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Synthesis and Crystal Structure of an Amino-Bridged Bis(silylene)iron Complex

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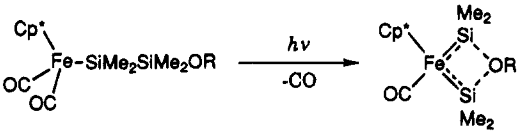
Photolysis of a C_6D_6 solution of the (aminodisilanyl)iron complex $Cp'Fe(CO)_2SiMe_2SiMe_2NEt_2$ ($Cp' = \eta$-C_5Me_5) resulted in the formation of the amino-bridged bis(silylene)iron complex **1**. The ^{29}Si NMR spectrum of **1** shows a signal at very low field (94.0 ppm). X-ray crystal structure analysis of **1** (monoclinic, space group $P2_1/a$, $a = 28.031(8)$ Å, $b = 19.541(6)$ Å, $c = 8.089(3)$ Å, $\beta = 93.62(2)°$, $V = 4422(3)$ Å^3, $Z = 8$) revealed very short Fe—Si bonds (2.22−2.23 Å), fairly long Si—N bonds (1.93−1.96 Å), and almost planar geometry at each silicon atom with respect to it and the attached C and Fe atoms, excluding the bridging nitrogen. These structural and spectroscopic data for **1** strongly indicate that the Fe—Si bonds take on partial double-bond character (bis(silylene) structure), while the Si—N bonds can be described as a hybrid of a covalent and weak dative bond.

Introduction

Transition-metal silylene complexes, containing a metal−silicon double bond, have been attracting much attention as a synthetic target. The first silylene complexes stabilized by coordination of donors to the electron-deficient silylene ligands were reported by Schmid and Welz in 1977.[1] They characterized the complexes using IR and mass spectroscopy, but X-ray crystal structure data were not obtained. The first silylene complexes characterized by X-ray crystal structure analysis appeared in 1987: Tilley's group[2a] and Zybill's group[3a] reported the syntheses and crystal structures of the donor-stabilized silylene complexes $[Cp'(PMe_3)_2Ru{=}SiPh_2{\cdot}NCMe]BPh_4$ ($Cp' = \eta$-C_5Me_5) and $(OC)_4Fe{=}Si(OBu^t)_2{\cdot}HMPA$, respectively. We then reported the synthesis and crystal structure of the donor-stabilized bis(silylene)iron complex.[4a] Since then, a number of donor-stabilized silylene complexes have been prepared,[2−8] and more recently, donor-free silylene complexes have also been reported.[9−12]

The alkoxy-bridged bis(silylene)iron complexes were synthesized by photolysis of the alkoxydisilanyliron complexes $Cp^*Fe(CO)_2SiMe_2SiMe_2OR$ ($Cp^* = Cp$, Cp'; R = Me, Bu^t) (eq 1).[4a,b] The methoxy-bridged bis(silylene)manganese complex was also synthesized by utilizing a similar photochemical method.[4c] The alkoxy-bridged bis(silylene)metal complexes are unique among the known base-stabilized silylene complexes since the two M—Si bonds of the bis(silylene)metal complexes take on partial double-bond character. The bridging alkoxy group stabilizes the bis(silylene) structure by coordination to the two electron-deficient silylene units. However, the effect of the bridging donor atom on the metal−silylene bonding has not been investigated. To elucidate the influence of donor atoms, it is important to synthesize a series of donor-stabilized bis(silylene)metal complexes with different bridging atoms, such as nitrogen, sulfur, and phosphorus. Here we wish to report the first application of the photochemical method



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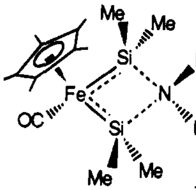
to synthesize a bis(silylene)iron complex with a non-oxygen bridging atom, namely the amino-bridged bis(silylene)iron complex **1**.[13] The influence of the bridging amino group on the bis(silylene)iron core is discussed on the basis of spectroscopic and crystallographic analysis.



1

Experimental Section

All manipulations were performed using standard Schlenk techniques under nitrogen, vacuum line techniques, or a drybox under nitrogen. Nuclear magnetic resonance (NMR) spectra were recorded on Varian XL-200, Bruker AC-300, and JEOL FX-90Q Fourier transform spectrometers and a Varian EM-390 CW spectrometer. Infrared (IR) spectra were obtained on a JASCO IRA-810 spectrometer. Mass and high-resolution mass spectra were recorded on a JEOL HX-110 spectrometer at the Instrumental Analytical Center for Chemistry of Tohoku University. Elemental analyses were also performed at the Instrumental Analytical Center for Chemistry of Tohoku University.

Tetrahydrofuran, benzene, hexane, and diethyl ether were dried and deoxygenated by refluxing over sodium/benzophenone ketyl followed by distillation under nitrogen. Diethylamine was dried over CaH_2 and distilled under nitrogen before use. Alkyllithium reagents were purchased from Wako Pure Chemical Industries, Ltd., and used as received. Preparation of $Cp'Fe(CO)_2SiMe_2SiMe_2Cl$ was as reported previously.[4b]

Synthesis of $Cp'Fe(CO)_2SiMe_2SiMe_2NEt_2$ (2). To an ether solution (20 mL) of $Cp'Fe(CO)_2SiMe_2SiMe_2Cl$ (1.33 g, 3.34 mmol) was added a solution of $LiNEt_2$ (3.4 mmol), prepared by mixing Et_2NH (0.35 mL, 3.4 mmol) in ether (5 mL) and 1.7 M *t*-BuLi in pentane (2.0 mL, 3.4 mmol). The reaction mixture was stirred for 24 h at room temperature. Volatiles were evaporated under reduced pressure, and the brown residue was extracted with 30 mL of hexane. The extract was filtered through a Celite pad and concentrated under vacuum. Molecular distillation (3.0×10^{-4} Torr) of the brown residue gave **2** as an air- and moisture-sensitive orange oil (0.22 g, 0.51 mmol, 15% yield) and yellow crystals of $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2SiMe_2)Fe(CO)_2$ (**3**) (0.40 g, 1.1 mmol, 33% yield). **2**: ^1H NMR (C_6D_6) δ 2.96 (q, $J = 6.8$ Hz, 4 H, NCH_2CH_3), 1.55 (s, 15 H, Cp′), 1.08 (t, $J = 6.8$ Hz, 6 H, NCH_2CH_3), 0.67 (s, 6 H, SiMe), 0.51 (s, 6 H, SiMe); ^{13}C NMR (C_6D_6) δ 218.4 (CO), 94.7 (C_5Me_5), 42.2 (NCH_2CH_3), 16.8 (NCH_2CH_3), 10.0 (C_5Me_5), 3.9 (SiMe), 1.2 (SiMe); ^{29}Si NMR (C_6D_6) δ 13.6, 3.1; IR (C_6D_6) ν_{CO} 1975, 1920 cm^{-1}; mass spectrum (EI, 70 eV) *m/z* (relative intensity) 435 (M^+, 1.1), 407 (5.8), 380 (17.3), 305 (100); exact mass calcd for $C_{20}H_{37}FeO_2NSi_2$ (M^+) 435.1712, found 435.1717. **3**: ^1H NMR (C_6D_6) δ 1.61 (s, 6 H, C_5Me_4), 1.46 (s, 6 H, C_5Me_4), 1.07 (s, 2 H, CH_2), 0.66 (s, 6 H, SiMe), 0.30 (s, 6 H, SiMe); ^{13}C NMR (C_6D_6) δ 218.0 (CO), 114.6 (C_5Me_4), 94.7 (C_5Me_4), 90.8 (C_5Me_4), 11.0 (CH_2), 10.4 (C_5Me_4), 10.3 (C_5Me_4), 1.9 (SiMe), −0.3 (SiMe); ^{29}Si NMR (C_6D_6) δ 44.5, 33.7; IR (C_6D_6) ν_{CO} 1965, 1910 cm^{-1}; mass spectrum (EI, 70 eV) *m/z* (relative intensity) 362 (M^+, 100), 334 (89.5), 306 (5.7). Anal. Calcd for $C_{16}H_{26}FeO_2Si_2$: C, 53.03; H, 7.23. Found: C, 52.81; H, 7.18.

Table 1. Crystallographic Data and Refinement Parameters for 1

chem formula	$C_{19}H_{37}FeNOSi_2$
fw	407.53
cryst syst	monoclinic
space group	$P2_1/a$ (variant of No. 14)
a, Å	28.031(8)
b, Å	19.541(6)
c, Å	8.089(3)
β, deg	93.62(2)
V, Å^3	4422(3)
Z	8
d_{calcd}, g cm^{-3}	1.224
μ, cm^{-1}	7.97
$F(000)$	1760
cryst size, mm	0.1 × 0.1 × 0.2
temp, K	150
radiation (λ, Å)	Mo Kα (0.710 73)
monochromator	graphite
scan type	ω
θ range, deg	1.79−29.01
index ranges	$-38 \le h \le 38, 0 \le k \le 26, 0 \le l \le 10$
no. of reflns measd	11 111
no. of unique data	11 111
no. of data with $\lvert F_o\rvert > 4\sigma(F_o)$	6947
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	11 111/0/479
goodness of fit on F^2	1.002
final R indices ($\lvert F_o\rvert > 4\sigma(F_o)$)	$R_1{}^a = 0.067$, w$R_2{}^b = 0.166$
final R indices (all data)	$R_1{}^a = 0.144$, w$R_2{}^b = 0.219$
largest diff peak and hole, e Å^{-3}	1.388 and −2.005

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$, where $w = 1/[\sigma^2(F_o^2) + (0.1325P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$.

Photolytic Procedure. Unless otherwise stated, photolysis of complex **2** was carried out as follows: A Pyrex NMR tube (5 mm o.d., 3 mm i.d.) was charged with **2** (ca. 10 mg) and connected to a vacuum line via a ground-glass joint. Benzene-d_6 (about 0.4 mL) was transferred to the sample tube by conventional trap-to-trap distillation. The NMR sample tube was then flame-sealed under vacuum. Irradiation was carried out 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.

Photolysis of 2 and Isolation of Its Product 1. A Pyrex sample tube (8 mm o.d., 6 mm i.d.) with a greaseless vacuum valve and a ground-glass joint was charged with **2** (100 mg, 0.23 mmol) and pentane (1.3 mL). The solution was degassed on a vacuum line by the conventional freeze−pump−thaw method and then irradiated for 1 h. After irradiation, the reaction mixture was concentrated and cooled to −20 °C in a refrigerator to give extremely air- and moisture-sensitive yellow crystals of **1**:[16] ^1H NMR (C_6D_6) δ 2.82 (q, $J = 7.1$ Hz, 2 H, NCH_2CH_3), 2.42 (q, $J = 7.1$ Hz, 2 H, NCH_2CH_3), 1.85 (s, 15 H, Cp′), 0.62 (t, $J = 7.1$ Hz, 3 H, NCH_2CH_3), 0.59 (t, $J = 7.1$ Hz, 3 H, NCH_2CH_3), 0.56 (s, 6 H, SiMe), 0.48 (s, 6 H, SiMe); ^{13}C NMR (C_6D_6) δ 223.1 (CO), 89.6 (C_5Me_5), 41.5 (NCH_2CH_3), 39.0 (NCH_2CH_3), 11.5 (C_5Me_5), 10.9 (NCH_2CH_3), 10.6 (NCH_2CH_3), 8.4 (SiMe), 5.3 (SiMe); ^{29}Si NMR (C_6D_6) δ 94.0; IR (C_6D_6) ν_{CO} 1850 cm^{-1}; mass spectrum (EI, 70 eV) *m/z* (relative intensity) 407 (M^+, 53.9), 336 (100); exact mass calcd for $C_{19}H_{37}FeONSi_2$ (M^+) 407.1763, found 407.1757.

X-ray Crystal Structure Determination of 1. A single crystal of **1** was sealed into a glass capillary under an atmosphere of dry nitrogen. Intensity data were collected on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo Kα radiation at 150 K. Crystallographic

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(13) The analogous amino-bridged bis(silylene)iron complexes $Cp(OC)Fe\{Me_2Si\cdot\cdot\cdot NR_2\cdot\cdot\cdot SiMe_2\}$ have been synthesized by Malisch *et al.* via a completely different route, but the details have not been published.[14] Another type of amino-bridged bis(silylene)ruthenium complex has also been reported recently.[15]

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(16) The photolysis of **2** proceeded very cleanly to afford the complex **1**, as shown in Figure 1. However, due to its instability, the reliable isolation yield of **1** could not be determined.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1

	x	*y*	*z*	*U*(eq)[a]
		Molecule A		
Fe(A)	2721(1)	9793(1)	832(1)	18(1)
Si(1A)	3204(1)	9012(1)	−189(2)	25(1)
Si(2A)	2417(1)	8760(1)	1249(2)	27(1)
O(A)	3302(2)	9781(2)	3904(5)	41(1)
N(A)	2978(1)	8203(2)	956(6)	31(1)
C(1A)	3061(2)	9748(2)	2643(6)	24(1)
C(2A)	3134(2)	8773(4)	−2422(7)	55(2)
C(3A)	3873(2)	9043(3)	299(7)	39(1)
C(4A)	1957(2)	8348(3)	−278(9)	49(2)
C(5A)	2187(2)	8567(3)	3330(8)	50(2)
C(6A)	2919(2)	7558(3)	3(9)	54(2)
C(7A)	3396(2)	7216(4)	−371(11)	76(3)
C(8A)	3266(2)	8069(3)	2542(7)	38(1)
C(9A)	3103(3)	7464(3)	3566(10)	67(2)
C(10A)	2062(2)	10308(3)	353(6)	30(1)
C(11A)	2296(2)	10231(2)	−1162(6)	27(1)
C(12A)	2740(2)	10563(3)	−1020(6)	28(1)
C(13A)	2796(2)	10852(3)	544(7)	36(1)
C(14A)	2381(2)	10708(3)	1411(7)	42(1)
C(15A)	1558(2)	10123(4)	638(11)	71(3)
C(16A)	2067(2)	9914(3)	−2716(8)	52(2)
C(17A)	3069(2)	10683(4)	−2360(10)	69(2)
C(18A)	3217(3)	11286(3)	1184(11)	78(3)
C(19A)	2285(3)	10948(4)	3150(8)	89(3)
		Molecule B		
Fe(B)	29(1)	8082(1)	4615(1)	20(1)
Si(1B)	−48(1)	7065(1)	5819(2)	24(1)
Si(2B)	675(1)	7461(1)	4171(2)	24(1)
O(B)	−476(1)	7587(2)	1644(4)	35(1)
N(B)	430(1)	6565(2)	4638(5)	26(1)
C(1B)	−256(2)	7765(2)	2850(5)	23(1)
C(2B)	140(2)	6931(3)	8094(7)	48(2)
C(3B)	−622(2)	6572(3)	5529(7)	36(1)
C(4B)	1238(2)	7509(3)	5573(7)	40(1)
C(5B)	911(2)	7446(3)	2028(6)	34(1)
C(6B)	755(2)	6092(3)	5652(7)	35(1)
C(7B)	528(2)	5429(3)	6182(8)	51(2)
C(8B)	199(2)	6194(3)	3152(6)	29(1)
C(9B)	534(2)	5808(3)	2090(7)	42(1)
C(10B)	362(3)	9044(4)	4938(12)	74(3)
C(11B)	245(2)	8789(4)	6487(9)	62(2)
C(12B)	−254(2)	8706(3)	6410(7)	40(1)
C(13B)	−430(2)	8907(3)	4808(8)	41(1)
C(14B)	−41(3)	9114(3)	3960(8)	60(2)
C(15B)	782(4)	9355(5)	3887(16)	42(3)
C(16B)	680(4)	8858(6)	7696(13)	34(3)
C(17B)	−420(5)	8580(6)	8160(15)	39(3)
C(18B)	−999(4)	8859(6)	4710(21)	44(3)
C(19B)	−274(6)	9389(5)	2158(13)	43(3)
C(15C)	923(4)	9153(6)	5279(21)	55(4)
C(16C)	442(5)	8568(6)	8379(13)	40(3)
C(17C)	−707(5)	8503(7)	7453(17)	43(3)
C(18C)	−875(5)	9030(6)	3695(20)	44(3)
C(19C)	125(6)	9418(5)	2366(15)	45(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 1

molecule A		molecule B	
Fe(A)—Si(1A)	2.2330(14)	Fe(B)—Si(1B)	2.230(2)
Fe(A)—Si(2A)	2.224(2)	Fe(B)—Si(2B)	2.2277(14)
Fe(A)—C(1A)	1.700(5)	Fe(B)—C(1B)	1.708(4)
Si(1A)—N(A)	1.958(4)	Si(1B)—N(B)	1.956(4)
Si(2A)—N(A)	1.940(4)	Si(2B)—N(B)	1.927(4)
Si(1A)—C(2A)	1.865(6)	Si(1B)—C(2B)	1.901(6)
Si(1A)—C(3A)	1.892(5)	Si(1B)—C(3B)	1.875(5)
Si(2A)—C(5A)	1.879(6)	Si(2B)—C(4B)	1.886(5)
Si(2A)—C(4A)	1.907(6)	Si(2B)—C(5B)	1.894(5)
O(A)—C(1A)	1.189(6)	O(B)—C(1B)	1.174(6)
N(A)—C(6A)	1.481(6)	N(B)—C(6B)	1.504(6)
N(A)—C(8A)	1.494(6)	N(B)—C(8B)	1.513(6)
C(6A)—C(7A)	1.543(8)	C(6B)—C(7B)	1.516(8)
C(8A)—C(9A)	1.529(8)	C(8B)—C(9B)	1.514(7)
Si(1A)···Si(2A)	2.605(2)	Si(1B)···Si(2B)	2.613(2)
C(2A)···C(6A)	3.162(10)	C(2B)···C(6B)	3.160(8)
C(3A)···C(8A)	3.194(8)	C(3B)···C(8B)	3.176(7)
C(4A)···C(6A)	3.104(8)	C(4B)···C(6B)	3.084(8)
C(5A)···C(8A)	3.279(8)	C(5B)···C(8B)	3.320(7)
C(2A)···C(16A)	3.727(10)	C(2B)···C(16C)	3.314(13)
C(2A)···C(17A)	3.737(12)	C(2B)···C(17B)	3.587(13)
C(4A)···C(15A)	3.731(10)	C(4B)···C(15C)	3.335(14)
C(4A)···C(16A)	3.663(9)	C(4B)···C(16B)	3.561(13)
Si(2A)—Fe(A)—Si(1A)	71.54(6)	Si(2B)—Fe(B)—Si(1B)	71.78(5)
Si(2A)—N(A)—Si(1A)	83.9(2)	Si(2B)—N(B)—Si(1B)	84.6(2)
N(A)—Si(1A)—Fe(A)	98.91(14)	N(B)—Si(1B)—Fe(B)	98.23(13)
N(A)—Si(2A)—Fe(A)	99.77(13)	N(B)—Si(2B)—Fe(B)	99.19(13)
O(A)—C(1A)—Fe(A)	174.0(4)	O(B)—C(1B)—Fe(B)	174.8(4)
C(2A)—Si(1A)—Fe(A)	120.0(2)	C(2B)—Si(1B)—Fe(B)	121.1(2)
C(3A)—Si(1A)—Fe(A)	121.2(2)	C(3B)—Si(1B)—Fe(B)	120.6(2)
C(2A)—Si(1A)—C(3A)	104.6(3)	C(2B)—Si(1B)—C(3B)	103.6(3)
C(4A)—Si(2A)—Fe(A)	122.3(2)	C(4B)—Si(2B)—Fe(B)	122.3(2)
C(5A)—Si(2A)—Fe(A)	118.4(2)	C(5B)—Si(2B)—Fe(B)	119.3(2)
C(4A)—Si(2A)—C(5A)	103.8(3)	C(4B)—Si(2B)—C(5B)	102.9(2)
C(6A)—N(A)—C(8A)	109.5(4)	C(6B)—N(B)—C(8B)	110.7(4)
C(6A)—N(A)—Si(2A)	118.4(3)	C(6B)—N(B)—Si(2B)	117.0(3)
C(8A)—N(A)—Si(2A)	113.0(3)	C(8B)—N(B)—Si(2B)	114.8(3)
C(6A)—N(A)—Si(1A)	118.1(4)	C(6B)—N(B)—Si(1B)	116.8(3)
C(8A)—N(A)—Si(1A)	112.0(3)	C(8B)—N(B)—Si(1B)	110.8(3)

data for **1** are listed in Table 1. The structure of **1** was solved by direct methods (SHELXS-86).[17] Non-hydrogen atoms were, at first, refined by full-matrix least-squares techniques with isotropic displacement parameters (SHELXL-93).[18] At this stage, several intense peaks were found near the Cp′ ring of one of the two independent molecules and also unusually large thermal parameters for the five methyl carbon atoms of the Cp′ group were obtained. These data indicated that the Cp′ ligand was disordered. Thus, a disorder model was built, assuming the presence of two different "Me$_5$" configurations around a C$_5$ ring and the structure was refined with a complementary occupancy factor (0.503). Non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters. Hydrogen atoms were placed at their geometrically calculated positions (d_{CH} = 0.98 Å for methyl hydrogens and 0.99 Å for methylene hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5\ U(C_{methyl})$ and $1.2\ U(C_{methylene})$). All measured, unique reflections (11 111 reflections) were used in the refinement. No absorption correction was applied. The final R_1 and the weighted wR_2 where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, were 0.067 and 0.166 for 6947 reflections with $F_o > 4\sigma(F_o)$, respectively. The highest residual peak in the final difference Fourier map was 1.39 e Å^{-3}. Tables 2 and 3 contain the atomic coordinates of non-hydrogen atoms and selected interatomic distances and angles, respectively. All the calculations were performed on an Apple Macintosh computer.

Results and Discussion

Synthesis of the (Aminodisilanyl)iron Complex Cp′Fe(CO)$_2$SiMe$_2$SiMe$_2$NEt$_2$ (2). Aminosilanes are usually prepared by the reactions of chlorosilanes with primary or secondary amines in an appropriate solvent. However, this method was not applicable for the synthesis of the (aminodisilanyl)iron complex **2**, since the (chlorodisilanyl)iron complex Cp′Fe(CO)$_2$SiMe$_2$SiMe$_2$Cl did not react with diethylamine. Thus, the (chlorodisilanyl)iron complex was treated with LiNEt$_2$. This

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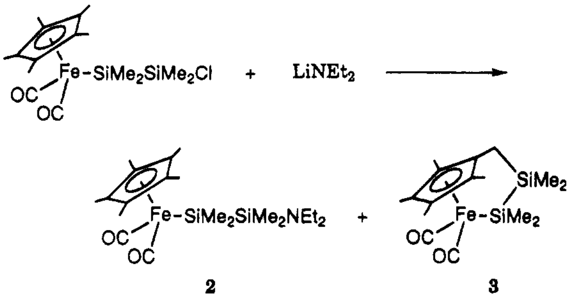
[17] Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.

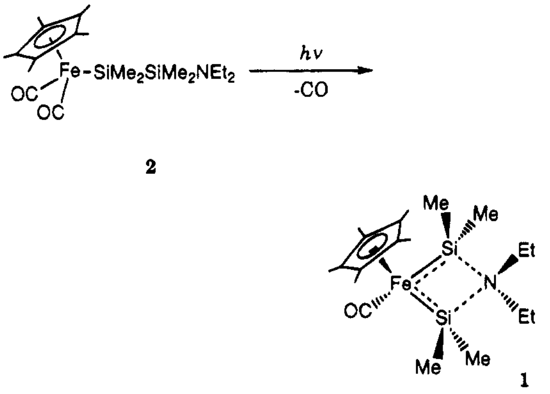
[18] Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1993.

reaction afforded **2** as well as the disilametallacycle (η^5:η^1-$C_5Me_4CH_2SiMe_2SiMe_2$)Fe(CO)$_2$ (**3**)[19] in 15 and 33% yields, respectively (eq 2).



(2)

Photolysis of the (Aminodisilanyl)iron Complex 2 and Characterization of Its Product 1. Irradiation of a C_6D_6 solution of Cp′Fe(CO)$_2$SiMe$_2$SiMe$_2$NEt$_2$ (**2**) resulted in the formation of the extremely air- and moisture-sensitive product **1** with CO evolution. The IR spectrum of **1** shows only one ν_{CO} absorption at 1850 cm^{-1}, indicating the existence of only one CO ligand. The significantly lower wavenumber of the ν_{CO} band compared to those of the precursor **2** (1975 and 1920 cm^{-1}) suggests the existence of strong back-donation from the metal to the carbonyl ligand. The ^{29}Si NMR spectrum of **1** shows only a singlet peak at 94.0 ppm. The considerable shift to lower field of the ^{29}Si NMR signal upon synthesis of **1** from precursor **2** (13.6 and 3.1 ppm) suggests significant sp^2 character of the silicon atoms in **1**. These spectral changes are consistent with the formation of the amino-bridged bis(silylene)iron complex **1** upon photolysis of **2** (eq 3). Spectral changes similar to this have been commonly observed for the photolysis of (alkoxydisilanyl)iron complexes, giving alkoxy-bridged bis(silylene)iron complexes.[4]



(3)

The formation of **1** is also supported by the ^{1}H NMR spectrum (Figure 1), which shows two Si—Me signals (0.56 and 0.48 ppm) and two N—Et signals (2.82 and 2.42 ppm for methylene hydrogens and 0.62 and 0.59 ppm for methyl hydrogens) due to the chemically different environments between the Cp′ side and the CO side with respect to the Fe—Si—N—Si chelate ring. The NOE data in the ^{1}H NMR spectra are also consistent with the structure of **1**: When the Cp′ signal was irradiated, the Si—Me signal at 0.48 ppm and the NCH_2CH$_3$ signals at 2.82 ppm were enhanced significantly, while other Si—Me and NCH_2CH$_3$ signals remained unchanged. This demonstrates that the methyl and ethyl groups which showed the enhanced signals are located spatially close to the Cp′ ligand. The signals of methyl groups on the NEt$_2$ bridge were not enhanced upon irradiation. This is certainly attributable to the large separation between the Cp′ ligand and the NEt methyl groups. The bis(silylene)iron complex **1** was finally characterized by X-ray crystal structure analysis (vide infra).

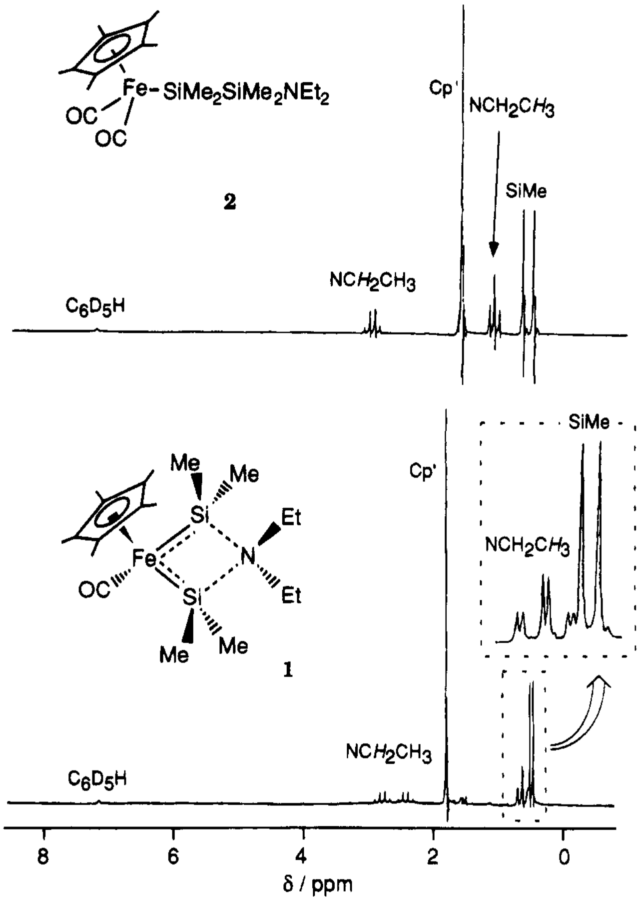


Figure 1. ^{1}H NMR spectra of Cp′Fe(CO)$_2$SiMe$_2$SiMe$_2$NEt$_2$ (**2**; top) and Cp′(OC)Fe{Me$_2$Si···NEt$_2$···SiMe$_2$} (**1**; bottom) in benzene-d_6 (90 MHz).

The ^{1}H NMR signals for both methylene and methyl groups on the NEt$_2$ moiety in **1** appear at somewhat higher field than those in the (aminodisilanyl)iron complex **2** (2.96 and 1.08 ppm, respectively). Such a high-field shift of the signal for the protons on the bridging group was also typically observed for the alkoxy-bridged bis(silylene)iron complexes Cp*(OC)Fe{Me$_2$Si···OR···SiMe$_2$} (Cp* = Cp, Cp′) and the methoxy-bridged bis(silylene)manganese complex (OC)$_4$Mn{Me$_2$Si···OMe···SiMe$_2$} (**4**).[4] These facts strongly suggest that localization of high electron density on the bridging group, which causes diamagnetic shielding of the substituents on the bridging atom. Contribution of the charge-separated bonding mode given in Chart 1 is, therefore, not negligible, though the bis(silylene) complex is quite soluble in nonpolar solvents such as hexane.

The ^{29}Si NMR signal of the amino-bridged bis(silylene)iron complex **1** appears at significantly higher field (94.0 ppm) than that of the alkoxy-bridged bis(silylene)iron complexes (121–128 ppm).[4] For monosubstituted silanes Me$_3$SiX, the ^{29}Si NMR signal shifts to lower field

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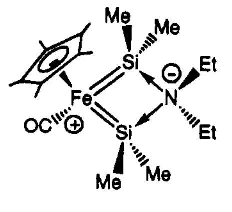
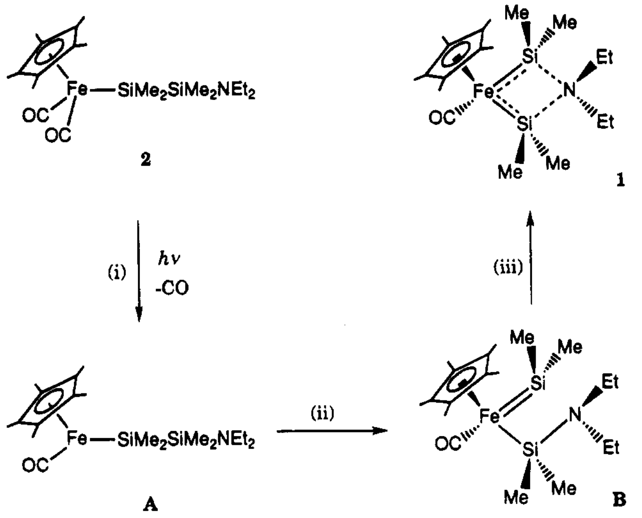
[19] The details of complex **3** will be reported elsewhere.

Chart 1



Scheme 1



as the substituent X becomes more electronegative.[20] In other words, the magnitude of the ^{29}Si NMR signal shift to higher field depends on X in the order X = F > Cl > Br > OMe > NMe_2 > Me. The high-field shift of the signal for **1** compared to those for the alkoxy-bridged bis(silylene)iron complexes is consistent with this trend (the electronegativity is 3.5 for oxygen and 3.1 for nitrogen).

The photoinduced formation of **1** from **2** can be explained by the mechanism shown in Scheme 1, which is essentially the same as that proposed previously for the photochemical conversion of the (alkoxydisilanyl)iron complexes to the alkoxy-bridged bis(silylene)iron complexes:[4a,b] (i) photochemically induced loss of a carbonyl ligand to generate a coordinatively unsaturated 16-electron intermediate **A**, (ii) intramolecular addition of an Si—Si bond to the metal center to produce the (aminosilyl)(silylene)iron intermediate **B**, and (iii) coordination of the amino nitrogen to the electron-deficient silylene ligand to form the amino-bridged bis(silylene)iron complex **1**.

Crystal Structure of the Iron Amino-Bridged Bis(silylene) Complex 1. The unit cell contains eight molecules of **1**. An asymmetric unit contains two crystallographically independent molecules, A and B, which are chemically equivalent. There is a disorder on the Cp′ ligand of molecule B. An ORTEP drawing of molecule A is shown in Figure 2. Selected interatomic distances and angles are listed in Table 3.

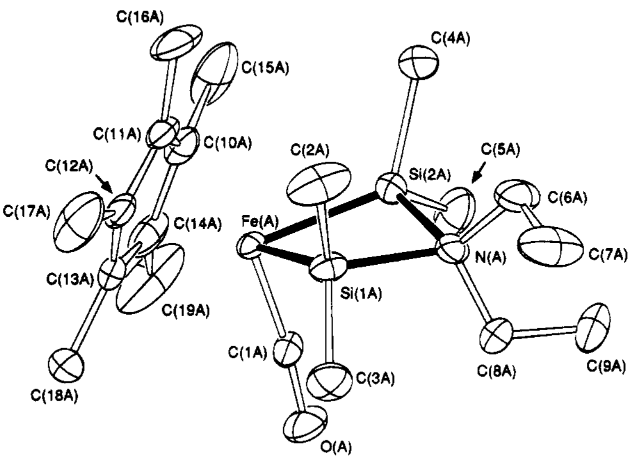


Figure 2. ORTEP view of molecule A of Cp′(OC)-Fe{$Me_2Si\cdot\cdot\cdot NEt_2\cdot\cdot\cdot SiMe_3$} (**1**).

The Fe—Si bond lengths of **1** (2.224(2) and 2.2330(14) Å for molecule A and 2.2277(14) and 2.230(2) Å for molecule B; averaged value 2.23 Å) are much shorter than those of (alkylsilyl)iron complexes (2.32–2.37 Å),[21] slightly shorter than those of $(OC)_4Fe{=}SiMe_2{\cdot}HMPA$ (2.279 and 2.292 Å),[3d,g] $(OC)_4Fe{=}Si(SBu^t)_2{\cdot}HMPA$ (2.278 Å),[10a] and $(OC)_4Fe{=}Si(OBu^t)_2{\cdot}HMPA$ (2.289 Å),[3a,c] and comparable to those of the methoxy-bridged bis(silylene)iron complex Cp′(OC)Fe{$Me_2Si\cdot\cdot\cdot OMe\cdot\cdot\cdot SiMeOMe$} (**5**; 2.207 and 2.222 Å)[4a,b] and $(OC)_4Fe{=}SiCl_2{\cdot}HMPA$ (2.214 and 2.221 Å).[3g] The short Fe—Si bonds in **1** indicate the unsaturated character of the Fe—Si bonding. The sp^2 character of the silicon atoms is also supported by the fact that each silicon atom and the atoms directly attached to it, except for the bridging nitrogen, are nearly coplanar. The silicon atoms lie 0.43–0.46 Å above the plane defined by the Fe atom and two carbon atoms attached to the silicon atom. The sum of the bond angles at each silicon, i.e., C—Si—C and two Fe—Si—C's, is 345.0° (average).

In contrast to the short Fe—Si distances, the bond distances between the silicon atoms and the tetracoordinate nitrogen atom (1.958(4) and 1.940(4) Å for molecule A and 1.956(4) and 1.927(4) Å for molecule B; averaged value 1.95 Å) are much longer than those of normal Si—N single bonds (1.70–1.76 Å for aminosilanes),[22] are comparable to that of the dative Si—N bond in the cationic acetonitrile-coordinated (silylene)ruthenium complex $[Cp'(Me_3P)_2Ru{=}SiPh_2{\cdot}NCMe]^+$ (1.932 Å),[2a,b] and are slightly shorter than that of $(OC)_5Cr{=}Si(C_6H_4CH_2NMe_2)_2$ (2.046 Å).[3f,h] Interestingly, the observed Si—N bond lengths in **1** (averaged value 1.95 Å) lie midway between the calculated Si—N bond distances for the aminosilane $H_3Si{-}NH_2$ (1.72 Å) and the amine-coordinated silylene $H_2Si{\leftarrow}NH_3$ (2.06 Å) obtained by ab initio calculations.[23,24] This is consistent with the description of the bonding between silicon and the bridging atoms as a hybrid of a covalent and dative bond.[4] The severe steric repulsion between the Si—Me and the N—Et groups in **1** also contributes to the elongation of the Si—N bonds: The interatomic distances between Si—Me and the methylene carbon atoms

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(20) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 8.

(21) (a) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24.

(22) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 3.

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(24) Conlin, R. T.; Laakso, D.; Marshall, P. *Organometallics* **1994**, *13*, 838.

of the NEt groups (3.08–3.32 Å) are much smaller than the sum of the van der Waals radii of methyl and methylene groups (4.0 Å).

The four-membered ring in **1** defined by Fe, two Si, and N atoms is nonplanar: The dihedral angles between the plane defined by Si(1)–Fe–Si(2) and that defined by Si(1)–N–Si(2) are 156.4 and 155.7° for molecule A and B, respectively. The four-membered ring in the alkoxy-bridged bis(silylene)iron complex **5** is also bent (dihedral angle 158.8°),[4a,b] while the corresponding four-membered ring in the alkoxy-bridged bis(silylene)-manganese complex **4** is planar.[4c] Bending of the four-membered ring in **1** is obviously attributable to the steric repulsion between the methyl groups of Cp′ and SiMe groups, since the interatomic distances between the Si–Me groups on the Cp′ side with respect to the four-membered ring and the methyl groups on the Cp′ ligand are considerably shorter (3.31–3.74 Å) than the sum of the van der Waals radii of two methyl groups (4.0 Å).

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Supplementary Material Available: For compound **1**, tables of hydrogen atom coordinates, all bond distances and angles, and anisotropic displacement parameters and figures giving an ORTEP view of molecule B and packing diagrams (11 pages). Ordering information is given on any current masthead page.

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