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# A Hydride-Substituted Homoleptic Silylborate: How Similar is it to its Diborane(6)-Dianion Isostere?

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Abstract: The B-nucleophilic 9H-9-borafluorene dianion reacts with 9-chloro-9-silafluorene to afford air- and moisture-stable silylborate salts $M[Ar_2(H)B–Si(H)Ar_2]$ (M[**HBSiH**], M=Li, Na). Li[**HBSiH**] and Me_3SiCl give the B–pyridine adduct $Ar_2(py)B–Si-(H)Ar_2$ (**(py)BSiH**) or the chlorosilane $Li[Ar_2(H)B–Si(Cl)Ar_2]$ (Li[**HBSiCl**]) in C_6H_6-pyridine or THF. In both cases, the first step is H⁻ abstraction at the B center. The resulting free borane subsequently binds a py or thf ligand. While the py adduct is stable at room temperature, the thf adduct undergoes a 1,2-H shift via the cyclic B(μ-H)Si intermediate **BHSi**, which is afterwards attacked at the Si atom by a Cl⁻ ion to give Li[**HBSiCl**]. DFT calculations were employed to support the proposed reaction mechanism and to characterize the electronic structure of **BHSi**. Treatment of Li[**HBSiCl**] with the N-heterocyclic carbene IMe introduces the neutral donor at the Si atom and leads to $Ar_2(H)B–Si(IMe)Ar_2$ (**HBSi(IMe)**), a donor-acceptor-stabilized silylene.

Introduction

The use of diboranes, in particular bis(pinacolato)diboron (B_2pin_2), for CH-borylation[1] and functionalization of alkenes and alkynes[2] has greatly advanced organic synthesis. In a similar vein, disilanes, especially the highly reactive Si_2Cl_6, are currently establishing themselves as useful reagents for the preparation of organosilanes with a wide range of applications, for example, in silicone chemistry.[3] The next systematic step in the extension of this chemistry is the progression from homoelement compounds to the corresponding heteroelement compounds, namely silylboranes $R_2B–SiR'_3$.[2b,4] Silylboranes are suitable for the introduction of boryl and/or silyl groups into a given substrate molecule (Scheme 1). As an example, Ito and coworkers used $pinB–SiMe_2Ph$ (**A**) as storage form of the $[Bpin]^-$ anion, which they released in situ by heterolysis of the B–Si bond with KOMe to prepare **B**.[5] Conversely, Wang, Uchiyama
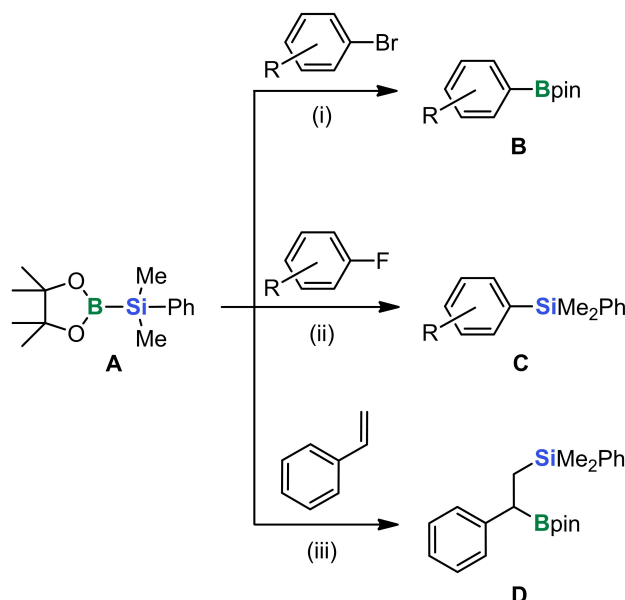
Scheme 1. The widely employed silylborane $pinB–SiMe_2Ph$ (**A**) can be used to introduce either Bpin (**B**), or $SiMe_2Ph$ (**C**) or both groups (**D**) into a substrate molecule without the need for a transition metal catalyst. (i) 1.5 equiv. Ar–Br, 1.2 equiv. KOMe, DME, 30 °C, 1 h, 50–85 % yield; (ii) 0.5 equiv. Ar–F, 1.5 equiv. NaOtBu, THF, room temperature, 12 h, 34–89 % yield; (iii) 1.0 equiv. styrene, 10 mol% KOtBu, THF, room temperature, 1 h, 91 % yield.

and coworkers introduced the $SiMe_2Ph$ group into benzene derivatives through the activation of the B–Si bond with NaOtBu (cf. **C**).[6] Again, Ito et al. performed the silaboration of olefins by means of the $pinB–SiMe_2Ph$/KOtBu system (cf. **D**).[7]

Although more and more evidence for the general utility of silylboranes is emerging, fundamental properties of pristine B–Si systems, largely unperturbed by electronic substituent

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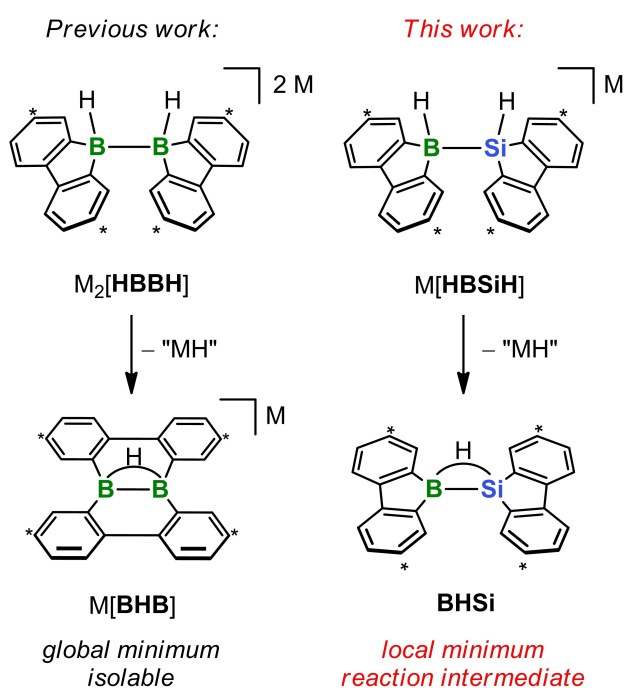Homepage: https://www.uni-frankfurt.de/58708118/wagner

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effects ($\pm$I, $\pm$M), still remain underexplored.[8] Due to a lack of availability, the parent H_2B-SiH_3 has been studied only theoretically:[9] Silylene (SiH_2) forms an adduct with monoborane (BH_3), which contains a B(μ-H)Si three-membered ring (2-electron-3-center, 2e3c, bond);[10] the associated stabilization energy was computed to fall in the range 37–50 kcal mol^{-1}, depending on the level of theory applied. The primary product represents only a local minimum and tends to undergo a 1,2-H shift with an activation barrier of only 1–4 kcal mol^{-1} to furnish silylborane H_2B-SiH_3 with an exothermicity of about 3–7 kcal mol^{-1}.[9c] Remarkably, the free borane-silylene complex $H_3B\cdot SiH_2$ without bridging H atom does not exist, but its formal adduct $H_3B\cdot SiH_2\cdot NHC$ was synthesized by Rivard and coworkers (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[11]

With the aim of validating the theoretical predictions by experiments, we searched for a synthetically accessible derivative of H_2B-SiH_3 and decided to rely on the same design principles as previously employed for the synthesis of isolable B–B bonded analogues.[12] We finally settled on the silylborate [Flu(H)B–Si(H)Flu]$^-$ ([**HBSiH**]$^-$, HBFlu/H_2SiFlu = bora-/silafluorene; Scheme 2),[13] the formal H$^-$ adduct of FluB–Si(H)Flu, as the entry point of our studies. Its diborane(6) analogue [**HBBH**]$^{2-}$ (Scheme 2) exists and has been proven useful for studying the B–B-bond reactivity in diborane(6) dianions [Flu(H)B–B(H)Flu]$^{2-}$.[14,15] Specifically, H$^-$ abstraction from [**HBBH**]$^{2-}$ leads to the isolable B(μ-H)B diborane(5) anion [**BHB**]$^-$,[15] which is valuable for modeling the parent [B_2H_5]$^-$ anion,[16] a valence-isoelectronic congener of H_2B-SiH_3. Herein, we disclose the synthesis protocol of [**HBSiH**]$^-$, describe how the B-bonded, the Si-bonded, or both H$^-$ ions can be replaced by other ligands, and show that **BHSi** is the key intermediate in observed SiH/ligand exchange reactions.

Results and Discussion

Synthesis and characterization of M[HBSiH]

The arguably best established synthetic route to B–Si bonds uses electrophilic boron species and nucleophilic silanide reagents.[13d,17] We also initially relied on this approach and selected HBFlu·thf[14] and Cl(H)SiFlu[18] as starting materials.[19] Since all our attempts to convert Cl(H)SiFlu to its Li$^+$ salt Li[HSiFlu] resulted in overreduction with formation of the 9-silafluorenyl-dianion salt Li$_2$[SiFlu],[20] we tested the suitability of Li$_2$[SiFlu] for B–Si-bond formation, but to no avail: the reaction scenario was dominated by redox processes and led to complex product mixtures. It was therefore necessary to resort to an *"Umpolung"* approach, for which we could use the exact same starting materials: Two-electron reduction of HBFlu·thf with alkali metal in THF gives our recently reported boron-centered nucleophile M$_2$[HBFlu] (M = Li, Na).[15,21,22] Freshly prepared M$_2$[HBFlu] reacted with Cl(H)SiFlu at room temperature in THF to afford the silylborate salts M[**HBSiH**] in yields of 83% (M = Li) and 56% (M = Na; Scheme 3). We wanted to have both salts

Scheme 2. Analogy between the B–B and B–Si species M[**BHB**] and **BHSi**, formally obtained by MH elimination from the isolable isosteres M$_2$[**HBBH**] and M[**HBSiH**]. Carbon atoms marked with asterisks bear *t*Bu substituents.

Previous work: M$_2$[**HBBH**] → – "MH" → M[**BHB**] *global minimum isolable*

This work: M[**HBSiH**] → – "MH" → **BHSi** *local minimum reaction intermediate*
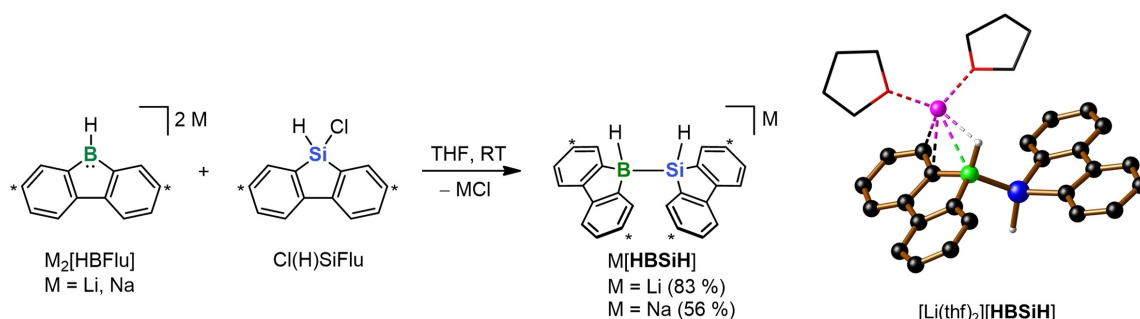
Scheme 3. *Left:* Synthesis of M[**HBSiH**] (M = Li, Na) through reaction of M$_2$[HBFlu] with Cl(H)SiFlu. Carbon atoms marked with asterisks bear *t*Bu substituents. *Right:* Solid-state structure of [Li(thf)$_2$][**HBSiH**]; C-bonded H atoms, all *t*Bu substituents, and two non-coordinating C_6H_6 molecules are omitted for clarity. H: gray, Li: magenta, B: green, C: black, O: red, Si: blue.

M$_2$[HBFlu]
M = Li, Na

Cl(H)SiFlu

THF, RT
– MCl

M[**HBSiH**]
M = Li (83%)
M = Na (56%)

[Li(thf)$_2$][**HBSiH**]

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available, because previous experience indicates a pronounced influence of the counter cation on the reactivity of subvalent boron compounds.[23,24]

Since the NMR data of M[**HBSiH**] (M = Li, Na; [D$_8$]THF) show only the usually observed negligible cation dependencies,[15,16a,23] it suffices here to discuss the spectra of Li[**HBSiH**]: In both the ^{1}H and ^{13}C{^{1}H} NMR spectra, one sees two signal sets of magnetically inequivalent 2,2′-biphenyldiyl fragments (proton-integral ratio = 1 : 1). The ^{11}B NMR spectrum contains a doublet at −22.7 ppm (^1J(B,H) = 89 Hz), testifying to the presence of tetracoordinated boron nuclei.[25] Upon proton decoupling, the doublet collapses to a singlet; the corresponding B-bonded proton gives rise to a 1 : 1 : 1 : 1 quartet at δ(^{1}H) = 2.72 ppm. A ^{29}Si NMR signal was not directly detectable, likely because it is severely broadened due to ^1J(Si,B) coupling with the quadrupolar [10/11]B nuclei. Yet, a ^{1}H,^{29}Si-HMBC NMR spectrum showed an intense cross-peak between δ([29]Si) = −22.7 ppm and the resonances of the *ortho*-H atoms of one of the 2,2′-biphenyldiyl signal sets (which can thereby be assigned to the silafluorene backbone). A ^{1}H NMR signal at 4.50 ppm with clearly visible [29]Si satellites arises from the Si-bonded proton (^1J(H,Si) = 157.0 Hz). The IR spectrum (recorded by ATR) shows characteristic B–H and Si–H stretches at 2272.7 (calcd. 2273.4) and 2032.6 (calcd. 2053.5) cm^{-1}, respectively.[18]

The molecular structure of [Li(thf)$_2$][**HBSiH**] was determined by single-crystal X-ray crystallography (SCXD; Scheme 3). The length of the central B–Si bond is 2.028(3) Å (calcd. 2.030 Å).[18] The two heteroatom-bonded H atoms were located in the difference Fourier map and freely refined. They adopt an *s-trans* conformation with an H–B–Si–H torsion angle of 180(2)°. [Li(thf)$_2$][**HBSiH**] forms contact-ion pairs in the solid state, in which the [Li(thf)$_2$]$^+$ cation is chelated by the BH-, one *ipso*-C-, and one *ortho*-C atom of the HBFlu unit.

Both M[**HBSiH**] salts are stable toward air and moisture in [D$_8$]THF. More detailed investigations were conducted using Na[**HBSiH**], which turned out to tolerate even added H$_2$O (NMR-spectroscopic control).[18] Until to-date, only very few comparably inert B–Si compounds have been reported,[26] and also the [**HBSiH**]$^-$ isostere [**HBBH**]$^{2-}$ is exceedingly sensitive toward hydrolysis.[18] Treatment of Na[**HBSiH**] with ethereal HCl as the stronger acid led to protonolysis of the B–Si bond with formation of HBFlu·thf and H$_2$SiFlu (approx. 90% selectivity by NMR). Both the B–H and the Si–H bond remained untouched. Thus, since we wanted to address primarily these potentially reactive sites, it seemed advisable to replace the Brønsted acid with a simple Lewis acid, such as Me$_3$SiCl.

By switching from the diborane(6) dianion [**HBBH**]$^{2-}$ to the silylborate monoanion [**HBSiH**]$^-$, a break in symmetry is induced. On the one hand, the resulting perturbation of the system should be small (cf. the diagonal relationship of the periodic table). On the other hand, H$^-$ abstraction from [**HBSiH**]$^-$ results either in a neutral borane or in a formal silylium-cation fragment, which should result in significant reactivity differences between the B–H and Si–H bonds. A particularly important question in this context would be to what extent the H atom that remains after H$^-$ abstraction can adopt a bridging position between B and Si (**BHSi** in Scheme 2;

compare the B(μ-H)B 2e3c bond in the crystallographically characterized isostere [**BHB**]$^-$).

Outcomes of H$^-$ abstractions from M[HBSiH] with Me$_3$SiX (X = Cl, Br) in the presence of no ligand, the strong ligand py, or the weak ligand thf

We first treated Li[**HBSiH**] with 1 equiv. of Me$_3$SiCl in the non-coordinating solvent C$_6$D$_6$, but obtained no indication of **BHSi** and only observed the unselective decomposition of the starting material (along with Me$_3$SiH as the only Me$_3$Si-containing species detectable by NMR). To test whether at least the initial step of the reaction cascade(s) can be conducted selectively, we repeated the experiment in the presence of 3 equiv. of pyridine (py) and quantitatively obtained the B–py adduct (**py**)**BSiH** (Scheme 4). Next, we confirmed that (**py**)**BSiH** generation indeed begins with B–H-bond activation and not with Si–H-bond activation accompanied by a subsequent 1,2-H shift: An isotopic-labeling experiment using Li[**DBSiH**] and Me$_3$SiCl fittingly furnished (**py**)**BSiH** and Me$_3$SiD as sole products. Can the strong donor py be replaced with the weaker ligand thf to approach the putative free borane **BHSi** more closely? When H$^-$ abstraction from Li[**HBSiH**] was carried out in [D$_8$]THF, Li[**HBSiCl**] was generated, while a significant amount of
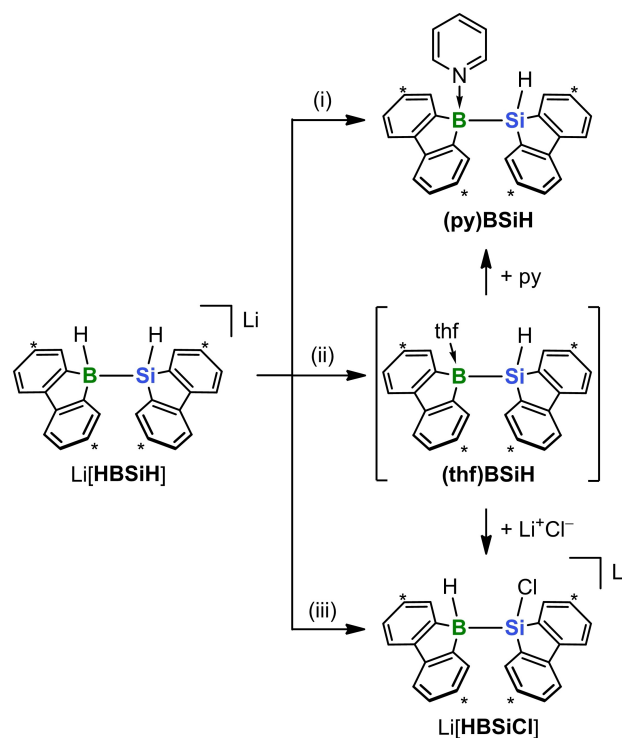
Scheme 4. Divergent reaction behavior after H$^-$ abstraction from Li[**HBSiH**] with Me$_3$SiX (X = Cl, Br). Carbon atoms marked with asterisks bear *t*Bu substituents. (i) 1 equiv. Me$_3$SiCl, 3 equiv. py, C$_6$D$_6$, room temperature, quantitative conversion to (**py**)**BSiH**; (ii) 5 equiv. Me$_3$SiBr, [D$_8$]THF, −30°C, characterized by NMR; (iii) *without 12-c-4*: 10 equiv. Me$_3$SiCl, [D$_8$]THF, room temperature, 90% conversion to Li[**HBSiCl**]; *with 12-c-4*: 2 equiv. 12-c-4, 30 equiv. Me$_3$SiCl, THF, room temperature, quantitative conversion to [Li(12-c-4)$_2$][**HBSiCl**], 85% yield.

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residual starting material Li[**HBSiH**] remained (approx. ratio = 2:1 after 2 d). Full conversion of Li[**HBSiH**] was reached by using 10 equiv. rather than 1 equiv. of Me_3SiCl. By this protocol, Li[**HBSiCl**] formed with about 90% selectivity (Scheme 4);[27] among the two side products, we identified HBFlu·thf. In the presence of 12-crown-4, these side products do no longer occur ([Li(12-c-4)₂][**HBSiCl**] was isolated in 85% yield; the amount of Me_3SiCl required to drive the reaction to completion increased from 10 to 30 equiv.). All in all, we conclude that the two pairs Li[**HBSiH**]/Me_3SiCl and Li[**HBSiCl**]/Me_3SiH are engaged in a dynamic equilibrium, as can be rationalized by the fact that the underlying transformation comes close to an identity reaction (see also the corresponding DFT calculations below).

The most obvious route to Li[**HBSiCl**] would proceed via mere H/Cl exchange at the Si center of Li[**HBSiH**] and thus, in stark contrast to the first case, require an initial Si—H-bond activation. As an alternative, the reaction could again be initiated by H⁻ abstraction from the B atom, followed by a rearrangement sequence eventually furnishing Li[**HBSiCl**]. To distinguish between both mechanistic scenarios, we monitored the conversion by low-temperature NMR spectroscopy.[28] Given that even at the moderately low temperature of −30 °C, Li[**HBSiH**] and Me_3SiCl (5 equiv.) behaved inert toward each other, we replaced Me_3SiCl by the more reactive Me_3SiBr. Now, the reaction mixture gave rise to prominent signals assignable to the (**py**)**BSiH**-analogue (**thf**)**BSiH** already at −30 °C (Scheme 4). Upon warming to room temperature, the primary intermediate (**thf**)**BSiH** was converted to Li[**HBSiBr**] (NMR-spectroscopic control). Since we have no reasons to assume that the reactions with Me_3SiCl and Me_3SiBr follow qualitatively different pathways, we postulate (**thf**)**BSiH** as the common intermediate of Li[**HBSiX**] formation (X = Cl, Br). From this it follows that the reaction between Li[**HBSiH**] and Me_3SiX in C_6D_6/py and [D₈]THF always yields an initial donor adduct (**do**)**BSiH** (do = py, thf). In the case of the stronger ligand py, (**py**)**BSiH** can be isolated; in the case of the weaker donor thf, (**thf**)**BSiH** reacts with the anionic donor X⁻ present in the solution to give Li[**HBSiX**] (presumably via the H-bridged intermediate **BHSi**).

So far, we have developed ways to remove *one* H⁻ substituent from the [**HBSiH**]⁻ anion. Is it possible to exchange *both* H⁻ ligands as well? Since the reaction of Li[**HBSiH**] in [D₈]THF stops at the Li[**HBSiCl**] monohydride stage even in the presence of a vast excess of Me_3SiCl, the amount of added H⁻ scavenger alone does not appear to be a sufficient handle. The key to success ultimately lies in the counter-cation effects mentioned above, as Na[**HBSiH**] could indeed be converted almost quantitatively to the isolable H⁻-free neutral product (**thf**)**BSiCl** (10 equiv. Me_3SiCl, THF; yield losses occurred during workup due to the high solubility of (**thf**)**BSiCl** in *n*-hexane; Scheme 5). Na[**HBSiCl**] was observed as an intermediate by in situ NMR monitoring at room temperature. These results indicate that the first steps of the reaction cascade are the same as for the Li⁺ salt, while the necessary driving force for the follow-up reaction Na[**HBSiCl**]→(**thf**)**BSiCl** must come from the precipitation of NaCl, which is essentially insoluble in THF.[29] As
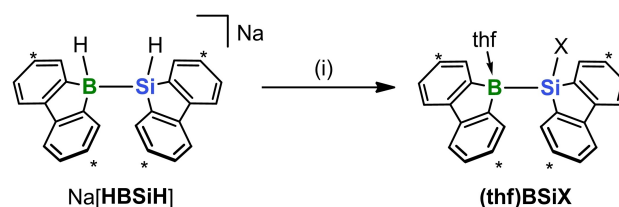
Scheme 5. Synthesis of (**thf**)**BSiX** by twofold H⁻ abstraction from Na[**HBSiH**] using Me_3SiX (X = Cl, Br). Carbon atoms marked with asterisks bear *t*Bu substituents. (i) 10 equiv. Me_3SiX (X = Cl, Br), THF, room temperature, > 95% conversion to (**thf**)**BSiX**, X = Cl: 55% yield, X = Br: 42% yield.

an aside, the use of Me_3SiBr instead of Me_3SiCl furnishes the bromosilane (**thf**)**BSiBr** (Scheme 5).[18]

Characterization of the H⁻-abstraction products (py)BSiH, [Li(12-c-4)₂][HBSiCl], and (thf)BSiCl

NMR spectra of (**py**)**BSiH** and [Li(12-c-4)₂][**HBSiCl**]/(**thf**)**BSiCl** were recorded in C_6D_6 and [D₈]THF, respectively.

The ¹¹B NMR resonance of (**py**)**BSiH** appears at −2.1 ppm, downfield-shifted by about 20 ppm compared to the starting material Li[**HBSiH**], but still in a range characteristic of tetracoordinated boron nuclei.[25] The ²⁹Si chemical shift value of −26.6 ppm remains largely the same as in Li[**HBSiH**]. A signal corresponding to a B-bonded H⁻ substituent is no longer detectable in the ¹H NMR spectrum of (**py**)**BSiH**, whereas a singlet at 5.33 ppm, possessing ²⁹Si satellites and integrating 1 H, can be assigned to the remaining Si*H* proton. The ^1J(H,Si) coupling constant of 174 Hz is larger by 17 Hz than ^1J(H,Si) in Li[**HBSiH**], which, according to Bent's rule,[30] is consistent with a higher group electronegativity of the boryl moiety in (**py**)**BSiH**. The relative integral values of the three py-proton resonances are fitting to the introduction of one py ligand.[31]

As expected, the changes in the NMR parameters of the HBSiCl core in [**HBSiCl**]⁻ are complementary to those of the (py)BSiH core in (**py**)**BSiH**: While the signals of the HB fragment at δ(¹H) = 2.97 ppm and δ(¹¹B) = −21.1 ppm (d, ^1J(B,H) = 94 Hz) remain close to those of [**HBSiH**]⁻, the signal of the silyl fragment at δ(²⁹Si) = 23.7 ppm is shifted to lower field strengths by about 50 ppm and an Si*H* resonance is no longer visible. An intense singlet at δ(¹H) = 3.41 ppm (32 H) corresponds to 2 equiv. of crown-ether ligands and thus supports the proposed ion-pair structure [Li(12-c-4)₂][**HBSiCl**]. The presence of one Cl substituent was confirmed by the characteristic isotope pattern of the [**HBSiCl**]⁻-anion peak at m/z = 603.36 in the LDI mass spectrum.[18]

Upon going from [**HBSiCl**]⁻ to (**thf**)**BSiCl**, the resonance of the B*H* substituent vanishes; the ¹¹B NMR signal loses its doublet multiplicity and shifts from −21.1 to 7.1 ppm. All these observations point toward successful abstraction also of the second H⁻ substituent, accompanied by the formation of a moderately strong thf adduct. ¹H NMR signals of the original protio-thf ligand, which stems from the synthesis of (**thf**)**BSiCl** in [H₈]THF, were found and integration was proportional to

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1 equiv. of protio-thf.[32] The ^{29}Si nuclei ($\delta = 8.6$ ppm) are shielded by 15.1 ppm relative to those of [**HBSiCl**]$^-$.

Compounds **(py)BSiH**, **(thf)BSiCl**, and **(thf)BSiBr** were structurally authenticated by SCXD (Figure 1). **(py)BSiH** crystallizes with two crystallographically independent molecules in the asymmetric unit (**(py)BSiH**^{A}, **(py)BSiH**^{B}), which vary slightly due to different environments in the crystal packing. The B–Si bond lengths are 2.039(3) and 2.061(3) Å, respectively. The sums of CBC and CBSi bond angles amount to 316.6(4)° (**(py)BSiH**^{A}) and 324.4(4)° (**(py)BSiH**^{B}), showing a pronounced pyramidalization of the B atom due to coordination of the py ligand. The B–N distances of 1.608(4) and 1.604(3) Å are similar to the B–N distance in BF$_3$·py (1.604(5) Å).[33] The Si-bonded H atom was located in the difference Fourier map and freely refined. In **(thf)BSiCl**, the key bond lengths are B–Si = 2.026(3) Å, B–O = 1.584(4) Å, and Si–Cl = 2.1106(12) Å. The pyramidalization of the B atom ($\Sigma_{CBE} = 324.8(4)°$; E = C or Si) is comparable to that in **(py)BSiH**^{B}. The torsion angles COG^B–B–Si–COG^{Si} in **(py)BSiH**$^{A/B}$ and **(thf)BSiCl** fall in the range $35 \pm 4°$ (COG$^{B/Si}$: centroid of the respective five-membered ring). Bromosilane **(thf)BSiBr** is isostructural with **(thf)BSiCl** in the crystalline state and therefore does not merit further discussion.

Assessment of the reaction Li[HBSiH]/Me₃SiCl and characterization of the key intermediate BHSi by theory
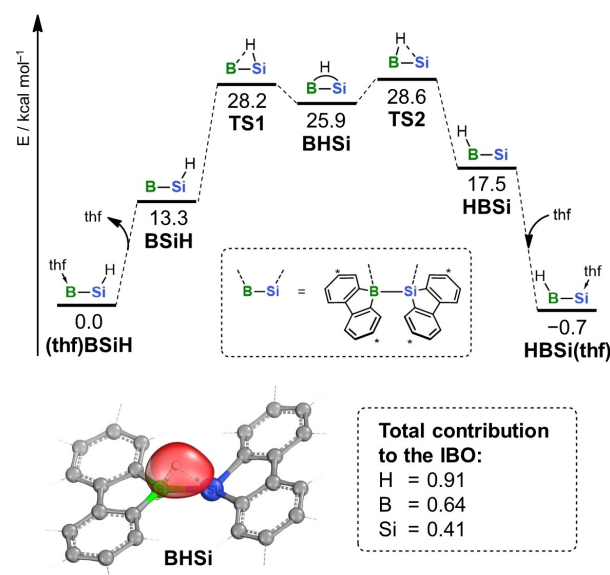
All energies were calculated at the SMD(THF)/PBE0-D3(BJ)/def2-TZVP level of theory, with optimized structures at SMD(THF)/PBE0-D3(BJ)/def2-SVP.

From our previous experiments, we concluded that the reaction between Li[**HBSiH**] and Me₃SiCl in THF leads to a dynamic equilibrium involving the intermediates **(thf)BSiH** and **BHSi** as well as an H$^-$ shift between B and Si. For the overall reaction [**HBSiH**]$^-$ + Me₃SiCl → [**HBSiCl**]$^-$ + Me₃SiH, we computed a free energy of $\Delta G_{298} = -0.2$ kcal mol^{-1} (equilibrium constant $K = 1.4$); inclusion of the complex cation [Li(thf)₂]$^+$ gave a similar picture with $\Delta G_{298} = -0.6$ kcal mol^{-1} ($K = 2.8$).[34] Both K values are close to the experimentally determined $K \approx 2$.

To exclude any necessity of considering counter cations, the energetics of the 1,2-H shift were calculated starting from the NMR-characterized, neutral adduct **(thf)BSiH** (Scheme 6): Barrierless dissociation of the thf ligand affords **BSiH** with a tricoordinated B center and a terminal Si*H* atom. The free
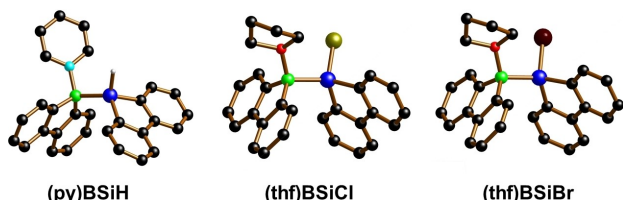
Scheme 6. *Top:* Calculated reaction mechanism for the 1,2-H shift from Si to B via **BHSi**. The reaction starts from **(thf)BSiH** and finally yields **HBSi(thf)**. Carbon atoms marked with asterisks bear *t*Bu substituents. Energies were calculated at the SMD(THF)/PBE0-D3(BJ)/def2-TZVP level of theory, with optimized structures at SMD(THF)/PBE0-D3(BJ)/def2-SVP. *Bottom:* Intrinsic bond orbital of the B(μ-H)Si core in the key intermediate **BHSi**. Total contributions are related to the fraction of electrons of the doubly occupied IBO assigned to each individual atom.
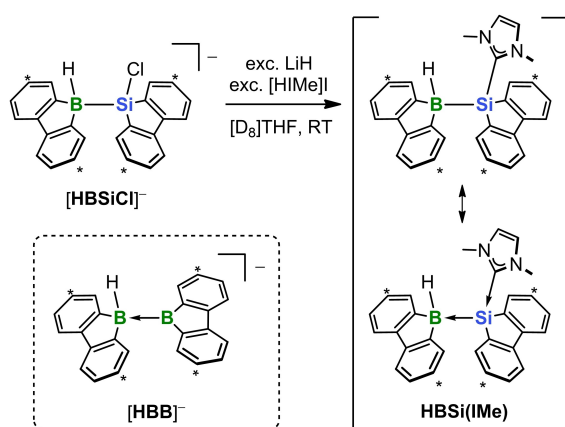
energy of **BSiH** is +13.3 kcal mol^{-1} relative to the starting point. The key intermediate **BHSi** lies 25.9 kcal mol^{-1} above **(thf)BSiH**, in a shallow minimum between **TS1** and **TS2** (28.2 kcal mol^{-1} and 28.6 kcal mol^{-1}, respectively). The H-atom shift from the bridging position in **BHSi** to the terminal position in **HBSi** is exothermic by 8.4 kcal mol^{-1}. We note that the tricoordinated Si atom in **HBSi** has a close intramolecular contact with one of the *ipso*-C atoms of the borafluorene moiety (Si···C = 2.173 Å), which can be traced back to some stabilizing hyperconjugation between the *ipso*-C–B σ bond and the Si(p$_z$) acceptor orbital.[18] Finally, an incoming thf ligand binds to the Si center of **HBSi** without a barrier and generates **HBSi(thf)**, which has essentially the same energy as its isomer **(thf)BSiH**.

The central H atom of **BHSi** interacts with both the B and the Si atom as shown by the intrinsic bond orbital (IBO) of the heteroatom core (total contributions: H = 0.91, B = 0.64, Si = 0.41; Scheme 6).[35] The Wiberg/Mayer bond indices for the B–H and Si–H bond contributions were computed as 0.604/0.453 and 0.333/0.481, respectively (cf. the Mayer bond orders for B₂H₆: B-(μ-H) = 0.47, B–H = 0.98).[36,37] These results consistently indicate the existence of a B(μ-H)Si 2e3c bond supporting the B–Si 2e2c bond in **BHSi**.
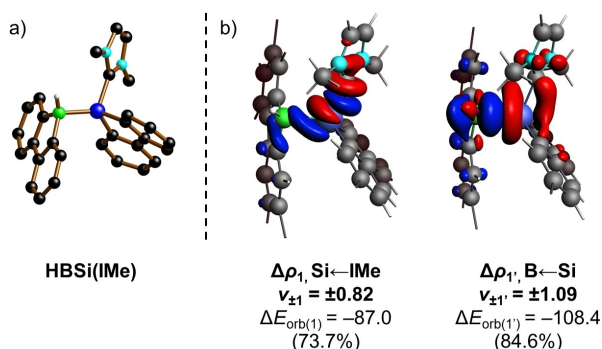
Synthesis and characterization of HBSi(IMe)

We have so far observed that, after H$^-$ abstraction, the neutral donor (do⁰) py tends to prefer the neutral B center, while the anionic donor Cl$^-$ aims for the formal silylium cation. Is it

Figure 1. Solid-state structures of **(py)BSiH**^{A} (left; one of two crystallographically independent molecules), **(thf)BSiCl** (middle), and **(thf)BSiBr** (right). C-bonded H atoms, all *t*Bu substituents, and non-coordinating solvent molecules are omitted for clarity. H: gray, B: green, C: black, N: light blue, O: red, Si: blue, Cl: yellow, Br: brown.

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nevertheless possible to force the system into an isolable HBSi(do⁰) structural motif? To reach this goal, we selected the sterically undemanding 1,3-dimethylimidazol-2-ylidene ligand (do⁰ = IMe), because its carbene-C atom also possesses properties of a carbanionic ligand (cf. the pronouncedly zwitterionic resonance structures of IMe).[38] In a nucleophilic substitution approach, a mixture of the appropriately pre-organized [Li(12-c-4)₂][HBSiCl] and LiH[39] in [D₈]THF was treated at room temperature with the imidazolium iodide [HIMe]I for the in situ release of IMe (Scheme 7). After 5 d, 90% conversion to HBSi(IMe) was achieved. In the NMR spectra, Cl/IMe exchange leads to an upfield shift of the ^{29}Si NMR signal from 23.7 to −16.0 ppm,

while the ^{1}H and ^{11}B resonances of the HB moiety shift by less than 0.2 and 1 ppm, respectively. Integration of the ^{1}H NMR spectrum confirms the presence of one IMe ligand in HBSi(IMe); the ^{13}C resonance of the carbene-C atom appears at 158.4 ppm. The molecular structure of HBSi(IMe) was characterized by SCXD (Figure 2); since the crystals obtained were only very weakly diffracting, we refrain from a detailed discussion of structural parameters.[18]

With (py)BSiH and HBSi(IMe), we have the two possible forms of neutral donor adducts at our disposal, but still with different ligands. To evaluate which of the isomers (do⁰)BSiH or HBSi(do⁰) with do⁰ = py or IMe has the lower energy, we also computed these two pairs (cf. Scheme 6 for the (thf)BSiH/HBSi(thf) pair). The minimum structure (py)BSiH is energetically favored over its isomer HBSi(py) by 4.2 kcal mol⁻¹, consistent with our experimental observations. The isomer pair (IMe)BSiH/HBSi(IMe) exhibits a similar trend with an even more pronounced energy difference of 8.1 kcal mol⁻¹. Thus, B-coordination is apparently thermodynamically preferred for strong neutral donors. The isolation of HBSi(IMe) is most likely enabled by kinetics: We assume that the Si-bonded Cl⁻ ion is replaced by IMe via an S$_N$2-type mechanism. Once coordinated to the Si center, the dissociation of IMe required for the rearrangement HBSi(IMe)→(IMe)BSiH would be associated with a prohibitively high energy penalty (compare the energy difference between HBSi(IMe) and HBSi/IMe of 41.4 kcal mol⁻¹).

The conceptual role model [BHB]⁻ (cf. Scheme 2) of the BHSi chemistry outlined herein shows a reactivity that is best explained by postulating the rearranged isomer [HBB]⁻ as crucial intermediate (Scheme 7) that acts as synthetically useful source of [:BFlu]⁻ anions.[16,40] This suggests that the sp³–sp² diborane [HBB]⁻ should be described as an acceptor-stabilized boryl anion. By the same token, HBSi(IMe) could be viewed as a donor-acceptor-stabilized silylene (Scheme 7). We have answered the question of how valid this view is with the help of energy decomposition analysis in combination with the natural orbitals for chemical valence method (EDA-NOCV) based on the optimized structure for HBSi(IMe): The interaction between neutral closed-shell fragments, i.e., [Flu(H)B-SiFlu] with [:IMe] and [HBFlu] with [:Si(IMe)Flu], rather than between ionic open-shell fragments resulted in the least negative orbital interaction terms ΔE_{orb}.[18] This reveals that the choice of neutral fragments leads to a better description of the considered bonds in HBSi(IMe). For these, only one NOCV pairwise interaction contributes majorly to the corresponding bonding situations. The resulting deformation densities indicate electron-charge flows from the electron-rich to the electron-poor fragments, which are representative of donor-acceptor coordination (Figure 2). Taken together, these results demonstrate that the bonding situation in HBSi(IMe) can best be delineated as that of a donor-acceptor-stabilized silylene.

Scheme 7. Treatment of [HBSiCl]⁻ with exc. LiH/[HIMe]I in [D₈]THF at room temperature gives HBSi(IMe) (> 90% conversion after 5 d). HBSi(IMe) can plausibly be described as donor-acceptor-stabilized silylene, which would render it the NHC-coordinated BSi analog of [HBB]⁻ (dashed box), a crucial isomer to explain observed reactivity patterns of [BHB]⁻ (similar arguments hold for HBSi and HBSi(thf)). Carbon atoms marked with asterisks bear tBu substituents.

HBSi(IMe)

$\Delta\rho_1$, Si←IMe
$\nu_{\pm1} = \pm0.82$
$\Delta E_{orb(1)} = -87.0$
(73.7%)

$\Delta\rho_{1'}$, B←Si
$\nu_{\pm1'} = \pm1.09$
$\Delta E_{orb(1')} = -108.4$
(84.6%)

Figure 2. a) Molecular structure of HBSi(IMe) in the solid state. C-bonded H atoms, all tBu substituents, and non-coordinating solvent molecules are omitted for clarity. H: gray, B: green, C: black, N: light blue, Si: blue. b) Plots of the deformation densities $\Delta\rho_1$ (Si←IMe bond) and $\Delta\rho_{1'}$ (B←Si bond) of the main pairwise contributions associated with the orbital interaction term ΔE_{orb} (kcal mol⁻¹) in HBSi(IMe). Interacting fragments: *left*: [Flu(H)B-SiFlu] with [:IMe]; *right*: [HBFlu] with [:Si(IMe)Flu]. Values in parentheses are the percentage of the pairwise orbital interaction with respect to the total ΔE_{orb} contribution. The eigenvalues $\nu_{\pm k}$ ($k = 1/1'$ for the Si←IMe/B←Si case) correspond to a charge transfer from orbital ψ_{-k} to orbital ψ_{+k} in the NOCV representation. Isovalues: 0.003. Charge flows from red to blue. All C-bonded H atoms and tBu substituents are omitted for clarity.

Conclusion

Molecules containing B–Si bonds are not only interesting in their own right, but are also becoming increasingly important as

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building blocks for organoelement compound synthesis. Compared to silylboranes, silylborates are still more scarce; herein, we disclosed an access route to both compound classes. As decisive asset, the parent silylborate of our studies, M[Flu(H)B–Si(H)Flu] (M[**HBSiH**], M=Li, Na), bears exclusively H and aryl substituents that allow key properties of the B–Si core to be evaluated in their purest form and largely unbiased by ligand artifacts. Apart from B vs. Si, both halves of the molecule are identical, so that their reactivity is only influenced by the different nature of the heteroatoms. Furthermore, the anion [**HBSiH**]⁻ is an isostere of the known diborane(6) dianion [Flu(H)B–B(H)Flu]²⁻ ([**HBBH**]²⁻),[14,15] so that a direct comparison of both species is possible. Important differences are: (i) [**HBSiH**]⁻ is stable under an ambient atmosphere, whereas [**HBBH**]²⁻ is extremely sensitive toward hydrolysis. (ii) H⁻ abstraction from [**HBBH**]²⁻ yields the isolable product [**BHB**]⁻, which contains a central three-membered ring with B(μ-H)B 2e3c bond; the analogous **BHSi** with B(μ-H)Si 2e3c bond is a transient intermediate, but nevertheless very useful for the preparation of differently substituted silylborates and -boranes. H⁻ abstraction from [**HBSiH**]⁻ always occurred at the B center, but a subsequent 1,2-H shift of the remaining Si-bonded H atom is facile. Considering its three sterically unencumbered reactive sites, i.e., the B–H, Si–H, and B–Si bonds, we are optimistic that [**HBSiH**]⁻ will prove to be a similarly fruitful entry into subvalent boron-silicon chemistry as [**HBBH**]²⁻ has been for diborane chemistry.[14–16]

X-ray Crystallography

Deposition numbers 2203993 (for [Li(thf)₂][**HBSiH**]), 2203991 (for [Na(thf)₄][**HBSiH**]), 2203990 (for (**py**)**BSiH**), 2203995 (for (**thf**)**BSiCl**), 2203992 (for (**thf**)**BSiBr**), 2203994 (for **HBSi(IMe)**), and 2203989 (for Cl₂SiFlu) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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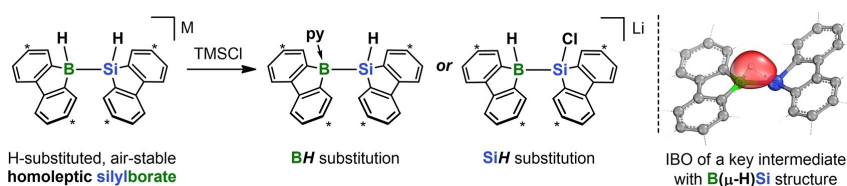
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RESEARCH ARTICLE

H-substituted, air-stable **homoleptic silylborate**

B*H* substitution

Si*H* substitution

IBO of a key intermediate with **B(μ-H)Si** structure

A 1,2-dihydride-substituted silylborate was synthesized via an *"Umpolung"* approach using a chlorosilane and a boron-centered nucleophile. Except for the B–Si vs. B–B cores, the silylborate is identical to a prominent diborane(6) dianion, allowing a direct comparison of their reactivities after H⁻ abstraction. The resulting B(μ-H)E product is isolable for E=B, but constitutes a (still synthetically useful) transient intermediate for E=Si.

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A Hydride-Substituted Homoleptic Silylborate: How Similar is it to its Diborane(6)-Dianion Isostere?