

Borasilenes

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An Isolable Potassium Salt of a Borasilene–Chloride Adduct

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Abstract: Among the variety of isolable compounds with multiple bonds involving silicon, examples of compounds that contain silicon–boron double bonds (borasilenes) still remain relatively rare. Herein, we report the synthesis of the potassium salt of a chloride adduct of borasilene 1 ($[2]^-$), which was obtained as an orange crystalline solid. Single-crystal X-ray diffraction analysis and reactivity studies on $[2]^-$ confirmed the double-bond character of the Si=B bond as well as the reduced Lewis acidity, which is due to the coordination of Cl^- to the boron center. A thermal reaction of $[2]^-$ afforded a bicyclic product by formal intramolecular C–H insertion across the Si=B bond of 1, which was corroborated by a theoretical study.

Numerous low-coordinate silicon compounds stabilized by bulky protecting groups and/or the coordination of Lewis bases and alkali-metal halides have been synthesized, and these species represent an important and active research area in silicon chemistry.^[1,2] Among the compounds that contain multiple bonds involving silicon, those with silicon-boron double bonds (borasilenes, R₂Si=BR') are relatively rare. Moreover, only one such compound has been isolated. Sekiguchi and Nakata reported compound A, which is stabilized by an electron-donating amino substituent on the boron center (Figure 1).^[3] An acetylide adduct of A (A') was synthesized by treatment of A with the corresponding acetylide^[3] while **B** was proposed as an intermediate in the reaction between $(tBu_2MeSi)_2SiLi_2$ and $MesBCl_2$ (Mes = 2,4,6-Me₃C₆H₂) in THF.^[4] Tokitoh et al. have suggested partial double-bond character for the Si=B bonds in (diarylboryl)silvl anions.^[5] Nevertheless, base-free borasilenes, which should possess the intrinsic properties of a Si=B double

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Figure 1. Borasilenes and related compounds.

bond, are still unknown. On account of the low-lying vacant 2p orbital on the boron atom,^[4] and owing to the weakness of the Si=B double bond,^[6] such compounds are expected to behave as electron acceptors and strong Lewis acids.

We have synthesized various stable compounds with silicon-heteroatom double bonds that bear bulky cyclic alkyl units, $R_2Si=X [R_2Si=2,2,5,5-tetrakis(trimethylsilyl)sila$ cyclopentan-1,1-diyl ($R_{2}^{H}Si$), X = NR',^[7] S,^[8] Se,^[8] Te;^[8] R₂Si = 2,2,5,5-tetrakis(isopropyldimethylsilyl)silacyclopentan-1,1divl, $X = O^{[9]}$ and investigated the intrinsic properties of their Si=X double bonds. The results prompted us to synthesize stable base-free borasilene 1, featuring an R^H₂Si moiety and a Mes group on the boron atom, to determine the intrinsic structure and properties of the Si=B double bond. During our synthetic study on 1, we unexpectedly obtained the chloride adduct of 1 as a potassium salt, which was isolated as an orange crystalline solid ([2][K(18-c-6)], 18-c-6 = 18-crown-6 ether).^[10] A thermal reaction of [2]⁻ afforded an intramolecular C-H insertion product (5), which is an isomer of 1. This result suggests that 5 is formed via intermediate 1. Herein, we report the synthesis, structure, and reactivity of $[2]^-$.

Treating silane **4**, which was obtained in 86% yield from the reaction of dialkylsilylene **3**^[11] with MesBCl₂^[12] in hexane (Scheme 1),^[5,13] with KC₈ and 18-c-6 in 1,2-dimethoxyethane (DME) at room temperature induced an immediate color change to orange. After stirring for 3 h, [**2**][K(18-c-6)] was obtained in 73% yield as air-sensitive and thermally unstable orange crystals,^[14] which were characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and single-crystal X-ray diffraction (XRD).



Scheme 1. Synthesis of [2][K(18-c-6)].

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The coordination of Cl^- to the unsaturated boron center suggests that the Lewis acidity of borasilene **1** is very high. In the absence of 18-c-6, a similar chloride adduct with a DME-coordinated potassium cation ([**2**][K(dme)₂]) was obtained, the structure of which was determined only by preliminary XRD analysis (see the Supporting Information). As [**2**][K(dme)₂] is thermally less stable than [**2**][K(18-c-6)], it could not be fully characterized.

The molecular structure of [2][K(18-c-6)] shows a contact ion pair in the solid state (Figure 2). The Cl1...K1 distance



Figure 2. Molecular structure of [**2**][K(18-c-6)].^[35] Thermal ellipsoids set at 30% probability, hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [⁰]: Si1–B1 1.859(2), B1–Cl1 1.879(2), Cl1···K1 3.0150(6); Si1-B1-C5 132.69(13), C5-B1-Cl1 113.03(12), Cl1-B1-Si1 114.25(10).

[3.0150(6) Å] is shorter than the sum of the ionic radii of Cl⁻ and K⁺ (3.14 Å).^[15] The Si1–B1 bond in [2]⁻ [1.859(2) Å] is similar in length to that in the neutral borasilene **A** [1.8379-(17) Å] and considerably shorter than that in borasilene– acetylide adduct **A'** [1.933(3) Å].^[3] The geometry around the Si1 and B1 atoms is almost planar, which is reflected by the angle sums around the Si1 (359.31°) and B1 (359.97°) atoms.^[16] The B1–Cl1 bond in [2]⁻ [1.879(2) Å] is significantly longer than that in precursor **4** [1.7751(17) Å], which suggests that the electron donation from the chloride to the boron atom is weaker than in **4**. These structural parameters show that the Si=B bond in [2]⁻ exhibits double-bond character, with little contribution from a silyl anion (R^H₂Si⁻–BMesCl) resonance structure.

A solution of [2][K(18-c-6)] in [D₈]THF showed the ²⁹Si NMR resonance (δ_{si}) of the central unsaturated silicon nucleus at 56.8 ppm and the ¹¹B NMR resonance (δ_{B}) as a broad signal at 38.0 ppm at 263 K. These values are in good agreement with the corresponding theoretical gauge independent atomic orbital (GIAO) values for the optimized structures of [R^H₂Si=BMesCl]⁻ ([2]⁻_{opt}; δ_{si} =59.6 ppm, δ_{B} = 33.6 ppm) and R^H₂Si=BMesCl]⁻ K(18-crown-6) ([2][K(18-c-6)]_{opt}; δ_{si} = 65.0 ppm, δ_{B} = 30.4 ppm) while they differ substantially from those of R^H₂Si=BMes(thf) (δ_{si} =86.8 ppm, δ_{B} =41.5 ppm; for details of the theoretical study, see the next paragraph and the Supporting Information). These results suggest that in solution, [2]⁻ is present as a borasilene– chloride adduct rather than as a borasilene–THF adduct although an equilibrium between these species cannot be ruled out.^[18,19] Compared to the δ_{Si} and δ_B values of **A**' (δ_{Si} = 23.4 ppm, δ_B = 55.3 ppm) in [D₈]THF at 298 K, those of [**2**][K(18-c-6)] are downfield- and upfield-shifted, respectively.^[3]

The electronic structure of $[2]^-$ was also investigated by DFT calculations. The structural parameters of the optimized structure of R^H₂Si=BMesCl···K(18-crown-6) ([2][K(18-c-6)]_{opt}) at the B3PW91-D3/6-31 + G(D) level of theory are in good agreement with the experimental values of 2 obtained from the XRD analysis. For [2][K(18-c-6)]_{opt}, Si=B, B-Cl, and Cl…K distances of 1.857, 1.889, and 3.018 Å, respectively, were calculated as well as angle sums of 359.7° (Si) and 359.9° (B). The geometry around the Si=B double bond in the anion $[R^{H}_{2}Si=BMesCl]^{-}([2]_{opt}^{-})$ is also similar to that of [2][K(18-c-6)]_{opt}. The Wiberg bond index for the Si=B double bond in $[2]_{opt}^{-}$ (1.70) is almost twice that for the corresponding Si–B bond in $\mathbf{4}_{opt}$ (0.88). The HOMO of $[\mathbf{2}]_{opt}^{-}$ is a π (Si=B) orbital, and its energy level is much higher than that of base-free borasilene $\mathbf{1}_{opt}$ owing to interactions between the $\pi(Si=B)$ orbital and the lone pair orbital on Cl (Figure S69). These results support the notion that $[2]^-$ should be interpreted as an anionic Si=B species rather than as a borylsilyl anion $(R^{H}_{2}Si^{-}-BMesCl)$. The addition of Cl⁻ to borasilene **1** was calculated to be exergonic ($\Delta G = -28.9 \text{ kJ mol}^{-1}$ in THF; $\Delta G = -77.5 \text{ kJ mol}^{-1}$ in toluene; T = 298.15 K; same level of theory), which is in good agreement with the experimental observation that $[2]^-$ was obtained rather than 1.

As Cl⁻ is a good leaving group, we expected that Cl⁻ could be eliminated from $[2]^-$ to generate free borasilene **1**. However, when a C₆D₆ solution of [2][K(18-c-6)] was left to stand at room temperature for one day, bicyclic compound **5**, which is an isomer of borasilene **1**, was obtained unexpectedly (Scheme 2). Interestingly, in this thermal reaction, *cis*-**5**



Scheme 2. Thermal reaction of [2][K(18-c-6)].

 $[(1S^*,5R^*)$ -5] was formed selectively, which was confirmed by NMR spectroscopy and XRD analysis.^[20] At lower temperatures (-80 to 0 °C) in C₇D₈, [2][K(18-c-6)] did not react, but at room temperature, 5 was formed in a similar fashion. During this reaction, ¹H NMR resonances assignable to intermediates such as 1 were not observed.

The formation of **5** from [**2**][K(18-c-6)] was accelerated in C_6D_6 at room temperature upon addition of one equivalent of triethylsilylium tetrakis(pentafluorophenyl)borate ([Et₃Si]-[TPFPB]),^[21] which is an effective Cl⁻ scavenger.^[22,23] The reaction mixture turned from orange to pale yellow, and two layers formed within 2 h. In the upper layer, the formation of **5** (67%), Et₃SiCl (70%), a small amount of Et₃SiH,^[24] and other unidentified compounds was observed by ¹H NMR spectroscopy. The formation of **5** and Et₃SiCl suggests that the

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abstraction of Cl^- accelerates the generation of borasilene intermediate 1.

The mechanism for the transformation of $[2]^-$ into **5** was investigated theoretically. A free energy change of $+77.5 \text{ kJ mol}^{-1}$ was calculated at the B3PW91-D3/6-31 + G(d) level of theory for the dissociation of Cl⁻ from $[2]^-_{opt}$ $([2]^-_{opt} \rightarrow 1_{opt} + \text{Cl}^-)$ at 298.15 K in toluene, which is consistent with the experimental results. The stereospecific C–H insertion reaction of model compound 1', in which the SiMe₃ and Mes groups were replaced with hydrogen atoms and a Me group, respectively, to the corresponding bicyclic product 5', involves a remarkably small activation energy (47.9 kJ mol⁻¹) in toluene at the B3PW91/6-31 + G(D) level of theory (Figure 3a). This activation barrier is much smaller than



Figure 3. Possible C–H insertion reactions of 1' and [2'][–]. Whereas both the *cis* and *trans* isomers of [2'][–] are possible, they exhibit very similar reaction routes with virtually identical activation energies; for further details see the Supporting Information.

that for the corresponding C–H insertion reaction from model compound [2']⁻ to 5'·Cl⁻ (188.7 kJ mol⁻¹; Figure 3b). Elimination of Cl⁻ from 5'·Cl⁻ is endergonic at 298.15 K in toluene ($\Delta G = +15.1$ kJ mol⁻¹). These results support the notion that the transformation of [2]⁻ into 5 proceeds via free borasilene 1. Although C–H insertions have been reported for methylene boranes^[25] and other heavier multiple-bond compounds, C(sp³)–H insertions have not been observed in other base-free double-bonded compounds bearing the same R^H₂Si moiety, suggesting that the reactivity of base-free borasilenes is relatively high.

Compound [2][K(18-c-6)] exhibits a double-bond character for the Si=B bond that is similar to that in borasilene A, and also reflected in its reactivity. Treatment of [2][K(18-c-6)] with S_8 (0.28 equiv) in toluene immediately produced the boracycle 1,3,2,4-dithiasilaboretane 6, which could be isolated in 39% yield as colorless crystals (Scheme 3).^[26] A similar borathiacycle, resulting from the insertion of an S atom into the Si=B double bond, was obtained from the reaction of borasilene A with S₈.^[27] Furthermore, [2][K(18-c-6)] reacted with two equivalents of Ph₃CCl. Upon addition, the color of the reaction mixture immediately turned to an intense purple, but faded quickly. The formation of 4 and the trityl dimer was observed by ¹H NMR spectroscopy (Scheme 3). One conceivable mechanism for this reaction involves the initial abstraction of a Cl radical from Ph₃CCl to generate a trityl radical and the radical anion of 4. Subsequently, the latter



Scheme 3. Reactivity of [2][K(18-c-6)] towards S₈ and Ph₃CCl.

should be oxidized with another equivalent of Ph_3CCl (see the Supporting Information).^[28] Similar chlorine abstraction reactions have already been reported for other compounds with multiple bonds to silicon, such as disilenes ($R_2Si=SiR_2$).^[29]

Reactions of [2][K(18-c-6)] with typical Lewis bases such as PPh₃ or *N*,*N*-dimethyl-4-aminopyridine did not proceed, which indicates that the Lewis acidity of $[2]^-$ was substantially reduced by the absence of the vacant 2p orbital on the boron atom after the coordination of Cl⁻.^[30]

Interestingly, $[2]^-$ exhibited unexpected reactivity towards 9,10-phenanthrenequinone (PQ), which is a typical trapping agent for compounds with multiple bonds involving silicon. Treating [2][K(18-c-6)] with two equivalents of PQ in C_6D_6 led to an immediate color change to dark red, which gradually faded. The formation of the silylene–PQ adduct 7 (98%) and 1,3,2-dioxaborolane $8^{[31]}$ (81%) instead of the expected [4+2] cycloadduct was observed by ¹H NMR spectroscopy (Scheme 4). Further information on this reaction was



Scheme 4. Reactivity of [2][K(18-c-6)] towards 9,10-phenanthrenequinone.

obtained from the stepwise addition of PQ to [2][K(18-c-6)]. Treatment of [2][K(18-c-6)] with one equivalent of PQ afforded 7 (21%), 3 (7%), 4 (43%), and other unidentified products, including a dark red precipitate. After addition of another equivalent of PQ to the mixture, this precipitate was consumed, and the color of the mixture turned to pale yellow. The ¹H NMR spectrum of the mixture showed that 3, 4, and the unidentified products were consumed with concomitant formation of 7 (81%) and 8 (88%). The mechanism for this reaction remains unclear at this stage but the initial formation of 4 suggests an electron transfer from $[2]^-$ to PQ^[32] and a subsequent disproportionation, which would lead to 4, while the precipitate should contain unidentified anionic species.

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Another equivalent of neutral PQ should then react with the anionic species to provide **7**, **8**, and the radical anion of PQ (PQ⁻⁻), the latter of which should then convert **4** into **7** and **8**^[33] (for details, see the Supporting Information, Scheme S1). The reaction of [**2**][K(18-c-6)] with PQ thus demonstrates the electron-rich nature of [**2**]⁻.

In summary, borasilene–chloride adduct $[2]^-$ was synthesized and isolated as [2][K(18-c-6)] in the form of orange crystals. Its molecular structure exhibits a Si=B bond and low Lewis acidity. The generation of borasilene 1 from $[2]^-$ was proposed on the basis of the stereoselective formation of intramolecular C-H insertion product 5 and theoretical calculations on model compounds. This reaction is very interesting as it includes the activation of relatively inert C(sp³)-H bonds. This, in turn, suggests unusually high reactivity for the base-free borasilene. As theoretical calculations predicted an absorption band for base-free borasilene 1 in the near-infrared region arising from the HOMO \rightarrow LUMO transition,^[34] isolation of the base-free borasilene stabilized by carefully designed protecting groups should be an important step towards unravelling the unusual reactivity and electronic nature of base-free Si=B double bonds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · C-H activation · multiple bonds · silicon

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- [35] CCDC 1520340 ([2][K(18-c-6)]), 1520341 ([2][K(dme)₂]), 1520342 (4), 1520343 (4'), 1520344 (5), 1520345 (6), and 1530520 ([S3][Li(CH₃CN)₄]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Communications



=R

SiMe₃

possible intermediate

Me₃Si SiMe₃

Me₃Si

Communications

a Borasilene-Chloride Adduct



The potassium salt of a borasilene–chloride adduct was synthesized and isolated. Its reactivity and single-crystal X-ray diffraction analysis revealed the doublebond character of its Si=B bond and reduced Lewis acidity. This adduct provides a cyclic product by formal intramolecular C-H insertion across the Si=B bond, possibly via the corresponding base-free borasilene.

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