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A Stable Silaborene: Synthesis and Characterization

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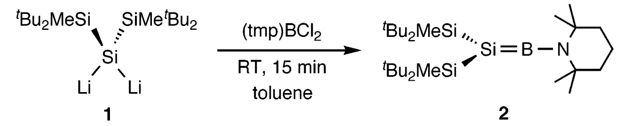
Since the first isolation of compounds with double bonds between carbon and boron atoms, methyleneborane ($R_2C{=}BR'$) in 1985 by Glaser and Nöth,[1] several examples of classical[2] and nonclassical methyleneboranes[3] have been reported.[4,5] By contrast, the heavy analogues of methyleneboranes of the type $R_2E{=}BR$ (E = Si, Ge) were unknown due to both the synthetic difficulty and the lack of suitable routes.[6] Recently, we demonstrated the novel 1,3-disila-2-gallata- and -indataallenic anions featuring double bonds between heavier elements of groups 13 and 14, which were produced by the coupling reaction of 1,1-dilithiosilane (**1**)[7] with MCl_3 (M = Ga, In).[8] Subsequently, we reported the reaction of **1** with $MesBCl_2$ (Mes = 2,4,6-trimethylphenyl) in THF, leading to the unexpected formation of a seven-membered ring compound containing an Si−B−O unit through the intermediate formation of the silaborene (>Si=B−) species, which induces the ring opening of the coordinated THF molecule.[9] This unusual reaction is ascribed to the high Lewis acidity of the boron center of the resulting >Si=B− species. Now, we introduced the 2,2,6,6-tetramethylpiperidino (tmp) group on the B atom, in the hope of synthesizing the stable >Si=B− species by the reaction of **1** with dichloro(tmp)borane. In this communication, we wish to report the synthesis and molecular structure of the first stable silaborene together with its unique reactivity with lithium acetylide to produce a lithium salt of the silaborenide, which was isolated as the solvent separated ion pair.

The reaction of **1** with 0.9 equiv of dichloro(2,2,6,6-tetramethylpiperidino)borane[10] in dry toluene at room temperature proceeded efficiently to form the corresponding coupling product, 1,1-bis(di-*tert*-butylmethylsilyl)-2-(2,2,6,6-tetramethylpiperidino)-1-sila-2-boraethene (**2**), which was isolated by recrystallization from toluene in 73% yield as air-sensitive yellow crystals (Scheme 1).[11]

Scheme 1



Silaborene **2** represents the first example of a compound with an >Si=B− double bond, and the structure of **1** was unambiguously determined by spectroscopic data and X-ray crystallographic analysis. The ^{29}Si NMR spectrum of **2** at 253 K in THF-d_8 showed two resonance signals at 23.3 and −128.1 ppm, which were assigned to the ^{t}Bu$_2$MeSi groups and the unsaturated skeletal silicon atom, respectively.[11] The ^{11}B NMR spectrum of **2** showed a broad signal at 87.7 ppm, which is shifted downfield relative to amino-substituted methyleneboranes (58.9−59.8 ppm).

The reason for such unusually large upfield and downfield shifts of the sp^2 silicon and sp boron atoms is probably due to the high polarization of the >Si=B− double bond, caused by the difference in the substitution at Si and B atoms; the two electropositive ^{t}Bu$_2$MeSi groups are bonded to the sp^2 silicon atom, whereas the electronegative tmp group is attached to the boron atom, leading to the reversed bond polarization as depicted, $>Si^{\delta-}{=}B^{\delta+}-$. In addition, the large, upfield-shifted resonance of the skeletal Si atom (−128.1 ppm) is consistent with a contribution from another, charge-separated, resonance structure, $>Si^{-}-B{=}N^{+}<$. The unusual chemical shifts of the ^{29}Si and ^{11}B NMR of **2** are reproduced by a GIAO calculation for the model compound, $[(Me_3Si)_2Si{=}B-(tmp)]$ (**3**) (*Si*=B: −94.3, Me$_3$*Si*: 20.6 and 19.8, Si=*B*: 75.9 ppm).[12] As expected, the natural population analysis (NPA) charge distributions for **3** showed a negative charge on the silicon atom (−0.268), whereas the boron atom has a positive charge (+0.357).

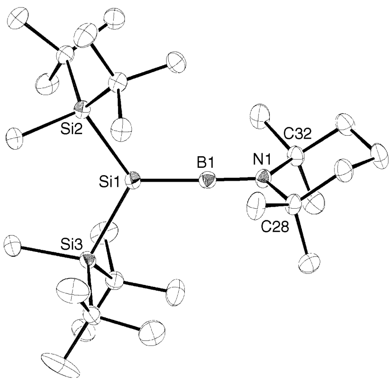


Figure 1. ORTEP drawing of silaborene **2** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−B1 = 1.8379(17), N1−B1 = 1.3695(19), Si1−Si2 = 2.3413(6), Si1−Si3 = 2.3419(6), N1−C28 = 1.5175(18), N1−C32 = 1.5212(18), Selected bond angles (deg): Si1−B1−N1 = 176.87(13), B1−Si1−Si2 = 119.45(5), B1−Si1−Si3 = 119.91(6), Si2−Si1−Si3 = 118.93(3), B1−N1−C28 = 120.01(12), B1−N1−C32 = 120.46(12), C28−N1−C32 = 119.27(11).

The molecular structure of **2** was determined by X-ray crystallographic analysis, and an ORTEP drawing of **2** is shown in Figure 1.[13] The Si1−B1 bond length of **2** (1.8379(17) Å) is about 10% shorter than typical Si−B single bonds of silylboranes (2.038−2.1249 Å),[9,14] lithium silylborates (1.984−1.993 Å),[15] and the silylborane−isocyanide complex (2.052 Å),[16] unambiguously showing the double bond character between silicon and boron atoms. The N1−B1 bond length (1.3695(19) Å) is similar to those of amino-substituted methyleneboranes (1.349−1.363 Å).[1b] The Si1−B1−N1 framework is almost linear (176.87(13)°), with a nearly perpendicular arrangement for the Si2−Si1−Si3 and C28−N1−C32 planes (96.5 and 89.1°). In addition, the slight pyramidalization around the Si1 atom (*trans*-bend angle: 13.0°, sum of the bond angles at the Si1 atom: 358.29°) indicates localization of the negative charge on the Si1 atom, as expected by the upfield shift of the ^{29}Si NMR resonance of **2**.

The reactivity of **2** toward nucleophiles is quite interesting because the LUMO of the molecule consists of the vacant p orbital on the boron atom. Thus, **2** reacted with lithium trimethylsilylacetylide at 60 °C in DME to give the corresponding silaborenide,

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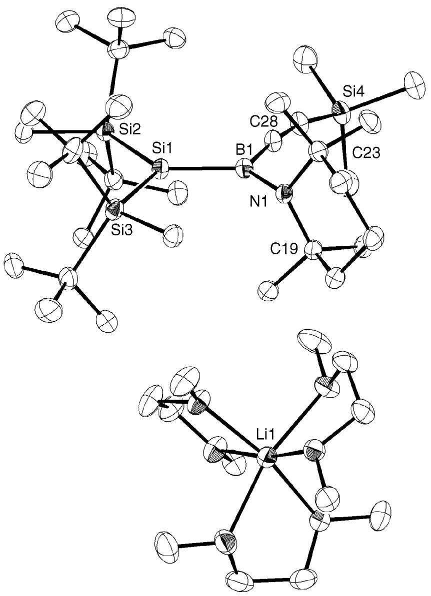
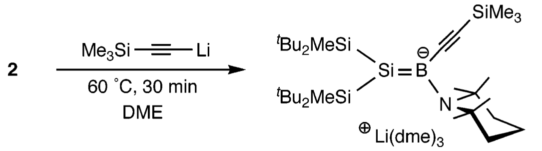


Figure 2. ORTEP drawing of silaborenide $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$ (30% thermal ellipsoids). Hydrogen atoms and a toluene molecule are omitted for clarity. Selected bond lengths (Å): Si1−B1 = 1.933(3), N1−B1 = 1.527(3), Si1−Si2 = 2.3728(8), Si1−Si3 = 2.3658(9), B1−C28 = 1.544(3), N1−C19 = 1.495(3), N1−C23 = 1.492(3). Selected bond angles (deg): B1−Si1−Si2 = 120.88(8), B1−Si1−Si3 = 117.98(8), Si2−Si1−Si3 = 121.12(3), Si1−B1−N1 = 125.51(17), Si1−B1−C28 = 116.93(16), N1−B1−C28 = 117.5(2), B1−N1−C19 = 116.46(17), B1−N1−C23 = 116.43(18), C19−N1−C23 = 116.90(17), B1−C28−C29 = 174.3(3), C28−C29−Si4 = 168.8(2).

lithium 1,1-bis(di-*tert*-butylmethylsilyl)-2-(trimethylsilylethynyl)-2-(2,2,6,6-tetramethylpiperidino)-1-sila-2-boren-2-ide ($\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$) in 76% yield, which was isolated as air- and moisture-sensitive reddish-orange crystals (Scheme 2).[11,14] The crystal structure of

Scheme 2



$\mathbf{4}^- \cdot [\mathrm{Li(dme)_3}]^+$

$\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$ was shown to be the solvent-separated ion pair (Figure 2).[17] The most important feature is the Si1−B1 bond length of 1.933(3) Å, which is 5% longer than that of **2**, but shorter than the reported Si−B single bonds (1.984−2.1249 Å).[9,14−16] The N1−B1 bond length (1.527(3) Å) is significantly longer than that of **2** (1.3695(19) Å). Furthermore, the sums of the bond angles around Si1, B1, and N1 of $\mathbf{4}^-$ were 359.98, 359.94, and 349.79°, respectively, suggesting planar geometry for the Si−B unit and pyramidal geometry around the N atom. These structural features indicate that the Si and B atoms of **4** are doubly bonded, but the bond order of **4** is reduced compared with that of **2**. The attack of the carbanion is expected to proceed on the boron p orbital (LUMO), rather than the π*-orbital of the Si=B bond.

The ^{29}Si NMR spectrum of $\mathbf{4}^-$ shows an unusual chemical shift for the anionic silicon atom. In the ^{29}Si NMR spectrum of $\mathbf{4}^-$ in THF-d_8 at 253 K, four sharp signals were observed at −26.1, 11.0, 15.8, and 23.4 ppm, which were assigned to an Me$_3$Si group, the two ^{t}Bu$_2$MeSi groups, and the skeletal silicon, respectively. The skeletal Si atom (23.4 ppm) of $\mathbf{4}^-$ is significantly shifted downfield by 151.5 ppm relative to **2**, probably due to the lack of resonance contribution from >Si−B=N$^+$<, as found by the X-ray structure of $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$. The ^{11}B NMR spectrum of $\mathbf{4}^-$ at 298 K in THF-d_8 revealed the resonance at 55.3 ppm as a very broad signal. The calculated ^{29}Si and ^{11}B NMR chemical shifts for the model compound, $[(\mathrm{Me_3Si})_2\mathrm{Si{-}B(tmp)(C{\equiv}CH)}]^-$ ($\mathbf{5}^-$) (*Si*−B: 30.5, Me$_3$*Si*: 11.2 and 13.9, Si−*B*: 44.4 ppm)[12] are in fair agreement with the experimental data.

Supporting Information Available: Experimental procedures and spectral data for **2** and $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$, calculated geometries for **3** and $\mathbf{5}^-$, and tables of crystallographic data including atomic positional and thermal parameters for **2** and $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$ (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the experimental procedures and spectral data of **2** and $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+$, see the Supporting Information.
(12) The geometries of **3** and $\mathbf{5}^-$ were optimized by using the Gaussian 98 program at the B3LYP/6-31G(d) level. The GIAO-B3LYP calculations for **3** and $\mathbf{5}^-$ were carried out with 6-311+G(3d,p) for Si and 6-311+G-(d) for C, H, B, and N.
(13) Crystal data for **2** at 120 K: $\mathrm{C_{27}H_{60}BNSi_3}$, MW = 493.84, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.2370(4)$, $b = 17.8420(8)$, $c = 15.5790(7)$ Å, $\beta = 106.461(3)$°, $V = 3262.0(2)$ Å^3, $D_{\mathrm{calcd}} = 1.006$ g cm^{-3}, R_1 ($I > 2\sigma(I)$) = 0.0494, wR_2 (all data) = 0.1464 for 7811 reflections, 391 parameters, and 1 restraint, GOF = 1.061.
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(17) Crystal data for $\mathbf{4}^-\cdot[\mathrm{Li(dme)_3}]^+\cdot$toluene at 120 K: $\mathrm{C_{51}H_{107}BliNO_6Si_4}$, MW = 960.49, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.2370(6)$, $b = 28.0650(13)$, $c = 17.9290(5)$ Å, $\beta = 95.189(3)$°, $V = 6132.1(4)$ Å^3, $D_{\mathrm{calcd}} = 1.040$ g cm^{-3}, R_1 ($I > 2\sigma(I)$) = 0.0678, wR_2 (all data) = 0.2046 for 14 310 reflections, 761 parameters, and 1 restraint, GOF = 1.057.

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