Contributions to the Chemistry of Boron, 244[+]

Preparation and Structural Characterization of Lithium Silylborates

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Dedicated to Prof. Dr. P. Jutzi on the occasion of his 60th birthday

Borane triethylamine reacts with lithium triphenylsilanide or lithium *tert*-butyldiphenylsilanide with formation of lithium (triphenylsilyl)trihydridoborate or lithium (*tert*-butyldiphenylsilyl)trihydridoborate. Complexation of the lithium cation with various ligands allows the isolation of compounds **1**, **2a**, and **2b**. Trimethoxyborane reacts with lithium trimethyl-

silanide to form lithium tetrakis(trimethylsilyl)borate **3** and lithium tris(trimethylsilyl)methylborate **4**. Mixed single crystals of **3** and **4** show an unexpected coordination of the lithium cation due to the lack of any supporting donor molecule. All silylborates exhibit short Si–B bond lengths compared to tricoordinated silylboranes.

Introduction

In 1961, Seyferth et al. described the preparation of the first tetracoordinated borate containing a silicon−boron bond.[2] The addition of triphenylborane to lithium triphenylsilanide leads to the formation of lithium (triphenylsilyl)triphenylborate. In 1982, we reported the synthesis of (trimethylsilyl)borates from alkoxyboranes and trimethylsilyllithium.[3] Although aryl-/alkylsilylborates have been known for some time, as yet no data concerning their molecular structures are available. In 1993, Schmidbaur et al. described the crystal structure of tricyclohexylphosphane-(trimethylsilyl)borane.[4] Nevertheless, to the best of our knowledge, the structures of anionic silylborates have not yet been determined.

Due to their use in organic synthesis, research is ongoing in the field of hydridoborates.[5] This field could be extended by the preparation of silylhydridoborates, which may possess electronic and/or reducing properties different from those of the known and well-investigated alkyl-/arylhydridoborates.[6]
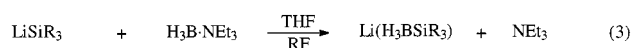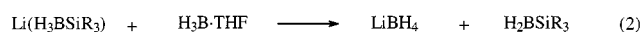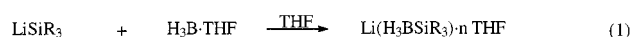
The present report deals with the preparation of new silylhydridoborates, as well as of known (trimethylsilyl)borates. Their molecular structures have been determined by means of X-ray diffraction analysis.

Results and Discussion

One might envisage the most straightforward pathway to monosilyltrihydridoborates as being the addition of BH_3 to

alkali metal silanides, $MSiR_3$, with $BH_3 \cdot THF$ as the source of borane, as shown in Eq. 1. However, reactions of $BH_3 \cdot THF$ with various lithium silanides invariably lead to only small amounts (10−20%) of compounds $Li(H_3BSiR_3)$, as shown by ^{11}B-NMR spectroscopy. The main product is $LiBH_4$, which is formed according to Eq. 2. Separation of $Li(H_3BSiR_3)$ from $LiBH_4$ by fractional crystallization has proved impossible.

In order to prevent rapid hydride transfer from $Li(H_3SiBR_3)$ to BH_3, a less reactive BH_3 source was necessary, a requirement that was met by $BH_3 \cdot NEt_3$. In this case, heating the THF solution under reflux was necessary to complete the reaction (Eq. 3) within a few hours. Under these conditions, the formation of $LiBH_4$ could not be completely suppressed. A silylhydridoborate was, however, the main species generated.

$$LiSiR_3 \quad + \quad H_3B \cdot THF \quad \xrightarrow{THF} \quad Li(H_3BSiR_3) \cdot n\, THF \qquad (1)$$

$$Li(H_3BSiR_3) \quad + \quad H_3B \cdot THF \quad \longrightarrow \quad LiBH_4 \quad + \quad H_2BSiR_3 \qquad (2)$$

$$LiSiR_3 \quad + \quad H_3B \cdot NEt_3 \quad \xrightarrow[RF]{THF} \quad Li(H_3BSiR_3) \quad + \quad NEt_3 \qquad (3)$$

Scheme 1

The triorganylsilyltrihydridoborates **1** and **2** were separated from $LiBH_4$ by crystallization. Compound **2a** was isolated as a THF solvate, while addition of nitrogen-containing ligands to the hexane solution resulted in compounds **1** and **2b**. It is interesting to note that NEt_3 clearly does not coordinate to Li, because **2a** crystallizes from a hexane solution containing NEt_3.
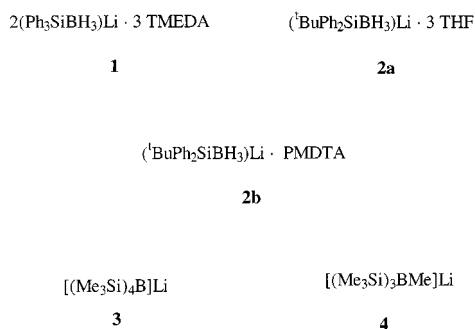
The monosilyltrihydridoborates could not be isolated in the absence of a supporting ligand. In contrast, the tetrasilylborate $LiB(SiMe_3)_4$ (**3**) is known to exist as a ligand-free

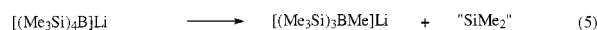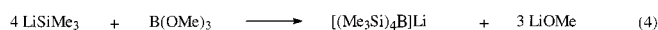compound. It was obtained as described in the literature[3] (Eq. 4). In addition to **3**, LiMeB(SiMe$_3$)$_3$ (**4**) was formed in approximately 10% yield (^{11}B NMR). Compound **4** is accessible directly from LiSiMe$_3$ and MeB(OMe)$_2$.[3]

2(Ph$_3$SiBH$_3$)Li · TMEDA   (^{t}BuPh$_2$SiBH$_3$)Li · 3 THF

1   **2a**

(^{t}BuPh$_2$SiBH$_3$)Li · PMDTA

2b

[(Me$_3$Si)$_4$B]Li   [(Me$_3$Si)$_3$BMe]Li

3   **4**

Scheme 2

4 LiSiMe$_3$ +   B(OMe)$_3$ $\longrightarrow$ [(Me$_3$Si)$_4$B]Li   +   3 LiOMe   (4)

[(Me$_3$Si)$_4$B]Li $\longrightarrow$ [(Me$_3$Si)$_3$BMe]Li   +   "SiMe$_2$"   (5)

Scheme 3

The 10% contamination of **3** by **4** can be removed by crystallization from hexane. However, a hexane solution of pure **3** shows the presence of **4** after storage for several weeks. Therefore, we suggest that compound **4** is formed according to Eq. 5.

It was of interest to compare the structures of these compounds with those of **1** and **2**.

NMR and IR Spectra

The ^{11}B-NMR spectra of the monosilyltrihydridoborates, recorded in C$_6$D$_6$ solution, are almost identical. The chemical shifts δ span the narrow range from δ = −42.5 to −43.8. This is the same region as found for the the ^{11}B resonance of LiBH$_4$ (THF solution, δ = −41.6).[7] A 1:3:3:1 quartet is seen in the proton-coupled ^{11}B-NMR spectra of the silyltrihydridoborates with $^1J(^{11}B,^1H)$ = 78−79 Hz, while LiBH$_4$ is characterized by a quintet with $^1J(^{11}B,^1H)$ = 82.4 Hz.[7] The main differences between the various silyltrihydridoborates lie in the linewidths, which are 22 Hz for **1**, 41 Hz for **2a**, and 20 Hz for **2b**. No ^{29}Si^{11}B coupling could be observed, nor any ^{29}Si signal was observed in the ^{29}Si-NMR spectrum. We attribute this to the same relaxation process as that which is operative in CB units, where the ^{13}C resonance is not usually observable due to strong quadrupolar line broadening.

The quartet structures of the ^{11}B-NMR signals suggest that all the hydrogen atoms bonded to the boron atom are magnetically and chemically equivalent, in spite of the fact that this is not the case in the solid state (vide infra). Therefore, free rotation of the BH$_3$ group about the B−Si bond occurs in solution.

In contrast, the IR spectra of **2a** and **2b** are quite different. **2a** shows two strong BH$_3$ stretching bands at 2284 and 2257 cm^{-1}, while for **2b** three bands are observed [at 2335 (m), 2266 (vs), and 2237 (s) cm^{-1}]. The two strong bands for **2a** and **2b** are consistent with local C_{3V} symmetry, while the band at 2335 cm^{-1} observed for **2b** most probably results from an overtone of the δ(BH$_3$) absorption found at 1167 cm^{-1} (2 × 1167 cm^{-1} = 2334 cm^{-1}). Although the anionic parts of **2a** and **2b** are, at least formally, identical, there is a 20 cm^{-1} difference in the position of the BH$_3$ stretching bands. We attribute this to the influence of the differently coordinated Li cation.

Molecular Structures in the Solid State

Single crystals of **1**, **2a**, and **2b** were obtained, which allowed the determination of their molecular structures in the solid state. These are depicted in Figures 1−3, and relevant molecular parameters are summarized in Table 1.
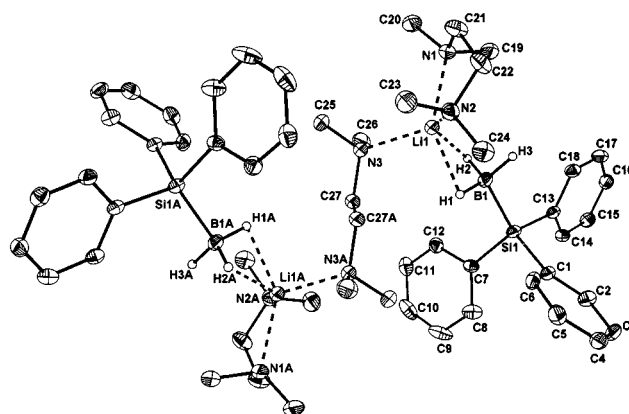

Figure 1. Molecular structure of the TMEDA adduct of lithium (triphenylsilyl)trihydridoborate **1** in the crystal. Thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms (except those on boron) are omitted for the sake of clarity
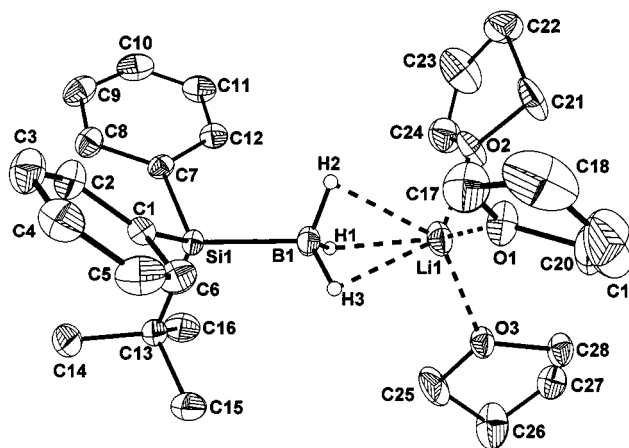
Figure 2. Molecular structure of the THF adduct of lithium (*tert*-butyldiphenylsilyl)trihydridoborate **2a** in the crystal. Thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms (except those on boron) are omitted for the sake of clarity

Lithium (triphenylsilyl)trihydridoborate **1** crystallizes with 1.5 TMEDA ligands per molecule and can be described by the formula [(Ph$_3$SiBH$_3$)Li · TMEDA]$_2$ ·

Figure 3. Molecular structure of the PMDTA adduct of lithium (*tert*-butyldiphenylsilyl)trihydridoborate **2b** in the crystal. Thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms (except those on boron) are omitted for the sake of clarity; only one position of the disordered PMDTA ligand is shown
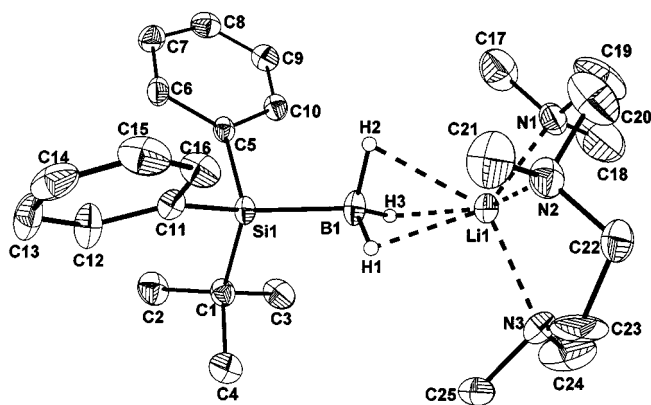
Table 1. Selected bond lengths [Å] and bond angles [°] of compounds **1**, **2a**, and **2b**; estimated standard deviations are given in parentheses

bond lengths	**1**	**2a**	**2b**
B1−Si1	1.984(5)	1.989(2)	1.993(5)
B1−Li1	2.337(8)	2.255(4)	2.252(8)
B1−Li1a	2.337(8)	−	−
Si1−C_{Ph}	1.901(4)	1.906(2)	1.899(4)
		1.907(2)	1.909(4)
Si1−C_{tBu}	−	1.925(2)	1.926(5)
B1−H1	1.07	1.13	1.02
B1−H2	1.13	1.14	1.03
B1−H3	1.15	1.13	1.19
Li1−H1	2.07	2.21	2.09
Li1−H2	2.24	2.13	2.25
Li1−H3	−	2.07	1.97
bond angles			
C_{tBu}−Si1−B1	−	112.9(1)	113.3(2)
C_{Ph}−Si1−B1	111.8(2)	110.5(1)	111.7(2)
	112.7(2)	110.7(1)	110.0(2)
	112.4(2)		
C_{tBu}−S1−C_{Ph}	−	107.1(1)	106.7.(2)
		105.6(1)	109.8(2)
C_{Ph}−Si1−C_{Ph}	106.1(2)	109.8(1)	105.0(2)
	106.3(2)		
	107.2(2)		
Si1−B1−Li1	165.2(3)	175.2(2)	176.2(4)

TMEDA. There is one chelating ligand per Li atom, while the third TMEDA molecule binds to the two centers via one N atom each. Moreover, each Li coordinates to two hydrogen atoms of the BH$_3$ units, making the lithium penta-coordinated. Thus, the SiBH$_3$ unit acts as a $\mu_2{}^1$ ligand with B−H distances of 1.07(3) (H1) and 1.13(3) Å (H2). The molecule has a center of inversion at the midpoint of the C27−C27a bond.

Lithium (*tert*-butyldiphenylsilyl)trihydridoborate · tris(tetrahydrofuran), **2a**, is present as a monomer in the crystal (see Figure 2).[8] In contrast to compound **1**, the Li center in **2a** is hexacoordinated, in this case by three oxygen atoms and three hydrogen atoms. In **2a**, all hydrides of the BH$_3$

unit are involved in Li−H bonding, with the BH$_3$ group acting as a $\mu_3{}^1$ ligand. As compound **2b** is also present as a monomeric molecular species (or contact ion pair) in the solid state, it is apparent that the change from oxygen col-igands (in **2a**) to nitrogen (in **2b**) has no influence on the molecular structure of **2** in the solid state. The B−H atom distances span a range from 1.02 to 1.19(3) Å.

According to Edelstein et al.,[9] the B−M distance is a function of the bonding mode of the BH$_4{}^-$ ligand, this distance decreasing as we move along the series M···H−BH$_3$, M···(H)$_2$BH$_2$, M···(H)$_3$BH, in other words when the BH$_4$ group acts as a $\mu_1{}^1$, $\mu_2{}^1$, or $\mu_3{}^1$ donor. For geometrical reasons, this of course also holds for RBH$_3{}^-$ groups.

Thus, it can be seen that when the R$_3$SiBH$_3{}^-$ group acts as a $\mu_2{}^1$ ligand (in compound of type **1**), the Li···B atom distance is 2.377(8) or 2.49(1) Å, whereas in **2a** and **2b**, with $\mu_3{}^1$-R$_3$SiBH$_3$ groups, this distance is as short as 2.255(4) or 2.252(8) Å. No influence of the coligands (oxygen in **2a**, nitrogen in **2b**) on the B···Li atom distance was observed. Owing to the different coordination of the Li atom in **1** compared with that in **2a** and **2b**, different Si−B−Li bonding angles are found. While **2a** [175.2(2)°] and **2b** [176.2(4)°] show an almost linear array of the Li, B, and Si atoms, an Si−B−Li angle of 165.2(3)° is found for compound **1**. Irrespective of the degree of association and the different BH$_3$···Li interactions, the B−Si bond lengths in **1**, **2a**, and **2b** are equal within the margin of the standard deviation, leading to an average Si−B bond length of 1.988 Å. This distance is significantly shorter than the Si−B bond length found in (*c*-C$_6$H$_{11}$)$_3$P · H$_2$BSiMe$_3$ [2.007(4) Å[4]]. Surprisingly, the Si−B distances in **1**, **2a**, and **2b** are even shorter than those in trivalent silylboranes,[10] where bond lengths between 2.038 and 2.127 Å have been found. This is a remarkable observation because bond lengths of a certain ligand generally increase with increasing coordination number of the central atom; in this case the B−Si bond length to a tetracoordinated boron atom would be expected to be longer than that to a tricoordinated boron species, but in fact the reverse is found. The shortest B−Si bond length found to date is 1.926(2) Å, observed in the three-membered heterocycle 1-(*tert*-butyl)-3-(diisopropylamino)-2,2-(dimesityl)azasilaboriridine.[11]

Single crystals of the trimethylsilylborates **3** and **4** could not be obtained. However, when these compounds were mixed in a 1:1 ratio, single crystals containing **3** and **4** in this ratio were obtained from hexane solution. Figure 4 shows the molecular structure of **3** and Figure 5 the structure of **4**. The packing of the two species in the unit cell is depicted in Figure 6. Selected structural parameters are summarized in Table 2.

As can be seen in Figure 4, the Li atom of compound **3** resides in a cleft formed by three methyl groups bonded to three different Si atoms, and this imposes an almost C_3 point group symmetry on the molecule. It is particularly surprising that the B−Si bond lengths in **3** are nevertheless all equal [B1 to Si1: 2.025(2), to Si2: 2.027(2), to Si3: 2.025(2), to Si4: 2.025(2) Å], in spite of the fact that the Si(3)Me$_3$ group is not involved in the interaction with Li1.
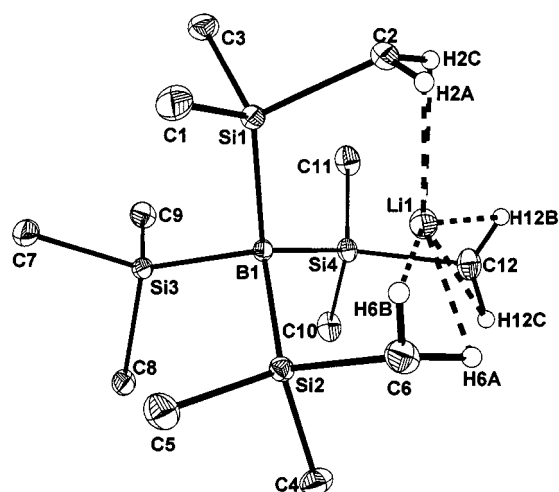
Figure 4. Molecular structure of lithium tetrakis(trimethylsilyl)borate **3** in the crystal. Thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms (except those which show contact to Li) are omitted for the sake of clarity

Figure 5. Molecular structure of lithium methyl tris(trimethylsilyl)-borate **4** in the crystal. Thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms (except those which show contact to Li) are omitted for the sake of clarity
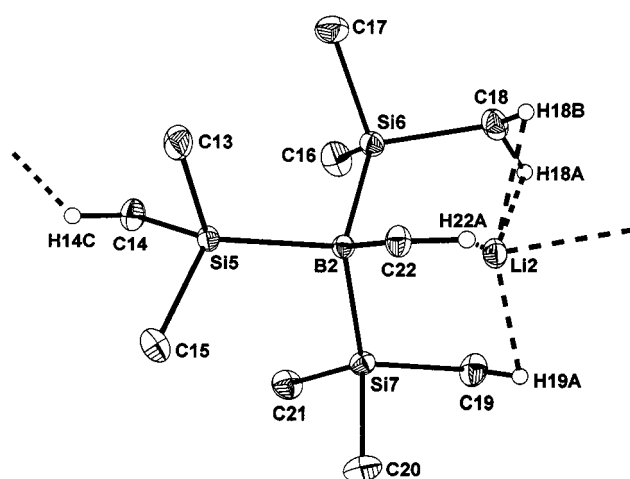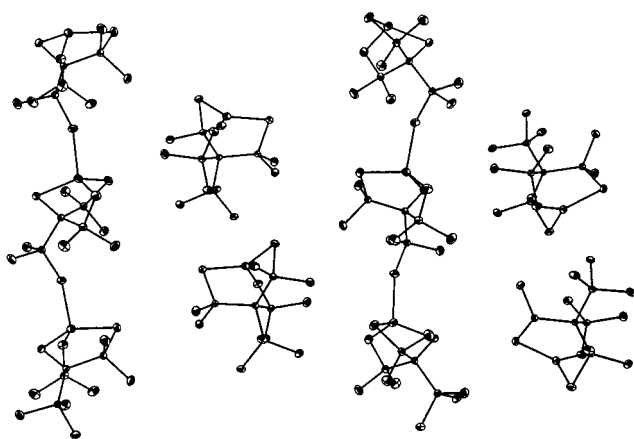

Figure 6. Arrangement of **3** and **4** in the crystal

Table 2. Selected bond lengths [Å] and bond angles [°] of compounds **3** and **4**; estimated standard deviations are given in parentheses

bond lengths	3	4
aver. $Si_{Li}-B$	2.025	2.032
$Si-B$	2.025(2)	2.017(2)
aver. $Si-C_{Li}$	1.917	1.920
aver. $Si-C$	1.884	1.881
$B-Li$	2.387(4)	2.276(4)
$Li\cdots H-C_B$	1.87	–
aver. $Li\cdots H-C_{Si}$	2.19	2.17

bond angles		
$Si-B-Li$	178.9(1)	173.2(1)
aver. $Si_{Li}-B-Si$	105.6	107.2
aver. $Si_{Li}-B-Si_{Li}$	113.0	113.2

The angle $Si3-B1\cdots Li1$ is 178.9(1)°. Moreover, the $Si-B1-Si$ angles of the silyl groups orientated towards Li1 are on average 113.0°, while the average of angles $Si3-B1-Si$ is 105.6°. This demonstrates that the $Li\cdots H$ interaction (average $Li\cdots H$ distance 2.17 Å) leads to a widening of the tetrahedral angle.

Lithium methyl tris(trimethylsilyl)borate **4** exhibits an unsymmetrical structure in the solid state. The Li atom is in contact with a total of five hydrogen atoms, four of which are from the same anionic species, while the fifth is from a neighbouring anion. Therefore, the molecules of **4** are associated so as to form a chain structure. $Li2-H$ distances are on average 2.19 Å for the hydrogen atoms of $SiMe_3$ groups, but are as short as 1.87 Å for the contacts with the hydrogens of the BMe group.

In contrast to the structure of the silylborate **3**, two different $B-Si$ bond lengths are found in compound **4**. The $Si5-B2$ bond measures 2.017(2) Å and is therefore shorter than the $Si6-B2$ and $Si7-B2$ bonds [2.034(2), 2.030(2) Å]. Hydrogen atoms of the $Si(6)Me_3$ and $Si(7)Me_3$ groups coordinate intramolecularly to the Li2 center. The $Si6-B2-Si7$ bond angle is 113.2(1)°, i.e. 3.6° larger than the ideal tetrahedral angle. This deviation, together with the longer $Si-C$ bonds to the $SiMe_3$ groups of Si6 and Si7, indicates that there should be more negative charge on these silyl groups than on that of Si5, and that "hyperconjugation" leads to bond lengthening. Indeed, the $Si-C$ bond lengths of the methyl groups involved in $CH\cdots Li$ interactions are longer [$Si6-C18$, $Si7-C19$: 1.920(2) Å] than all the other $Si-C$ distances (average: 1.881 Å). The fact that Li2 is not located between three $SiMe_3$ groups indicates that BCLi "hyperconjugation" is preferred to BSiLi "hyperconjugation". This is also reflected in a rather long BC bond length of 1.679(3) Å, compared with BC bonds of between 1.621(5) and 1.642(4) Å in LiBMe₄.[12] In this molecule the $Li-B$ atom distance is 2.541(5) Å, in contrast to **4** where it is only 2.276(4) Å, which is even shorter than that in compound **3** [$B\cdots Li1$: 2.387(4) Å].

The packing of the molecules **3** and **4** in the lattice is depicted in Figure 6. There are only van der Waals' contacts

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between hydrogen atoms. The chains of molecule **4** are oriented along the *b* axis.

As has been reported previously,[3] all hydrogen atoms of the tetrakis(trimethylsilyl)borate are equivalent on the NMR timescale. The molecule is thus fluxional, and the same holds true for compound **4**. While it can readily be seen from the crystal structures of **3** and **4** that these compounds will be present as molecules in solution, the process that leads to fluxionality is still unknown. We assume that this does not occur by a dissociative process, but rather by a simultaneous movement of the Li centers with rotation of the SiMe₃ groups about the B−Si bonds.

Conclusion

Lithium silyltrihydridoborates Li(R₃SiBH₃) are accessible by reacting lithium silanides with BH₃ · NEt₃. In contrast to the reaction of lithium organyls with H₃B · NMe₃,[13] no deprotonation at the organyl groups of the amine occurs. Depending on the coligand (THF, TMEDA, PMDTA), either bridged dimeric or monomeric molecules are formed. Two different kinds of hydride bridges B−H···Li are observed, corresponding to μ_2^1- and μ_3^1- BH₃R groups, which are responsible for the association. In contrast, LiB(SiMe₃)₄ is monomeric in the solid state, with the Li center "buried" in a cleft between three SiMe₃ groups. There are six C−H···Li interactions. Only minor distortion of the B(SiMe₃)₄⁻ anion occurs, the most notable feature being the lengthening of the Si−C bonds when H atoms are involved in C−H···Li interactions. This can be explained in terms of "hyperconjugation". LiMeB(SiMe₃)₃ is less symmetrical than **3** because the BMe group is involved in bonding to Li. B−C bond lengthening, which exceeds that observed for LiBMe₄, indicates that BCLi "hyperconjugation" is more pronounced than SiCLi "hyperconjugation".

The structures of **3** and **4** are unique for main group organometallic compounds and it would be interesting to compare them with the structures of LiB(*t*Bu)₄ and LiMeB(*t*Bu)₃. However, LiB(*t*Bu)₄ is unstable and decomposes readily with loss of isobutene to give LiHB(*t*Bu)₃, while LiMeB(*t*Bu)₃ (d¹¹B = −10.4) has only been observed in THF solution,[14] and has yet to be isolated and characterized, other than by NMR.

Experimental Section

General Remarks: All experiments were performed under anhydrous conditions under N₂ or Ar using Schlenk techniques. All reagents were purified prior to use either by distillation or crystallization. The reactions were monitored by using a Bruker WP 200 PFT NMR spectrometer equipped with a multinuclear probe. − BH₃ · THF was prepared from NaBH₄ in diglyme and BF₃; the diborane released was dissolved in pure THF. BH₃ · NEt₃ was prepared by adding an equimolar amount of NEt₃ to a solution of BH₃ · THF. Lithium silanides were obtained by standard literature procedures.[15] − Elemental analyses, using a Heraeus MX instru-

ment, were performed at the microanalytical laboratory of the Institute. A systematic lack of 1−2% carbon in the analyses is due to the formation of SiC and BC. − IR: Perkin-Elmer FT spectrometer. − NMR: Bruker WP 200 PFT, JEOL GSX 270, and JEOL EX 400 instruments; internal TMS (¹H, ¹³C), external BF₃·OEt₂ (¹¹B) as standards.

Bis[lithium (triphenylsilyl)trihydridoborate] · Tris(tetramethylethylenediamine) (1): A THF solution (30 mL) of freshly prepared triphenylsilyllithium (10 mmol)[15] was added dropwise to a stirred solution of BH₃ · NEt₃ (10 mmol) in THF (20 mL) at −30°C. In the course of the addition, the deep-green colour of the lithium silanide changed to reddish-brown. The mixture was allowed to warm to ambient temperature over a period of 4 h, and was then heated under reflux for 48 h, which resulted in a colourless solution. According to NMR analysis of this solution, LiBH₄ and the silyltrihydridoborate **1** were present in a ratio of 1:17. All volatiles were then removed in vacuo, leaving a white powder. **1** was separated from LiBH₄ by washing the powder with hexane (3× 30 mL). An attempted crystallization from hexane solution was unsuccessful, a 100% excess of TMEDA (20 mmol) was added. At −20°C, **1** precipitated within 2 weeks as colourless crystals, which were suitable for X-ray diffraction analysis. Yield: 2.90 g (3.2 mmol, 64%), m.p. 110−114°C (decomp.). − C₅₄H₈₄B₂Li₂N₆Si₂ (908.97): calcd. C 71.35, H 9.31, N 9.25; found C 70.44, H 8.96, N 8.94. − ¹¹B NMR (64 MHz, C₆D₆): δ = −42.6 [q, ¹*J*(B,H) = 78 Hz, $h_{1/2}$ = 34 Hz]. − ¹H NMR (400 MHz, C₆D₆): δ = 7.93 (m, Si−C₆*H*₅), 7.57 (m, Si−C₆*H*₅), 7.24 (m, Si−C₆*H*₅), 7.11 (m, Si−C₆*H*₅), 2.02 (br. s, 12 H, N−C*H*₂−), 1.98 (br. s, 36 H, N−C*H*₃), 0.00 [br. q, ¹*J*(B,H) = 78 Hz]. − ¹³C NMR (100 MHz, C₆D₆): δ = 136.7 (arom. C$_i$), 136.2 (arom. C$_o$), 130.1 (arom. C$_p$), 128.4 (arom. C$_m$), 51.6 (N−*C*H₂−), 46.1 (N−*C*H₃).

Lithium [(*tert*-Butyldiphenylsilyl)trihydridoborate] · Tris(tetrahydrofuran) (2a): A THF solution (30 mL) of freshly prepared *tert*-butyldiphenylsilyllithium (10 mmol) was added dropwise to a stirred solution of BH₃ · NEt₃ (10 mmol) in THF (20 mL) at −30°C. In the course of the addition, the dark-brown colour of the lithium silanide became lighter, but did not disappear entirely. The mixture was allowed to warm to ambient temperature over a period of 4 h, and was then heated under reflux for 48 h, which resulted in a colourless but cloudy solution. According to NMR analysis of this solution, LiBH₄ and the silyltrihydridoborate were present in a ratio of 1:9. The volatiles were then removed in vacuo, leaving a white powder. **2a** was separated from LiBH₄ by washing the powder with hexane (3× 30 mL). At −20°C, **2a** precipitated from the hexane solution within 2 weeks as colourless crystals, which were suitable for X-ray diffraction analysis. Yield: 2.7 g (5.7 mmol, 57%), m.p. 98−101°C (decomp.). − C₂₈H₄₆BLiO₃Si (476.49): calcd. C 70.58, H 9.73; found C 69.28, H 9.53. − ¹¹B NMR (64 MHz, C₆D₆): δ = −43.8 [q, ¹*J*(B,H) = 78 Hz, $h_{1/2}$ = 41 Hz]. − ¹H NMR (400 MHz, C₆D₆): δ = 8.11 (m, Si−C₆*H*₅), 7.31 (m, Si−C₆*H*₅), 3.52 (m, 12 H, THF: −O−C*H*₂−), 1.47 [s, 9 H, Si−C(C*H*₃)₃], 1.33 (m, 12 H, THF: −O−CH₂−C*H*₂−), −0.09 [q, ¹*J*(B,H) = 78 Hz, 3 H, B*H*₃]. − ¹³C NMR (100 MHz, C₆D₆): δ = 137.0 (arom. C$_o$), 136.1 (arom. C$_i$), 127.2 (arom. C$_p$), 127.0 (arom. C$_m$), 68.3 (O−*C*H₂−CH₂), 29.5 [Si−C(*C*H₃)₃], 27.7 [Si−*C*(CH₃)₃], 25.4 (O−CH₂−*C*H₂−). − IR (Nujol): ṽ = 2284.3 (br. vs), 2257.2 (br. vs), 1962.4 (vw), 1946.4 (vw), 1483.6 (m), 1467.6 (m), 1459.2 (m), 1425.6 (vs), 1383.0 (m), 1370.0 (w), 1356.1 (m), 1341.6 (w), 1305.3 (w), 1293.8 (w), 1258.4 (m), 1182.2 (m), 1096.1 (vs), 1049.2 (vs), 1010.2 (m), 998.8 (w), 988.8 (vw), 935.2 (w), 916.7 (m), 894.3 (s), 820.8 (s), 738.3 (s), 731.6 (s), 702.5 (vs), 687.7 (s), 636.7 (s), 617.6 (m), 571.8 (m), 490.8 (s), 482.8 (s), 448.3 (m), 397.6 (w), 373.4 (w), 330.8 (w), 323.6 (w), 306.9 (w), 293.5 (m), 250.4 (vw).

Lithium [(*tert*-Butyldiphenylsilyl)trihydridoborate] · Pentamethyldiethylenetriamine (2b): A stoichiometric amount of PMDTA was added to a solution of **2a** in hexane. From the resulting solution, colorless crystals grew at −20°C within 7 days; m.p. 106−108°C (decomp.). − $C_{25}H_{45}BLiN_3Si$ (433.48): calcd. C 69.27, H 10.46, N 9.69; found C 68.43, H 9.98, N 8.97. − ^{11}B NMR (64 MHz, C_6D_6): δ = −43.8 [q, $^1J(B,H)$ = 79 Hz, $h_{1/2}$ = 20 Hz]. − ^1H NMR (400 MHz, C_6D_6): δ = 8.27 (m, $Si-C_6H_5$), 7.35 (m, $Si-C_6H_5$), 2.00 (br. s, 8 H, $-N-CH_2-CH_2-$), 1.87 (br. s, 16 H, $N-CH_3$), 1.54 [s, 9 H, $Si-C(CH_3)_3$], −0.10 [q, 3 H, $^1J(B,H)$ = 79 Hz, BH_3]. − ^{13}C NMR (100 MHz, C_6D_6): δ = 137.4 (arom. C_o), 136.3 (arom. C_i), 126.9 (arom. C_m), 126.8 (arom. C_p), 57.1 ($N-CH_2-$), 45.9 ($N-CH_3$), 29.9 [$Si-C(CH_3)_3$], 28.1 [$Si-C(CH_3)_3$]. − IR (Nujol): ṽ = 2335.4 (br. m), 2266.4 (br. ss), 2237.5 (br. s), 2008.4 (vw), 1956.5 (vw), 1882.8 (vw), 1826.5 (vw), 1770.2 (vw), 1653.2 (vw), 1588.3 (vw), 1484 (m), 1470.7 (vs), 1463.9 (vs), 1454.9 (vs), 1425.1 (vs), 1410.3 (w), 1390.0 (w), 1379.9 (w), 1361.4 (m), 1351.9 (m), 1324.0 (vw), 1299.3 (m), 1289.1 (m), 1250.4 (w), 1214.8 (vw), 1167.5 (m), 1151.5 (m), 1106.7 (vs), 1094.1 (vs), 1065.0 (m), 1055.7 (m), 1035.6 (s), 1030.1 (s), 1017.7 (m), 999.02 (w), 983.9 (m), 935.0 (m), 897.5 (w), 856.8 (vw), 818.7 (m), 788.3 (w), 773.1 (w), 738.6 (s), 703.7 (vs), 689.3 (s), 645.6 (m), 620.7 (m), 605.5 (vw), 597.9 (vw), 571.6 (m), 509.0 (vw), 482.4 (s), 433.6 (m), 404.9 (w), 3992.2 (w), 343.9 (vw), 316.0 (vw).

Lithium Tetrakis(trimethylsilyl)borate (3) and **Lithium Tris(trimethylsilyl)methylborate (4)** were prepared as described in the literature.[3]

X-ray Structure Determinations: Single crystals of compounds **1**, **2a**, **2b**, **3**, and **4** were obtained from hexane solutions at −20°C. The selected crystals were covered with perfluoroether oil, mounted on a glass fibre, placed on the goniometer head of the diffractometer, and cooled to −90°C under a flow of N_2. Preliminary dimensions of the unit cells were calculated from the reflections collected at four different settings of the crystal by recording 15 frames each with a CCD area detector. Data collection was performed with a 10 s exposure time per frame by rotating the crystal by 0.3° in φ at two different χ settings. The data from 1350 frames were reduced using the program SAINT[16] and the structures were solved by direct methods using the XS and SHELX97 programs for structure solution and refinement. The structure of compound **2b** showed disorder of one $NC_2H_4NMe_2$ bridge of the PMDTA coligand with an SOF of 0.5. Refinement of this disorder needed restraints in bond length for N−C and C−C distances. Atoms C17, C18, C20, C22, C22a, C24a, and C25a were refined with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically, and the positions of hydrogens as found by difference Fourier maps were refined freely. Relevant data are presented in Table 3.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 105281−105284. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/ 336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected crystallographic data for the structures of **1**, **2a**, **2b**, **3**, and **4** and data referring to data collection and structure refinement

	1	**2a**	**2b**	**3, 4**
Empirical formula	$C_{27}H_{42}BLiN_3Si$	$C_{28}H_{46}BLiO_3Si$	$C_{25}H_{45}BLiN_3Si$	$C_{22}H_{66}B_2Li_2Si_7$
Mol. mass	454.48	476.49	433.48	562.88
Crystal size [mm]	$0.05 \times 0.10 \times 0.20$	$0.40 \times 0.40 \times 0.40$	$0.10 \times 0.10 \times 0.20$	$0.2 \times 0.3 \times 0.3$
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	P-1	$P2(1)/c$	P-1	$Pbca$
a [Å]	11.3191(1)	12.073	10.3485(3)	17.439(5)
b [Å]	11.3967(3)	13.5337(1)	11.9161(2)	15.528(5)
c [Å]	12.4007(5)	19.1765(2)	12.3191(3)	28.02(1)
α [°]	93.292(2)	90	90.908(1)	90
β [°]	90.514(1)	107.519(1)	111.653(1)	90
γ [°]	113.966(1)	90	94.406(1)	90
V [Å³]	1458.45(7)	2987.94(4)	1406.14(6)	7588(4)
Z	2	4	2	8
ρ_{calcd} [Mg/m³]	1.035	1.059	1.024	0.985
μ [mm⁻¹]	0.098	0.103	0.099	0.262
$F(000)$	494	1040	476	2496
Index range	$-13 \le h \le 13$	$-15 \le h \le 15$	$-13 \le h \le 10$	$-18 \le h \le 18$
	$-14 \le k \le 14$	$-17 \le k \le 11$	$-14 \le k \le 15$	$-20 \le k \le 20$
	$-8 \le l \le 16$	$-23 \le l \le 23$	$-15 \le l \le 15$	$-34 \le l \le 34$
2θ [°]	58.02	58.24	57.60	55.72
T [K]	193	193	193	183(3)
Refl. collected	8508	16426	8029	40823
Refl. unique	4564	5432	4383	7484
Refl. observed (4σ)	2672	4140	3153	5617
R (int.)	0.0664	0.0276	0.0257	0.0501
No. of variables	322	414	348	562
Weighting scheme[a]	0.0394/0.9659	0.0489/1.4893	0.1398/2.3485	0.0319/2.7715
GooF	1.072	1.065	1.038	1.066
Final R (4σ)	0.0669	0.0570	0.0964	0.0364
Final $wR2$	0.1208	0.1289	0.2555	0.0714
Larg. res. peak	0.283 [e/Å³]	0.240	0.718 [e/Å³]	0.298 [e/Å³]

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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[8] Also isolated and characterized by X-ray structure determination was $[(t\text{BuPh}_2\text{Si})\text{BH}_3 \cdot \text{Li(thf)}_2]_2$. This compound was obtained in an experiment similar to that described for the preparation of **2a**. Its SiBH_3 group acts as a μ_2^1, μ_1^1-ligand, bridging two Li units, which are pentacoordinated by two O atoms and 3 H atoms (of the THF molecules and two BH_4 units). However, the crystal quality was less than satisfactory since refinement could not be improved beyond $R1 = 10.31$. Furthermore, solution was only possible in the triclinic space proup $P\overline{1}$bar, whereas the unit cell dimensions showed the presence of a monoclinic crystal system. Crystal data are: $a = 12.2823(6)$, $b = 13.4825(6)$, $c = 15.4181(7)$ Å, $\alpha = 89.996(2)$, $\beta = 86.881(1)$, $\gamma = 89.984(1)°$, $Z = 2$. The data of the structure refinement have also been deposited with the CCDC.

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