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Registry No. H_2, 1333-74-0; p-$F_3CC_6H_4OH$, 402-45-9; p-ClC_6H_4OH, 106-48-9; PhOH, 108-95-2; p-HOC_6H_4Bu-t, 98-54-4; p-$MeOC_6H_4OH$, 150-76-5.

Synthesis, Characterization, and X-ray Crystal Structure of a Donor-Stabilized Bis(silylene)iron Complex

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Silylene complexes have been proposed as reactive intermediates in a number of reactions[1] and as products in a few reactions,[2] but there has been no report on the X-ray crystal structure analysis of stable silylene complexes until recently. In 1987, two groups reported one after the other the syntheses and crystal structures of donor-stabilized silylene complexes: $[(OC)_4Fe{=}Si(O\text{-}t\text{-}Bu)_2\cdot HMPT]$[3] and $[Cp'(Me_3P)_2Ru{=}SiPh_2\cdot NCMe](BPh_4)$ ($Cp' = \eta^5\text{-}C_5Me_5$).[4] We now report the first synthesis and X-ray crystal structure determination of a donor-stabilized bis(silylene)iron complex.

Recently, Pannell's group[5] and we[6] independently observed an unusually fast alkyl scrambling between silicon atoms in the photoinduced conversion of $CpFe(CO)_2SiR_2SiR_3$ to $CpFe(CO)_2SiR_3$ (R = alkyl, aryl). Silyl(silylene)iron intermediates were postulated as key intermediates of this reaction, but these were too unstable to isolate. Thus, our efforts have focused on searching substituents on silicon atoms which effectively stabilize the silyl(silylene)iron complexes, and we have finally found that these can be stabilized as donor-stabilized bis(silylene)iron complexes by introducing alkoxy groups.

The starting complex $Cp'Fe(CO)_2SiMe_2SiMe(OMe)_2$ (**1**)[7] was prepared as follows: $Na[Cp'Fe(CO)_2]$ was allowed to react with $ClMe_2SiSiMeCl_2$, and then the product was treated with methanol and pyridine to give **1** and its isomer $Cp'Fe(CO)_2SiMe(OMe)SiMe_2(OMe)$ in 32% and 9% overall yields, respectively. Irradiation of **1** in C_6D_6 or toluene (ca. 0.1 M) with a medium pressure Hg arc lamp resulted in the quantitative conversion to a mixture of diastereomers of bis(silylene) complexes **2**[8] and **3**[8] (optical isomerism is ignored) with loss of 1 equiv of CO within several minutes (eq 1). The ratio of **2** and **3** is approximately 2:1

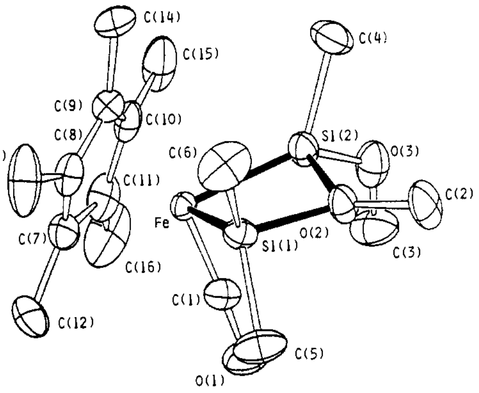


Figure 1. ORTEP view of **2** with thermal elipsoids at 30% probability level. Selected distances (Å) and angles (deg): Fe–Si(1), 2.222 (3); Fe–Si(2), 2.207 (3); Fe–C(1), 1.676 (11); Si(1)–C(5), 1.88 (2); Si(1)–C(6), 1.88 (2); Si(1)–O(2), 1.793 (9); Si(2)–O(2), 1.799 (8); Si(2)–O(3), 1.632 (9); Si(2)–C(4), 1.94 (2); O(2)–C(2), 1.45 (2); O(3)–C(3), 1.41 (2); O(1)–C(1), 1.198 (14); Si(1)···Si(2), 2.622 (4); Fe···O(2), 2.962 (7); O(1)···C(3), 3.33 (2); C(4)···C(14), 3.59 (2); C(6)···C(13), 3.54 (2); Si(1)–Fe–Si(2), 72.6 (1); Fe–Si(1)–O(2), 94.5 (3); Fe–Si(2)–O(2), 94.8 (3); Si(1)–O(2)–Si(2), 93.8 (4); Fe–Si(1)–C(5), 123.1 (5); Fe–Si(1)–C(6), 123.6 (6); C(5)–Si(1)–C(6), 105.8 (7); Fe–Si(2)–O(3), 126.9 (4); Fe–Si(2)–C(4), 127.2 (5); O(3)–Si(2)–C(4), 98.5 (6); Si(1)–O(2)–C(2), 131.6 (7); Si(2)–O(2)–C(2), 132.4 (8); Si(1)–Fe–C(1), 84.9 (4); Si(2)–Fe–C(1), 91.7 (4).

Chart I

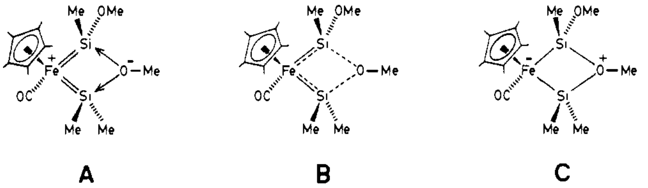
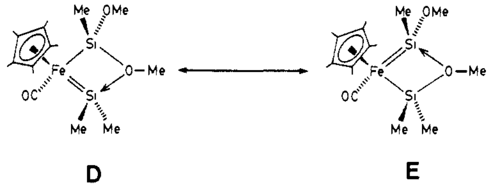
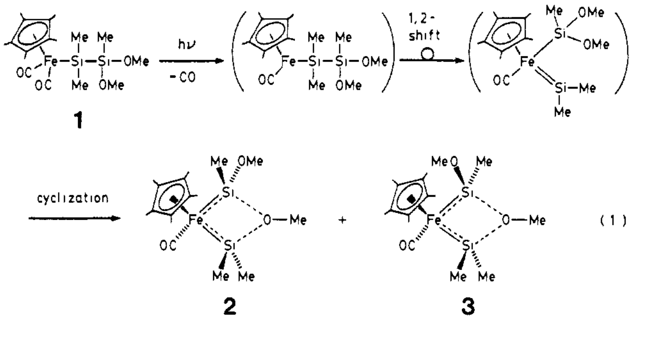


Chart II





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(7) For **1**: ^1H NMR (90 MHz, C_6D_6) δ 3.50 (s, 6 H, OMe), 1.62 (s, 15 H, Me of Cp′), 0.72 (s, 6 H, Si–Me), 0.41 (s, 3 H, Si–Me); ^{13}C NMR (22.5 MHz, C_6D_6) δ 217.8 (CO), 95.2 (Cp′ ring carbon), 50.1 (OMe), 9.8 (Me of Cp′), 3.5 (Si–Me), −2.2 (Si–Me); ^{29}Si NMR (17.8 MHz, C_6D_6) δ 10.7, 4.6; IR (C_6D_6) ν(CO) 1920 vs, 1972 vs cm^{-1}; Anal. Calcd for $C_{17}H_{30}FeO_4Si_2$: C, 49.75; H, 7.39. Found: C, 49.74; H, 7.35.

(8) For a mixture of **2** and **3** in the ratio of ca. 2:1 (assignments of signals for NMR spectra were done if possible): ^1H NMR (90 MHz, C_6D_6) δ 3.70 (s, 3 H, OMe, **2**), 3.37 (s, 3 H, OMe, **3**), 2.89 (s, 3 H, OMe, **2**), 2.82 (s, 3 H, OMe, **3**), 1.90 (s, 15 H, Me of Cp′, **3**), 1.82 (s, 15 H, Me of Cp′, **2**), 0.57 (s, 3 H, Si–Me, **2** and **3**), 0.55 (s, 3 H, Si–Me, **3**), 0.47 (s, 3 H, Si–Me, **3**), 0.43 (s, 3 H, Si–Me, **2**), 0.40 (s, 3 H, Si–Me, **2**); ^{13}C NMR (22.5 MHz, C_6D_6) δ 221.0 (CO, **2**), 220.0 (CO, **3**), 90.0 (Cp′ ring carbon, **3**), 89.8 (Cp′ ring carbon, **2**), 51.9 (OMe), 51.8 (OMe), 51.0 (OMe), 11.6 (Me of Cp′), 9.9 (Si–Me), 7.3 (Si–Me), 6.5 (Si–Me), 5.8 (Si–Me), 5.2 (Si–Me), 3.3 (Si–Me); IR (C_6D_6) ν(CO) 1875 cm^{-1}; MS (10 eV), *m/e* 382 (100, M^+); exact mass calcd for $C_{16}H_{30}FeO_3Si_2$ 382.1083, found 382.1086.

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according to ^{1}H NMR, and the major component is presumed to be **2** which has less steric repulsion between the substituent of the asymmetric silicon and bulky Cp′ ring than **3**. A possible mechanism of the photoreaction of **1** (eq 1) is essentially the same as that proposed previously for peralkyldisilanyliron complexes[5,6] except for the final cyclization step to form **2** and **3**.

Yellow crystals of **2** suitable for X-ray crystal structure analysis were obtained from a concentrated reaction mixture in toluene at −20 °C. The ORTEP view of **2** is shown in Figure 1.[9] The Fe–Si bond lengths (2.207 (3) and 2.222 (3) Å) are very short, and the former is the shortest Fe–Si bond length yet observed.[10] In contrast, the bond lengths of Si(1)–O(2) (1.793 (9) Å) and Si(2)–O(2) (1.799 (8) Å) are significantly longer than that of Si(2)–O(3) (1.632 (9) Å), a usual Si–O single bond, and are even longer than a dative Si–O(HMPT) bond in $[(OC)_4Fe{=}Si(O\text{-}t\text{-}Bu)_2{\cdot}HMPT]$ (1.730 (3) Å).[3] Each silicon atom and the atoms directly attached to this except O(2) are almost coplanar: Si(1) and Si(2) lie only 0.32 and 0.30 Å above the planes defined by Fe, C(5), and C(6) and Fe, O(3), and C(4), respectively. Interestingly, the trivalent oxygen O(2) and three atoms bonded to this, Si(1), Si(2), and C(2), are also coplanar: the deviation of O(2) from the plane defined by Si(1), Si(2), and C(2) is only 0.14 Å.

In consideration of the nearly planar arrangement of atoms at each silicon except O(2), the short Fe–Si and long Si–O(2) bond lengths, and the equivalence of two Fe–Si bonds and two Si–O(2) bonds, we propose a bonding model which is schematically represented by the structure B in Chart I. Structure B lies in the midst of two canonical structures A and C. Charge separation seems to be very little because **2** is very soluble in typical nonpolar organic solvents. Therefore, it is considered that two Fe–Si bonds take on the partial double bond character, whereas two Si–O(2) bonds are regarded as a mixture of dative bonding and covalent bonding. By using classical bonding description, structure B could be described as a combination of two resonance forms D and E (Chart II).

The sp^2 character of silicon atoms is further supported by the ^{29}Si NMR data: A mixture of **2** and **3** in the ratio of ca. 2:1 shows four signals at remarkably low field (δ 127.4, 121.1, 101.9, and 93.9 ppm) with ca. 1:2:2:1 intensity.

The CO stretching frequency for the terminal carbonyl ligand of **2** (and also **3**) (1875 cm^{-1}) is appreciably lower than those of **1** (1920 and 1972 cm^{-1}) and that of a structurally similar complex $CpFeH(SiCl_3)_2(CO)$ (2025 cm^{-1}).[11] This result indicates the strong back donation of electron density from iron to carbonyl ligand and therefore suggests the poor electron-accepting ability of the two silylene ligands, which may be due to the partial occupancy of vacant 3p orbitals of silicon atoms by the lone pairs of methoxy oxygen O(2). The strong back donation to the carbonyl ligand is also reflected in the short Fe–C(1) bond (1.68 Å) and the long C(1)–O(1) bond (1.20 Å) compared to those of $CpFeH(SiCl_3)_2(CO)$ (1.75 and 1.13 Å, respectively).[12]

The complexes **2** and **3** are extremely air and moisture sensitive, and the light yellow color of those crystals or solutions immediately turns to dark brown when they are exposed to air or moisture.

The similar photochemical behavior was observed for $Cp'Fe(CO)_2SiMe_2SiMe_2OMe$, $Cp'Fe(CO)_2SiMe_2SiMe_2O\text{-}t\text{-}Bu$, $CpFe(CO)_2SiMe_2SiMe(O\text{-}t\text{-}Bu)_2$, and $CpFe(CO)_2SiMe_2SiMe_2O\text{-}t\text{-}Bu$ which will be reported elsewhere in detail.

Acknowledgment. We express our grateful acknowledgment to Prof. H. Sakurai, Tohoku University, for his warm encouragement and helpful discussions throughout this work. This work has been supported by Grants-in-Aid for Special Project Research, no. 61125007, and for Scientific Research, no. 662740340, from the Ministry of Education, Science and Culture.

Supplementary Material Available: Tables of atomic positional and thermal parameters and bond distances and bond angles for **2** (6 pages); listings of observed and calculated structure factors for **2** (9 pages). Ordering information is given on any current masthead page.

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(9) Crystal data of **2**: orthorhombic, space group $P2_12_12_1$, $a = 10.547$ (2) Å, $b = 21.932$ (4) Å, $c = 8.742$ (3) Å, $V = 2022.2$ (8) Å^3, $d_{calcd} = 1.26$ g cm^{-3}, $Z = 4$. X-ray diffraction data were collected at 15 °C on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation. Reflections (3488) with $3° < 2\theta < 60°$ were collected by the ω-2θ scan technique. The crystal structure was solved by the heavy atom method and refined with block-diagonal least-squares by using individual anisotropic thermal parameters. None of the hydrogen atoms was found. As a result of refinement, the structure drawn in Figure 1 was slightly more favored than that with inverse chirality, applying anomalous dispersion correction. For 1900 unique reflections ($|F_o| > 3\sigma(F_o)$) $R = 0.076$ ($R_w = 0.114$) was obtained.

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Two-Dimensional NMR Strategies for Carbon–Carbon Correlations and Sequence-Specific Assignments in Carbon-13 Labeled Proteins

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Applications of carbon NMR spectroscopy to proteins in the past have been limited to one-dimensional spectroscopy[1] with a few explorations into two-dimensional heteronuclear chemical shift correlation.[2-7] Carbon–carbon scalar couplings have been totally unexploited in NMR spectroscopy of proteins. Uniform or selective carbon-13 enrichment can be used to increase sensitivity of heteronuclear shift correlation experiments as well as to introduce a readily observable level of ^{13}C–^{13}C coupling. Although a prototype ^{13}C–^{13}C correlation experiment was carried out with an amino acid ([85% U1-^{13}C]lysine) several years ago,[8] protein experiments have been slow to follow. We report here that the NMR spin system assignments of the nine leucine residues in [85% U1-^{13}C]leucine streptomyces subtilisin inhibitor ([85% U1-^{13}C]leucine SSI)[9,10] have been extended from the carbonyl carbons[11-13] to the intraresidue α carbons by means of two-dimen-

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