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Photochemical Reaction of $CpFe(CO)_2SiMe_3$ (Cp = η^5-C_5H_5) with a Trihydrosilane Containing a Bulky Amino Substituent, Bis(trimethylsilyl)aminosilane

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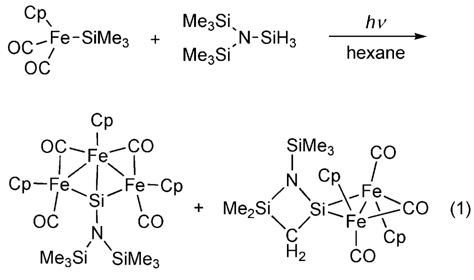
*Summary: A photochemical reaction between $CpFe(CO)_2SiMe_3$ and $(Me_3Si)_2NSiH_3$ in hexane gave the silylyne-bridged triiron complex $Cp_3Fe_3(CO)_4SiN(SiMe_3)_2$ (**2**) and a diiron complex bridged by a four-membered cyclic silylene, $Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$SiN(SiMe_3)_2SiMe_2CH_2)$ (**3**). In contrast, the silylene- and alkyne-bridged triiron complex $Cp_3Fe_3\{\mu_2$-$SiHN(SiMe_3)_2\}\{\mu_3$-$COSiH_2N(SiMe_3)_2\}\{\mu_3$-$\eta^2$-$C_2O_2$-$SiHN(SiMe_3)_2\}$ (**4**) was formed as the main product by a similar reaction in toluene.*

The transition-metal-mediated transformation of organosilicon compounds is an important reaction in organic and organometallic chemistry.[1] Oxidative addition of a Si−H bond to an unsaturated metal center is a key step for the transformation reactions. A variety of complexes containing metal−silicon bonds have been synthesized via oxidative addition of hydrosilanes to metal complexes.[2−6] Photochemical reactions of iron complexes $CpFe(CO)_2R$ with primary silanes ($RSiH_3$) have been reported to give hydrosilylene-bridged complexes.[4] This type of compound is attractive, since a reactive Si−H bond remains on the silylene ligand.[3−6] Thus, Kawano et al. synthesized the donor-stabilized diiron μ-silylyne complex $[Cp_2Fe_2(CO)_3(\mu$-Si-^{t}Bu•Base$)]^+$ from the μ-hydrosilylene complex $Cp_2Fe_2(CO)_3$-$(\mu$-SiH^{t}Bu), which was prepared by the reaction of CpFe-$(CO)_2SiMe_3$ with ^{t}BuSiH$_3$.[4,5]

In this paper, we report the photochemical reaction between $CpFe(CO)_2SiMe_3$ and $(Me_3Si)_2NSiH_3$.[7,8] This reaction was expected to afford the amino(hydro)silylene-bridged diiron complex $Cp_2Fe_2(CO)_3\{\mu$-$SiHN(SiMe_3)_2\}$ (**1**), which would be a good precursor for a novel donor-free silylyne-bridged diiron complex, since the bulky amino substituent must stabilize the electron-deficient silylyne ligand electronically and kinetically. Contrary to our expectation, the photolytic reaction gave unprecedented products, the silylyne-bridged triiron complex $Cp_3Fe_3(CO)_4SiN(SiMe_3)_2$ (**2**), the four-membered cyclic silylene bridged diiron complex $Cp_2Fe_2(CO)_2(\mu$-$CO)(\mu$-$SiN(SiMe_3)_2$-$SiMe_2CH_2)$ (**3**), and the silylene- and alkyne-bridged triiron complex $Cp_3Fe_3\{\mu_2$-$SiHN(SiMe_3)_2\}\{\mu_3$-$COSiH_2N(SiMe_3)_2\}\{\mu_3$-$\eta^2$-$C_2O_2SiHN(SiMe_3)_2\}$ (**4**), depending on the reaction conditions.

A yellow hexane solution containing $CpFe(CO)_2SiMe_3$ (2 equiv) and $(Me_3Si)_2NSiH_3$ (1 equiv) was irradiated for 24 h with a medium-pressure Hg arc lamp (450 W). This reaction afforded a mixture of a red solution and a black crystalline precipitate. The black precipitate was isolated by filtration and was characterized as the silylyne-bridged triiron complex **2** (10% yield, eq 1).[9] The red solution was revealed to contain the silylene-bridged diiron complex **3** as a main product and several unidentified products by NMR investigation. Complex **3** was isolated as red crystals (22% yield) from the solution (eq 1).[10]



2 **3**

When the reaction was monitored periodically by ^1H NMR, a trace singlet signal was observed at 8.63 ppm during the

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(9) Data for **2**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.52 (s, 9H, $SiMe_3$), 0.85 (s, 9H, $SiMe_3$), 4.43 (s, 5H, Cp), 4.58 (s, 10H, Cp); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 5.7 ($SiMe_3$), 6.1 ($SiMe_3$), 87.6 (Cp), 88.3 (Cp), 212.5 (CO), 273.8 (μ-CO); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −0.96 ($SiMe_3$), 2.40 ($SiMe_3$), 426.30 (silylyne); IR (KBr): ν_{CO} 1965, 1763 cm^{-1}. Anal. Calcd for $C_{25}H_{33}Fe_3NO_4Si_3$: C, 45.27; H, 5.01; N, 2.11. Found: C, 45.67; H, 5.27; N, 1.99.

(10) Data for **3**: ^1H NMR (500 MHz, C_6D_6) δ 0.21 (s, 9H, $SiMe_3$), 0.47 (s, 3H, SiMe), 0.48 (s, 3H, SiMe), 1.30 (d, 1H, CH, $J = 15.8$ Hz). 1.50 (d, 1H, CH, $J = 15.8$ Hz). 4.30 (s, 5H, Cp), 4.40 (s, 5H, Cp); ^{13}C NMR (125 MHz, C_6D_6) δ 2.57 ($SiMe_3$), 3.46 (SiMe), 3.50 (SiMe), 21.55 (CH_2), 85.05 (Cp), 86.56 (Cp), 212.73 (CO), 213.25 (CO), 276.72 (μ-CO); ^{29}Si NMR (99.3 MHz, C_6D_6) δ −1.33 ($SiMe_3$), 11.25 ($SiMe_2$), 220.07 (silylene); IR (KBr) ν_{CO} 1924, 1772 cm^{-1}. Anal. Calcd for $C_{19}H_{27}Fe_2NO_3Si_3$: C, 44.45; H, 5.30; N, 2.73. Found: C, 44.81; H, 5.36; N, 2.71.

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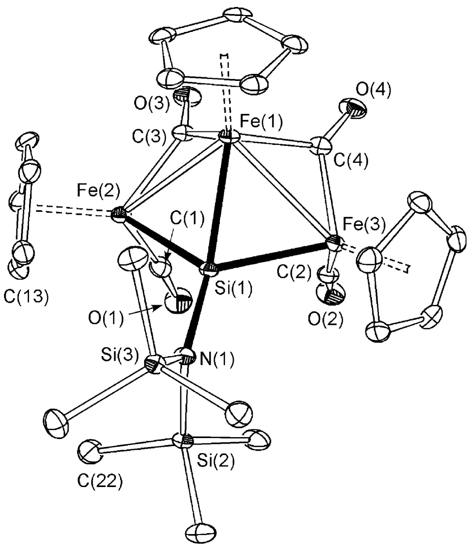

Figure 1. ORTEP drawing of **2** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.6589(4), Fe(1)−Fe(3) = 2.6511(4), Fe(1)−Si(1) = 2.3544(6), Fe(2)−Si(1) = 2.2741(6), Fe(3)−Si(1) = 2.2810(6), Si(1)−N(1) = 1.7566(18); Fe(1)−Si(1)−Fe(2) = 70.099(19), Fe(1)−Si(1)−Fe(3) = 69.748(18), Fe(2)−Si(1)−Fe(3) = 120.83(3), N(1)−Si(1)−Fe(1) = 151.53(7), N(1)−Si(1)−Fe(2) = 118.72(6), N(1)−Si(1)−Fe(3) = 117.46(6).

photolysis. This signal might be attributable to the Si−H of the desired amino(hydro)silylene-bridged complex $Cp_2Fe_2(CO)_3\{\mu\text{-}SiHN(SiMe_3)_2\}$ (**1**), since hydrosilylene-bridged diiron complexes have been reported to give the Si−H signals at very low field (7−8 ppm).[4b,d,11] However, we have not succeeded in isolating the product from the reaction mixture.

An X-ray crystal structure analysis of **2** revealed that the bridging Si atom in the aminosilylyne ligand $SiN(SiMe_3)_2$ is bound to three Fe atoms, each of which has a Cp ligand (Figure 1).[12] The Fe(1) atom was connected to the Fe(2) and Fe(3) atoms by Fe−Fe single bonds (Fe(1)−Fe(2) = 2.6589(4) Å, Fe(1)−Fe(3) = 2.6511(4) Å) and bridging carbonyl ligands, but there is no direct bond between Fe(2) and Fe(3) (Fe(2)···Fe(3) = 3.9611(4) Å). Three Fe−Si bond lengths are within the range of usual Fe−Si single-bond lengths (2.21−2.43 Å);[2,4−6,13] however, the Fe(1)−Si(1) bond (2.3544(6) Å) is apparently longer than the others (Fe(2)−Si(1) = 2.2741(6) Å and Fe(3)−Si(1) = 2.2810(6) Å), suggesting that the bonding character of Fe(1)−Si(1) is different from the others. The geometry around the bridging silicon atom Si(1) is extremely distorted from a regular tetrahedral structure. The bridging silicon Si(1) and the Fe(2), Fe(3), and N atoms lie on a plane: the sum of the three bond angles around Si(1) is 357.01(3)°. The remaining Fe(1) atom is largely displaced from the plane. The entire structure of **2** has pseudo-C_s symmetry: the Fe(1), Si(1), Si(2), Si(3), and N atoms form a pseudo mirror plane. The ^{1}H NMR spectrum of **2** showed two Cp signals at 4.58 and 4.43 ppm with a 2:1 intensity ratio and two $SiMe_3$ signals at 0.85 and 0.52 ppm. The $SiMe_3$ signals remained sharp even at 110 °C in toluene-d_8, which indicates that the rotation of the $Si-N(SiMe_3)_2$ bond is prevented by the severe steric repulsion between $SiMe_3$ and Cp groups on Fe(2) and Fe(3). The interatomic distance between C(13) and C(22) (3.585(4) Å) is smaller than the sum of van der Waals radii of Me and C−H of Cp (3.85 Å). The silylyne-bridged complex **2** contains three FeCp fragments, instead of two, in a molecule. Thus, the yield of complex **2** was considerably increased to 54% in the 3:1 reaction of $CpFe(CO)_2SiMe_3$ and $(Me_3Si)_2NSiH_3$ for 72 h.

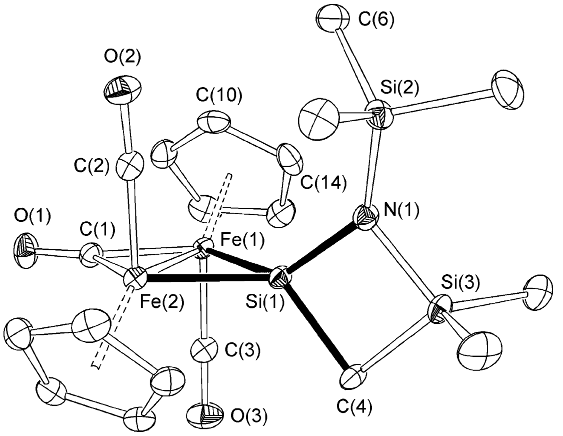

Figure 2. ORTEP drawing of **3** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.6320(4), Fe(1)−Si(1) = 2.2919(5), Fe(2)−Si(1) = 2.2771(5), Si(1)−N(1) = 1.7681(15), Si(1)−C(4) = 1.9108(18); Fe(1)−Si(1)−Fe(2) = 70.347(16), N(1)−Si(1)−C(4) = 89.24(7).

Complex **3** showed two Cp signals in its ^{1}H and ^{13}C NMR spectra. Signals arising from the $N(SiMe_3)_2$ unit were complicated compared with those of complex **2**. Three Si−Me signals were observed at 0.48, 0.47, and 0.21 ppm with 9:3:3 intensities in the ^{1}H NMR spectrum, which are assignable to a $SiMe_3$ group and a $SiMe_2$ unit with inequivalent Me groups, respectively. In addition to these Si−Me signals, two doublet signals were observed at 1.30 and 1.50 ppm, each with 1H intensity. These results suggest that one of six methyl groups in the reactant $(SiMe_3)_2NSiH_3$ is transformed into a methylene group during the reaction. The structure of complex **3** was confirmed by X-ray crystal structure analysis (Figure 2).[14] Complex **3** has two FeCp(CO) fragments, in which two iron centers are bridged by CO and a cyclic silylene ligand. The Cp and terminal CO ligands occupy mutually trans positions with respect to the Fe(1)−Si(1)−Fe(2)−C(1) four-membered ring, respectively. The silylene ligand has an almost planar Si−N−Si−C four-membered ring. The N(1)−Si(2) bond tilts from the least-squares plane of Si-

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[12] Crystallographic data for **2**: formula $C_{25}H_{33}Fe_3NO_4Si_3$, fw = 663.33, triclinic, space group $P\bar{1}$, $a = 10.0782(7)$ Å, $b = 11.2516(9)$ Å, $c = 12.1662(8)$ Å, $\alpha = 90.697(3)°$, $\beta = 91.267(3)°$, $\gamma = 100.896(4)°$, $V = 1354.21(17)$ Å^3, $Z = 2$, $T = 113(2)$ K, $\rho_{calcd} = 1.627$ g cm^{-3}, $\mu = 1.751$ mm^{-1}, $F(000) = 684$, θ range 1.67−32.16°, 331 variables refined with 6928 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0486 and wR2 = 0.1300, GOF = 1.076.

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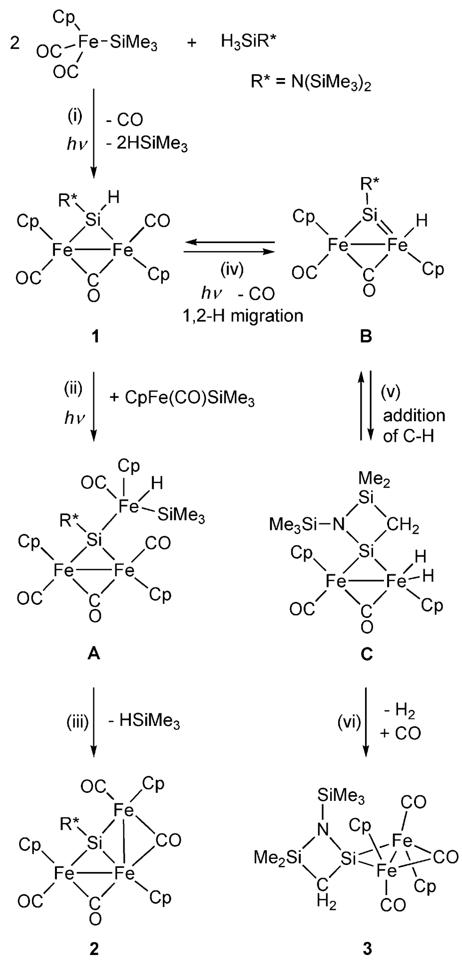
[14] Crystallographic data for **3**: formula $C_{19}H_{27}Fe_2NO_3Si_3$, fw = 513.37, monoclinic, space group $P2_1/n$, $a = 8.4040(5)$ Å, $b = 17.3179(8)$ Å, $c = 15.7939(11)$ Å, $\beta = 101.368(2)°$, $V = 2253.5(2)$ Å^3, $Z = 4$, $T = 113(2)$ K, $\rho_{calcd} = 1.513$ g cm^{-3}, $\mu = 1.467$ mm^{-1}, $F(000) = 1064$, θ range 1.76−32.26°, 258 variables refined with 6197 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0521 and wR2 = 0.1331, GOF = 1.066.

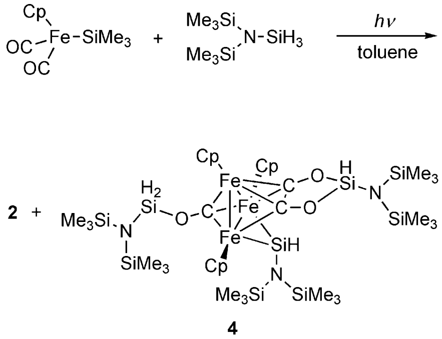
Scheme 1



(1), N(1), Si(3), and C(4) by 17.9(1)°. This deviation would be caused by the steric repulsion between the $SiMe_3$ group and a Cp ligand. Indeed, the interatomic distances between C(6) and C(10) (3.696(3) Å) and C(6) and C(14) (3.717(3) Å) are smaller than the sum of the van der Waals radii of Me and C−H of Cp (3.85 Å). The Fe−Fe distance of 2.6320(4) Å indicates the Fe−Fe single-bond character. The Fe−Si bonds (2.2771(5) and 2.2919(5) Å) are within the range of usual Fe−Si single bonds found in the known silylene-bridged diiron complexes (2.25−2.36 Å).[2,4−6,13]

A possible formation mechanism of complexes **2** and **3** is depicted in Scheme 1. In step i, the photochemical reaction of $CpFe(CO)_2SiMe_3$ and $(SiMe_3)_2NSiH_3$ generates the silylene-bridged diiron complex **1** via a mechanism similar to that reported previously.[4a,b] Complex **1** is quite reactive under the reaction conditions, probably due to the electronic influence of the amino substituent on the silylene ligand. Thus, in step ii complex **1** reacts with the 16-electron intermediate CpFe(CO)-$SiMe_3$, generated by photochemical elimination of a carbonyl group from $CpFe(CO)_2SiMe_3$ to form the triiron intermediate **A**. (iii) Reductive elimination of $HSiMe_3$ from **A** followed by bridging of CO affords complex **2**. Complex **3** was formed via photochemical elimination of a carbonyl group from **1** followed by 1,2-migration of H to give silylyne-bridged intermediate **B** (step iv), addition of a C−H bond in a methyl group of SiN-$(SiMe_3)_2$ to the Fe═Si bond to form intermediate **C** (step v), and reductive elimination of H_2 and recombination of CO (step vi). 1,2-Migration of hydrogen from silicon to metal, found in step iv, has been established as an important route for the formation of silylene complexes.[15] To the best of our knowledge, addition of an alkyl C−H bond to a M═Si bond such as in step v has not been reported, though activation of an aromatic C−H bond by silylene complexes was proposed as a key step for the formation of M−Si−C−C−P five-membered-ring metallacycle complexes.[16]

The products for the photoinduced reaction of CpFe-$(CO)_2SiMe_3$ and $(Me_3Si)_2NSiH_3$ depend on the solvent used. Photolysis of $CpFe(CO)_2SiMe_3$ (1 equiv) in the presence of $(Me_3Si)_2NSiH_3$ (1 equiv) in *toluene* for 72 h caused reduction of CO by hydrosilane and C−C coupling to give the novel silylene- and alkyne-bridged triiron complex $Cp_3Fe_3\{\mu_2\text{-SiHN(SiMe}_3)_2\}\{\mu_3\text{-COSiH}_2\text{N(SiMe}_3)_2\}\{\mu_3\text{-}\eta^2\text{-C}_2\text{O}_2\text{SiHN(SiMe}_3)_2\}$ (**4**) in addition to a small amount of **2** (eq 2).[17] Complex **4** was



(2)

isolated as brown crystals in 22% yield and fully characterized, including X-ray analysis (Figure 3).[18] Three FeCp units with a trigonal structure are linked by $\mu_3\text{-COSiH}_2\text{N(SiMe}_3)_2$ and $\mu_3\text{-}\eta^2\text{-C}_2\text{O}_2\text{SiHN(SiMe}_3)_2$ ligands. Two of the three iron atoms are further bridged by a hydrosilylene ligand, $HSiN(SiMe_3)_2$. The Fe−Si bond lengths (2.2830(6) and 2.2889(6) Å) in **4** are within the range of usual Fe−Si bond lengths found in silylene-bridged diiron complexes (2.25−2.36 Å).[2,4−6,13] The C(1)−C(2) distance (1.410(3) Å) is comparable to those of alkyne-bridged triiron complexes: $Fe_3(CO)_9(PPh_3)(\mu_3\text{-}\eta^2\text{-CH}_3\text{CCOC}_2\text{H}_5)$ (1.399(5) Å)[19] and $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-EtOCCPMePh}_2)]^-$ (1.393(5) Å).[20] To our knowledge, this is the first example of the coupling of two carbon monoxide molecules by the reaction with hydrosilane

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[17] Data for **4**: ^1H NMR (500 MHz, C_6D_6) δ 0.05 (s, 9H, $SiMe_3$), 0.51 (s, 18H, $SiMe_3$), 0.54 (s, 18H, $SiMe_3$), 0.58 (s, 9H, $SiMe_3$), 4.43 (s, 10H, Cp), 4.60 (s, 5H, Cp), 5.59 (s, 1H, O_2SiH), 5.91 (s, 2H, $OSiH_2$), 8.01 (s, 1H, SiH); ^{13}C NMR (125 MHz, C_6D_6) δ 4.47 ($SiMe_3$), 4.81 ($SiMe_3$), 5.81 ($SiMe_3$), 6.51 ($SiMe_3$), 83.46 (Cp), 84.01 (Cp), 192.87 (μ_2-CO), 195.38 (μ_3-CO); ^{29}Si NMR (99.3 MHz, C_6D_6) δ −45.60 (O_2Si), −17.36 (OSi), 2.18 ($SiMe_3$), 2.95 ($SiMe_3$), 4.99 ($SiMe_3$), 6.98 ($SiMe_3$), 176.21 (silylene). Anal. Calcd for $C_{36}H_{73}Fe_3N_3O_3Si_9$: C, 42.55; H, 7.24; N, 4.13. Found: C, 42.94; H, 7.27; N, 3.77.

[18] Crystallographic data for **4**: formula $C_{39}H_{80}Fe_3N_3O_3Si_9$, fw = 1059.38, triclinic, space group $P\bar{1}$, $a = 12.3130(4)$ Å, $b = 12.4321(2)$ Å, $c = 18.7094(5)$ Å, $\alpha = 72.974(3)°$, $\beta = 84.917(4)°$, $\gamma = 77.009(4)°$, $V = 2667.56(12)$ Å^3, $Z = 2$, $T = 113(2)$ K, $\rho_{calcd} = 1.319$ g cm^{-3}, $\mu = 1.043$ mm^{-1}, $F(000) = 1126$, θ range 1.75−32.38°, 548 variables refined with 13 769 independent reflections to final R indices ($I > 2\sigma(I)$) of R1 = 0.0436 and wR2 = 0.1254, GOF = 1.061.

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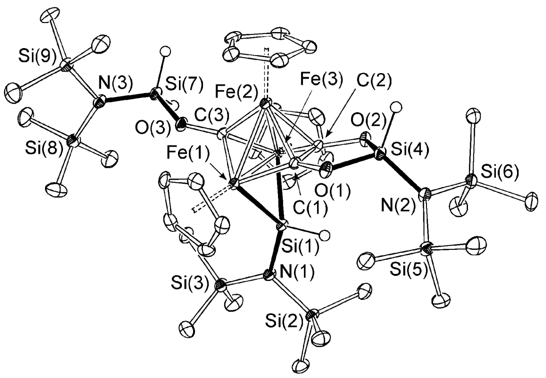

Figure 3. ORTEP drawing of **4** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Fe(1)−Fe(2) = 2.6608(4), Fe(1)−Fe(3) = 2.4997(4), Fe(2)−Fe(3) = 2.4966(4), Fe(1)−Si(1) = 2.2830(6), Fe(2)−Si(1) = 2.2889(6), C(1)−C(2) = 1.410(2); Fe(1)−Si(1)−Fe(2) = 71.182(17).

to give an alkyne molecule. Interestingly, hydrosilane-induced reductive coupling of carbon monoxide has been reported to form 1,2-ethanedioxy groups.[21] Furthermore, Murai et al. have reported the Rh-catalyzed reductive oligomerization of CO with hydrosilanes and the Ru-catalyzed synthesis of catechols from two CO's, $HSiR_3$, and 1,6-diynes, in which a dioxyacetylene−metal complex has been proposed as a key intermediate.[22] The formation mechanism of **4** and the relevance to the transition-metal-catalyzed reactions of CO are under investigation.

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Supporting Information Available: Text giving complete experimental details, including synthesis and characterization data for all new compounds and tables giving crystal structure data (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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