Synthesis and Structure of a Stable Silylene

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Although two compounds of divalent silicon, the tetracoordinate $Si[CH(PMe_2)_2]$[1] and the π-complex decamethylsilicocene,[2] have been described, *dicoordinate* silicon compounds[3] have only been intercepted in trapping experiments[4] or studied in matrices at low temperatures.[5,6] We now report on the synthesis, isolation, and structure of **2**, a stable dicoordinate silicon compound.

Compound **2** is obtained as the only reaction product (^{1}H NMR) by reducing **1**[7] with potassium in boiling THF (Scheme 1).[8,9] It is a colorless, crystalline solid with remarkable thermal stability. **2** can be distilled at 85 °C (0.1 Torr) without decomposition. Solutions of **2** (toluene, sealed NMR tubes) were found to be unchanged after 4 months of heating to 150 °C. In the context of these findings, it is remarkable that the diamidosilylene $Me_2Si({}^tBuN)_2Si$: reported by Veith[5a] is stable only below 77 K.

Positive identification of **2** was accomplished by gas-phase electron diffraction.[10] The structure, shown in Figure 1, is in good agreement with the results of quantum chemical calculations (Table 1). X-ray crystallography confirmed that **2** is also monomeric in the solid state, but precise structural data could not be obtained due to twinning problems.[11]

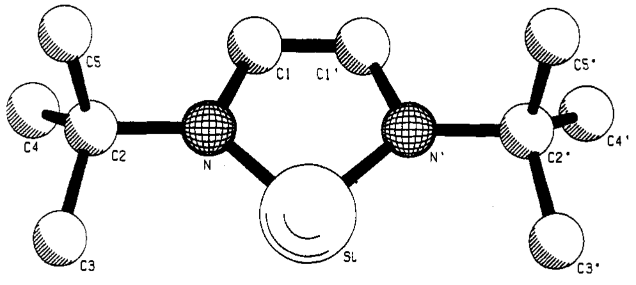
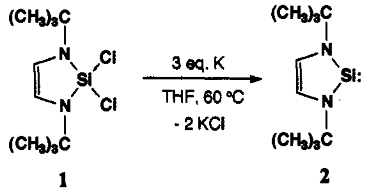


Figure 1. Molecular model (PLUTON[19]) of **2**. Hydrogen atoms have been omitted for clarity.

Scheme 1



1 **2**

Table 1. Experimental (**1**, **2**) and Calculated (**3**) Bond Lengths [pm] and Angles [deg] of Diamidosilylenes (**2**, **3**) and Silanes (**1**)

	1[a]	**2**[b]	**3**[c]
Si–N	169.5(3), 1.700(3)	175.3(5)	174.25
N–C1	141.6(5), 141.4(4)	140.0(9)	138.99
C1–C1′	132.2(4)	134.7(21)	133.25
N–Si–N	95.4(1)	90.5(10)	86.04
N–C1–C1′	115.3(3), 114.4(3)	114.1(5)	112.20

[a] Single crystal X-ray diffraction data. [b] Gas-Phase electron diffraction data. [c] Quantum chemical data.

Compound **2** is quite unreactive compared with transient silylenes. Triethylsilane, a known silylene scavenger,[12] did *not* react with **2** even after prolonged heating to 110 °C. No reaction was observed with pyridine, trimethylphosphine, triethylamine, or THF, all of which are known to form Lewis acid–base complexes with silylenes.[13] Compound **2** does react with air and with metal carbonyls. For example, reaction of **2** with $Ni(CO)_4$ in THF gives the base free bis-silylene complex $(LSi:)_2Ni(CO)_2$ (LSi: = **2**).[14]

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(8) Synthesis of **2**: 53.39 g of **1**[7] (0.201 mol) dissolved in 600 mL of THF was heated to reflux with 23.52 g of potassium (0.603 mol) under argon for 5 days. The cold reaction mixture was filtered through a medium glass frit, and the solids were washed twice with 100 mL of pentane. After removal of solvent, 30 g of pure **2** (78%) was isolated by distillation (bp 85–86 °C/0.1 Torr).

(9) Selected spectroscopic data. NMR data (in ppm and Hz) were recorded at room temperature in C_6D_6 solution at 200 MHz (^{1}H), 126 MHz (^{13}C), and 99.3 MHz (^{29}Si). **2** ^{1}H NMR δ 1.41 (18H, s, $C(CH_3)_3$), 6.75 (s, 2H); ^{13}C NMR δ 30.3 (^1J = 125.7 Hz, $C(CH_3)_3$), 54.0 ($C(CH_3)_3$), 120.0 (dd, ^1J = 176.1 Hz, ^2J = 11.0 Hz, =CH); ^{29}Si NMR δ +78.3 (s); ^{15}N NMR δ −170.3 (s, vs $MeNO_2$); MS (40 eV, positive ions) m/z 196 (59) [$M^{\bullet+}$], 181 (23), 140 (18), 125 (42), 99 (6), 84 (100), 57 (78). **1**: ^{1}H NMR δ 1.24 (18H, s, $C(CH_3)_3$), 5.73 (s, 2H); ^{13}C NMR δ 30.4 (^1J = 125.9 Hz, $C(CH_3)_3$), 52.6 ($C(CH_3)_3$), 112.6 (dd, ^1J = 183.9 Hz, ^2J = 8.4 Hz, =CH); ^{29}Si NMR δ −40.7 (s); ^{15}N NMR δ −282.9 (s, vs $MeNO_2$); MS (70 eV, positive ions) m/z 287 (10) [$M^{\bullet+}$], 231 (2), 210 (4), 196 (8), 155 (100), 57 (22), 41 (33), 29 (24).

(10) (a) Electron diffraction data of **2** were recorded on a Balzers Edigraph KDG 2[10b] with a nozzle temperature of about 75 °C and nozzle-to-plate distances of about 50 and 25 cm. Optical densities were recorded on the Snoopy densitometer and processed by standard procedures.[10c] Atomic scattering factors were taken from ref 10d. Backgrounds were drawn at least-squares adjusted polynomials to the difference between the total observed intensity and the molecular intensity calculated for the best model. The final modified molecular intensity curves extended from s = 20.00 to 152.50 with increment δs = 1.25 nm^{-1} (50 cm, five plates) and from s = 60.00 to 30.00 with increment δs = 2.50 nm^{-1} (25 cm, three plates). Least-squares refinements were based on a five-membered C_2N_2Si ring (C_s symmetry) with an envelope conformation, the symmetry plane containing the Si atom and bisecting the C–C double bond. The flap angle was defined as the angle between the SiN_2 and the NC_2 planes. Methyl groups and the tertiary butyl groups were assumed to have local C_{3v} symmetries. Methyl groups were fixed in staggered conformations, and only a mean C–H bond distance was refined. The molecular structure was refined by least-squares calculations on the intensity data under the constraints of a geometrical consistent r_a structure. Best modeling of observed intensities was obtained with a nearly planar five-membered ring, flap angle = 5(12)°, and nearly planar nitrogen atoms. (b) Bastiansen, O.; Graber, R.; Wegman, L. *Balzers High Vacuum Report* **1969**, *25*, 1. (c) Andersen, B.; Seip, H. M.; Strand, T. G.; Stölevik, R. *Chem. Phys. Letters* **1969**, *3*, 617. (d) Schäfter, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.

(11) X-ray diffraction data for **2**: a = 13.643(2) Å, b = 13.821(8) Å, c = 6.345(6) Å, $\alpha = \beta = \gamma = 90°$. The closest Si–Si contact is 634.6 pm and clearly nonbonding. $R(F)$ = 16.5%, $R_w(F)$ = 24.77%.

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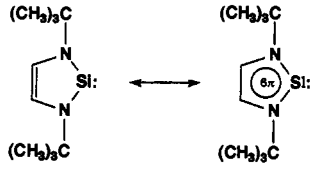
Scheme 2



2

The unusual stability of **2** as compared to the diamidosilylene described by Veith et al.[5a] may result in part from aromatic stabilization (Scheme 2). It is instructive to compare the structural data for **2** and **1** (Table 1).

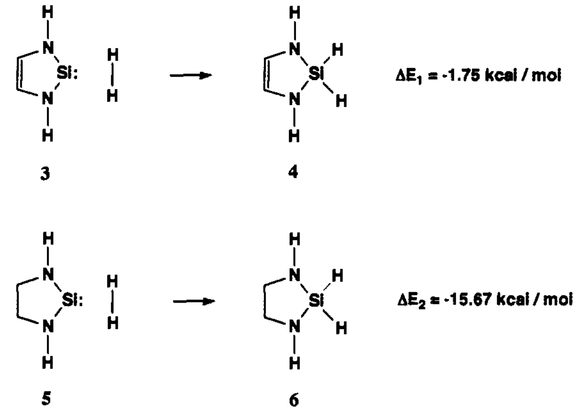
The difference between the bond lengths C1–C1′ (a formal double bond) and N–C1 (a formal single bond) decreases from **1** to **2**, consistent with an increase in delocalization. The interpretation of Si–N bond lengths is less straightforward. Bonds to divalent group 14 elements are typically 8–10 pm longer than corresponding bond lengths of tetravalent elements.[15] The elongation of the Si–N bond in **2** (5.6 pm as compared to **1**) is significantly less than expected on these grounds and in agreement with a partial Si–N double bond. Further evidence for N–Si π-bonding in **2** is the strong deshielding of the nitrogen atoms (^{15}N NMR −170.3 ppm in **2** vs −282.9 ppm in **1**).[9] The deshielding of the ring protons in **2** (^{1}H NMR 5.73 ppm for **1** and 6.75 ppm for **2**) is consistent with aromatic delocalization in the silylene.

To quantify our assumption, the relative stabilities of the two silylenes **3** (six π-electrons) and **5** (four π-electrons) were evaluated by quantum chemical methods.[16] Their insertion into dihydrogen was chosen as a set of isodesmic reactions (Scheme 3).

Comparison of the reaction energies ΔE_1 and ΔE_2 shows **3** to be stabilized relative to **5** by 13.92 kcal·mol^{-1}. This surprisingly large energy difference may be taken as an upper limit for a possible aromatic stabilization of **3** vs the C–C-saturated derivative **5**.

A detailed comparison of **2** with its carbene[17] and germylene[18] derivatives is under way. To study the influence of the C–C double bond on the stability of **2**, the synthesis of the corresponding C–C-saturated derivative would be highly desirable, and we have begun to work on this task.

Scheme 3



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(16) (a) The equilibrium geometries of **3**–**6** were computed with the GAUSSIAN 92 program[16b] in the LANLIDZ[16c] basis and in the split-valence d-polarized 3-21G*[16d] and 6-21G*[16e] basis sets. The geometric parameters were optimized with the symmetry restrictions C_{2v} (**3**, **4**) and C_2 (**5**, **6**). Minima on the potential energy surface were verified by analysis of the harmonic vibrational frequencies of **3**–**6** at the RHF/3-21G* level. Final electronic energies were obtained by single-point calculations including electron correlation at the MP2 level in the 6-31G* basis with the optimized RHF/6-31G* geometries (RHF/MP2/6-31G*//RHF/6-31G*). Zero point energies were multiplied by 0.89 to correct for anharmonicity. Zero point vibrational contributions were included. (b) Frisch, M. J.; *et al. GAUSSIAN 92*, revision C; Gaussian, Inc.: Pittsburgh, PA, 1992. (c) Hay, P. J.; Waldt, W. R. *J. Chem. Phys.* **1985**, *82*, 270; 284; 299. (d) Hehre, W. J.; Radom, C.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985. (e) Franel, M. M.; *et al. J. Chem. Phys.* **1982**, *77*, 3654.

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