

Synthesis of Alkali Metal Salts of Borylsilyl Anions Utilizing Highly Crowded Silylboranes and Their Properties[#]

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The lithium salt of a borylsilyl anion, [Tbt(Mes)SiBpin][−]Li⁺ (**11**: Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl, pin = pinacolato), was synthesized by the boron–metal exchange reaction of a diborylsilane, Tbt(Mes)Si(Bpin)₂ (**8**), which was synthesized by the insertion of a highly crowded diarylsilylene, Tbt(Mes)Si: (**1**), into the B–B bond of a diborane(4) compound, B₂pin₂. Although a salt of the borylsilyl anion **11** could not be isolated due to its thermal instability, the investigation of the reactivity of the anion revealed that **11** is a possible precursor for Si-functionalized silylboranes as well as Si,Si-difunctionalized silanes. Furthermore, the borylsilyl anion [Tbt(Mes)SiBScat][−] (**27**: Scat = dithiocatecholato), which was synthesized by a procedure similar to that used for **11**, showed a reactivity different from that of **11**. Theoretical calculations for the borylsilyl anions revealed that the anion **27** has a boratasilene character; namely, the Si–B bond has a double-bond character due to the donation of an electron pair of the negatively charged silicon atom into the vacant p-orbital of the adjacent boron atom.

Introduction

In recent decades, the chemistry of silyl anions, which are versatile reagents for the synthesis of various organosilicon compounds, has been greatly developed.¹ In particular, functionalized silyl anions² such as (fluorosilyl)lithiums (R₂SiFLi),³ (alkoxysilyl)lithiums (R₂Si(OR')Li),⁴ and (aminosilyl)lithiums (R₂Si(NR')Li)⁵ have attracted attention from the viewpoints of both fundamental and applied chemistry. In contrast to these actively explored species, borylsilyl anions, silyl anions substituted by boron atoms, have not been investigated until very recently.

The carbon analogue, the carbanions substituted by boron atoms, have been known as boron-stabilized carbanions or borataalkenes.⁶ They were first postulated in 1960s as intermediates in the hydrolysis reactions of gem-diborylalkanes.⁷ In the 1970s, boron-stabilized carbanions were found to be generated by the removal of α- and γ-protons of alkyl- and vinylboranes,

respectively,⁸ and the anions thus generated have been shown to be versatile intermediates in organic syntheses.^{9–13} Furthermore, isolable boron-stabilized carbanions were synthesized and their structural characterization showed them to have significantly short B–C bond lengths.^{14–16}

The chemistry of boron-stabilized carbanions is comparable to that of carbonyl-stabilized carbanions (enolates),^{17,18} which

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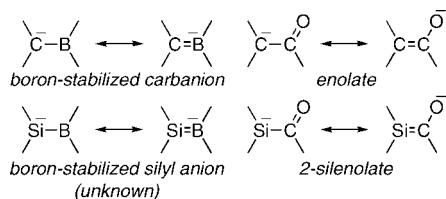
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are one of the most important reagents in organic synthesis. Silicon analogues of enolates (2-silenolates) have been known since 1989,¹⁹ and the first isolable example was reported in 2003,²⁰ while, as mentioned above, silicon analogues of boron-stabilized carbanions have been unexplored.



The absence of reports on borylsilyl anions is mainly due to the lack of appropriate synthetic methods for their precursors.

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Although silylboranes have been extensively investigated,^{21–23} methods for their preparation are severely limited^{24–27} and the routes to silylboranes bearing leaving groups on their silicon atoms have not been established. On the other hand, we have recently investigated the reactions of a highly crowded diarylsilylene (**1**) with various boron compounds in a search for a novel synthetic method for silylborane derivatives. Insertion of silylene **1** into B–H and B–X (X = halogen) bonds proceeded to give the corresponding (hydrosilyl)boranes and (halosilyl)boranes, respectively, which are difficult to synthesize by other methods.²⁸ We describe here a study of the synthesis of borylsilyl anions taking advantage of the silylboranes prepared by our method. During the course of this study, we found that silylene **1** is reactive toward B–B bonds as well as B–H and B–X bonds and that the resulting diborylsilanes are good precursors for borylsilyl anions.²⁹ Although salts of the borylsilyl anions could not be isolated in the present study,³⁰ some reactivities of the anions were examined. Theoretical calculations on the structure of model molecules of the borylsilyl anions are also described.

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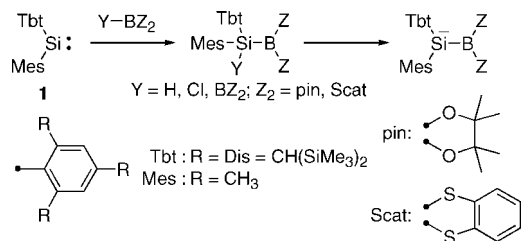
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Results and Discussion

Attempted Synthesis: (a) Deprotonation. First, we examined the deprotonation of (hydrosilyl)borane **2**^{28b} with a base. Although the deprotonation of hydrosilanes to form the corresponding silyl anions is rather exceptional due to their bond polarity (i.e., $\text{Si}^{\delta+}\text{-H}^{\delta-}$ whereas it is $\text{C}^{\delta-}\text{-H}^{\delta+}$ in hydrocarbons), the silyl-metalation reaction of trialkylsilyl-substituted hydrosilanes has been reported very recently.³¹ Inspired by the effect of electropositive silyl groups, we thought that the deprotonation of boryl-substituted hydrosilanes might be possible, because of the electropositive character of boron.³² Accordingly, (hydrosilyl)borane **2**^{28b} was treated with a base (Scheme 1).

The reaction of **2** with LDA (lithium diisopropylamide) for 1 h followed by treatment with chlorotrimethylsilane resulted in formation of hydrodisilane **3** in 15% yield together with recovered starting material (85%, Scheme 1). The structure of **3** was confirmed spectroscopically and crystallographically (Figure 1). This reaction was significantly affected by the reaction time. Thus, after the addition of Me_3SiCl , reaction for 6 h increased the yield of **3** to 35% and decreased the amount of unreacted **2** (11%). In this case, 1,2-dihydrobenzo[*b*]silete **4**³³ and dihydrodisilane **5**³⁴ also were obtained in 7 and 18% yields, respectively (Scheme 1). Much longer reaction time (32 h) afforded **4** as the main product (65%), and no **2** and **3** were obtained (Scheme 1).

The reaction course is reasonably interpreted in terms of the boron–lithium exchange reaction of silylborane **2** (Scheme 2). The reaction of hydrosilyl anion **6** thus generated with chlorotrimethylsilane gives the corresponding trimethylsilylated hydrosilane **3**, while protonation of the anion leads to dihydrodisilane **5**. The formation of **4** is explained by the α -elimination of lithium hydride from the anion **6** giving silylene **1** followed by intramolecular C–H insertion^{33,34} (Scheme 2). Boron–metal exchange reaction of silylboranes has recently been reported as a new route to silyl anions, where more than 2 molar amounts of alkyllithiums, alkylmagnesium bromide, or potassium alkoxide were used.^{22a} Our results show that the boron–metal exchange reaction also proceeds with only an equimolar amount of LDA.

To suppress the nucleophilic attack of the base at the boron atom of **2**, the non-nucleophilic base LiTMP (lithium 2,2,6,6-tetramethylpiperide) was used (Scheme 3). As expected, the

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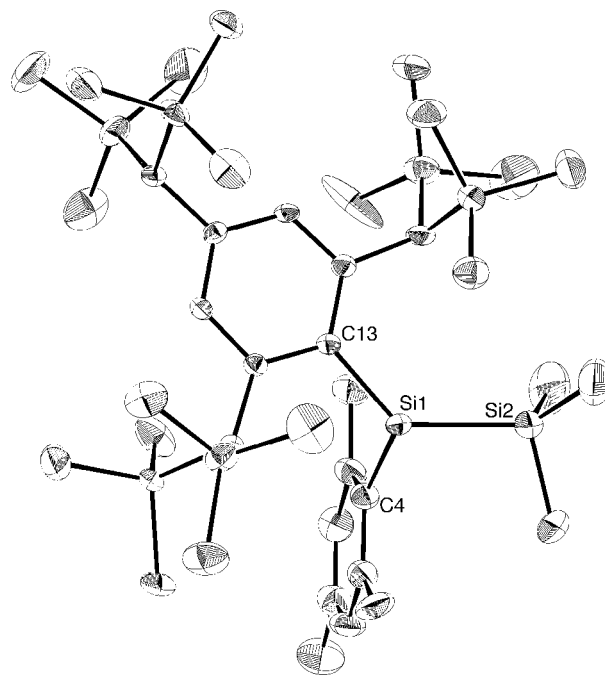
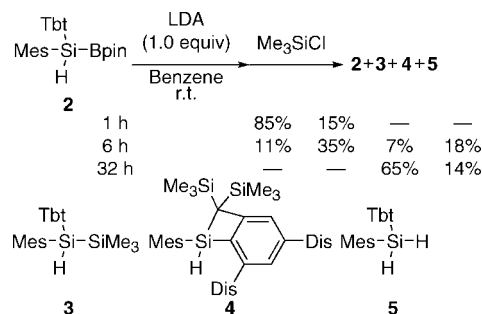
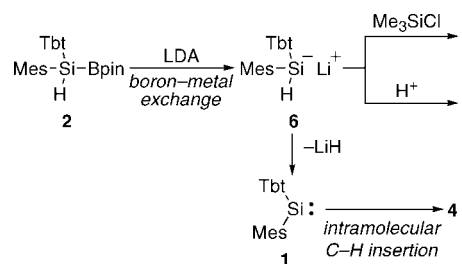


Figure 1. ORTEP drawing of **3** with thermal ellipsoid plots (50% probability).

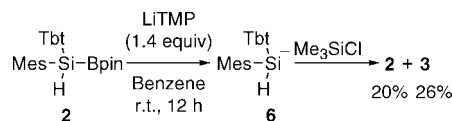
Scheme 1. Reaction of (Hydrosilyl)borane **2** with LDA



Scheme 2. Mechanism for the Reaction of **2** with LDA



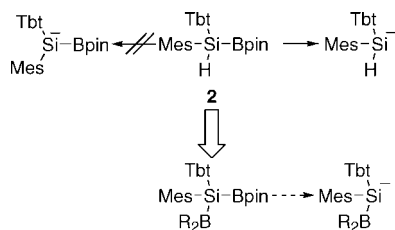
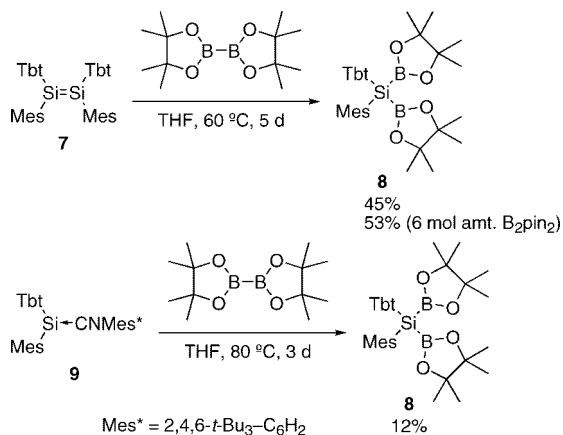
Scheme 3. Reaction of **2** with LiTMP



yield of products derived from the anion **6** decreased; that is, hydrodisilane **3** was obtained in 26% yield and **4** and **5** were not obtained even after a 12 h reaction time (Scheme 3). However, no products derived from Si–H deprotonation were observed.

Synthesis of Diborylsilane: Silylene Insertion into a B–B Bond. Treatment of (hydrosilyl)borane **2** with a lithium base led to boron–lithium exchange rather than deprotonation (*vide supra*). This result suggested that a borylsilyl anion might be

Scheme 4. New Strategy for the Generation of a Borylsilyl Anion

Scheme 5. Synthesis of Diborylsilane **8**

generated if a diborylsilane was used instead of a (hydrosilyl)borane (Scheme 4). Accordingly, the synthesis of a diborylsilane was explored.

When a THF or benzene suspension of disilene **7**³⁴ and bis(pinacolato)diborane(4)³⁵ was heated at 60 °C, the original orange color faded very slowly, giving a colorless solution in 5 days. Diborylsilane **8** was isolated from the reaction mixture by silica gel column chromatography in 45% yield (Scheme 5).²⁹ The formation of **8** is reasonably interpreted in terms of the insertion of silylene **1**, generated from disilene **7**, into the B–B bond of bis(pinacolato)diborane(4). Thus, silylene **1** was found to be reactive toward a B–B bond as well as toward B–H and B–halogen bonds, although B–B bond insertion was much slower than B–H and B–Cl insertion.^{28b} The reaction of silylene–isocyanide complex **9**³⁶ with bis(pinacolato)diborane(4) also gave diborylsilane **8**, but the reaction required a higher temperature and the yield was much lower (Scheme 5).²⁹ This result agrees with the reduced reactivity of a silylene–Lewis base complex compared with a free silylene.³⁷

Although the formal insertion of a silylene, *t*-Bu₂Si:, into a B–B bond of an azadiboriridine has been reported, the reaction was explained in terms of nucleophilic attack of the silylenoid, *t*-Bu₂SiCILi, on the boron atom, because a silylene Me₂Si:, generated by the photolysis of the corresponding cyclohexasilane Si₆Me₁₂, did not show such reactivity.³⁸ Thus, the formation of diborylsilane **8** by the reaction of **7** or **9** with bis(pinacolato)diborane(4) should be of great interest as the first example of the insertion of a silylene into a B–B bond. Moreover, there have been only few reports of compounds containing a B–Si–B

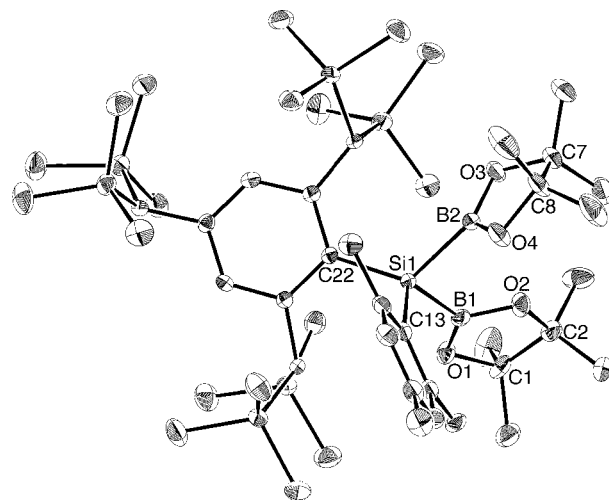


Figure 2. ORTEP drawing of **8** with thermal ellipsoid plots (50% probability).

skeleton.^{38,39} However, silyl-bridged boranes and silaboranes, i.e., cage compounds containing three-center B–Si–B interactions, are well-known.⁴⁰

The ²⁹Si NMR spectrum of diborylsilane **8** shows a broad signal, which is characteristic of a nucleus attached to a boron atom, at –67.6 ppm. This value is similar to those of the related hydrosilanes, i.e., (hydrosilyl)borane **2** (–62.7 ppm) and dihydrosilane **5** (–61.3 ppm). The molecular structure of **8** was determined by X-ray crystallographic analysis, and the ORTEP drawing of **8** is shown in Figure 2. The Si–B bond lengths (2.038(3) Å for Si1–B1 and 2.054(3) Å for Si1–B2) are comparable to those of previously reported silylborane derivatives.^{24h,25,26a,28,39c,41} Interestingly, one of the two dioxaborolane rings in **8** is slightly distorted, while the other is almost planar. The ring puckering coordinates defined by Cremer and Pople⁴² were $q_2 = 0.04$ Å and $\phi_2 = 115.80^\circ$ for the O1–B1–O2–C2–C1 ring and $q_2 = 0.31$ Å and $\phi_2 = 128.00^\circ$ for the O3–B2–O4–C8–C7 ring. The ϕ_2 value of the latter is close to the value (126°) appropriate to one of the twist forms with the twist axis through B2. Similarly distorted BO₂C₂ rings have been reported for R₂C[B(pin)]₂ compounds, though both of the two rings are distorted.⁴³

Attempted Synthesis: (b) Boron–Metal Exchange Reaction. With the diborylsilane in hand, we examined the reaction of **8** with a nucleophile. Although the reactions of **8** with LDA, lithium diethylamide, or potassium hydride did not

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(36) (a) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456–1457. (b) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem.–Eur. J.* **2003**, *9*, 3530–3543. (c) Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1999**, *43*, 1–42.

(38) Luckert, S.; Eversheim, E.; Englert, U.; Wagner, T.; Paetzold, P. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1815–1823.

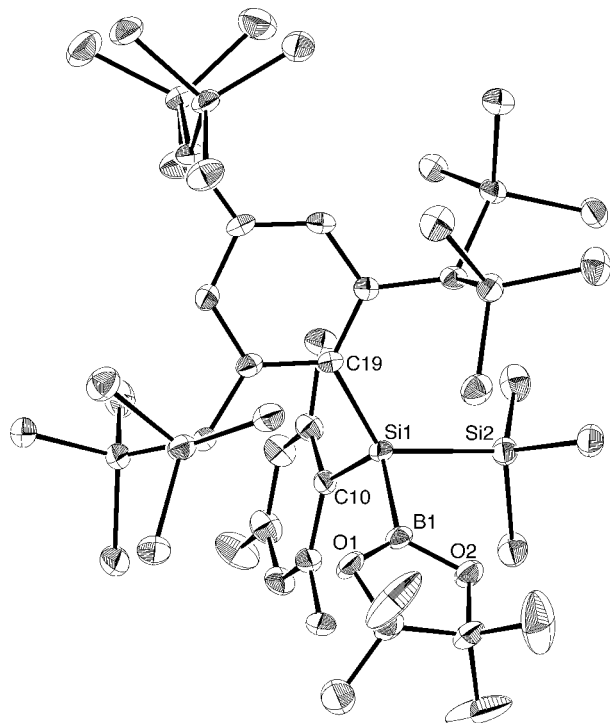
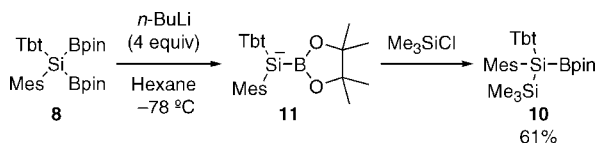


Figure 3. ORTEP drawing of **10** with thermal ellipsoid plots (50% probability, one of the two crystallographically independent molecules).

Scheme 6. Reaction of Diborylsilane **8 with *n*-BuLi**

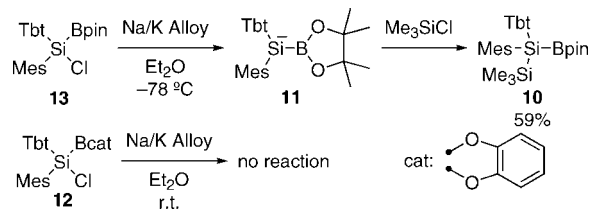


proceed at all, the reaction of **8** with 4 molar equiv of *n*-BuLi in hexane at $-78\text{ }^{\circ}\text{C}$ afforded a deep red solution. Addition of chlorotrimethylsilane gave *Si*-trimethylsilylated silylborane **10** in 61% yield (Scheme 6).²⁹ The formation of trimethylsilyl-substituted silylborane **10** is most likely explained in terms of the reaction of borylsilyl anion **11**, which is generated by boron–lithium exchange between *n*-BuLi and **8**,^{22a} with chlorotrimethylsilane. The formation of **11** by the boron–lithium exchange reaction of **8** is the first example of the generation of a borylsilyl anion.^{29,30}

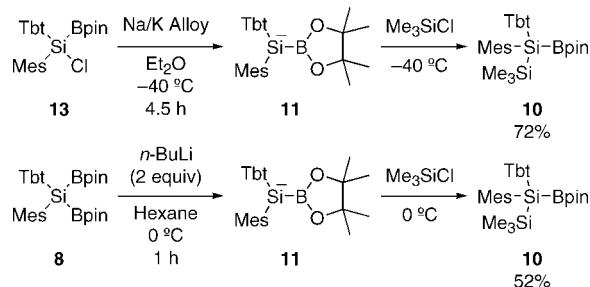
The ²⁹Si NMR spectrum of boryldisilane **10** shows a broad signal at -57.8 ppm. This value is roughly the same range as that of the boron analogue, i.e., diborylsilane **8** (-67.6 ppm), as documented in the literature.⁴⁴ The molecular structure of **10** was determined by X-ray crystallographic analysis, and the ORTEP drawing of **10** is shown in Figure 3.

Attempted Synthesis: (c) Reductive Dehalogenation. We examined the synthesis of borylsilyl anions by the reduction of the corresponding (halosilyl)boranes. The reduction of (chlorosilyl)catecholborane **12**^{28b} with Li, LiNaph, K, or KC₈ afforded complicated mixtures. Treatment of pinacolato derivative **13**^{28b} with K or KC₈ also gave a complicated mixture, while Na/K alloy was found to be an appropriate reductant for the reductive dehalogenation of **13**. Thus, the reaction of **13** with Na/K alloy in diethyl ether at $-78\text{ }^{\circ}\text{C}$ resulted in the formation of borylsilyl anion **11**, which was trapped with chlorotrimeth-

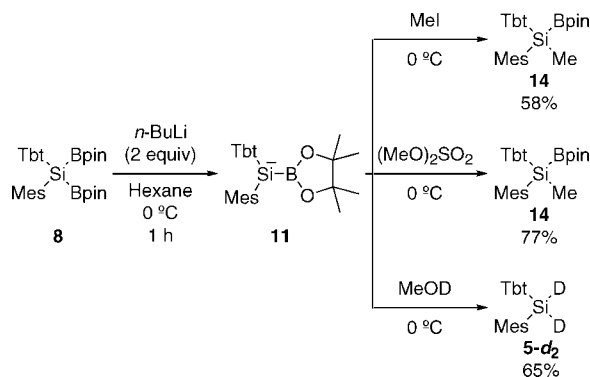
Scheme 7. Reaction of (Chlorosilyl)boranes **12 and **13** with Na/K Alloy**



Scheme 8. Generation of Borylsilyl Anion **11 at a Higher Temperature**



Scheme 9. Reactions of Borylsilyl Anion **11 with Electrophiles**



ylsilane to give **10** in 59% yield (Scheme 7). In contrast, the reaction of **12** with Na/K alloy did not proceed (Scheme 7).

Reactions of Borylsilyl Anion **11 with Electrophiles.** Although spectroscopic observation of the lithium salt of borylsilyl anion **11** has been unsuccessful due to its thermal instability (*vide infra*), the reactions of **11** with several electrophiles were examined. Borylsilyl anion **11** was found to be stable for hours at $-40\text{ }^{\circ}\text{C}$ in diethyl ether or at $0\text{ }^{\circ}\text{C}$ in hexane, respectively, to give the corresponding *Si*-trimethylsilylated silylborane after the addition of chlorotrimethylsilane (Scheme 8). In the latter case, 2 molar equiv of *n*-BuLi were sufficient to consume diborylsilane **8**, while 4 molar equiv were required in the reaction at $-78\text{ }^{\circ}\text{C}$ (Scheme 6).

When borylsilyl anion **11** was treated with iodomethane, the corresponding *Si*-methylated silylborane **14** was obtained in 58% yield (Scheme 9), the structure of which was confirmed spectrographically and crystallographically (Figure 4). The reaction of borylsilyl anion **11** with dimethyl sulfate also afforded **14** in 77% yield (Scheme 9). On the other hand, the reaction of **11** with methanol-*d* gave a different type of product, dideuteriosilane **5-d₂**, in 65% yield (Scheme 9).

One might think that the formation of **5-d₂** is the result of the reaction of dianion species **15** with MeOD. However, the dianion mechanism is excluded because the reaction with other electrophiles gave no disubstituted product. Indeed, the reaction of diborylsilane **8** with an excess (even 10 molar equiv) of *n*-BuLi gave (methylsilyl)borane **14** rather than the dimethyl

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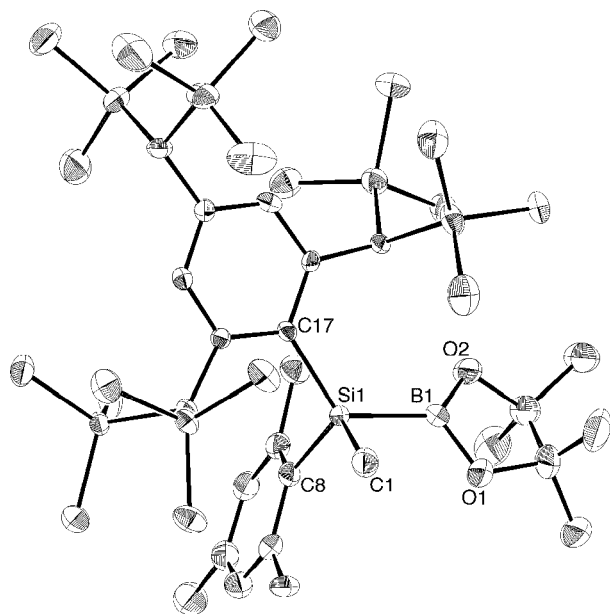
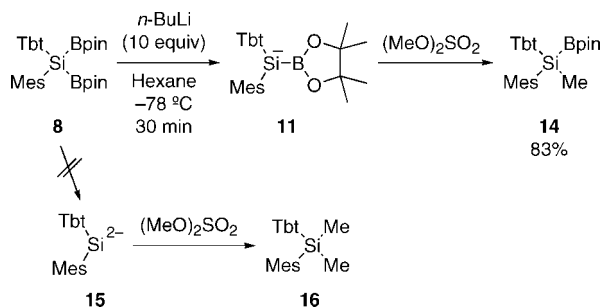
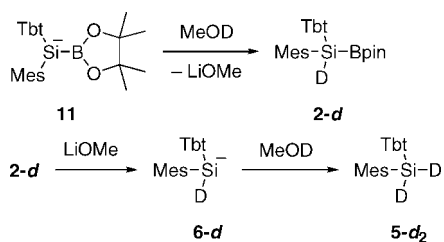


Figure 4. ORTEP drawing of **14** with thermal ellipsoid plots (50% probability).

Scheme 10. Reaction of Diborylsilane **8** with an Excess of *n*-BuLi



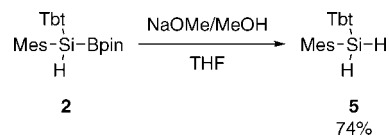
Scheme 11. Plausible Mechanism for the Production of Dideuteriosilane **5-d₂**



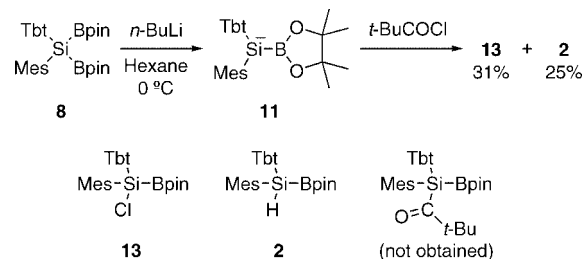
derivative **16** after treatment with an excess (23 molar equiv to **8**) of dimethyl sulfate (Scheme 10). Thus, the formation mechanism of **5-d₂** is interpreted in terms of the stepwise process as follows. The reaction of borylsilyl anion **11** with MeOD initially afforded the corresponding *Si*-deuterated silylborane **2-d** and lithium methoxide. Nucleophilic attack of LiOMe thus formed *in situ* at the boron atom of **2-d** resulted in generation of a deuteriosilyl anion **6-d** by boron–lithium exchange and anion **6-d** was trapped by MeOD to give the final product **5-d₂** (Scheme 11). Although the formation of the intermediary silylborane **2-d** could not be confirmed, this mechanism was supported by the fact that the reaction of the isolated (hydrosilyl)borane **2** with sodium methoxide in methanol gave the corresponding dihydrosilane **5** in 74% yield (Scheme 12).

The reaction of **11** with pivaloyl chloride did not afford the corresponding (acylsilyl)borane but resulted in the formation

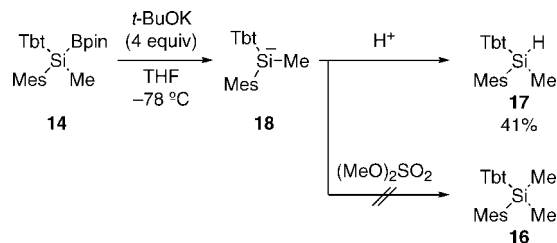
Scheme 12. Reaction of (Hydrosilyl)borane **2** with Sodium Methoxide



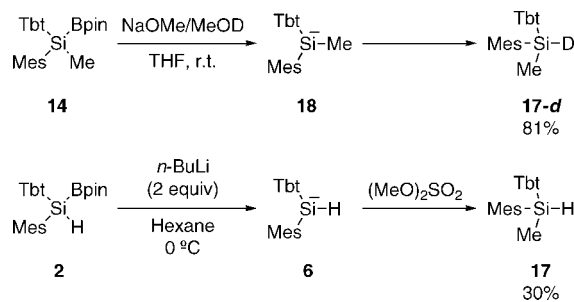
Scheme 13. Reaction of Borylsilyl Anion **11** with Pivaloyl Chloride



Scheme 14. Boron–Metal Exchange Reaction of (Methylsilyl)borane **14**



Scheme 15. Synthesis of Hydrosilane **17**



of (chlorosilyl)borane **13** and (hydrosilyl)borane **2** in 31 and 25% yields, respectively (Scheme 13). Nucleophilic attack of **11** at the carbonyl carbon atom of pivaloyl chloride was suppressed due to the extreme steric congestion, while electron transfer occurred readily to give **13**.

Diborylsilane as a Masked Silicon Dianion. The boron–metal exchange of (methylsilyl)borane **14**, the product of the reaction of borylsilyl anion **11** with dimethyl sulfate, was examined. Such a reaction did not proceed when alkylolithiums were used. The reaction of **14** with 4 molar equiv of potassium *tert*-butoxide followed by treatment with dimethyl sulfate (12 equiv) afforded not dimethylsilylborane **16** but hydrosilane **17** (41%) together with a 59% recovery of starting material (Scheme 14). These results are due to the severe steric hindrance of both (methylsilyl)borane **14** and methylsilyl anion **18**.

The treatment of **14** with an excess of sodium methoxide in methanol-*d* gave hydrosilane **17-d** in 81% yield (Scheme 15). Furthermore, boron–lithium exchange between (hydrosilyl)borane **2** and *n*-BuLi and subsequent treatment with dimethyl sulfate also resulted in formation of **17** in 30% yield together with dihydrosilane **5** (30%) and a 29% recovery of **2** (Scheme 15). The ORTEP drawing of **17** is shown in Figure 5.

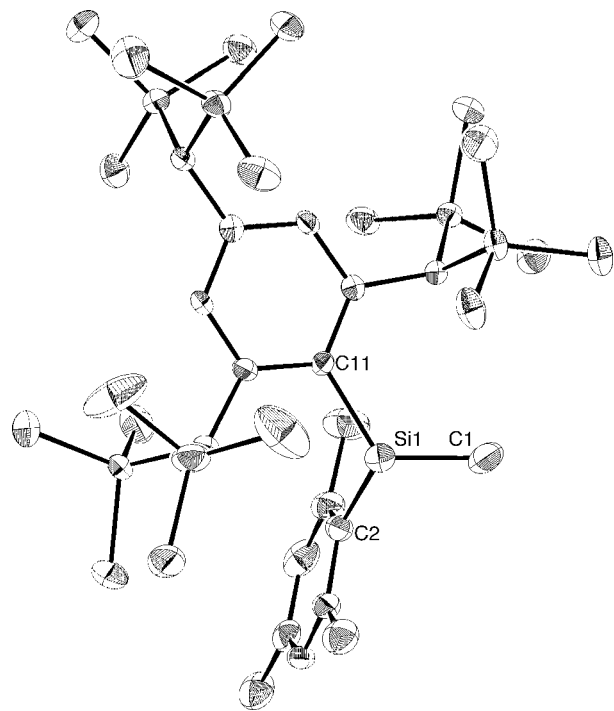
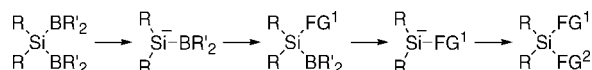
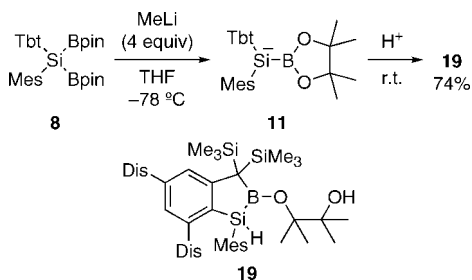


Figure 5. ORTEP drawing of **17** with thermal ellipsoid plots (50% probability).

Scheme 16. Possible Route to *Si*,*Si*-Difunctionalized Silanes Starting from Diborylsilanes



Scheme 17. Formation of 2,3-Dihydro-1*H*-benzo[*d*][1,2]silaborole **19**



These results indicate that borylsilyl anion **11** is a good precursor for *gem*-*Si*-difunctionalized silanes as well as *Si*-functionalized silylboranes.⁴⁵ In this context, a diborylsilane may be regarded as a “masked silicon dianion”, whose reactions provide difunctionalized silanes (Scheme 16).

Rearrangement of Borylsilyl Anion **11.** Although borylsilyl anion **11** is stable at low temperature, it was found that **11** is unstable at room temperature, undergoing a migration reaction. When the mixture of borylsilyl anion **11** generated from **8** and 4 molar equiv of MeLi at $-78\text{ }^\circ\text{C}$ was warmed to room temperature and quenched with dimethyl sulfate (16 equiv), 2,3-dihydro-1*H*-benzo[*d*][1,2]silaborole **19** was obtained as the main product (74%, Scheme 17).

The structure of **19** was supported by NMR, IR, and mass spectra and determined by X-ray crystallographic analysis. The

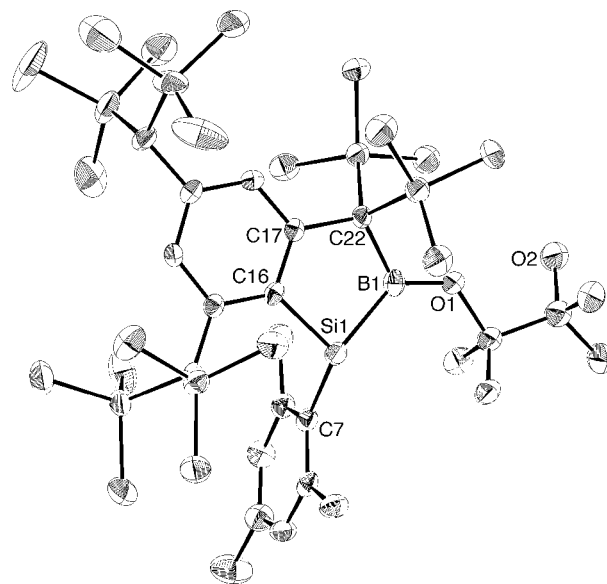


Figure 6. ORTEP drawing of **19** with thermal ellipsoid plots (50% probability).

¹H and ¹³C NMR spectra showed the unsymmetrical structure of the pinacolyl group. In the ¹H NMR spectrum, 7 signals due to methyl groups (4 signals assignable to the pinacolyl and 3 signals assignable to the mesityl group) were observed. In addition, the signal at 2.57 ppm disappeared when D₂O was added to the solution of **19**. In the ¹³C NMR spectrum, 7 signals due to methyl groups and 2 signals due to the quaternary carbon atoms attached to oxygen were observed. The original dioxaborolane ring of **8** obviously had been opened, giving a C–OH group. The presence of the O–H bond was shown by an absorption at 3588 cm⁻¹ in the IR spectra. The ¹¹B NMR spectrum showed a signal at 65.4 ppm, suggesting that at least one of the two B–O bonds had been cleaved. The ²⁹Si NMR spectrum showed a very broad and weak signal at -55.3 ppm, strongly suggestive of a B–Si bond, together with signals assignable to trimethylsilyl groups. The molecular structure of **19** was determined by X-ray crystallographic analysis, and the ORTEP drawing of **19** is shown in Figure 6. The Si–B bond length (2.036(5) Å) is comparable to those of the previously reported silylborane derivatives.^{24h,25,26a,28,39c,41} The five-membered ring in the 2,3-dihydro-1*H*-benzo[*d*][1,2]silaborole skeleton is nearly planar (the ring puckering coordinates:⁴² $q_2 = 0.10$ Å and $\phi_2 = 214.30^\circ$ for the Si1–B1–C22–C17–C16 ring). The formation of **19** is interesting because only a few examples of cyclic silylboranes are known.^{38,39d,46}

On the other hand, a different type of product was obtained when MeOD was used as the trapping agent. The reaction of diborylsilane **8** with MeLi in THF at room temperature after quenching with MeOD afforded deuteriohydrosilane **20-d** (62%), which has a (pinacolato)boryl group at the *o*-benzyl position of the Tbt group (Scheme 18). The reaction of (chlorosilyl)borane

(45) Very recently, the alternative synthetic method for functionalized silylboranes was reported; see: Ohmura, T.; Masuda, K.; Furukawa, H.; Sugimoto, M. *Organometallics* **2007**, *26*, 1291–1294.

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Table 1. Calculated Structures of Boron-Stabilized Silyl Anions and Carbanions (1)^a

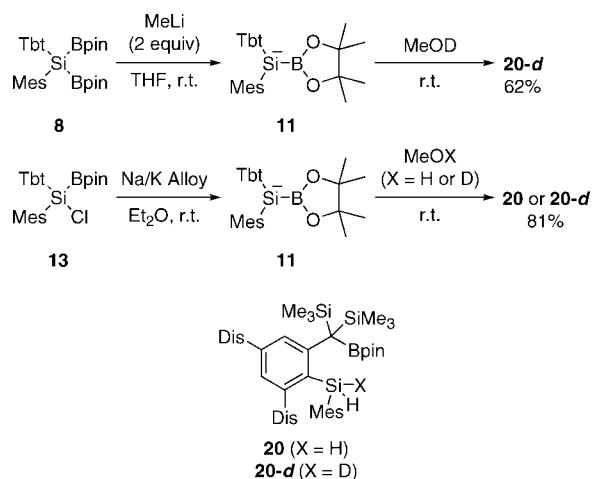
X	Y	Si–B (Å)	X–Si–B (deg)	X–Si–X (deg)	∑Si (deg) ^b	δ _{Si}	δ _B	¹ J(²⁹ Si– ¹¹ B)
H	H	1.880	126.0	106.9	358.8	–52.5	33.6	146.3
H	F	2.008	100.3	99.6	300.2	–222.1	50.6	43.2
F	H	1.907	120.8	98.8	340.5	150.9	–6.5	16.4
F	F	2.101	98.9	98.3	296.2	113.3	25.6	1.9
	[H ₂ C–BH ₂] [–]	1.466	123.8	112.4	360.0	(77.8) ^c	19.2	(90.6) ^d
	[H ₂ C–BF ₂] [–]	1.457	122.7	114.7	360.0	(0.1) ^c	32.5	(137.5) ^d

^a Calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d) level with C_s symmetry. ^b Sum of angles around the central silicon atom. ^c δ_C. ^d ¹J(¹³C–¹¹B).

Table 2. Energy Differences between the Highest and the Lowest Energy Isomers Varying the Torsion Angle^a

molecule	energy difference (kcal/mol)
[H ₂ Si–BH ₂] [–]	60.2
[H ₂ Si–BF ₂] [–]	10.2
[F ₂ Si–BH ₂] [–]	61.8
[F ₂ Si–BF ₂] [–]	5.2
[H ₂ C–BH ₂] [–]	57.3
[H ₂ C–BF ₂] [–]	32.1
H ₃ Si–BH ₂	1.1
H ₂ Si=CH ₂	53.1
[H ₂ Si–CH ₃] [–]	1.7
H ₃ Si–CH ₃	1.4

^a Calculated at the B3LYP/6-31+G(d) level.

Scheme 18. Formation of Dihydrosilane **20** and Deuteriohydrosilane **20-d**

13 with Na/K alloy in diethyl ether at room temperature followed by addition of MeOH or MeOD also afforded dihydrosilane **20** or its deuterio analogue **20-d**, respectively, in 81% yield (Scheme 18).

The structure of **20** was fully supported by its NMR, IR, and mass spectra. The ¹H and ¹³C NMR spectra showed signals assignable to a (pinacolato)boryl group; that is, the original dioxaborolane ring was not opened in contrast to the case of **19**. The ¹¹B NMR spectrum showed a signal at 33.5 ppm, which is in the range for the chemical shifts of (pinacolato)borane derivatives.⁴⁷ The ²⁹Si NMR spectrum showed a sharp signal at –53.8 ppm together with signals due to trimethylsilyl groups. The sharp signal strongly suggests the absence of a B–Si bond.

A plausible but speculative mechanism for the formation of **19** and **20** is shown in Scheme 19. The deprotonation of the

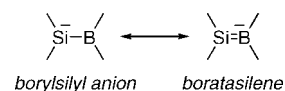
o-benzyl proton of the Tbt group by the silyl anion in borylsilyl anion **11** gives benzyl anion **21**. Similar intramolecular proton abstraction from the *o*-benzyl position of the Tbt group has been found in the group 14 dianionic species [Tbt(Dip)M]^{2–} (Dip = 2,6-diisopropylphenyl, M = Si, Ge, and Sn).⁴⁸ Nucleophilic attack of benzyl anion **21** at the intramolecular boron atom leads to cyclic silylborate **22**. The latter is unreactive toward dimethyl sulfate, and the protonation of alkoxide **23**, which exists in the equilibrium with **22**, affords the cyclic silylborane **19**, bearing a hydroxy group (Scheme 19, path a). On the other hand, the formation of hydrosilane **20** might be interpreted in terms of boron–metal exchange by the methoxide anion generated *in situ*, as in the case of the reaction of borylsilyl anion **11** with MeOH. Hydrosilyl anion **24**, having a borate moiety at the *o*-benzyl position of the Tbt group, was trapped by MeOH to give **20** (Scheme 19, path b).

When the isolated alcohol **19** was allowed to react with potassium hydride and subsequently treated with MeOD, deuteriohydrosilane **20-d** was obtained in 37% yield (Scheme 20). This result strongly supports the existence of an equilibrium between cyclic silylborate **22** and alkoxide **23**.

The thermal instability of borylsilyl anion **11** is probably attributable to localization of the anionic charge at the silicon atom due to the strong electron-donating ability of pinacolato group attached to the boron atom. To elucidate the substituent effect, theoretical calculations were carried out.

Theoretical Calculations on the Structure of Boron-Stabilized Silyl Anions. In this section, we use the term “boron-stabilized silyl anion” for borylsilyl anion according to the carbon analogue, boron-stabilized carbanion. As described in the Introduction section, boron-stabilized silyl anions have two canonical forms: one has a silicon–boron single bond and the localized anion charge at the silicon atom and the other has a silicon–boron double bond and the formal charge at the boron atom. To distinguish them, the former form is referred to as “borylsilyl anion” and the latter is denoted as “boratasilene” (Chart 1).

Chart 1. Canonical Forms for Boron-Stabilized Silyl Anions



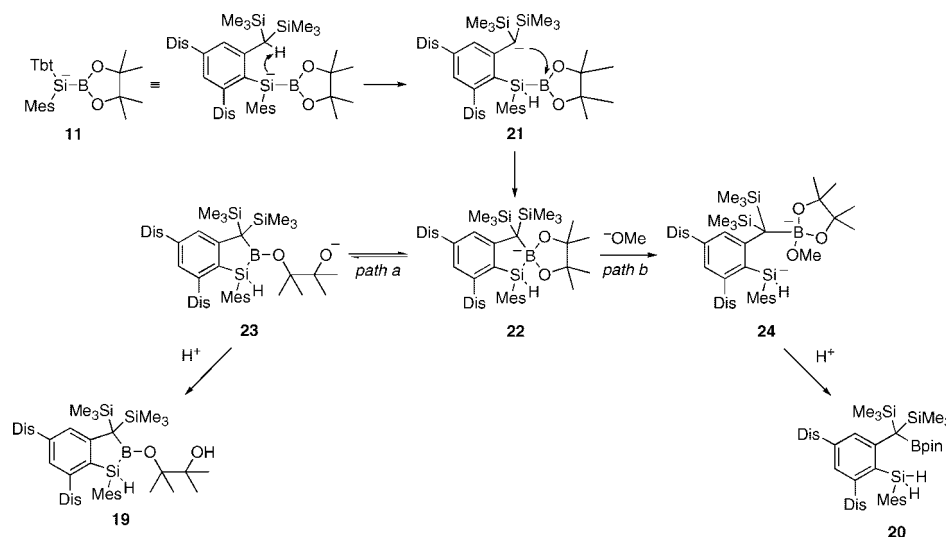
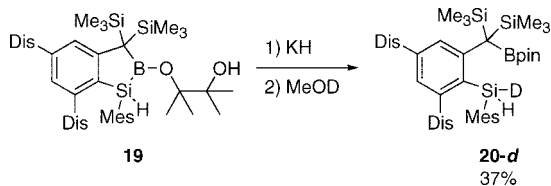
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Table 3. Calculated Structures of Boron-Stabilized Silyl Anions(2)^a

Z	Z'	Si-B (Å)	C-Si-B (deg)	C-Si-C (deg)	ΣSi(°) ^b	δ _{Si}	δ _B	¹ J(²⁹ Si- ¹¹ B)
Me	Me	1.929	117.3/117.3	104.5	339.1	31.3	63.6	95.7
Me	OMe	1.993	107.8/108.5	102.6	318.9	0.4	67.8	62.9
OMe	OMe	2.043	105.6/102.1	99.7	307.4	-34.2	43.5	40.9
OH	OH	2.048	101.9/101.9	100.6	304.3	-34.6	39.9	37.8
NMe ₂	NMe ₂	2.051	106.1/110.8	98.8	315.7	-9.4	47.1	48.0
NH ₂	NH ₂	2.064	100.5/100.4	99.0	299.9	-27.6	41.7	28.5
pin ^c		2.020	102.5/103.0	101.3	306.8	-36.9	44.6	41.1
cat ^d		1.999	103.9/103.9	102.4	310.2	-40.3	48.0	47.2
Scat ^e		1.977	106.8/106.8	103.3	316.8	-1.0	68.4	56.7

^a Calculated at the B3LYP/6-311+G(2d,p)/B3LYP/6-31+G(d) level without any symmetry constraints. ^b Sum of angles around the central silicon atom. ^c Pinacolato. ^d Catecholato. ^e Dithiocatecholato.

Scheme 19. Plausible Mechanism for the Formation of Cyclic Silylborane 19 and Hydrosilane 20**Scheme 20.** Production of Hydrosilane 20 Starting from Alcohol 19

We started from the calculations for the parent molecule ([H₂Si-BH₂]⁻) and its fluorine analogues.⁴⁹ The results are shown in Table 1, together with those of related carbanions (boratamethylenes).^{17a} The parent molecule ([H₂Si-BH₂]⁻) has a planar geometry at the silicon atom and the Si-B distance is quite short (1.880 Å).⁵⁰ This value is comparable to the calculated values for the parent borasilene, a neutral silicon-boron doubly bonded molecule (H₂Si=BH, 1.819 Å)⁵¹ and for the 1,3-disila-2-borataallenic anion ([(H₃Si)₂Si=B=Si(SiH₃)₂]⁻, 1.858 Å).⁵² However, the substitution of hydrogen atoms by fluorine atoms leads to longer Si-B distances and pyramidalized geometry at the silicon atom, indicating that the

borylsilyl anion form becomes dominant. These results are explained as follows: (a) the σ -electron-withdrawing fluorine substituents on the silicon atom stabilize the borylsilyl anion form; (b) the π -electron-donating fluorine substituents on the boron atom destabilize the boratasilene form and thus the borylsilyl anion form becomes more favored. Interestingly, the substitution of hydrogen by fluorine atoms on the boron atom does not affect the structure of boron-stabilized carbanions, in contrast to the corresponding silyl anions. This difference may be attributed to the electropositive character of the silicon atom and/or the lesser tendency of silicon to sp² hybridization.

A rotational barrier around the Si-B bond in boron-stabilized silyl anions is an index of its double-bond character. Although rotational transition states were not calculated, rotational barriers were approximately estimated by PES (potential energy surface) scans.⁵³ The results are summarized in Table 2. The parent molecule ([H₂Si-BH₂]⁻) has a large energy difference between the highest and lowest energy isomers (60.2 kcal/mol). Since this value is much larger than that for the parent silylborane (H₃Si-BH₂, 1.1 kcal/mol), which has an Si-B single bond, it is suggested that the Si-B bond of the parent molecule ([H₂Si-BH₂]⁻) has a double-bond character. In contrast, the fluorine analogue ([F₂Si-BF₂]⁻) shows only a small energy

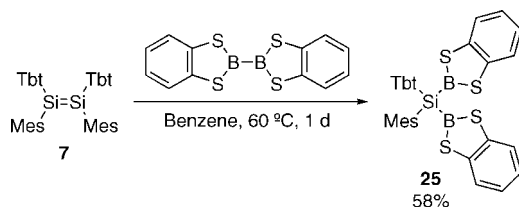
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Scheme 21. Synthesis of Diborylsilane **25**

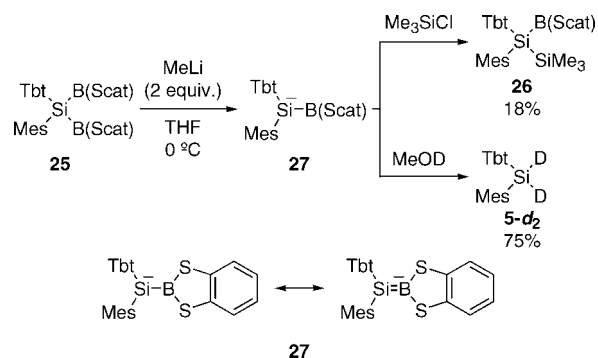
difference (5.2 kcal/mol). However, this value is still larger than that of the parent silylborane. This suggests a small extent of double-bond character in the Si–B bond of the fluorine analogue. It is noteworthy that the methylsilyl anion ($[\text{H}_2\text{Si}-\text{CH}_3]^-$) has a small energy difference (1.7 kcal/mol), and the value is comparable to that of methylsilane ($\text{H}_3\text{Si}-\text{CH}_3$, 1.4 kcal/mol). The results suggested from the PES scans are consistent with those indicated by the calculated structures.

Next, boron-stabilized silyl anions bearing methyl groups on the silicon atom and C, N, O, and S substituents on the boron atoms were calculated; the results are summarized in Table 3. Due to their π -electron donating property, the introduction of nitrogen or oxygen substituents makes the borylsilyl anion form that has longer Si–B distances and pyramidalized geometry at the silicon atom preferable. In contrast, the tetramethyl-substituted derivative ($[\text{Me}_2\text{Si}-\text{BMe}_2]^-$) has a slightly pyramidalized geometry at the silicon atom, and its Si–B distance is rather short (1.929 Å). This molecule can be regarded as a boratasilene. It is noteworthy that the molecule bearing one methyl and one methoxy group on the boron atom still shows a slightly shortened Si–B distance (1.993 Å). Indeed, the isolable example of a boron-stabilized silyl anion, recently reported by Nakata and Sekiguchi, is substituted by one carbon substituent (ethynyl) and one amino group on the boron atom, and the anion has a short Si–B distance.³⁰

While the pinacolato derivative favors the borylsilyl anion form, the less electron-donating catecholato group results in a shortening of the Si–B distance together with an increase of the sum of bond angles around the silicon atom. The substitution of oxygen atoms by sulfur atoms (dithiocatecholato group) leads to further shortening of the Si–B distance and an increase of the angles. The shortening of the Si–B distances is reflected in the larger coupling constants ($^1J(^{29}\text{Si}-^{11}\text{B})$). More significantly, the calculated ^{29}Si NMR chemical shift (–1.0 ppm) of the dithiocatecholato derivative is significantly downfield shifted from the other two oxygen derivatives. This may be due to the larger sp^2 character of the silicon atom; that is, dithiocatecholato derivative has a boratasilene character.

These calculations reveal that the structure of the boron-stabilized silyl anions is significantly influenced by the substituents on the boron atom. Introduction of less electron-donating groups on the boron atom may lead to a greater contribution of the boratasilene form by the delocalization of the anionic charge to the vacant p orbital of the boron atom.

Synthesis of a Borylsilyl Anion Bearing a Dithiocatecholato Group. Inspired by the results of calculations, we chose a borylsilyl anion bearing a dithiocatecholato group as a next target. The thermal reaction of disilene **7** and bis(dithiocatecholato)diborane(4)⁵⁴ afforded diborylsilane **25** containing a dithiocatecholato group (Scheme 21). The reaction is reasonably interpreted in terms of the insertion of silylene **1** into the B–B bond of bis(dithiocatecholato)diborane(4). Although di-

Scheme 22. Boron–Lithium Exchange Reaction of Diborylsilane **25**

borylsilane **25** is air-sensitive, silica gel column chromatography under an argon atmosphere resulted in the successful isolation of **25** in 58% yield. Its ^{29}Si NMR spectrum showed a signal at –58.4 ppm, the value of which is comparable to that of pinacolato derivative **8** (–67.6 ppm).

The reaction of diborylsilane **25** with MeLi followed by addition of chlorotrimethylsilane afforded a complicated mixture, from which the corresponding *Si*-trimethylsilylated silylborane **26** was isolated by PTLC (preparative thin-layer chromatography) in 18% yield (Scheme 22). On the other hand, when the reaction mixture of **25** and MeLi was quenched with methanol-*d*, the corresponding dideuteriosilane **5-*d*₂** was obtained in 75% yield (Scheme 22). These results suggest that the borylsilyl anion **27**, bearing a dithiocatecholato group, had been successfully generated by the boron–lithium exchange reaction of **25**. However, the yield of silylated product **26** was much lower than the yields of the corresponding pinacolato derivative **10** in the trapping reactions of borylsilyl anion **11** with chlorotrimethylsilane (Schemes 6–8). This difference probably is due to the lower reactivity of anion **27** toward chlorosilane than that of **11**. The low reactivity of anion **27** may be attributed to its boratasilene character, in which the anionic charge on the silicon atom is delocalized toward the boron atom.

Experimental Section

General Remarks. All experiments were performed under anhydrous conditions under an argon atmosphere unless otherwise noted. ^1H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{11}B NMR (96 MHz), and ^{29}Si NMR (59 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. The ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the internal residual CHCl_3 (7.25 ppm), $\text{C}_6\text{D}_5\text{H}$ (7.15 ppm), or *sym*- C_2DHCl_4 (5.98 ppm). The ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the carbon-13 signals of CDCl_3 (77.0 ppm), C_6D_6 (128.0 ppm), or *sym*- $\text{C}_2\text{D}_2\text{Cl}_4$ (73.8 ppm). Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. The ^{11}B and ^{29}Si NMR chemical shifts are referenced to the external standards $\text{BF}_3 \cdot \text{OEt}_2$ (0 ppm) and tetramethylsilane (0 ppm), respectively. IR spectra were recorded on a JASCO FT/IR-5300 or a JASCO FT/IR-460 Plus spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. GPC-HPLC was performed on an LC-918 or an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns using chloroform or toluene as an eluent. PTLC was performed with Merck Kieselgel 60 PF₂₅₄.

Materials. All reaction solvents were dried and distilled from CaH_2 , stored over molecular sieves 4A, and then freshly distilled

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from Na/benzophenone ketyl under argon prior to use. Solvents for reactions to generate a borosilyl anion were dried over Na and then a K mirror. Disilene **7**,³⁴ Mes*NC,⁵⁵ silylene–isocyanide complex **9**,³⁶ (hydrosilyl)borane **2**,^{28b} (chlorosilyl)boranes **12** and **13**,^{28b} bis(pinacolato)diborane(**4**),³⁵ and bis(dithiocatecholato)diborane(**4**)⁵⁴ were prepared according to procedures reported in the literature.

Reaction of (Hydrosilyl)borane 2 with LDA. (a) **Reaction time: 1 h.** (Hydrosilyl)borane **2** (33.0 mg, 39.9 μmol) was dissolved in benzene (0.8 mL). To this solution was added a 2.0 M solution of LDA (lithium diisopropylamide) in heptane/THF/ethylbenzene (20.0 μL , 40.0 μmol), and the mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of an excess of chlorotrimethylsilane (20 μL). After removal of the solvent, the residue was separated by HPLC (LC-918, CHCl_3) to give hydrodisilane **3** (4.7 mg, 6.1 μmol , 15%) together with recovery of some of starting material **2** (28.0 mg, 33.8 μmol , 85%). **3**: colorless crystals. Mp: 185.7–187.4 °C. $^1\text{H NMR}$ (CDCl_3): δ –0.18 (s, 9H), –0.13 (s, 9H), 0.02 (s, 9H), 0.04 (s, 9H), 0.09 (s, 9H), 0.10 (s, 18H), 1.28 (s, 1H), 1.89 (br, s, 3H), 2.11 (s, 1H), 2.15 (s, 1H), 2.20 (s, 3H), 2.51 (br, s, 3H), 5.07 (s, 1H, $^1J_{\text{SiH}} = 176$ Hz), 6.28 (s, 1H), 6.41 (s, 1H), 6.61 (br, s, 1H), 6.80 (br, s, 1H). $^{13}\text{C NMR}$ (CDCl_3): δ 0.87 (q), 0.94 (q), 1.06 (q), 1.11 (q), 1.14 (q), 1.57 (q), 1.66 (q), 21.0 (q), 24.9 (q), 26.1 (q), 29.0 (d), 29.3 (d), 30.4 (d), 122.8 (d), 128.10 (s), 128.15 (d), 128.3 (d), 129.1 (d), 132.8 (s), 137.6 (s), 143.0 (s), 144.1 (s \times 2), 150.5 (s), 151.0 (s). $^{29}\text{Si NMR}$ (CDCl_3): δ –54.3, –12.2, 1.6, 1.7, 2.0, 2.1. IR (KBr) 2121 [ν (SiH)] cm^{-1} . LRMS (FAB): m/z 773 [(M + H) $^+$], 757 [(M – Me) $^+$], 699 [(M – SiMe $_3$) $^+$]. HRMS (FAB): m/z 773.4464, calcd for $\text{C}_{39}\text{H}_{81}\text{Si}_8$ 773.4492.

(b) **Reaction time: 6 h.** (Hydrosilyl)borane **2** (75.6 mg, 91.4 μmol) was dissolved in benzene (1.5 mL). To this solution was added a 2.0 M solution of LDA in heptane/THF/ethylbenzene (48.0 μL , 96.0 μmol), and the mixture was stirred at room temperature for 6 h. The reaction was quenched by the addition of an excess of chlorotrimethylsilane (30 μL). After removal of the solvent, the residue was separated by HPLC (LC-918, CHCl_3) to give hydrodisilane **3** (25.0 mg, 32.3 μmol , 35%), the starting material **2** (8.6 mg, 10 μmol , 11%), and a mixture of dihydrobenzo[*b*]silete **4**³³ and dihydrosilane **5**³⁴ (15.9 mg). The mixture of **4** and **5** could not be separated, and the yields of these products were estimated as 7 and 18%, respectively, as judged by the ratio of the integrated intensities of the $^1\text{H NMR}$ signals.

(c) **Reaction time: 32 h.** (Hydrosilyl)borane **2** (52.6 mg, 63.6 μmol) was dissolved in benzene (1.0 mL). To this solution was added a 2.0 M solution of LDA in heptane/THF/ethylbenzene (33.0 μL , 66.0 μmol), and the mixture was stirred at room temperature for 32 h. The reaction was quenched by the addition of an excess of chlorotrimethylsilane (20 μL). After removal of the solvent, the residue was separated by HPLC (LC-908, toluene) to give a mixture of dihydrobenzo[*b*]silete **4** and dihydrosilane **5** (35.3 mg). The mixture of **4** and **5** could not be separated, and the yields of these products were estimated as 65 and 14%, respectively, as judged by the ratio of the integrated intensities of the $^1\text{H NMR}$ signals.

Reaction of (Hydrosilyl)borane 2 with LiTMP (Lithium 2,2,6,6-tetramethylpiperidide). A 1.37 M solution of *n*-BuLi (90 μL , 123 μmol) was added to 2,2,6,6-tetramethylpiperidine (20 μL , 118 μmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. To this was added (hydrosilyl)borane **2** (71.3 mg, 86.2 μmol) in benzene (1.0 mL) at 0 °C, and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of an excess of chlorotrimethylsilane (30 μL). After removal of the solvent, the residue was separated by HPLC (LC-918, CHCl_3) to

give hydrosilane **3** (17.1 mg, 22.1 μmol , 26%) together with recovery of starting material **2** (14.3 mg, 17.3 μmol , 20%).

Synthesis of Diborylsilane 8. (a) **Reaction of Disilene 7 with Bis(pinacolato)diborane(4).** In a 10 mm ϕ Pyrex tube was placed a THF solution (2.4 mL) of a mixture of disilene **7** (151 mg, 108 μmol) and bis(pinacolato)diborane(**4**) (66.7 mg, 263 μmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 122 h, during which time the original orange color gradually disappeared. The tube was opened and solvent was removed. Purification by silica gel chromatography (*n*-hexane/ CHCl_3 = 1:1) afforded diborylsilane **8** (92.4 mg, 96.9 μmol , 45%). **8**: colorless crystals, mp 226–229 °C (dec). $^1\text{H NMR}$ (CDCl_3): δ –0.09 (br, 18H), 0.02 (s, 18H), 0.06 (br, 18H), 1.15 (s, 12H), 1.19 (s, 12H), 1.23 (s, 1H), 2.00 (br, s, 1H), 2.17 (s, 3H), 2.29 (s, 6H), 3.05 (br, s, 1H), 6.23 (s, 1H), 6.36 (s, 1H), 6.64 (s, 2H). $^{13}\text{C NMR}$ (CDCl_3): δ 1.0 (q), 1.5 (q), 1.8 (q), 20.9 (q), 24.8 (q), 25.6 (q), 26.7 (q), 28.0 (d), 28.1 (d), 30.0 (d), 83.6 (s), 122.8 (d), 127.5 (s), 127.8 (d), 128.1 (d), 135.4 (s), 136.7 (s), 142.2 (s), 144.0 (s), 151.8 (s), 152.9 (s). $^{11}\text{B NMR}$ (CDCl_3) δ 35.3. $^{29}\text{Si NMR}$ (CDCl_3) δ –67.6, 1.6, 2.2, 2.7. LRMS (FAB): m/z 975 [(M + Na) $^+$], 953 [(M + H) $^+$]. HRMS (FAB): m/z 953.5840, calcd for $\text{C}_{48}\text{H}_{95}\text{B}_2\text{O}_4\text{Si}_7$: 953.5801. Anal. Calcd for $\text{C}_{48}\text{H}_{94}\text{B}_2\text{O}_4\text{Si}_7$: C, 60.46; H, 9.94. Found: C, 59.96; H, 10.13.

(b) **Reaction of 7 with an Excess of Bis(pinacolato)diborane(4).** In a 10 mm ϕ Pyrex tube was placed a THF solution (1.5 mL) of a mixture of disilene **7** (153 mg, 109 μmol) and bis(pinacolato)diborane(**4**) (178 mg, 701 μmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 186 h, during which time the original orange color gradually disappeared. The tube was opened and solvent was removed. Purification by silica gel chromatography (*n*-hexane/ CHCl_3 = 1:1) afforded diborylsilane **8** (111 mg, 116 μmol , 53%).

(c) **Reaction of Silylene–Isocyanide Complex 9 with Bis(pinacolato)diborane(4).** In a 10 mm ϕ Pyrex tube was placed a THF solution (2.4 mL) of silylene–isocyanide complex **9**, prepared from disilene **7** (155 mg, 111 μmol) and Mes*NC (63.5 mg, 234 μmol) in THF (2.4 mL). Bis(pinacolato)diborane(**4**) (59.1 mg, 233 μmol) was added to this solution. After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 120 h and then at 70 °C for 96 h, during which time the original deep blue color did not change. Further heating at 80 °C for 72 h afforded a pale yellow solution. The tube was opened and solvent was removed. Purification by silica gel chromatography (*n*-hexane/ CHCl_3 = 1:1) afforded diborylsilane **8** (25.8 mg, 27.1 μmol , 12%) together with Mes*NC (62.1 mg, 229 μmol , 98%).

Reaction of Diborylsilane 8 with *n*-BuLi at –78 °C. Diborylsilane **8** (31.2 mg, 32.7 μmol) was dissolved in hexane (1.0 mL) and the solution was cooled to –78 °C. To this solution was added a 0.46 M solution of *n*-butyllithium in hexane (290 μL , 133 μmol). The colorless solution turned yellow. The mixture was stirred at –78 °C for 1 h, and the reaction was quenched by addition of an excess of chlorotrimethylsilane (100 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO_2 /*n*-hexane) to give *Si*-trimethylsilylated silylborane **10** as the main product (18.0 mg, 20.0 μmol , 61%). **10**: colorless crystals, mp 250–253 °C (dec). $^1\text{H NMR}$ (*sym*- $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): δ –0.28 (s, 9H), 0.10 (br, s, 18H), 0.12 (br, s, 18H), 0.13 (s, 9H), 0.31 (s, 9H), 1.33 (s, 1H), 1.35 (s, 6H), 1.37 (s, 6H), 1.68 (s, 3H), 2.16 (s, 1H), 2.20 (s, 3H), 2.28 (s, 1H), 2.60 (s, 3H), 6.34 (br, s, 1H), 6.47 (br, s, 1H), 6.56 (s, 1H), 6.75 (s, 1H). $^{13}\text{C NMR}$ (*sym*- $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): δ 0.9 (q), 1.0 (q), 1.7 (q), 1.9 (q), 2.3 (q), 20.6 (q), 25.6 (q), 25.8 (q), 27.3 (q), 27.9 (q), 29.6 (d), 30.4 (d), 30.5 (d), 83.9 (s), 124.6 (d), 128.0 (d), 128.4 (d), 129.2 (d), 131.1 (s), 133.6 (s), 137.0 (s), 142.1 (s), 142.6 (s), 145.9 (s), 150.0 (s), 153.2 (s). $^{11}\text{B NMR}$ (*sym*- $\text{C}_2\text{D}_2\text{Cl}_4$): δ 35.8. $^{29}\text{Si NMR}$ (*sym*- $\text{C}_2\text{D}_2\text{Cl}_4$): δ –57.8 (NNE, 296 K), –9.0, 1.6, 1.7 (INEPT, 373 K). LRMS (FAB):

(55) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681–1687.

m/z 921 [(M + Na)⁺], 899 [(M + H)⁺], 825 [(M - TMS)⁺], 783 [(M - C₆H₁₂O₂ + H)⁺]. HRMS (FAB): m/z 899.5339, calcd for C₄₅H₉₂BO₂Si₈ 899.5345.

Reaction of (Chlorosilyl)pinacolborane 13 with Na/K Alloy at -78 °C. To a mixture of (chlorosilyl)borane **13** (56.8 mg, 65.9 μmol) and Na/K alloy (14.2 mg) was added ether (2.5 mL) at -78 °C. The resulting suspension was stirred at -78 °C for 12 h and then quenched by the addition of an excess of chlorotrimethylsilane (200 μL). After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give *Si*-trimethylsilylated silylborane **10** as the main product (34.9 mg, 38.8 μmol, 59%).

Reaction of (Chlorosilyl)borane 13 with Na/K Alloy at -40 °C. To a suspension of (chlorosilyl)borane **13** (46.9 mg, 54.4 μmol) in diethyl ether (2.0 mL) was added Na/K alloy (ca. 10 mg) at -40 °C, and the mixture was stirred at -40 °C for 4.5 h. Chlorotrimethylsilane (200 μL) was added, and the mixture was stirred overnight, during which time it was warmed to room temperature. The solvent was evaporated and hexane was added to the residue. After filtration through Celite, the solvent was removed and the residue was separated by PTLC (SiO₂/*n*-hexane) to give *Si*-trimethylsilylated silylborane **10** (35.2 mg, 39.1 μmol, 72%).

Reaction of Diborylsilane 8 with *n*-BuLi at 0 °C. Diborylsilane **8** (44.4 mg, 46.6 μmol) was dissolved in hexane (1.5 mL), and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (220 μL, 94.6 μmol). The initially colorless solution turned deep red. The mixture was stirred at 0 °C for 1 h, and the reaction was quenched by addition of an excess of chlorotrimethylsilane (200 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give *Si*-trimethylsilylated silylborane **10** as the main product (21.8 mg, 24.2 μmol, 52%).

Reaction of Borylsilyl Anion 11 with Iodomethane. Diborylsilane **8** (59.0 mg, 61.9 μmol) was dissolved in hexane (2.0 mL), and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (290 μL, 125 μmol). The colorless solution turned deep red. The mixture was stirred at 0 °C for 30 min., and the reaction was quenched by the addition of an excess of iodomethane (100 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane/CHCl₃ = 2:1) to give *Si*-methylated silylborane **14** as the main product (30.5 mg, 36.2 μmol, 58%). **14**: colorless crystals. Mp: 205–208 °C (dec). ¹H NMR (CDCl₃): δ -0.17 (br, s, 18H), 0.02 (s, 9H), 0.03 (s, 9H), 0.06 (s, 9H), 0.09 (s, 9H), 0.81 (s, 3H), 1.02 (s, 6H), 1.07 (s, 6H), 1.26 (s, 1H), 2.16 (s, 3H), 2.36 (br, 6 + 2H), 6.22 (s, 1H), 6.35 (s, 1H), 6.64 (s, 2H). ¹³C NMR (CDCl₃): δ 0.85 (q), 0.91 (q), 1.0 (q), 1.3 (q), 1.8 (q), 2.1 (q), 5.6 (q), 20.9 (q), 24.1 (q), 25.0 (q), 25.5 (q), 27.4 (d), 27.6 (d), 30.1 (d), 83.5 (s), 122.7 (d), 127.8 (d), 128.9 (d), 130.0 (s), 133.5 (s), 137.4 (s), 142.8 (s), 144.1 (s), 151.3 (s × 2). ¹¹B NMR (CDCl₃): δ 35.7. ²⁹Si NMR (CDCl₃): δ -37.5, 1.6, 1.7, 2.1, 2.4, 2.6, 2.7. LRMS (FAB): m/z 841 [(M + H)⁺], 825 [(M - Me)⁺], 756 [(M - C₆H₁₂)⁺], 725 [(M - C₆H₁₂O₂ + H)⁺]. HRMS (FAB): m/z 841.5137, calcd for C₄₃H₈₆BO₂Si₇ 841.5106.

Reaction of Borylsilyl Anion 11 with Dimethyl Sulfate. Diborylsilane **8** (48.4 mg, 50.8 μmol) was dissolved in hexane (2.0 mL), and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (240 μL, 103 μmol). The resulting red mixture was stirred at 0 °C for 30 min, and the reaction was quenched by the addition of an excess of dimethyl sulfate (100 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane/CHCl₃ = 2:1) to give *Si*-methylated silylborane **14** as the main product (32.8 mg, 39.0 μmol, 77%).

Reaction of Borylsilyl Anion 11 with Methanol-*d*. Diborylsilane **8** (21.6 mg, 22.7 μmol) was dissolved in hexane (1.0 mL), and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (105 μL, 45.2 μmol).

The resulting deep red mixture was stirred at 0 °C for 30 min, and the reaction was quenched by the addition of an excess of methanol-*d* (100 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give dideuteriosilane **5-d₂** as the main product (10.4 mg, 14.8 μmol, 65%).

Reaction of Diborylsilane 8 with an Excess of *n*-BuLi. Diborylsilane **8** (44.0 mg, 46.1 μmol) was dissolved in hexane (2.0 mL) and the solution was cooled to -78 °C. To this solution was added a 1.50 M solution of *n*-butyllithium in hexane (310 μL, 465 μmol). The resulting yellow mixture was stirred at -78 °C for 30 min, and the reaction was quenched by the addition of an excess of dimethyl sulfate (100 μL) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane/CHCl₃ = 2:1) to give *Si*-methylated silylborane **14** as the main product (32.2 mg, 38.3 μmol, 83%).

Reaction of (Hydrosilyl)borane 2 with Sodium Methoxide. (Hydrosilyl)borane **2** (57.9 mg, 70.0 μmol) was dissolved in THF (1.5 mL). To this solution was added a solution of sodium methoxide (66.2 mg) in methanol (1.0 mL), and the mixture was stirred overnight at room temperature. The resulting mixture was poured into water, and the organic layer was extracted with hexane and dried over Na₂SO₄. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give dihydrosilane **5** as the main product (36.1 mg, 51.5 μmol, 74%).

Reaction of Borylsilyl Anion 11 with Pivaloyl Chloride. Diborylsilane **8** (51.3 mg, 53.8 μmol) was dissolved in hexane (2.0 mL) and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (260 μL, 112 μmol). The resulting deep red mixture was stirred at 0 °C for 30 min, and pivaloyl chloride (100 μL) was added at 0 °C. The mixture was stirred at 0 °C for 30 min and overnight, during which time it was warmed to room temperature. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane/CHCl₃ = 3:2) to give (chlorosilyl)borane **13** (14.4 mg, 16.7 μmol, 31%) together with (hydrosilyl)borane **2** (11.1 mg, 13.4 μmol, 25%).

Reaction of Silylborane 14 with Potassium *tert*-Butoxide. To a mixture of silylborane **14** (36.4 mg, 43.3 μmol) and potassium *tert*-butoxide (20.2 mg, 180 μmol) was added THF (1.5 mL) at -78 °C, and the mixture was stirred at -78 °C for 1 h. The reaction was quenched by the addition of an excess of dimethyl sulfate (50 μL). After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give hydrosilane **17** (12.7 mg, 17.7 μmol, 41%) together with recovery of **14** (21.5 mg, 25.5 μmol, 59%). **17**: colorless crystals, mp 198.6–200.4 °C. ¹H NMR (CDCl₃): δ -0.09 (s, 9H), -0.06 (s, 9H), -0.03 (s, 18H), 0.03 (s, 18H), 0.69 (d, 3H, ³J_{HH} = 4.6 Hz), 1.29 (s, 1H), 2.08 (s, 1H), 2.16 (s, 1H), 2.23 (s, 3H), 2.37 (s, 6H), 5.20 (q, 1H, ³J_{HH} = 4.6 Hz), 6.20 (s, 1H), 6.35 (s, 1H), 6.78 (s, 2H). ¹³C NMR (CDCl₃): δ 0.71 (q), 0.79 (q), 0.85 (q), 1.0 (q), 1.1 (q), 1.4 (q), 3.2 (q), 21.0 (q), 24.9 (q), 27.1 (d), 27.3 (d), 30.3 (d), 122.5 (d), 126.0 (s), 127.5 (d), 128.9 (d), 133.5 (s), 138.8 (s), 143.7 (s), 143.9 (s), 151.5 (s), 151.7 (s). ²⁹Si NMR (CDCl₃): δ -34.2, 1.7, 2.1, 2.4. IR (KBr) 2173 [ν(SiH)] cm⁻¹. LRMS (FAB): m/z 714 [(M)⁺], 699 [(M - Me)⁺], 595 [(M - Mes)⁺]. HRMS (FAB): m/z 714.4178, calcd for C₃₇H₇₄Si₇: 714.4175. Anal. Calcd for C₃₇H₇₄Si₇: C, 62.10; H, 10.42. Found: C, 61.98; H, 10.52.

Synthesis of Hydrosilane 17. (a) Reaction of (Methylsilyl)borane 14 with Sodium Methoxide. (Methylsilyl)borane **14** (20.9 mg, 24.8 μmol) was dissolved in THF (1.0 mL). To this solution was added a solution of sodium methoxide (29.7 mg) in methanol-*d* (1.0 mL), and the mixture was stirred overnight at room temperature. The resulting mixture was poured into water, and the organic layer was extracted with hexane and dried over Na₂SO₄. After removal of solvent, the residue was separated with PTLC (SiO₂/*n*-hexane) to give hydrosilane **17-d** as the main product (14.4 mg, 20.1 μmol, 81%).

(b) Reaction of (Hydrosilyl)borane 2 with *n*-BuLi. (Hydrosilyl)borane **2** (71.4 mg, 86.3 μ mol) was dissolved in hexane (2.5 mL) and the solution was cooled to 0 °C. To this solution was added a 0.43 M solution of *n*-butyllithium in hexane (420 μ L, 181 μ mol). The resulting pale yellow mixture was stirred at 0 °C for 6 h, and the reaction was quenched by the addition of an excess of dimethyl sulfate (50 μ L) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give a mixture of hydrosilane **17** and dihydrosilane **5** (36.5 mg) together with recovery of **2** (20.6 mg, 24.9 μ mol, 29%). The mixture of **17** and **5** could not be separated, and the yields of these products were estimated as 30 and 30%, respectively, as judged by the ratio of the integrated intensities of the ¹H NMR signals.

Formation of 2,3-Dihydro-1*H*-benzo[*d*][1,2]silaborole 19. To diborylsilane **8** (122.7 mg, 128.7 μ mol) was added THF (0.2 mL), and the suspension was cooled to -78 °C. To this suspension was added a 1.20 M solution of methyllithium in diethyl ether (430 μ L, 516 μ mol). The resulting deep red mixture was stirred at -78 °C for 30 min and overnight, during which time it was warmed to room temperature. To the resulting yellow suspension was added dimethyl sulfate (200 μ L). After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane/CHCl₃ = 1:1) to give 2,3-dihydro-1*H*-benzo[*d*][1,2]silaborole **19** as the main product (78.9 mg, 95.3 μ mol, 74%). **19**: colorless crystals, mp 195–197 °C (dec). ¹H NMR (CDCl₃, 333 K): δ -0.35 (s, 9H), 0.04 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 0.12 (s, 9H), 0.25 (s, 9H), 1.07 (s, 3H), 1.20 (s, 3H), 1.27 (s, 3H), 1.38 (s, 1H), 1.39 (s, 3H), 1.56 (s, 1H), 1.94 (s, 3H), 2.22 (s, 3H), 2.57 (s, 1H), 2.62 (s, 3H), 4.97 (s, 1H), ¹J_{SiH} = 179 Hz), 6.40 (br, s, 1H), 6.60 (br, s, 1H), 6.67 (s, 1H), 6.87 (s, 1H). ¹³C NMR (CDCl₃, 333 K): δ 0.5 (q), 0.9 (q \times 2), 1.1 (q), 2.1 (q), 4.0 (q), 21.0 (q), 23.5 (q), 24.3 (q), 24.9 (q), 25.3 (q), 25.6 (q), 26.2 (q), 31.0 (d), 31.6 (d), 75.3 (s), 86.8 (s), 122.1 (d), 128.2 (d \times 2), 128.9 (s), 129.2 (d), 131.4 (s), 131.6 (s), 138.9 (s), 144.4 (s), 144.5 (s), 150.2 (s), 155.8 (s), the signal of BC was not observed. ¹¹B NMR (CDCl₃): δ 65.4. ²⁹Si NMR (CDCl₃): δ -55.3, -2.5, -0.3, 1.4, 1.8, 1.9, 2.5. IR (KBr): 3588 [ν (OH)], 2128 [ν (SiH)] cm⁻¹. LRMS (FAB): *m/z* 849 [(M + Na)⁺], 826 [(M)⁺]. HRMS (FAB): *m/z* 826.4877, calcd for C₄₂H₈₃BO₂Si₇ 826.4871. Anal. Calcd for C₄₂H₈₃BO₂Si₇: C, 60.96; H, 10.11. Found: C, 60.74; H, 10.13.

Reaction of (Chlorosilyl)pinacolborane 13 with Na/K Alloy at Room Temperature. (a) **Quenched by MeOH.** To a suspension of (chlorosilyl)borane **13** (65.9 mg, 76.5 μ mol) in diethyl ether (2.0 mL) was added an excess of Na/K alloy (18.5 mg). The mixture was stirred at room temperature for 27.5 h and then quenched by the addition of methanol (100 μ L). After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give dihydrosilane **20** as the main product (51.5 mg, 62.2 μ mol, 81%). **20**: colorless crystals, mp 219–222 °C (dec). ¹H NMR (CDCl₃): δ -0.13 (s, 18H), 0.05 (s, 18H), 0.21 (s, 18H), 1.31 (s, 12 + 1H), 1.69 (s, 1H), 2.17 (br, s, 6H), 2.20 (s, 3H), 5.06 (s, 2H), ¹J_{SiH} = 201 Hz), 6.37 (d, 1H, ⁴J_{HH} = 1.5 Hz), 6.72 (s, 2H), 6.80 (d, 1H, ⁴J_{HH} = 1.5 Hz). ¹³C NMR (CDCl₃): δ 0.3 (q), 1.2 (q), 3.8 (q), 21.0 (q), 24.5 (q), 26.0 (q), 29.6 (d), 30.2 (d), 83.2 (s), 122.5 (d), 128.6 (s), 128.8 (d), 130.6 (s), 131.9 (d), 138.7 (s), 142.6 (s), 144.7 (s), 150.1 (s), 152.6 (s), the signal of BC was not observed. ¹¹B NMR (CDCl₃): δ 33.5. ²⁹Si NMR (CDCl₃): δ -53.8, 2.0, 2.1, 2.3. IR (KBr): 2218 [ν (SiH)], 2175 [ν (SiH)] cm⁻¹. LRMS (FAB): *m/z* 849 [(M + Na)⁺], 826 [(M)⁺], 742 [(M - C₆H₁₂)⁺], 726 [(M - C₆H₁₂O)⁺], 707 [(M - Mes)⁺]. HRMS (FAB): *m/z* 826.4863, calcd for C₄₂H₈₃BO₂Si₇ 826.4871. Anal. Calcd for C₄₂H₈₃BO₂Si₇: C, 60.96; H, 10.11. Found: C, 61.01; H, 10.16.

(b) **Quenched by MeOD.** The same procedure was used in a reaction of (chlorosilyl)borane **13** (67.7 mg, 78.5 μ mol) in diethyl ether (2.0 mL) with an excess of Na/K alloy (18.4 mg) except that methanol-*d* (100 μ L) was added. Dihydrosilane **20-d** was isolated (52.8 mg, 63.7 μ mol, 81%).

Reaction of Diborylsilane 8 with MeLi at Room Temperature. Diborylsilane **8** (127.9 mg, 134.1 μ mol) was dissolved in THF (3.0 mL). To this solution was added a 1.20 M solution of methyllithium in diethyl ether (240 μ L, 288 μ mol). The resulting deep red mixture was stirred at room temperature for 19.5 h, during which time the color of the solution disappeared and a white precipitate formed. The reaction was quenched by the addition of an excess of methanol-*d* (100 μ L) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give dihydrosilane **20-d** as the main product (68.6 mg, 82.8 μ mol, 62%).

Reaction of 2,3-Dihydro-1*H*-benzo[*d*][1,2]silaborole 19 with Potassium Hydride. To a mixture of 2,3-dihydro-1*H*-benzo[*d*][1,2]silaborole **19** (52.4 mg, 63.3 μ mol) and potassium hydride (6.5 mg, 160 μ mol) was added THF (1.5 mL), and the mixture was stirred at room temperature 18.5 h. To this mixture was added an excess of methanol-*d* (150 μ L), and the resulting mixture was stirred overnight. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give dihydrosilane **20-d** (19.6 mg, 23.7 μ mol, 37%).

Reaction of Disilene 7 with Bis(dithiocatecholato)diborane(4). In a 10 mm ϕ Pyrex tube was placed a benzene solution (0.6 mL) of a mixture of disilene **7** (53.1 mg, 38.0 μ mol) and bis(dithiocatecholato)diborane(4) (27.8 mg, 92.0 μ mol). After three freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 20 h, during which time the original orange color gradually disappeared. The tube was opened in a glovebox and solvent was removed. Purification by silica gel chromatography (*n*-hexane/toluene = 2:1) under argon afforded diborylsilane **25** (44.0 mg, 43.9 μ mol, 58%). **25**: colorless crystals, mp 167–171 °C (dec). ¹H NMR (C₆D₆): δ 0.21 (s, 18H), 0.246 (s, 18H), 0.250 (br, 18H), 1.56 (s, 1H), 2.14 (s, 3H), 2.43 (s, 6H), 2.95 (s, 1H), 2.99 (s, 1H), 6.62 (s, 1H), 6.76 (s, 1H), 6.79 (s, 2H), 6.80–6.85 (m, 4H), 7.42–7.48 (m, 4H). ¹³C NMR (C₆D₆): δ 1.3 (q), 2.4 (q), 2.5 (q), 21.0 (q), 29.6 (q), 30.5 (d), 30.8 (d), 31.8 (d), 124.4 (d), 125.5 (d), 126.0 (d), 128.7 (s), 129.8 (d), 130.3 (d), 135.4 (s), 138.9 (s), 144.1 (s), 144.5 (s), 145.2 (s), 153.3 (s), 153.6 (s). ¹¹B NMR (C₆D₆): δ 66.9. ²⁹Si NMR (C₆D₆): δ -58.4, 2.1, 2.7, 3.0. LRMS (FAB): *m/z* 1001 [(M + H)⁺], 985 [(M - Me)⁺], 881 [(M - Mes)⁺], 849 [(M - B(Scat))⁺], 793 [(M - Mes - TMS - Me)⁺], 761 [(M - B(Scat) - TMS - Me)⁺], 731 [(M - Mes - B(Scat) + H)⁺], 715 [(M - Mes - B(Scat) - Me)⁺], 699 [(M - B₂(Scat)₂ + H)⁺]. HRMS (FAB): *m/z* 1001.3616, calcd for C₄₈H₇₉B₂S₄Si₇ 1001.3636. Anal. Calcd for C₄₈H₇₉B₂S₄Si₇: C, 57.56; H, 7.85. Found: C, 56.86; H, 7.80.

Reaction of Diborylsilane 25 with MeLi. (a) **Quench by TMSCl.** Diborylsilane **25** (72.5 mg, 72.4 μ mol) was dissolved in THF (2.0 mL) and the solution was cooled to 0 °C. To this solution was added a 1.20 M solution of methyllithium in diethyl ether (125 μ L, 150 μ mol). The resulting deep red mixture was stirred at 0 °C for 40 min, and the reaction was quenched by addition of an excess of chlorotrimethylsilane (200 μ L) to afford a colorless solution. After removal of solvent, the residue was separated by PTLC (SiO₂/*n*-hexane) to give *Si*-trimethylsilylated silylborane **26** (12.1 mg, 13.1 μ mol, 18%). **26**: colorless crystals. ¹H NMR (C₆D₆): δ 0.11 (s, 9H), 0.15 (s, 9H), 0.23 (s, 9H), 0.24 (s, 9H), 0.34 (s, 9H), 0.35 (s, 9H), 0.47 (s, 9H), 1.54 (s, 1H), 2.07 (s, 3H), 2.32 (s, 3H), 2.44 (s, 3H), 2.62 (s, 1H), 2.69 (s, 1H), 6.63 (s, 1H), 6.70 (s, 1 + 1H), 6.74 (s, 1H), 6.83–6.88 (m, 2H), 7.51–7.56 (m, 2H). ¹³C NMR (C₆D₆): δ 1.3 (q), 1.4 (q), 2.57 (q), 2.64 (q), 3.1 (q), 3.4 (q), 20.9 (q), 29.3 (q), 29.8 (q), 30.3 (d), 30.6 (d), 30.7 (d), 123.9 (d), 125.5 (d), 125.8 (d), 129.3 (d), 129.9 (d), 130.1 (d), 131.4 (s), 134.1 (s), 138.4 (s), 143.3 (s), 144.2 (s), 144.6 (s), 145.4 (s), 152.8 (s), 153.2 (s). ¹¹B NMR (C₆D₆): δ 65.7. LRMS (FAB): *m/z* 923 [(M + H)⁺], 907 [(M - Me)⁺], 849 [(M - SiMe₃)⁺]. HRMS (FAB): *m/z* 923.4250, calcd for C₄₅H₄₄BS₂Si₈: 923.4262. Anal. Calcd for C₄₅H₄₄BS₂Si₈: C, 58.51; H, 9.06. Found: C, 58.30; H, 9.24.

Table 4. Crystallographic Data for **3**, **8**, **10**, **14**, **17**, and **19**

	3	8	10	14	17	19
formula	C ₃₉ H ₈₀ Si ₈	C ₄₈ H ₉₄ B ₂ O ₄ Si ₇	C ₄₅ H ₉₁ BO ₂ Si ₈	C ₄₃ H ₈₅ BO ₂ Si ₇	C ₃₇ H ₇₄ Si ₇	C ₄₂ H ₈₃ BO ₂ Si ₇
fw	773.75	953.48	899.71	841.55	715.59	827.52
cryst size (mm)	0.25 × 0.25 × 0.25	0.35 × 0.25 × 0.15	0.40 × 0.35 × 0.20	0.30 × 0.15 × 0.05	0.40 × 0.25 × 0.20	0.35 × 0.20 × 0.10
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>C</i> 2/ <i>c</i> (#15)
<i>a</i> (Å)	9.708(3)	12.189(4)	13.100(7)	9.220(6)	11.384(4)	35.738(19)
<i>b</i> (Å)	14.996(4)	13.204(5)	20.193(10)	12.874(8)	13.277(5)	13.262(6)
<i>c</i> (Å)	17.847(5)	19.744(7)	24.014(11)	23.730(14)	15.422(5)	22.777(12)
α (deg)	79.350(7)	79.858(14)	65.154(12)	100.332(6)	79.505(9)	
β (deg)	87.704(10)	72.051(13)	78.169(12)	92.284(9)	80.473(9)	110.042(8)
γ (deg)	81.536(7)	78.938(16)	88.869(18)	108.119(12)	87.062(9)	
<i>V</i> (Å ³)	2525.4(12)	2943.3(17)	5626(5)	2620(3)	2259.9(14)	10141(9)
<i>Z</i>	2	2	4	2	2	8
<i>D</i> _{calc} (g cm ⁻³)	1.018	1.076	1.062	1.067	1.052	1.084
μ (cm ⁻¹)	2.36	1.99	2.22	2.13	2.34	2.19
no. of indep reflns/params	8683/449	10 158/579	18 704/1065	9040/505	7801/420	8933/495
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0948	0.0523	0.0605	0.0790	0.0854	0.0859
<i>wR</i> ₂ (all data)	0.2775	0.1221	0.1481	0.2138	0.2193	0.1804
goodness of fit	1.065	1.075	1.079	1.071	1.065	1.149

(b) **Quench by MeOD.** The same procedure was used in the reaction of diborylsilane **25** (54.2 mg, 54.1 μ mol) with methyl-lithium in diethyl ether (90 μ L, 108 μ mol), with subsequent quench by an excess of methanol-*d* (50 μ L). Dideuteriosilane **5-d**₂ (28.7 mg, 40.8 μ mol, 75%) was obtained.

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 98 M or Gaussian 03 M programs⁴⁹ with density functional theory at the B3LYP level.⁵⁶ The structural optimization was performed at the B3LYP/6-31+G(d) level. The NMR chemical shifts were calculated at the GIAO-B3LYP/6-311+G(2d,p) level. Reference molecules for the chemical shifts were also calculated at the same level: Si(CH₃)₄ for Si (0 ppm) and B₂H₆ for B (16.6 ppm).⁵⁷

X-Ray Crystallographic Analysis. Single crystals of **3**, **8**, **10**, **14**, **17**, and **19** suitable for X-ray analysis were obtained by recrystallization from dichloromethane/methanol at room temperature (for **3**, **8**, **14**, **17**, and **19**) and from hexane at room temperature (for **10**). A colorless crystal was mounted on a loop. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å). The structures were solved by a direct method (SIR-97)⁵⁸ and

refined by full-matrix least-squares procedures on *F*² for all reflections (SHELXL-97).⁵⁹ All the non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions. Crystallographic data for **3**, **8**, **10**, **14**, **17**, and **19** are given in Table 4.

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Supporting Information Available: Calculated atomic charges for R₂SiH₂ molecules,³² calculated molecular coordinates for boron-stabilized silyl anions, PES scans for boron-stabilized silyl anions and related molecules, ¹H and ¹³C NMR spectra for new compounds, and full citation of ref 49. X-ray crystallographic data of **3**, **8**, **10**, **14**, **17**, and **19** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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