

Cleavage of Carbene-Stabilized Disilicon

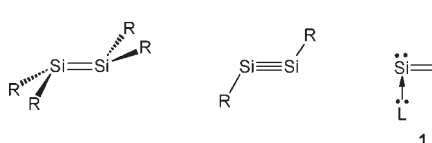
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Supporting Information

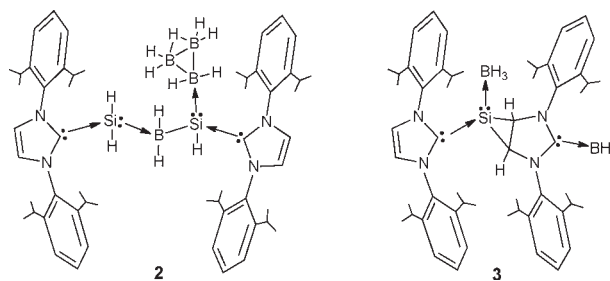
ABSTRACT: Reaction of carbene-stabilized disilicon L:Si=Si:L (L: = :C{N(2,6-Prⁱ₂C₆H₃)CH}₂, **1**) with BH₃·THF results in facile cleavage of the silicon–silicon double bond and the formation of two quite different “push–pull” stabilized products with borane- and carbene-coordinated silylene moieties: **2**, containing a parent silylene (:SiH₂); and **3**, containing a unique three-membered cyclosilylene.

The intervening decades between the seminal discovery of the first disilene¹ in 1981 and that of the first disilyne² in 2004 underscore the challenges, as well as the rewards, of silicon–silicon multiple bond chemistry. The recent realization of an N-heterocyclic carbene-stabilized compound containing a silicon–silicon double bond, L:Si=Si:L (L: = :C{N(2,6-Prⁱ₂C₆H₃)CH}₂, **1**),³ extends this series to disilicon(0) derivatives.



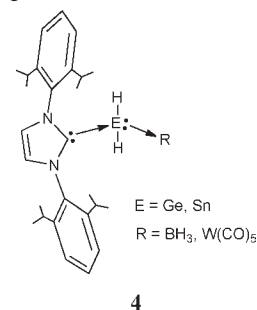
Compounds with silicon–silicon multiple bonds are intriguing not only because of the unique bonding nature of silicon, but also due to the unusual reactivity of unsaturated Si–Si fragments.^{4–12} In contrast to extensively explored hydroboration reactions of carbon–carbon multiple bonds,¹³ the experimental hydroboration of a disilyne (RSi≡SiR, R = SiPrⁱ[CH(SiMe₃)₂]) has recently been reported to yield boryl-substituted disilenes.^{14,15} Hydroboration of disilenes, on the other hand, has only been examined computationally.¹⁶ We now report the unexpected silicon–silicon double bond cleavage and borane insertion reactions of **1** when combined with BH₃·THF and describe the formation,¹⁷ molecular structures,¹⁷ and computational investigations¹⁸ of **2** and **3**, the novel ensuing products. The “push–pull” stabilization of the parent silylene (:SiH₂) unit in **2** is significant since SiH₂ has been observed as an important intermediate in the chemical vapor deposition (CVD) of silicon film by pyrolysis of silane (SiH₄).¹⁹

Colorless crystals of **2** (72% yield) were obtained by reaction of pure **1** with BH₃·THF (1:4) in toluene. However, in the presence of NHC (N-heterocyclic carbene) impurity in **1** (NHC:1 = 1:5), both **2** and **3** were isolated in a moderate yield (30% yield for **2**, 28% yield for **3**) from the BH₃·THF reaction. Although the mechanistic details are unclear, structural and computational studies suggest that the formation of **2** may involve multiple complexations of boranes to **1**,



concomitant with cleavage of silicon–silicon bond and boron-to-silicon hydrogen transfer reactions. These processes could eventually afford **2** via BH₂ insertion between two silicon(II) atoms. The formation of **3** may involve the cycloaddition of the highly reactive Si(0) center of an L:Si(BH₃) intermediate to the C=C bond of an imidazole ring in a NHC:BH₃ fragment. Indeed, similar reactions of silicon(0) atoms with π-conjugated systems have been observed in matrix isolation studies.^{20–22} Notably, the presence of a free NHC ligand in the reaction system appears to be required for the formation of **3**, where the NHC ligand essentially functions as a “trapping agent” for the “push–pull” stabilized Si(0) atom.

The X-ray structure of **2** (Figure 1) suggests its formation from **1** by a complex sequence of reactions involving four BH₃ molecules. During this process, three borane hydrogen atoms could have been transferred to the two silicon atoms of **1** leading eventually to **2** via Si=Si bond cleavage by BH₂ insertion. Note that electron pair donation from the Si(1) atom of **2** helps stabilize the neutral three-membered B₃H₇ ring as in analogous L:B₃H₇ complexes (where L: = NH₃,²³ phosphine,²⁴ and CO²⁵). While “push–pull” N-heterocyclic carbene–transition metal carbonyl complexed GeH₂ and SnH₂ analogues (**4**) have recently been reported,^{26,27} **2** is the first example of a “push–pull” stabilized parent silylene (:SiH₂) persistent at room temperature.²⁸ The L:SiH(BH₂)(B₃H₇) fragment in **2** mimics the Lewis acid



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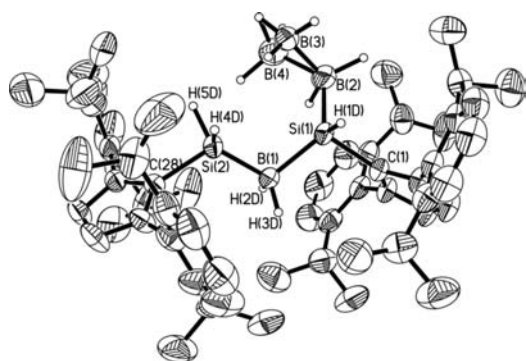


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. (Hydrogen atoms at boron and silicon atoms were located in the difference Fourier map. All the hydrogen atoms on carbon have been omitted for clarity. The disorder in B(1)H₂ unit is not shown (see Figure S1, Supporting Information)¹⁷). Selected bond distances (Å) and angles (deg) for (**2**): Si(1)–C(1) 1.944(4), Si(2)–C(28) 1.934(4), B(1)–Si(1) 1.994(8), B(1)–Si(2) 1.922(7), Si(2)–H(4D) 1.49(2), Si(2)–H(5D) 1.42(4), B(1)–H(3D) 1.119(19), B(1)–H(2D) 1.145(19), Si(1)–H(1D) 1.49(4), B(2)–Si(1) 1.965(7); C(1)–Si(1)–B(1) 107.2(2), B(1)–Si(2)–C(28) 117.7(3), Si(1)–B(1)–Si(2) 109.1(4) B(2)–Si(1)–B(1) 122.2(3), B(2)–Si(1)–C(1) 107.7(2), B(2)–Si(1)–H(1D) 111.0(14), H(2D)–B(1)–H(3D) 106(3), H(4D)–Si(2)–H(5D) 101(3).

behavior of R groups in L:E(H)₂R (E = Ge, Sn; R = BH₃, W(CO)₅) (**4**).

The Si–C_{carbene} bond distances, 1.934(4) and 1.944(4) Å in **2** as well as 1.938(3) Å in **3**, are close to those reported for **1** (1.9271(15) Å).³ The central boron atom (B(1)) environment in **2** is disordered,¹⁸ the average B(1)–Si(1) (1.980 Å) and B(1)–Si(2) (1.902 Å) bond distances are comparable to the 1.965(7) Å of B(2)–Si(1). The B₃H₇ ring in **2** gives rise to the broad ¹H NMR singlet resonance at –0.29 ppm and the ¹¹B NMR multiplet at –30.0 ppm. The silylene coordination shifts the ¹H NMR resonance of B₃H₇ to higher field (–0.29 ppm) than that of NH₃B₃H₇ (1.62 ppm)²³ and of L':B₃H₇ (L' = PH₃, CH₃PH₂, (CH₃)₂PH, (CH₃)₃P) adducts (1.23–0.72 ppm),²⁴ indicating the stronger electron-donating ability of silylene than phosphine or ammonia. Although the BH₂ proton resonances were not observed in the ¹H NMR spectrum,^{29,30} they appeared clearly in the proton-coupled ¹¹B NMR as a triplet at –50.4 ppm, a position comparable to the reported –43.0 ppm signal of [Tbt(Mes)SiHBH₂CNAr] (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl).³⁰ While the ²⁹Si resonance of the silicon atoms in **2** could not be observed due to the strong line-broadening caused by quadrupolar boron nuclei,³¹ the ¹H NMR spectrum of **2** gave a SiH doublet (2.90 ppm, *J* = 7.0 Hz)²⁹ and a SiH₂ triplet (3.13 ppm, *J* = 12.0 Hz).

The bonding of **2** was further probed by DFT analysis at the B3LYP/DZP level.¹⁸ The 0.953, 0.999, and 0.869 Wiberg bond indices of B(1)–Si(1), B(1)–Si(2), and B(2)–Si(1), respectively, support their single bond essence. The positive natural charges on the silicon atoms in **2**, +0.95 for Si(1) and +0.90 for Si(2), and the negative charges of the B(1) atom (–0.92) and the B₃H₇ ring (–1.03) are consistent with the dative character of the B(1)–Si(2) and B(2)–Si(1) bonding.

The silicon atom of the central three-membered silylene ring, a significant structural feature of **3** (Figure 2), exhibits simultaneous nucleophilic and electrophilic (“push-pull”) bonding character by donating its electron pair to a BH₃ while—*simultaneously*—accepting

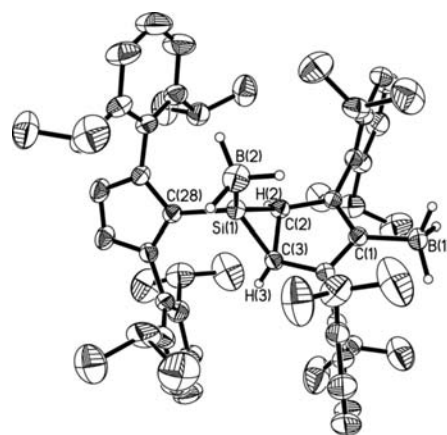


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Some hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for (**3**): Si(1)–B(2) 1.996(4), Si(1)–C(28) 1.938(3), Si(1)–C(2) 1.903(3), Si(1)–C(3) 1.888(3), C(2)–C(3) 1.530(4), C(1)–B(1) 1.593(5); C(2)–Si(1)–B(2) 134.88(17), C(3)–Si(1)–B(2) 133.06(18), C(28)–Si(1)–B(2) 116.25(17), C(2)–Si(1)–C(28) 102.27(13), C(3)–Si(1)–C(28) 104.04(13), C(3)–Si(1)–C(2) 47.62(12), C(3)–C(2)–Si(1) 65.68(16), C(2)–C(3)–Si(1) 66.70(16).

an electron pair from the carbene ligand. Although five and six-membered cyclosilylenes^{32,33} are well-known, three-membered cyclic silylenes based on C₂H₄Si: have only been studied by matrix-isolation techniques.²⁰ The three-membered silylene ring in **3** has a 1.53 Å C(2)–C(3) single bond and two ~1.89 Å Si–C bonds, marginally shorter than the dative Si(1)–C(28) bond length (1.938(3) Å). The –35.0 ppm (¹*J* = 87 Hz) quartet resonance of the BH₃ at the C(1) carbene in the ¹H-coupled ¹¹B-NMR spectrum of **3** is like that reported for L: BH₃ (–35.4 ppm; ¹*J* = 83 Hz).³⁴ The –47.0 ppm broad doublet resonance of BH₃ coordinating to the central silicon atom is close to the –43.4 ppm (¹*J* = 84 Hz) of potassium tris(trimethylsilyl)silylboranate.³¹ As in **2**, the ²⁹Si resonance of the silicon atom in **3** could not be observed.³¹

The carbene-stabilized disilicon compound, **1**, exhibits unusual reactivity with BH₃, affording two unique silylene compounds, **2** and **3**, which contain a parent silylene (:SiH₂) and a three-membered silylene ring, respectively. The driving force for the formation of **2** is provided by its stabilizing B₃H₇ structural feature.¹⁸

■ ASSOCIATED CONTENT

S Supporting Information. Full details of the syntheses, computations, and X-ray crystal structure determinations (including CIF files); complete ref 18. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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