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An Amidinato Amidosilylene-Dibromodiborene

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ABSTRACT. The amidinato amidosilylene [LSiNMe₂] (**1**, L = PhC(N*t*Bu)₂) was reacted with B₂Br₄(SMe₂)₂ in toluene at room temperature to form the bis(silylene)-tetrabromodiborane [L{Me₂N}Si]₂B₂Br₄ (**2**). It was then reacted with excess KC₈ in THF at room temperature to afford the bis(silylene)-dibromodiborene [L{Me₂N}Si]₂B₂Br₂ (**3**).

Silylenes of composition [R₂Si:] (R = supporting substituents) have a lone pair of electrons and vacant orbital on the silicon atoms (Figure 1).¹ These electronic properties enable them to possess both nucleophilic and electrophilic characters. To enhance the stability and ease of isolation, the vacant p orbital of silylenes can be stabilized by coordinating with a Lewis base donor to form base-stabilized derivatives [R₂(L)Si:] (L = Lewis base donor). Silylenes, [R₂Si:]

and $[R_2(L)Si:]$ shows fruitful chemistry toward small molecules activation.¹ In case of boron compounds, silylenes typically donate their lone pair of electrons to vacant p orbital of boranes, particularly BH_3 and BPh_3 , to form Lewis acid-base adducts.² Besides, they were prone to undergo oxidative addition reaction with boranes containing boron-heteroatom bonds.³ As an illustration, Braunschweig et al. showed that an N-heterocyclic silylene (NHSi) $[\{(H)C(Xyl)N\}_2Si:]$ ($Xyl = 2,6-Me_2C_6H_3$) underwent insertion with the B-Br bond of $PhBBr_2$, followed by expansion of the NHSi ring to afford a six-membered silaborinine ring (Figure 1).⁴ In addition, our group reported the B-H and C-H bond activation in the reaction of the amidinato amidosilylene $[L\{R(SiMe_3)N\}Si:]$ ($L = PhC(NtBu)_2$, $R = Ar$ or $SiMe_3$, $Ar = 2,6-iPr_2C_6H_3$) with BH_2OTf .⁵ Only the NHC-hydridosilylene $[(H)(tBu_3Si)Si(IME)]$ ($IME = :C\{N(Me)C(Me)\}_2$) was shown to coordinate with haloboranes, instead of undergoing oxidative addition.⁶

The reactivity of silylenes toward boron compounds was further extended to diboranes. For example, Braunschweig and co-workers showed that the N-heterocyclic silylene $[\{(H)C(Xyl)N\}_2Si:]$ functionalized B-X ($X = \text{halide}$) and C-H bonds in diaryldihalodiboranes(4) to form NHSi adducts of 1-aryl-2-silyl-1,2-diboraindanes.⁷ They also reported that the bis(amidinato)silylene $[\{PhC(NiPr)_2\}_2Si:]$ underwent reductive ligand transfer onto diaryldihalodiboranes(4) to form diborane radical (Figure 1).⁸ In these reactions, no stable Lewis acid-base adducts between silylenes and diaryldihalodiboranes(4) were detected. It seems that the synthesis of silylene-diborane complexes is a formidable challenge.

Though silylenes exhibit diverse reactivity with boranes, they were seldom used to coordinate with low-oxidation state boron compounds.⁹ It is probably due to the absence of stable silylene-haloborane complexes, which can undergo reduction to form low-oxidation state boron complexes. Only Xie and co-workers reported a carborane-substituted bis(silylene)-

bromoborylene and -borylene cation for dihydrogen activation and hydroboration of carbon monoxide.¹⁰ For other low-oxidation state boron compounds, namely diborene and diboryne, their chemistry with silylene are still unknown as yet. This aroused our interest to investigate the feasibility of silylene-multiply bonded boron complexes. Herein, we report the synthesis of an amidinato amidosilylene-tetrabromodiborane and -dibromodiborene complex.

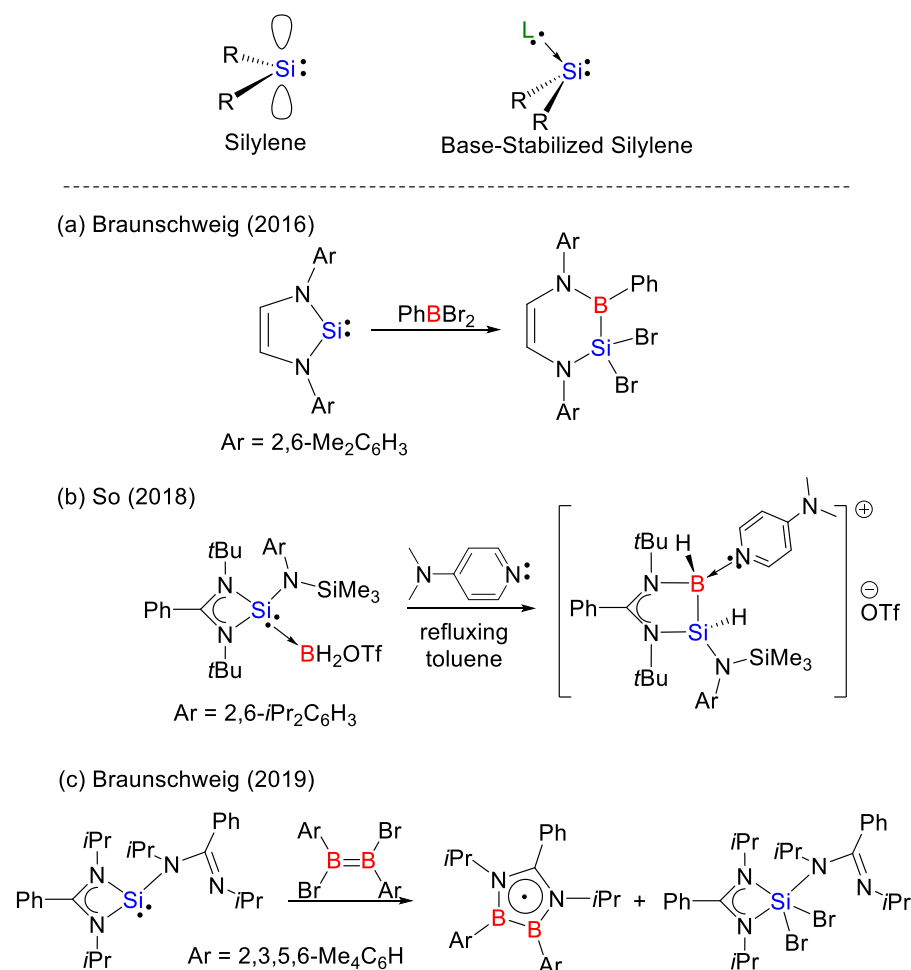
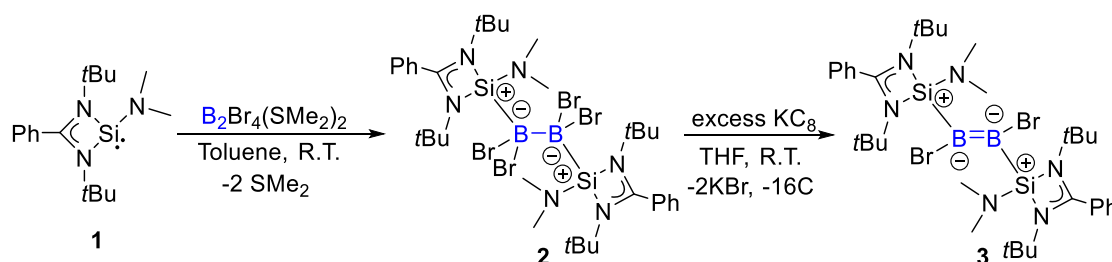


Figure 1. The reactivity of silylenes and base-stabilized derivatives with boron compounds.

The amidinato amidosilylene [LSiNMe₂] (**1**, L = PhC(N*t*Bu)₂)¹¹ was reacted with 0.5 equivalents of B₂Br₄(SMe₂)₂ in toluene at room temperature for 6 hours to form the bis(silylene)-tetrabromodiborane [L{Me₂N}Si]₂B₂Br₄ (**2**, Scheme 1) in 93% yield. In the reaction, compound

1 uses its lone pair of electrons to displace SMe_2 in $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ to form compound **2**. Other Lewis base-tetrahalodiborane(4) adducts using phosphines and N-heterocyclic carbenes as electron donors were reported,¹² though compound **2** is the first example using silylene to coordinate with tetrabromodiborane(4). The $^{11}\text{B}\{^1\text{H}\}$ NMR signal (-4.4 ppm) is in the range of the $^{11}\text{B}\{^1\text{H}\}$ NMR signals (-16.5 - -0.3 ppm) of other bis(Lewis base)-tetrabromodiborane compounds.¹² The $^{29}\text{Si}\{^1\text{H}\}$ NMR signal (-5.1 ppm) is upfield shifted in comparison with that of the amidinato amidosilylene-borane compound $[\text{L}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{SiBH}_3]$ (22.1 ppm).⁵ The X-ray crystal structure of **2** shows that the silicon and boron centers adopt a tetrahedral geometry (Figure 2). The Si-B bond length (2.029(2) Å) is slightly longer than the Si-B coordinative covalent bond in the amidinato amidosilylene-borane compound $[\text{L}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{SiBH}_3]$ (1.974(3) Å).⁵



Scheme 1. Synthesis of compounds **2** and **3**.

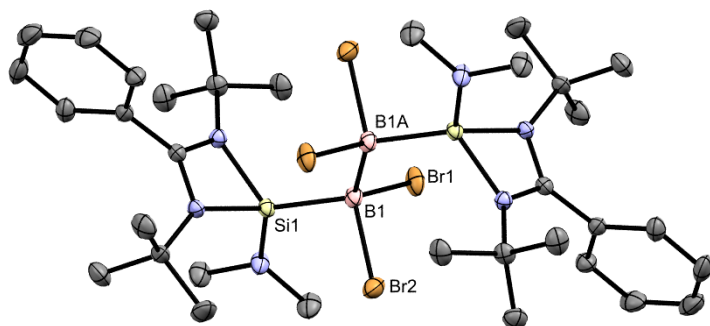


Figure 2. Molecular structure of **2** obtained by X-ray crystallography. Thermal ellipsoids are shown at 50 % probability. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Si1-B1 2.029(2), B1-B1A 1.705(5), B1-Br1 2.084(2), B1-Br2 2.084(2), Si1-B1-Br1 105.13(11), Si1-B1-Br2 102.71(11), Si1-B1-B1A 122.16(19).

Compound **2** was then reacted with excess KC_8 in THF at ambient temperature for 14 hours to afford a red suspension (Scheme 1). After filtration and concentration of the filtrate, the bis(silylene)-diborene compound $[\text{L}(\text{Me}_2\text{N})\text{SiB}(\text{Br})=\text{B}(\text{Br})\text{Si}(\text{NMe}_2)\text{L}]$ (**3**) was afforded as a red crystalline solid in 58% yield. The $^{11}\text{B}\{\text{H}\}$ NMR signal (26.6 ppm) is downfield shifted in comparison with that of **2**. It is in the range of the $^{11}\text{B}\{\text{H}\}$ NMR signals (12 – 32 ppm) of other Lewis base-diborene compounds.¹³⁻²⁷ The $^{29}\text{Si}\{\text{H}\}$ NMR signal (1.7 ppm) is downfield shifted in comparison with that of **2** (-5.1 ppm) due to the presence of a B=B double bond. The molecular structure obtained by X-ray crystallography shows that compound **3** has a trans-configuration and the B centers adopt a trigonal planar geometry (Figure 3). The B1-B1A bond length (1.56(3) Å) falls in the range of B=B double-bond length (1.546–1.625 Å) in similar Lewis base-diborene compounds.¹³⁻²⁷ The Si1-B1 bond (1.961(13) Å) is shorter than that of **2**, but it is longer than that of the carborane-substituted bis(silylene)-bromoborylene (1.857(4) Å).¹⁰

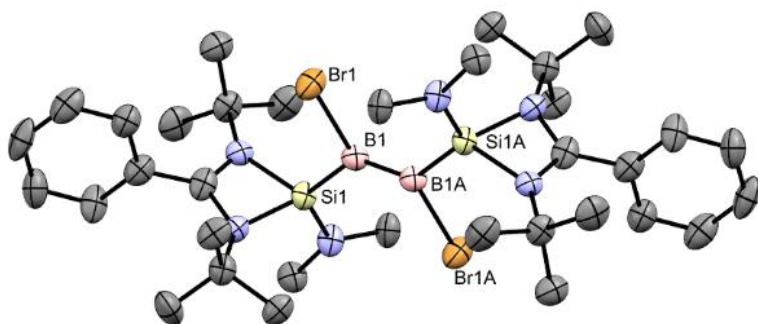


Figure 3. Molecular structure of **3** obtained by X-ray crystallography. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are deleted for clarity. Selected bond lengths (Å) and angles (deg): Si1-B1 1.961(13), B1-B1A 1.56(3), B1-Br1 2.060(13), Si1-B1-B1A 131.4(12), Br1-B1-B1A 120.4(11).

The electronic structure of compound **3** was elucidated by DFT calculations (B3LYP-D3BJ/def2-SVP). HOMO-1 shows a combination of the Si-B and B-B σ orbitals, while HOMO exhibits the π orbital of the B=B double-bond (Figure 4). Similar finding of B=B π orbital was found in NHC-diborene compounds.²⁶⁻²⁷ Accordingly, the Natural Bond orbital (NBO) analysis illustrates that the B1-B2 σ bond is arisen from the mixing of sp hybrids on the boron atoms, while the B1-B2 π bond is generated by the overlapping of B p orbitals (Table S2). The B=B double bond character is further supported by the Wiberg Bond Index of 1.66. Natural Population Analysis (NPA) shows that the natural charge on the B and Si atoms are -0.69 and 1.89 e, respectively, indicating a strong charge transfer from the silylene to diborene moieties. The Si-B bonds are formed by the overlapping of B $sp^{2.16}$ and Si $sp^{1.21}$ hybrids. The electron density of the Si-B bonds is slightly polarized toward the B atoms (56.4%). The Wiberg bond indices are 1.02, indicating that the Si-B bonds are a single bond. The EDA-NOCV calculations (B3LYP-D3BJ/TZP//B3LYP-D3BJ/def2-SVP) show that the Si-B bonds are described in term of electron-sharing single bonds between charged fragments $\{L(Me_2N)Si\}^+$ (triplet, two molecules) and $\{B(Br)=B(Br)\}^{2-}$ (triplet, Table S3). In the Laplacian distribution, the electron densities are concentrated in the middle of the Si-B bonds ($\rho(r_c)$: 0.2676 e/Å³, $\nabla^2\rho(r_c)$: -0.6635 e/Å⁵, Figure 4). These results suggest that strong σ -donating property of compound **1** led to an effective orbital overlap between the Si and B atoms in the Si-B σ bonds.

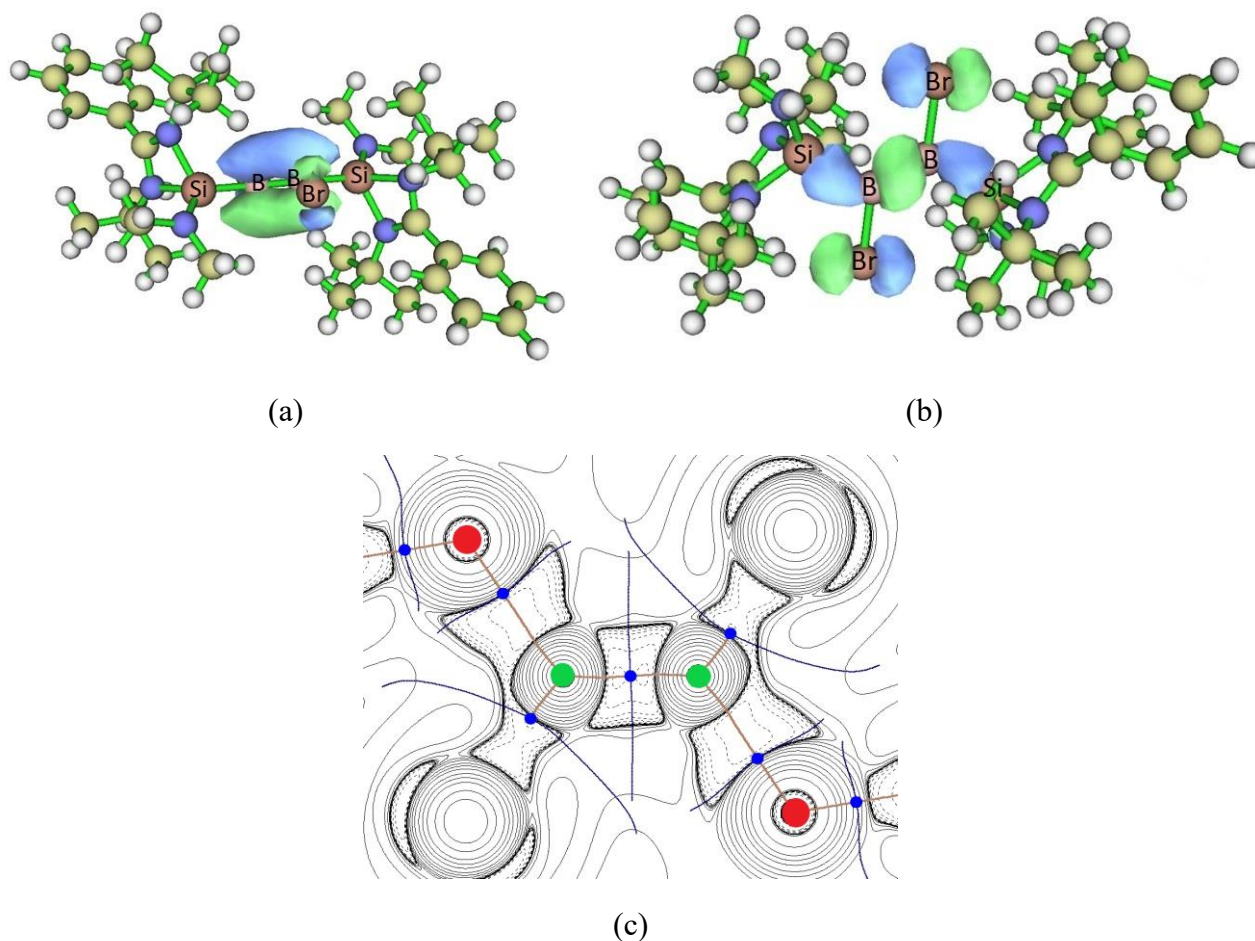


Figure 4. Selected molecular orbitals of compound **3** (a) HOMO. (C: yellow, H: white, N: blue) (b) HOMO-1. (c) Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the Si-B-B plane in **3**. Solid lines indicate the areas of the charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). Green and red circles denote B and Si atoms, respectively. Blue circles denotes (3,-1) critical points. Bold dark brown lines depict bond paths and purple lines separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

In conclusion, the amidinato amidosilylene **1** was capable of coordinating with $B_2Br_4(SMe)_2$ to form the bis(amidinato amidosilylene)-tetrabromodiborane **2**. It served as a synthon in the reduction with KC_8 to form the bis(amidinato amidosilylene)-dibormodiborene **3**. Further reduction of compound **3** is currently under investigation and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information.

The Supporting information is available free of charge at <http://pubs.acs.org>

Experimental procedures and DFT calculations (PDF)

Accession Codes

CCDC 2103603 - 2103604 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS. The bis(silylene)-tetrabromodiborane reacted with excess KC_8 to afford the bis(silylene)-dibromodiborene.

