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Cleavage of Carbene-Stabilized Disilicon

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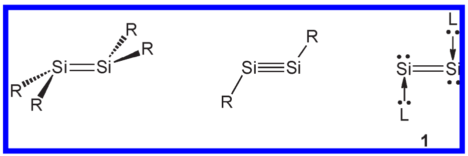
S *Supporting Information*

ABSTRACT: Reaction of carbene-stabilized disilicon L:Si═Si:L (L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$, **1**) with $BH_3\cdot$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 (:SiH_2); and **3**, containing a unique three-membered cyclosilylene.

The intervening decades between the seminal discovery of the first disilene[1] in 1981 and that of the first disilyne[2] 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-$Pr^i_2C_6H_3$)CH}$_2$, **1**),[3] extends this series to disilicon(0) derivatives.



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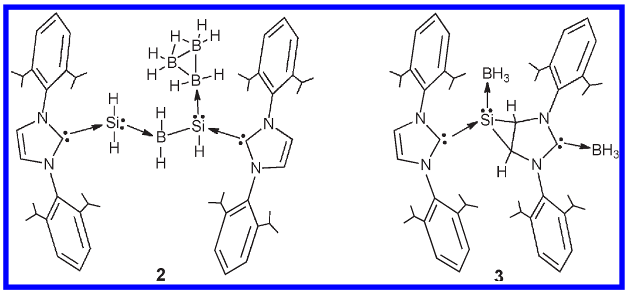
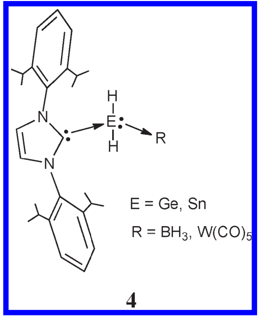
Compounds with silicon−silicon multiple bonds are intriguing not only because of the unique bonding nature of silicon, but also due to the unusual reactivity of unsaturated Si−Si fragments.[4−12] In contrast to extensively explored hydroboration reactions of carbon−carbon multiple bonds,[13] the experimental hydroboration of a disilyne (RSi≡SiR, R = $SiPr^i$[CH($SiMe_3$)$_2$]$_2$) 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 $BH_3\cdot$THF and describe the formation,[17] molecular structures,[17] and computational investigations[18] of **2** and **3**, the novel ensuing products. The "push−pull" stabilization of the parent silylene (:SiH_2) unit in **2** is significant since SiH_2 has been observed as an important intermediate in the chemical vapor deposition (CVD) of silicon film by pyrolysis of silane (SiH_4).[19]

Colorless crystals of **2** (72% yield) were obtained by reaction of pure **1** with $BH_3\cdot$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 $BH_3\cdot$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 BH_2 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(BH_3) intermediate to the C═C bond of an imidazole ring in a NHC:BH_3 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.



2 **3**

The X-ray structure of **2** (Figure 1) suggests its formation from **1** by a complex sequence of reactions involving four BH_3 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 BH_2 insertion. Note that electron pair donation from the Si(1) atom of **2** helps stabilize the neutral three-membered B_3H_7 ring as in analogous L:B_3H_7 complexes (where L: = NH_3,[23] phosphine,[24] and CO[25]). While "push−pull" N-heterocyclic carbene−transition metal carbonyl complexed GeH_2 and SnH_2 analogues (**4**) have recently been reported,[26,27] **2** is the first example of a "push−pull" stabilized parent silylene (:SiH_2) persistent at room temperature.[28] The L:SiH(BH_2)(B_3H_7) fragment in **2** mimics the Lewis acid



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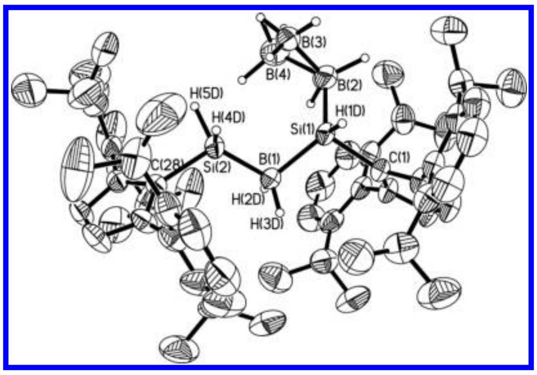

Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. (Hydrogen atoms at boron and silicon atoms were located in the difference Fourier map. All the hydrogen atoms on carbon have been omitted for clarity. The disorder in B(1)H_2 unit is not shown (see Figure S1, Supporting 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)$_2$R (E = Ge, Sn; R = BH_3, $W(CO)_5$) (**4**).

The Si−C$_{\text{carbene}}$ 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 B_3H_7 ring in **2** gives rise to the broad ^{1}H NMR singlet resonance at −0.29 ppm and the ^{11}B NMR multiplet at −30.0 ppm. The silylene coordination shifts the ^{1}H NMR resonance of B_3H_7 to higher field (−0.29 ppm) than that of $NH_3B_3H_7$ (1.62 ppm)[23] and of L:′B_3H_7 (L:′ = PH_3, CH_3PH_2, $(CH_3)_2PH$, $(CH_3)_3P$) adducts (1.23−0.72 ppm),[24] indicating the stronger electron-donating ability of silylene than phosphine or ammonia. Although the BH_2 proton resonances were not observed in the ^{1}H NMR spectrum,[29,30] they appeared clearly in the proton-coupled ^{11}B NMR as a triplet at −50.4 ppm, a position comparable to the reported −43.0 ppm signal of [Tbt(Mes)SiHBH$_2$CNAr] (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl).[30] While the ^{29}Si resonance of the silicon atoms in **2** could not be observed due to the strong line-broadening caused by quadrupolar boron nuclei,[31] the ^{1}H NMR spectrum of **2** gave a SiH doublet (2.90 ppm, J = 7.0 Hz)[29] and a SiH_2 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 B_3H_7 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 BH_3 while—*simultaneously*—accepting an electron pair from the carbene ligand. Although five and six-membered cyclosilylenes[32,33] are well-known, three-membered cyclic silylenes based on C_2H_4Si: 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 (^1J = 87 Hz) quartet resonance of the BH_3 at the C(1) carbene in the ^{1}H-coupled ^{11}B-NMR spectrum of **3** is like that reported for L:BH_3 (−35.4 ppm; ^1J = 83 Hz).[34] The −47.0 ppm broad doublet resonance of BH_3 coordinating to the central silicon atom is close to the −43.4 ppm (^1J = 84 Hz) of potassium tris(trimethylsilyl)silylboranate.[31] As in **2**, the ^{29}Si resonance of the silicon atom in **3** could not be observed.[31]

The carbene-stabilized disilicon compound, **1**, exhibits unusual reactivity with BH_3, affording two unique silylene compounds, **2** and **3**, which contain a parent silylene (:SiH_2) and a three-membered silylene ring, respectively. The driving force for the formation of **2** is provided by its stabilizing B_3H_7 structural feature.[18]

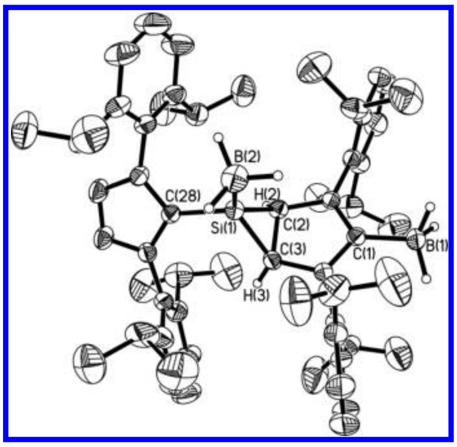

Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Some hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for (**3**): Si(1)−B(2) 1.996(4), Si(1)−C(28) 1.938(3), Si(1)−C(2) 1.903(3), Si(1)−C(3) 1.888(3), C(2)−C(3) 1.530(4), C(1)−B(1) 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).

■ ASSOCIATED CONTENT

Ⓢ 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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(17) See the Supporting Information for synthetic and crystallographic details.

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