Silicon Chemistry

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A Remarkable Base-Stabilized Bis(silylene) with a Silicon(I)–Silicon(I) Bond**

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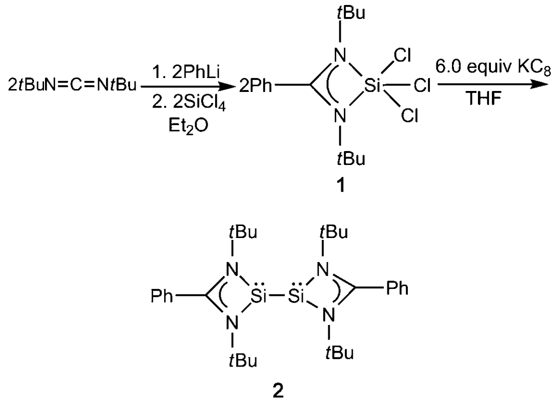
Dedicated to Professor Dietmar Seyferth on the occasion of his 80th birthday

Double and triple covalent bonds are ubiquitous in carbon chemistry and have been studied for more than two centuries but were unusual with its congener in the periodic table, silicon. Initial attempts to synthesize such compounds were unsuccessful, resulting in the formation of polymeric substances. This situation changed when West and co-workers in 1981 synthesized a compound containing a Si=Si double bond ($R_2Si{=}SiR_2$, $R = Me_3C_6H_2$), in which each Si atom has a formal oxidation state of +II.[1] Key to the discovery of stable compounds containing Si=Si double bonds was the protection of the double bonds by bulky substituents, which provide kinetic stability. Apeloig et al. showed that silylene has a singlet ground state, and the $^3B_1$ triplet state lies significantly higher in energy.[2] Moreover, recent calculations indicate that the energy difference between the singlet and triplet states of silylene is around 18–21 kcal mol^{-1}.[3] This singlet–triplet energy difference of the silylene fragments is the main reason for the weakness of the Si=Si double bond. This now generally accepted model originated from Carter, Goddard, Malrieu, and Trinquier (CGMT), who described the double-bond topology as being a function of the energy difference between the singlet and the triplet state of the carbene-like fragments formally constituting the double bond.[4,5] Compounds with double-bonded silicon are established and have been studied in detail during the last decade.[6] In 2004, Sekiguchi and co-workers as well as Wiberg et al. were successful in isolating compounds containing Si≡Si triple bonds ($RSi{\equiv}SiR$; $R = Si(i\text{Pr})\{CH(SiMe_3)_2\}_2$ and $R = SiMe(Sit\text{Bu}_3)_2$) in which the formal oxidation state of Si is +I.[7] Subsequently, Robinson and co-workers synthesized two compounds, one with a Si–Si single bond having formal oxidation state +I and another with a Si=Si double bond in which the formal oxidation state of Si is 0 (RClSi–SiClR and RSi=SiR, R = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene).[8]

In addition to disilenes and disilynes, a number of other unusual stable compounds with low-coordinate Si atoms have been described.[9] To our knowledge, only one compound consisting of a Si–Si single bond and a lone pair of electrons on each Si atom was reported to date.[8] The compound was stabilized by an N-heterocyclic carbene, and one chlorine atom was attached to each silicon center making the formal oxidation state of the silicon atoms +I. This situation is unique, because each Si center which features a lone pair of electrons is simultaneously involved in bonding. These two attributes are usually associated with extreme instability. In view of this chemistry, we became interested in synthesizing a compound with a Si–Si single bond stabilized by a monoanionic ligand, thus avoiding the lone pair of electrons taking part in any bonding. We were recently successful in using an amidinate ligand with *t*Bu substituents on the nitrogen atoms to stabilize heteroleptic silylenes and a Ge^I dimer.[10,11] It seems that such a ligand might also stabilize a Si^I compound with a Si^I–Si^I single bond. Our preliminary results in this direction are reported herein.

The reaction of *tert*-butylcarbodiimide with one equivalent of PhLi in diethyl ether and subsequent treatment with $SiCl_4$ afforded $[PhC(Nt\text{Bu})_2]SiCl_3$ (**1**, Scheme 1). Compound **1** was obtained as a colorless crystalline solid in 47% yield, and its structure was confirmed by NMR spectroscopy, EI mass spectrometry, and elemental analysis.[10]



Scheme 1. Preparation of compound **2**.

Treatment of **1** with two equivalents of potassium in THF afforded monomeric chlorosilylene.[10] We mentioned earlier that we are interested in preparing a compound with a Si^I–Si^I single bond. Therefore, we reacted **1** in a ratio of 2:6

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(Scheme 1) with potassium graphite (KC$_8$) in THF, which afforded air-sensitive, orange-red crystals of **2** (5.21 % yield). Compound **2** is highly soluble in solvents such as diethyl ether, toluene, and THF. It has been characterized by elemental analysis, spectroscopic methods, and X-ray structural analysis. The ^{1}H and ^{13}C NMR spectra of **2** (in [D$_8$]THF) display one set of resonances that result from the amidinate ligand. The resonances show a downfield shift relative to that of **1** and also from chlorosilylene.[10] The shift is probably due to the lower oxidation state of the silicon center (+I in **2**) compared to silylene, where normally a formal oxidation state at the Si center of +II is observed. The resonance of **2** in the ^{29}Si NMR spectrum in [D$_8$]THF (75.71 ppm) is further downfield than that of RClSi–SiClR, ($\delta = 38.4$ ppm; R = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene).[8] We were also curious to measure the NMR spectrum in nonpolar solvent (C$_6$D$_6$), and in the ^{29}Si NMR spectrum, **2** resonates at $\delta = 76.29$ ppm. So there is very little downfield shift in the ^{29}Si NMR spectrum. The molecular ion of **2** appeared as the most abundant peak in the EI mass spectrum at *m*/*z* 518.3.

The molecular structure of **2** is shown in Figure 1.[12] Compound **2** crystallizes in the monoclinic space group *C*2/*c*. The coordination environment of each of the Si atoms exhibits a distorted tetrahedral geometry. The coordination sites of the Si centers are each occupied by the N atoms of the amidinato ligand and by the other Si atom. The lone pair of each Si atom occupies the remaining coordination site of the tetrahedral geometry. The X-ray structural analysis of **2** reveals that the Si–Si core is sterically well-shielded by the two amidinate ligands. The central Si–Si bond (2.413(2) Å) is only about 0.07 Å longer than the sum of the Si covalent radii (2.34 Å)[13] and about 0.05 Å longer than the Si–Si single bond in α-silicon (2.36 Å).[14] The value is 5.17 % larger than the longest disilene bond (2.29 Å)[6] and 14.6 % longer than the reported disilyne bond (2.06 Å),[7] and it also compares well with that of the Si^{I} dimer reported by Robinson et al. (2.393 Å).[8] The sum of the bond angles of the Si atoms in **2** (282.35° average) compares very well with literature values.[15] Compound **2** possesses a *gauche*-bent conformation. This structural feature of **2** is akin to that of the Ge^{I} dimer,[11] which also favors a *gauche*-bent geometry, as do the isolobal equivalents hydrazine and diphosphine.[16] It is interesting to mention that a bis(carbene) with a C^{I}–C^{I} bond has not been reported to date.

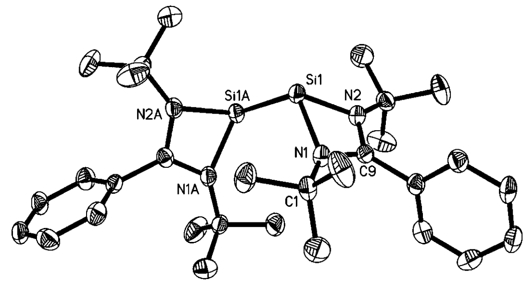

Figure 1. ORTEP view (50% ellipsoid probability) of compound **2**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°] Si1–Si1A 2.413(2), Si1–N2 1.866(4), Si1–N1 1.874(4), C1–N1 1.467(6), C9–N1 1.331(6); N2-Si1-N1 69.52(18), N2-Si1-Si1A 102.15(14), C9-N1-C1 130.09(3).

In conclusion, we have prepared and fully characterized a compound with a Si^{I}–Si^{I} bond, which is stabilized by bulky amidinate ligands. Compound **2** exhibits a *gauche*-bent geometry, and the Si–Si bond shows no multiple-bond character. Currently we are exploring the reactivity of compound **2**.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques or in a dinitrogen-filled glove box. Solvents were dried over molecular sieves and distilled prior to use. The NMR spectra were recorded in C$_6$D$_6$ and [D$_8$]THF. The chemical shifts δ are given relative to SiMe$_4$. The EI mass spectrum was obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. The melting point was measured in a sealed glass tube on a Büchi B-540 melting point apparatus and was uncorrected.

2: THF (50 mL) was added to a mixture of **1** (1.49 g, 4.08 mmol) and potassium graphite (1.65 g, 12.24 mmol) at −78 °C. The resulting red mixture was stirred overnight. The solvent was then removed in vacuo, and the residue was extracted with toluene (50 mL). The insoluble precipitate was filtered off and the red filtrate was concentrated to yield orange-red crystals of **2** (0.11 g, 5.21 %). M.p.:155–160 °C. ^{1}H NMR (200 MHz, [D$_8$]THF, 25 °C): $\delta = 1.23$ ppm (s, 36 H, *t*Bu), 7.34–7.38 ppm (m, 10 H, Ph); ^{13}C{^{1}H} NMR (75.47 MHz, [D$_8$]THF, 25 °C): $\delta = 32.19$ (CMe$_3$), 53.36 (CMe$_3$), 128.42, 129.91, 130.95, 131.95, 134.35, 136.49, (Ph), 146.32 ppm (NCN); ^{29}Si{^{1}H} NMR (59.62 MHz, [D$_8$]THF, 25 °C): $\delta = 75.71$ ppm; ^{1}H NMR (200 MHz, C$_6$D$_6$, 25 °C): $\delta = 1.18$ ppm (s, 36 H, *t*Bu), 7.22–7.30 ppm (m, 10 H, Ph); ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$, 25 °C): $\delta =$ 32.01 (CMe$_3$), 53.73 (CMe$_3$), 127.71, 128.19, 128.40, 129.21, 130.32, 135.98 (Ph), 145.67 ppm (NCN); ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$, 25 °C): $\delta = 76.29$ ppm; EI-MS: *m*/*z*(%): 518.3 [M^+] (100). Elemental analysis (%) calcd for C$_{30}$H$_{46}$N$_4$Si$_2$ (518.33): C 69.44, H 8.94, N 10.80; found: C 68.26, H 8.63, N 11.06.

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