 1. The structures were solved by Patterson and Fourier transform methods (SHELXS-86).[26] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters (SHELXL-93).[27] All hydrogen atoms were placed at their geometrically calculated positions (d_{CH} = 0.98 Å for

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Table 1. Crystal Data and Structure Refinement for 1a, 1b, and 2

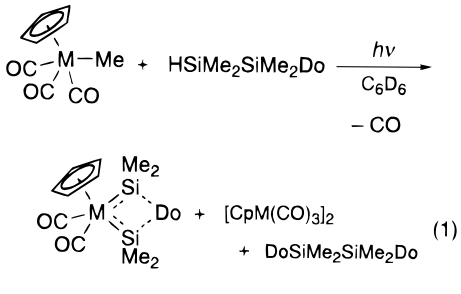
	1a	1b	2
empirical formula	$C_{12}H_{20}MoO_3Si_2$	$C_{15}H_{27}MoNO_2Si_2$	$C_{12}H_{20}CrO_3Si$
fw	364.40	405.50	320.46
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/a$	$Pnma$
unit cell dimens			
a/Å	15.0938(13)	16.667(2)	12.900(2)
b/Å	12.0680(9)	8.8103(7)	14.456(2)
c/Å	9.0823(7)	12.9121(12)	8.5349(8)
β/deg	95.89(2)	94.59(2)	
volume/Å^3	1645.6(2)	1889.9(3)	1591.5(3)
Z	4	4	4
density (calcd)/g cm^{-3}	1.471	1.425	1.337
abs coeff/mm^{-1}	0.940	0.824	0.867
F(000)	744	840	672
cryst size/mm^3	0.55 × 0.55 × 0.37	0.40 × 0.35 × 0.18	0.42 × 0.52 × 0.37
θ range for data collection/deg	2.17−29.99	1.58−30.00	2.77−30.00
index ranges	$-21 \le h \le 21$	$-23 \le h \le 23$	$0 \le h \le 18$
	$0 \le k \le 16$	$0 \le k \le 12$	$0 \le k \le 20$
	$0 \le l \le 12$	$0 \le l \le 18$	$0 \le l \le 12$
no. of reflns collected	4786	5518	2403
no. of ind reflns	4786	5518	2403
no. of reflns with $I > 2\sigma(I)$	3621	3903	1006
no. of data/restraints/params	4786/0/168	5517/0/298	2395/0/91
goodness-of-fit on F^2	1.052	1.034	1.023
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0356	R1 = 0.0362	R1 = 0.0654
	wR2 = 0.0835	wR2 = 0.0786	wR2 = 0.1427
R indices (all data)[a]	R1 = 0.0605	R1 = 0.0725	R1 = 0.1959
	wR2 = 0.0940	wR2 = 0.0908	wR2 = 0.2056
largest diff peak and hole/e Å^{-3}	0.402 and −0.797	0.527 and −0.903	0.482 and −0.342

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

methyl hydrogens, 0.99 Å for methylene hydrogens, and 0.96 Å for Cp protons) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5U(C_{methyl})$, $1.2U(C_{methylene})$, and $1.2U(C_{ring})$). There is irresolvable disorder in the Cp ligand in **2**. The final R indices against the reflections with $I > 2\sigma(I)$ were R1 = 0.0356 and wR2 = 0.0835 for **1a**, R1 = 0.0362 and wR2 = 0.0786 for **1b**, and R1 = 0.0654 and wR2 = 0.1427 for **2**. All calculations were performed on an Apple Macintosh computer.

Results and Discussion

Synthesis of Donor-Bridged Bis(silylene)molybdenum and −chromium Complexes. We have reported that photolysis of $CpW(CO)_3Me$ in the presence of a hydrodisilane $HSiMe_2SiMe_2Do$ afforded the donor-bridged bis(silylene)tungsten complexes $CpW(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}$ (Do = OMe (**3a**), NEt_2 (**3b**)).[17] In this work, the molybdenum and chromium analogues of the tungsten complexes were synthesized by a similar photolytic method. Photolysis of a C_6D_6 solution containing $CpMo(CO)_3Me$ and an excess of $HSiMe_2SiMe_2Do$ in a Pyrex NMR sample tube with a medium-pressure Hg lamp afforded bis(silylene)molybdenum complexes, **1a** and **1b**, together with small amounts of byproducts $[CpMo(CO)_3]_2$ and $DoSiMe_2SiMe_2Do$ (eq 1).[28] Complexes **1a** and **1b** were isolated as pale yellow crystals in 33 and 44% yield, respectively, in large scale photolyses followed by crystallization. Bis(silylene)-chromium complex **2** was also synthesized by photolysis of a C_6D_6 solution containing $CpCr(CO)_3Me$ and an excess of $HSiMe_2SiMe_2OMe$. However, significant amounts of byproducts including $[CpCr(CO)_3]_2$, $MeOSiMe_2SiMe_2OMe$, and unidentified compounds were formed during the photolysis. Thus the isolated yield of **2** was rather low (12%) compared to those of the molybdenum and the tungsten complexes (50−54% yield for the tungsten complexes). The poor yield is mostly attributable to the photochemical and thermal instability of **2** in contrast with the tungsten and molybdenum analogues. Indeed, either photolysis or thermolysis (360 K) of a toluene solution of **2** gave a complex mixture of decomposition products, whereas no decomposition was observed for the molybdenum and tungsten complexes under the same experimental conditions. Complexes **1a**, **1b**, and **2** were fully characterized by spectroscopic methods, elemental analysis, and X-ray crystallography.



1a: M = Mo, Do = OMe
1b: M = Mo, Do = NEt_2
2: M = Cr, Do = OMe

The ^{29}Si NMR signals of these complexes (**1a**, 117.6 ppm; **1b**, 80.5 ppm; **2**, 128.6 ppm) appear at significantly low field compared to those of known alkylsilylmolybdenum complexes (δ 20−69 ppm)[29] and are comparable to those of the known silylenemolybdenum (δ 111 ppm),[22] alkyl- and arylsilylenechromium (δ 73−133 ppm),[2,30,31] and bis(silylene)tungsten complexes (**3a**, 99.3 ppm; **3b**, 62.1 ppm).[17] This indicates unsaturated character of the metal−silicon bonding in the bis(silylene) complexes.

The ^{29}Si NMR signals of the bis(silylene) complexes with group 6 metals shift to higher field on going from

(28) At the present time we are unable to offer a good explanation for the formation of $DoSiMe_2SiMe_2Do$.

(29) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489.

Cr to W in the group. A similar tendency has also been found for bis(silylene) complexes of group 8 metals, $CpM(CO)\{(SiMe_2)\cdots OMe\cdots(SiMe_2)\}$ (M = Fe,[14b] Ru[16e]), and some transition metal−group 14 element complexes.[32−35] Lappert et al. found a similar trend in the ^{119}Sn NMR shift of tin−transition metal complexes and rationalized by a contribution of both paramagnetic and diamagnetic shielding effects.[36] On the basis of their interpretation, the higher field shifts observed for the bis(silylene) complexes with heavier metal atoms can be explained by a combination of the smaller paramagnetic contribution and larger diamagnetic contribution of neighboring atoms. The former is derived from larger values of the averaged excitation energy and higher polarizability of the heavier transition metal.[36] The latter is known to be proportional to Z/r, where Z is the atomic number of the contributing atom and r is its distance from the relevant nucleus.[36,37]

The ^{29}Si NMR signals for methoxy-bridged bis(silylene) complexes, **1a** and **3a**, are shifted downfield compared to those of amino-bridged complexes, **1b** and **3b**, respectively.[17] For monosubstituted silanes Me_3SiX, the ^{29}Si NMR signal shifts to lower field as the substituent X becomes more electronegative.[38] In other words, the ^{29}Si NMR signal shifts to lower field in the order X = F > Cl > Br > OMe > NMe_2 > Me. The low-field shift of the signals for the alkoxy-bridged complexes compared to that of the diethylamino-bridged complexes is consistent with this trend.

The ^1H NMR signals for the bridging methoxy group (δ 2.62 ppm for **1a** and 2.56 ppm for **2**) and diethylamino group (δ 2.40(br) and 0.67(br) ppm for **1b**) appear at higher field than those of the starting disilanes $HSiMe_2SiMe_2OMe$ (δ 3.29 ppm) and $HSiMe_2SiMe_2NEt_2$ (δ 2.76 and 0.97 ppm), respectively. These high-field shifts of bridging group signals are characteristic for the donor-bridged bis(silylene) complexes.[14,16−18]

The formation of the bis(silylene) complexes by the photolysis of a solution of $CpM(CO)_3Me$ and $HSiMe_2SiMe_2Do$ can be explained by the following mechanism, which is essentially the same as that proposed for the formation of bis(silylene)tungsten complexes:[17] (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 $CpM(CO)_2(H)(Me)SiMe_2SiMe_2Do$ (**B**), (ii) reductive elimination of CH_4 from **B** affording a 16-electron disilanyltungsten complex $CpM(CO)_2SiMe_2SiMe_2Do$, and (iii) 1,2-silyl group migration of the silyl group $SiMe_2Do$ to the metal center followed by cyclization to give the bis(silylene) complex $CpM(CO)_2\{(SiMe_2)\cdots Do\cdots(SiMe_2)\}$.

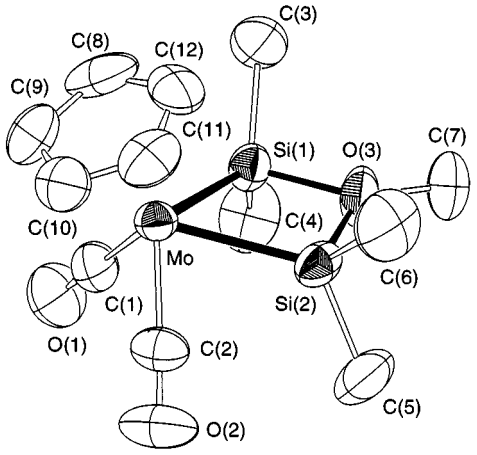


Figure 1. ORTEP drawing of **1a** with thermal ellipsoids shown at the 50% probability level.

Table 2. Selected Interatomic Distances [Å] and Angles [deg] for 1a

Mo−Si(1)	2.4804(9)	Mo−Si(2)	2.4795(9)
Mo−C(1)	1.946(3)	Mo−C(2)	1.936(3)
Si(1)−O(3)	1.782(2)	Si(1)−C(4)	1.872(4)
Si(1)−C(5)	1.871(4)	Si(2)−O(3)	1.788(3)
Si(2)−C(6)	1.871(4)	Si(2)−C(7)	1.865(4)
O(1)−C(1)	1.156(4)	O(2)−C(2)	1.164(4)
O(3)−C(3)	1.446(4)	C(1)···C(4)	3.156(5)
O(1)···C(4)	3.283(5)	C(2)···C(5)	3.138(6)
O(2)···C(5)	3.267(5)	C(3)···C(7)	3.518(6)
C(4)···C(7)	3.437(6)	C(5)···C(7)	3.440(6)
C(6)···C(7)	3.558(6)		
C(2)−Mo−C(1)	79.04(14)	C(2)−Mo−Si(2)	73.59(11)
C(1)−Mo−Si(2)	111.75(10)	C(2)−Mo−Si(1)	115.64(10)
C(1)−Mo−Si(1)	75.30(10)	Si(2)−Mo−Si(1)	63.63(3)
C(5)−Si(1)−C(4)	106.3(2)	O(3)−Si(1)−Mo	100.22(8)
C(5)−Si(1)−Mo	125.7(2)	C(4)−Si(1)−Mo	116.51(13)
C(7)−Si(2)−C(6)	105.4(2)	O(3)−Si(2)−Mo	100.09(7)
C(7)−Si(2)−Mo	125.4(2)	C(6)−Si(2)−Mo	117.4(2)
C(3)−O(3)−Si(1)	131.9(3)	C(3)−O(3)−Si(2)	132.6(2)
Si(1)−O(3)−Si(2)	94.19(11)	O(1)−C(1)−Mo	177.8(3)
O(2)−C(2)−Mo	177.6(3)		

Crystal Structures of 1a, 1b, and 2. Bis(silylene)-molybdenum and -chromium complexes were characterized by X-ray crystal structure analysis (Figure 1 and Table 2 for **1a**, Figure 2 and Table 3 for **1b**, and Figure 3 and Table 4 for **2**). The complexes **1a** and **1b** are the first structurally characterized molybdenum complexes with a silylene ligand. The Mo−Si bonds (2.4804(9) and 2.4795(9) Å for **1a**; 2.4996(9) and 2.5008(9) Å for **1b**) are shorter than those of the known silylmolybdenum complexes (2.51−2.67 Å).[29,39−41] The Cr−Si bond length of **2** (2.355(2) Å) is comparable to or shorter than those of the reported alkyl- and arylsilylenechromium complexes (2.36−2.53 Å).[2,30] The short metal−silicon bond

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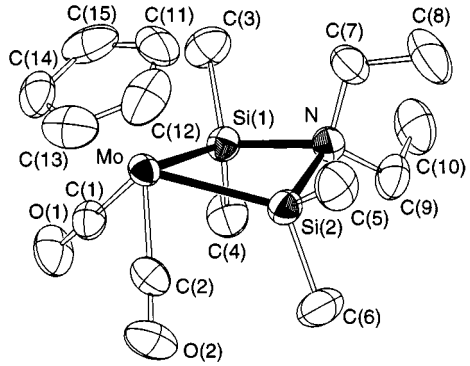

Figure 2. ORTEP drawing of **1b** with thermal ellipsoids shown at the 50% probability level.

Table 3. Selected Interatomic Distances [Å] and Angles [deg] for 1b

Mo−Si(1)	2.4996(9)	Mo−Si(2)	2.5008(9)
Mo−C(1)	1.944(3)	Mo−C(2)	1.931(3)
Si(1)−C(3)	1.872(4)	Si(1)−C(4)	1.879(4)
Si(1)−N	1.933(2)	Si(2)−C(5)	1.876(4)
Si(2)−C(6)	1.874(4)	Si(2)−N	1.923(3)
N−C(7)	1.500(4)	N−C(9)	1.499(4)
C(1)−O(1)	1.162(4)	C(2)−O(2)	1.169(4)
C(7)−C(8)	1.526(6)	C(9)−C(10)	1.507(6)
C(1)···C(4)	3.109(5)	C(2)···C(6)	3.129(6)
O(1)···C(4)	3.264(5)	O(2)···C(6)	3.283(6)
C(3)···C(7)	3.160(6)	C(4)···C(9)	3.178(6)
C(5)···C(7)	3.290(7)	C(6)···C(9)	3.136(7)
C(2)−Mo−C(1)	81.33(13)	C(2)−Mo−Si(1)	113.71(10)
C(1)−Mo−Si(1)	74.01(10)	C(2)−Mo−Si(2)	72.54(10)
C(1)−Mo−Si(2)	111.69(9)	Si(1)−Mo−Si(2)	62.29(3)
C(3)−Si(1)−C(4)	104.5(2)	C(3)−Si(1)−Mo	115.86(14)
C(4)−Si(1)−Mo	121.8(2)	N−Si(1)−Mo	102.32(8)
C(6)−Si(2)−C(5)	103.4(2)	C(6)−Si(2)−Mo	122.6(2)
C(5)−Si(2)−Mo	114.9(2)	N−Si(2)−Mo	102.58(8)
C(9)−N−C(7)	110.3(3)	C(9)−N−Si(2)	119.0(2)
C(7)−N−Si(2)	112.1(2)	C(9)−N−Si(1)	118.7(2)
C(7)−N−Si(1)	110.1(2)	Si(2)−N−Si(1)	84.26(10)
O(1)−C(1)−Mo	176.7(3)	O(2)−C(2)−Mo	176.7(3)

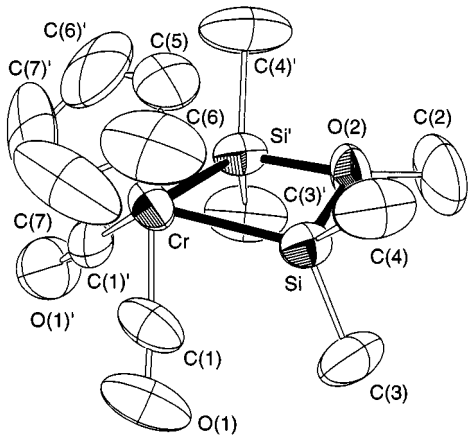

Figure 3. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level.

lengths indicate unsaturated character of the metal−silicon bonding, which is also supported by the low-field shift of ^{29}Si NMR signals (vide supra). The Si−O bonds in **1a** (1.782(2) and 1.788(3) Å) and **2** (1.788(3) Å) and Si−N bonds (1.933(2) and 1.923(3) Å) in **1b** are much longer than usual Si−O (1.63−1.65 Å) and Si−N single bonds (1.70−1.76 Å), respectively,[42] and are comparable to those of the donor-bridged bis(silylene)iron, manganese, ruthenium, and tungsten complexes (1.93−1.96 Å for Si−N; 1.78−1.86 Å for Si−O).[14,16a,b,e,17] The Si−O and Si−N bond lengths lie between that of the theoretically calculated value of H_3Si-OH (1.65−1.67 Å)[43,44] and that of $H_2Si\leftarrow OH_2$ (2.10−2.13 Å)[43,44] and between that of H_3Si-NH_2 (1.72 Å)[43] and that of $H_2Si\leftarrow NH_3$ (2.04−2.09 Å),[43,45] respectively. These structural data support that the Si−O and Si−N bonds are regarded as a hybrid of covalent bonding and dative bonding.

Table 4. Selected Interatomic Distances [Å] and Angles [deg] for 2[a]

Cr−Si	2.355(2)	Cr−C(1)	1.792(6)
Si−O(2)	1.788(3)	Si−C(3)	1.866(6)
Si−C(4)	1.875(6)	O(1)−C(1)	1.160(7)
O(2)−C(2)	1.464(10)	C(1)···C(3)	3.060(9)
O(1)···C(3)	3.205(8)	C(2)···C(3)	3.355(10)
C(2)···C(4)	3.591(10)		
C(1)′−Cr−C(1)	81.0(4)	C(1)′−Cr−Si	117.1(2)
C(1)−Cr−Si	75.6(2)	Si′−Cr−Si	65.79(8)
C(3)−Si−C(4)	105.7(3)	O(2)−Si−Cr	99.84(13)
C(3)−Si−Cr	123.3(2)	C(4)−Si−Cr	120.1(3)
C(2)−O(2)−Si	130.8(2)	Si−O(2)−Si′	91.3(2)
O(1)−C(1)−Cr	176.7(6)		

[a] Symmetry transformation used to generate equivalent atoms: (′) $x, -y + 1/2, z$.

The four-membered ring defined by M, two Si, and the bridging atom is significantly bent to make the bridging atom and the Cp ring close. Dihedral angles between the Si−M−Si plane and the Si−X−Si (X = bridging atom) plane in **1a**, **1b**, and **2** are 166.5°, 152.4°, and 162.4°, respectively. Bending of the planes is attributable to the steric repulsion between the carbonyl ligands and methyl groups on the silicon atoms. The interatomic distances between the carbon atoms of carbonyl ligands and those of methyl groups (3.156(5) and 3.138(6) Å for **1a**, 3.109(5) and 3.129(6) Å for **1b**, and 3.060(9) Å for **2**) are much smaller than the sum of the van der Waals radii of methyl group and carbon atom (3.7 Å). The larger dihedral angle in the diethylamino-bridged bis(silylene)molybdenum complex **1b** than that in methoxy-bridged complex **1a** is due to the repulsion between the Si−Me and N−Et groups in **1b**. Interatomic distances between C(4)···C(9) (3.136(7) Å) and C(6)···C(9) (3.178(6) Å) in **1b** are significantly smaller than the sum of van der Waals radii of Me and the methylene group (4.0 Å).

Fluxional Behavior of Bis(silylene) Complexes. We have reported that the bis(silylene)tungsten complexes **3a** and **3b** show fluxional behavior in solution due to the rotation of silylene ligand.[17] The molybdenum and chromium complexes also show similar fluxional behavior in solution. Figure 4 shows the variable-temperature ^{1}H NMR (VT ^{1}H NMR) spectra of **1b**. At 250 K, complex **1b** affords two singlets for the $SiMe_2$ groups and two quartets and two overlapping triplets for the NEt_2 group, which is consistent with the crystal structure shown in Figure 2. As the temperature is raised, these signals gradually broaden, coalesce, and finally become a singlet for the $SiMe_2$ groups and a set

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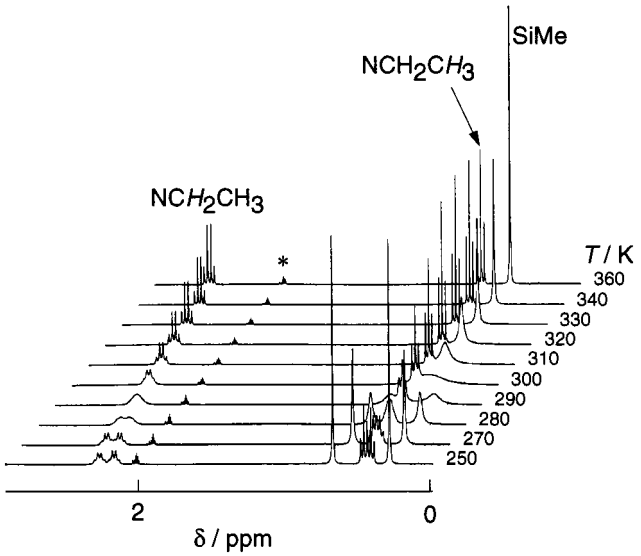


Figure 4. Variable-temperature ^{1}H NMR (300 MHz) spectra of **1b** measured in toluene-d_8. *: $C_6D_5CD_2H$.

Table 5. Activation Parameters for the SiMe Exchange of 1a and 3a and the SiMe and the NEt Exchange of 1b and 3b

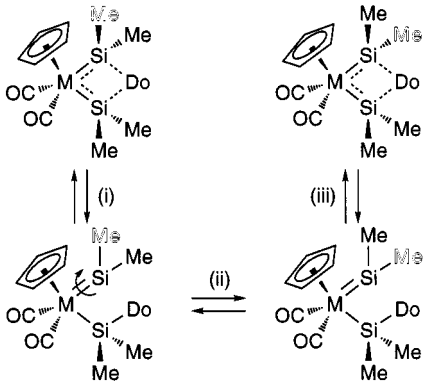
complex	probing signal	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
1a[a]	SiMe	61.0 (4.8)	11.6 (15.2)
1b[a]	SiMe	65.0 (3.3)	22.4 (5.1)
	methylene of NEt	49.1 (6.3)	−41.2 (21.6)
3a[a,c]	SiMe	70.2 (2.1)	39.9 (7.5)
3b[a,c]	SiMe	72.8 (3.3)	49.0 (10.5)
	methylene of NEt	63.4 (3.9)	10.6 (13.5)
3b[b,c]	SiMe	67.6 (1.5)	30.4 (5.1)
	methylene of NEt	67.7 (2.1)	24.9 (6.9)

[a] Determined from VT ^{1}H NMR spectra. [b] Determined from VT ^{13}C{^{1}H} NMR spectra. [c] Reference 17.

of a quartet and a triplet for the NEt_2 group. The complexes **1a** and **2** also showed a similar spectral change for the Si−Me signals. However, in the case of complex **2**, severe decomposition occurred during the VT NMR measurement, which prevented further investigation. The activation parameters, $\Delta H^{\ddagger}$/kJ mol^{-1} and $\Delta S^{\ddagger}$/J mol^{-1} K^{-1}, were determined by the complete band shape analysis[46] of the VT ^{1}H NMR spectra of the $SiMe_2$ signals of **1a** and that of the $SiMe_2$ signals and the methylene signals of the NEt_2 group of **1b** and are summarized in Table 5 along with those of the tungsten complexes. The activation parameters for the molybdenum complexes are comparable to those for the tungsten complexes.

We propose the following mechanism for the fluxional process (Scheme 2): (i) cleavage of a Si···Do bond to form a base-free silyl(silylene) intermediate, (ii) rotation of the resulting M═Si double bond and, in the case of **1b**, 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 those proposed previously for the fluxional behavior of silylene(germylene)- and bis(germylene)iron complexes,[23] bis(silylene)tungsten complexes **3a** and **3b**,[17]

Scheme 2



and bis(silylene)ruthenium complexes.[18] The rate-determining step would be the cleavage of the Si···Do bond (step i) since the rotation barriers around the M═Si bond in silylene complexes $(OC)_5M$═SiHR (M = Cr, Mo; R = H, OH) have been calculated to be very small (0.46−1.5 kJ mol^{-1}) due to fairly weak π-bonding interaction between metal and silylene ligand.[47−49]

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.[50] The electron-rich group 6 metal fragment weakens the Si···Do bond by the strong back-donation to the σ^* orbital of Si···Do bonds.[51] This facilitates formation of the base-free silyl(silylene) intermediate and also stabilizes the intermediate by π back-donation to the empty p orbital of the silylene ligand. In addition to the electronic factor, steric factors also are important for the fluxionality of bis(silylene) complexes **1a**, **1b**, and **2** as well as **3a** and **3b**. As described, there is severe steric repulsion between carbonyl ligands and methyl groups in the silylene ligands, which bends the four-membered ring defined by M, two Si, and the bridging atoms significantly to make the bridging atom and the Cp ring close. Cleavage of the Si···O bond to give the base-free silyl(silylene) intermediate releases the steric strain.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (No. 09440223 and 10132203) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Tables of crystal data and structural refinement, atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms, full bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1a**, **1b**, and **2.** This material is available free of charge via the Internet at http://pubs.acs.org.

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