5058 *Inorg. Chem.* **2009**, *48*, 5058–5060
DOI: 10.1021/ic900204c

Inorganic Chemistry
Communication

A Base-Stabilized Silylene with a Tricoordinate Silicon Atom as a Ligand for a Metal Complex

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Received February 2, 2009

Treatment of base stabilized silylene $[\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2]\mathrm{SiO}t\mathrm{Bu}$ (**1**) with a tricoordinate silicon atom and diiron nonacarbonyl $[\mathrm{Fe}_2(\mathrm{CO})_9]$ in tetrahydrofuran led to the formation of $\{[\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2]\mathrm{SiO}t\mathrm{Bu}\}\mathrm{Fe}(\mathrm{CO})_4$ (**2**), the first stable metal complex derived from a base-stabilized tricoordinate silylene ligand. The solid-state structure and bonding situation of **2** were investigated with single-crystal X-ray diffraction and quantum chemical calculations.

In the past 20 years, the chemistry of stable N-heterocyclic silylenes (NHSs) has attracted much attention,[1] while the N-heterocyclic carbenes have been proven to be a versatile and important class of ligands.[2,3] Recently, we reported the synthesis and structures of the first monomeric heteroleptic silylene $[\{\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{SiCl}]$,[4] and the derivatives $[\{\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{SiNMe}_2]$, $[\{\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{SiOR}]$ (R = *t*Bu, *i*Pr), and $[\{\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{SiP}i\mathrm{Pr}_2]$.[5] The molecular structures of these silylenes show that the Si(II) center is tricoordinate (with two nitrogen atoms of the amidinato ligand and another substituent) and has a trigonal-pyramidal geometry with a lone pair of electrons and bonded with nearly pure p orbitals. These molecular structures are quite different from those of the dicoordinate NHSs.

Although various stable dicoordinate NHSs and their metal complexes are known, no metal complex supported by tricoordinate silylene was reported. We have recently been intrigued by the question as to whether such tricoordinate silylenes can act as ligands to stabilize metal complexes. Therefore, tricoordinate silylene $\{\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2\}\mathrm{SiO}t\mathrm{Bu}$ (**1**) and diiron nonacarbonyl, $\mathrm{Fe}_2(\mathrm{CO})_9$, were selected as a probe to investigate their reaction behavior. In this paper, we describe the preparation and characterization of the target

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(7) Silylene **1** was synthesized as published.[5] THF (30 mL) was added to a mixture of silylene **1** (0.057 g, 0.17 mmol) and diiron nonacarbonyl (0.076 g, 0.21 mmol) at ambient temperature under N_2. After stirring for 40 h, the initially light orange solution became darker in color to ultimately afford a garnet brown solution. Solvent was then removed in vacuo, and the residue was extracted with toluene (30 mL). The insoluble solid was filtered off. The garnet brown filtrate was concentrated and stored at −30 °C to yield red-brown crystals of **2** (72%).

(8) $\{[\mathrm{PhC}(\mathrm{N}t\mathrm{Bu})_2]\mathrm{SiO}t\mathrm{Bu}\}\mathrm{Fe}(\mathrm{CO})_4$ (**2**). Mp: 203.6 °C. Anal. calcd (%) for $\mathrm{C}_{23}\mathrm{H}_{32}\mathrm{FeN}_2\mathrm{O}_5\mathrm{Si}$ (M = 500.44): C, 55.20; H, 6.45; N, 5.60. Found (%): C, 55.27; H, 6.38; N, 5.66. ^{1}H NMR(CDCl3): δ 1.25 (s, 18 H, CMe_3), 1.51 (s, 9 H, OCMe_3), 7.37−7.53 (m, 5H, *Ph*). ^{13}C{^{1}H} NMR (CDCl3): δ 31.39 (CMe_3), 31.42 (OCMe_3), 54.95 (CMe$_3$), 77.03 (OCMe$_3$), 127.88, 128.28, 128.36, 128.47, 130.08, 130.73 (Ph), 171.10 (N*C*N), 216.69 (*C*O). ^{29}Si{^{1}H} NMR (CDCl_3): δ 40.30. IR (cm^{-1}, KBr) 2026 (m), 1949 (s), 1899 (s). Crystal data: empirical formula $\mathrm{C}_{23}\mathrm{H}_{32}\mathrm{FeN}_2\mathrm{O}_5\mathrm{Si}$, M = 500.45, monoclinic, space group $P2(1)/n$, $a = 9.1551(7)$ Å, $b = 16.6045(14)$ Å, $c = 17.2613(15)$ Å, $\alpha = 90°$, $\beta = 91.710(2)°$, $\gamma = 90°$, $V = 2622.8(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.267$ mg/m^3, $\mu = 0.654$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 1056$. Data in the range $1.70° \leq \theta \leq 28.31°$ were collected with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K (6346 reflections). Final R1 = 0.0507, wR2 = 0.1096 for 3584 reflections with $I > 2\sigma(I)$.

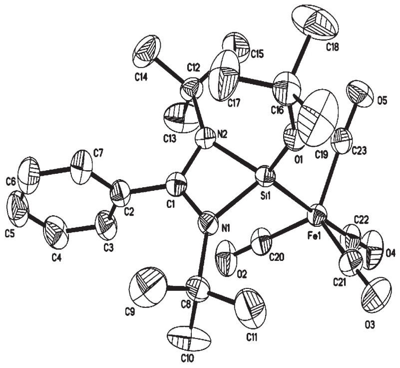
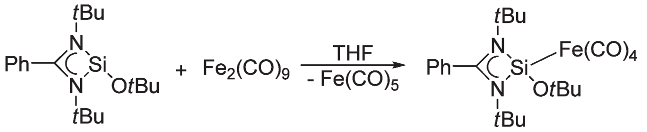


Figure 1. Molecular structure of **2**. Thermal ellipsoids are set at the 50% probability level. H atoms are omitted for clarity.

Scheme 1. The Synthesis of Complex $\{[PhC(NtBu)_2]SiOtBu\}Fe(CO)_4$ (**2**)



1 **2**

complex $\{[PhC(NtBu)_2]SiOtBu\}Fe(CO)_4$ (**2**), an example of complex formation using a tricoordinate silylene ligand.

The synthetic procedure of **2** (Scheme 1) is similar to that of the NHS analogue $\{(CHNtBu)_2Si\}Fe(CO)_4$.[6,7] Treatment of **1** with 1.2 equiv of diiron nonacarbonyl, $[Fe_2(CO)_9]$, in THF for 40 h afforded complex **2**. The solvent was then removed in a vacuum, and the residue was extracted with toluene. The insoluble solid was filtered off. The filtrate was concentrated and stored at −30 °C to yield red-brown crystals of complex **2** suitable for X-ray diffraction study.[8] Complex **2** was characterized by elemental analyses; IR; and ^{1}H, ^{13}C, and ^{29}Si NMR investigation. All of the data are in accordance with the proposed formula of **2**.

The solid-state structure of **2** as determined by single-crystal X-ray diffraction is shown in Figure 1 with selected bond lengths and angles. Figure 1 indicates that complex **2** is monomeric. The silicon center is four-coordinate. The sum of the angles N(1)−Si(1)−N(2), N(1)−Si(1)−O(1), and N(1)−Si(1)−Fe(1) around the silicon center (333.2°) of **2** exhibits a distorted tetrahedral geometry.

The acute bond angle of N(1)−Si(1)−N(2) (71.16°) in **2** is a little larger than those of $[\{PhC(NtBu)_2\}SiCl]$ (68.4°),[4] $[\{PhC(NtBu)_2\}SiNMe_2]$ (68.3°), and $[\{PhC(NtBu)_2\}SiPiPr_2]$ (69.3°).[5] The Si(1)−O(1) bond distance in **2** (1.602 Å) is the shortest compared to those of $\{(tBuO)_2Si\}Fe(CO)_4\cdot HMPT$ (HMPT = hexamethylphosphoric triamide) (**3**) (1.610, 1.636, and 1.730 Å)[9] and of the siloxyl silylene $[HC\{C(Me)NAr\}_2SiOSi(H)\{NArC(CH_2)\}\{NArC(Me)\}CH]$ (1.656 Å).[10] The Fe(1)−Si(1) bond distance in **2** (2.237 Å) is slightly longer when compared with that in the NHS complex $\{Si[N(tBu)CH]_2\}Fe(CO)_4$ (**4**) (2.196 Å)[6,11] with tricoordinate silicon atom but shorter than that in **3** (2.289 Å).[9]

In the IR spectrum of **2**, the CO stretching frequencies (2026 (m), 1949 (s), 1899 cm^{-1} (s)) are quite similar to those of **3** (2005 (w), 1920 (vs),1883 cm^{-1} (vs)).[9] The ^{13}C NMR chemical shift of the carbonyl group in **2** (216.69 ppm) is similar to that observed for the NHS complex **4** (216.90 ppm) with tricoordinate silicon atom.[6] The ^{29}Si NMR spectrum of **2** exhibits one singlet (40.30 ppm), which shows a low-field shift when compared with that of **1** (−5.19 ppm) due to the Lewis base properties of silicon, where electron density is donated to the iron center. The chemical shift of **2** lies between that of **3** (7.1 ppm)[9] and the bis(amino)silylene metal complex **4** (111.64 ppm).[6] This indicates that the silicon center of **2** is not purely sp^2 hybridized but has also some sp^3 character. It is interesting to note that the silicon atom in **2** behaves like a Lewis base, while the silicon atoms in the N-heterocyclic stable silylenes rather act as Lewis acids, accepting electrons from the adjacent nitrogen atoms.

Table 1. Selected Geometric Parameter by X-Ray Single-Crystal Diffraction and Calculations at the B3LYP/6-31G* Level for Compound **2**[a]

bond lengths (Å)	exptl	B3LYP/6-31G*
Fe(1)−C(23)	1.758(4)	1.7653
Fe(1)−Si(1)	2.237(7)	2.2784
Si(1)−O(1)	1.602(2)	1.6415
Si(1)−N(1)	1.833(2)	1.8854
Si(1)−N(2)	1.838(2)	1.8855
bond angles (deg)	**exptl**	**B3LYP/6-31G***
O(1)−Si(1)−N(1)	110.6(8)	111.78
O(1)−Si(1)−N(2)	112.8(4)	111.79
N(1)−Si(1)−N(2)	71.1(6)	70.09
O(1)−Si(1)−Fe(1)	114.6(2)	115.76
N(2)−Si(1)−Fe(1)	119.1(9)	119.74
C(16)−O(1)−Si(1)	143.5(2)	145.54
O(5)−C(23)−Fe(1)	176.5(3)	179.79
C(23)−Fe(1)−Si(1)	85.2(4)	86.19

[a] See Figure 1 for the atom numbering scheme.

Table 2. Natural Bond Orbital (NBO) Properties

atom	Q_p[a]	NEC (valence)[b]
Fe(1)	−1.35	$(4S)^{0.77}(3d)^{8.22}(4p)^{0.07}(5S)^{0.01}(4d)^{0.02}(5p)^{0.26}$
Si(1)	1.08	$(3S)^{1.26}(3p)^{1.27}$
N(2)	−0.37	$(2S)^{1.46}(2p)^{3.90}$
C(1)	0.24	$(2S)^{1.06}(2p)^{2.70}$
C(23)	0.30	$(2S)^{1.40}(2p)^{2.30}$
O(1)	−0.43	$(2S)^{1.72}(2p)^{4.71}$

[a] NBO charge on selected atoms. [b] Natural electronic configuration on selected atoms.

To examine the stability and bonding properties of this stable tricoordinate silylene−transition metal complex, compound **2** was investigated by means of quantum chemical calculations (Tables 1−3), using B3LYP density functional theory. The calculated structural parameters (Table 1) are in good agreement with the crystallographic data and give convincing support for quantum chemical analysis. The free energy and thermal energy of the reaction for the synthesis of **2** are −118.02 kJ/mol and −127.09 kJ/mol, respectively. These data show that **2** is stable and an easy-to-form compound.

The natural bond orbital analysis was carried out to explain the bonding between Fe−Si and Si−O and to determine some electronic properties characteristic for coordination to iron.[12]

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Table 3. Selected Calculated Bond Types and Hybrid Descriptors

bond	occupancy	MO1	contr.[a]	type	MO2	contr.[a]	type
Fe(1)−Si(1)	1.75384	Fe(1)	51.63%	s(33.68%) $p^{0.08}$(2.85%) $d^{1.88}$(63.47%)	Si(1)	48.37%	s(39.61%) $p^{1.52}$(60.39%)
Si(1)−O(1)	1.94217	Si(1)	26.34%	s(30.61%) $p^{2.27}$(69.39%)	O(1)	73.66%	s(26.80%) $p^{2.73}$(73.20%)
Si(1)−N(2)	1.72829	Si(1)	21.78%	s(26.95%) $p^{2.71}$(73.05%)	N(2)	78.22%	s(3.77%) $p^{25.55}$(96.23%)
Fe(1)−C(23)	1.88049	Fe(1)	28.14%	s(58.81%) $p^{0.09}$(5.31%) $d^{0.61}$(35.88%)	C(23)	71.86%	s(60.40%) $p^{0.66}$(39.60%)

[a] contr. = contribution.

The natural charge (Q_p; Table 2) shows the charge on the atoms. The natural electron configuration gives the effective valence electron configuration for the atoms. Table 3 lists the selected calculated bond types and hybrid descriptors. The calculated bond can be described as c1 × hybrid1 + c2 × hybrid2, where the coefficients c1 and c2 denote the polarization coefficient. The calculated Fe−Si bond is $0.7186 \times sp^{0.08}d^{1.88}(Fe) + 0.6955 \times sp^{1.52}(Si)$, whereas the calculated Si−O bond is $0.5133 \times sp^{2.27}(Si) + 0.8582 \times sp^{2.73}(O)$. From the polarization coefficient, greater electronic density can be found on Fe than on Si.

In summary, we succeeded in the synthesis and characterization of $\{[PhC(N\textit{t}Bu)_2]SiO\textit{t}Bu\}Fe(CO)_4$ (**2**), the first stable metal complex containing a tricoordinate silylene as a ligand. The solid-state structure and bonding situation of **2** were investigated with single-crystal X-ray diffraction and quantum chemical calculations.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20571033) and by the Program for New Century Excellent Talents in University (NCET-06-0483) and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Further details of the synthesis and characterization, figures, and X-ray structural information (CIF) for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.