Syntheses and Reactions of a Stable 1,2-Dichloro-1,2-diborolane and Aromatic Tetraboranes

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Keywords: Aromatics / Boranes / Carbanions / Cyclizations / Heterocycles / Rearrangements

The 1,2-dichloro-1,2-diborolane **1b** was isolated in good yield after the reaction of the 1,2-bis(dimethylamino)-1,2-diborolane **2c** with BCl_3. We prepared **2c** from 1,2-bis(dimethylamino)-1,2-dichlorodiborane(4) (**3**) and TMEDA-free [1,3-bis(trimethylsilyl)allyl]lithium (**5a·Li**), which is accessible by deprotonation of 1,3-bis(trimethylsilyl)propene (**4a**) with *n*-butyllithium in diethyl ether. Upon its reaction with lithium in THF, the 1-allyl-2-chlorodiborane(4) **6a** obtained in the first step undergoes an unprecedented ring closure with 1,2-migration of a trimethylsilyl substituent to yield the boron-stabilized carbanion **7a**. Reaction of **7a** with either chlorotrimethylsilane or HCl gives **2c** or **2d**, respectively. The latter compound cannot be transformed into an isolable 1,2-dichloro-1,2-diborolane; this observation demonstrates that a trimethylsilyl substituent next to each boron atom is essential for the stability of 1,2-dichloro-1,2-diborolanes. Compound **1b** is a versatile starting material, inter alia for the syntheses of the aromatic tetraboranes(6) *cis*-**11** and *trans*-**13** and the aromatic tetraborane(4) *cis*-**12**. The isomerization *cis*-**11** → *trans*-**13** can be explained on the basis of reactions occurring under the conservation of two-electron aromaticity.

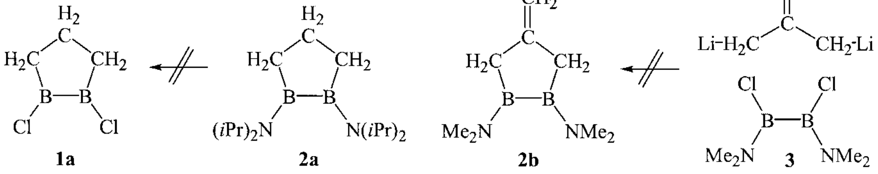
Introduction

1,2-Dichloro-1,2-diborolanes appear to be versatile starting materials for the syntheses of 1,2-diborolanes that lack strong donor substituents at the boron centers, but only 1,2-diborolanes possessing such donors, i.e., 1,2-diamino-1,2-diborolanes, are known experimentally.[1−3] Computations have revealed a strong tendency for the unsubstituted 1,2-diborolane to isomerize to nonclassical forms that have two-electron homoaromatic structures.[4] Attempts to prepare 1,2-dichloro-1,2-diborolane (**1a**) by reaction of the 1,2-diamino-1,2-diborolane **2a** with BCl_3 were unsuccessful,[2] as were efforts to obtain **2b** by reaction of 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) (**3**) with 1,3-dilithio-2-methylenepropane (Scheme 1).[3]

In this paper we describe the synthesis of the stable 1,2-dichloro-1,2-diborolane **1b** (Scheme 3) via the new 1,2-diamino-1,2-diborolane **2c** (Scheme 2). Compound **1b** turned out to be a versatile starting material, inter alia for the syntheses of the aromatic tetraboranes *cis*-**11**,[5] *cis*-**12**,[6] and *trans*-**13**[5] as well as for triboracyclopropanates[7] and a pentaborane(7).[6]

Syntheses

The TMEDA-free allyllithium compounds **5a·Li** and **5b·Li** were prepared by deprotonation of 1,3-bis(silyl)propenes **4a**[8,9] and **4b**[10] with *n*-butyllithium in diethyl ether at room temperature. Compound **4b** was synthesized from 3-[dimethyl(phenyl)silyl]propene,[11] which was deprotonated in the same way and then treated with chlorodimethyl(phenyl)silane.



Scheme 1

The bis(trimethylsilyl)propene **4a** is deprotonated usually in the presence of *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA), THF, or HMPA.[8,12−14] The deprotonation

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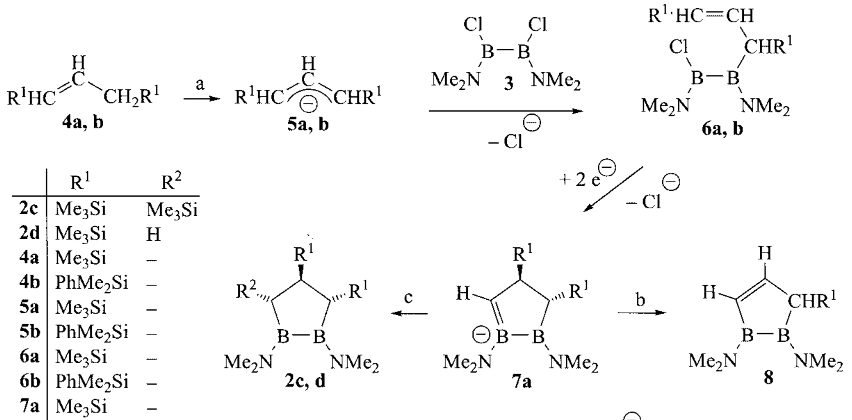
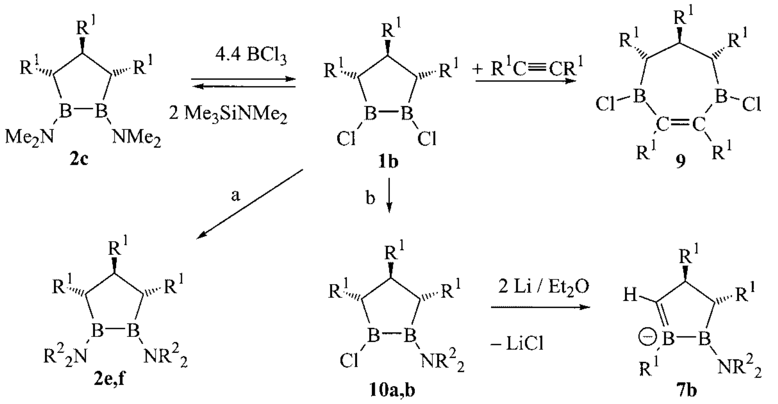
DOI: 10.1002/ejic.200400078



	R^1	R^2
2c	Me_3Si	Me_3Si
2d	Me_3Si	H
4a	Me_3Si	–
4b	$PhMe_2Si$	–
5a	Me_3Si	–
5b	$PhMe_2Si$	–
6a	Me_3Si	–
6b	$PhMe_2Si$	–
7a	Me_3Si	–
8	Me_3Si	–

a: + *n*-BuLi, – C_4H_{10} b: + ICH_2-CF_3, – $F^{\ominus}$, – Me_3SiI, – $H_2C{=}CF_2$
c: + Me_3SiCl, – $Cl^{\ominus}$ (**2c**), + HCl, – $Cl^{\ominus}$ (**2d**)

Scheme 2



	2e	**2f**	**7b**	**10a**	**10b**
$R^2{}_2$	$(CH_2)_5$	Et_2	$(CH_2)_5$	Me_2	$(CH_2)_5$

$R^1 = Me_3Si$

a: + 2 $Me_3SiNR^2{}_2$, – 2 Me_3SiCl
b: + $Me_3SiNR^2{}_2$, – Me_3SiCl

Scheme 3

with *n*-butyllithium in diethyl ether requires a reaction time of 8 d, but the workup of the products obtained after the reaction of lithiopropene **5a·Li** with 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) (**3**) is considerably easier and yields of allylchlorodiboranes(4) **6a,b** are much higher than they are when using the lithium salts of **5a**,**b** containing TMEDA. The 1-allyl-2-chlorodiboranes(4) **6a**,**b** thus obtained are mixtures of (*E*) and (*Z*) stereoisomers, which could not be separated by distillation. The constitutions of (*E*/*Z*)-**6a**,**b** were deduced from their ^1H and ^{13}C NMR spectra and confirmed by the X-ray crystal structure analysis of the product obtained by reaction of the former with lithium in THF (see below). Nearly identical coupling constants $J(^1H,^1H)$ of the alkene moieties of the isomers prevented assignments of configurations by means of ^1H NMR spectroscopy. Probably, the main products (**6a**: 85%; **6b**: 90%) are the (*E*) isomers because of their lower degree of steric hindrance when compared to the (*Z*) isomers.

Reaction of (*E*/*Z*)-**6a** with lithium powder in THF at room temperature yielded 1,2-diborolan-3-ide **7a** as the sole product. This ring-closing reaction was not observed with **6b** even when stoichiometric amounts of lithium naphthalenide were used. The constitution of **7a** is in agreement with all the NMR spectroscopic data and was confirmed definitely by an X-ray crystal structure analysis (see below). While the methyl groups of the dimethylamino substituent of the uncharged boron atom of **7a** show two signals in the ^1H and ^{13}C NMR spectra (300 K, 300/75 MHz), those of the charged boron atom are averaged, which indicates a less hindered rotation.

During the formation of **7a** from (*E*/*Z*)-**6a**, a C−B bond, as well as a boron-stabilized carbanion, is formed, and a trimethylsilyl group must migrate from a carbon atom to the neighboring carbon atom, which, for **6a**, does not possess a silyl substituent. A mechanism for this unprecedented ring closure is proposed below.

The reaction of the anion **7a** with either chlorotrimethylsilane or HCl gave 1,2-diborolanes **2c** and **2d**, respectively. Their constitutions and stereochemistries are in agreement with all of their NMR spectroscopic data. The ^1H NMR spectrum of **2c** exhibits two signals for the silyl groups (2:1), the aminomethyl groups (1:1), and the ring protons (2:1; d and t, respectively). The crude product of **2c** was used for subsequent reactions without further purification because it contained very few impurities after removal of the volatile components and filtration.

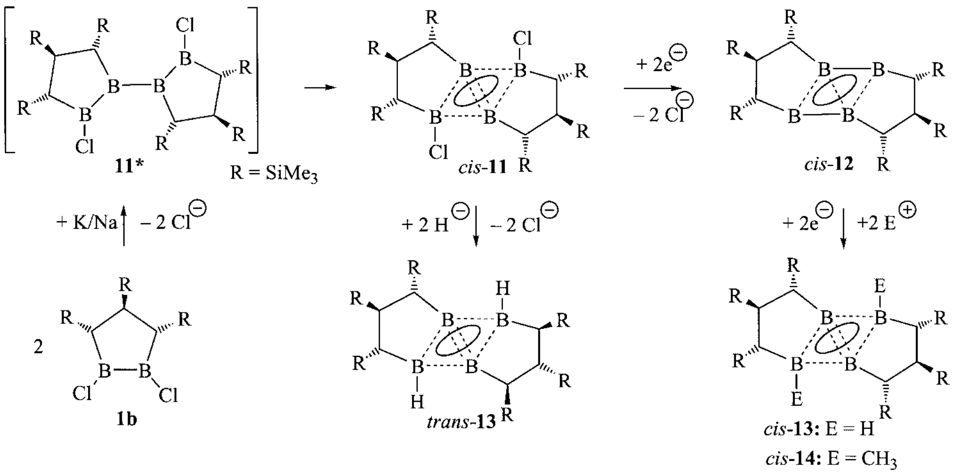
Reaction of **7a** with 1,1,1-trifluoro-2-iodoethane did not yield the expected 3-iodo-1,2-diborolane after warming to room temperature, but, instead, the elimination product diboracyclopentene **8**. The constitution of compound **8** was derived from its one- and two-dimensional ^{1}H, ^{11}B, and ^{13}C NMR spectra.

After the addition of ca. 4 equiv. of neat boron trichloride to a solution of **2c** in *n*-pentane at −78 °C, the solution was warmed to ambient temperature during which time both amino groups were replaced cleanly by chlorine atoms. While small-scale experiments yielded nearly pure **1b**, the crude products of experiments starting with $>$ 10 g of **2c** had to be crystallized from *n*-pentane at −30 °C to obtain satisfactory yields (ca. 68%) of pure **1b**. Diborolane **2d**, which lacks one trimethylsilyl group when compared to **2c**, could not be chlorinated in a similar manner. Reaction with BCl_3 resulted in the recovery of **2d** or led to an inseparable mixture of products containing varying amounts of starting material.

The diborolane **1b** reacts with bis(trimethylsilyl)ethyne at room temperature to form the 3,7-diboracycloheptene **9**. Its constitution was confirmed by NMR spectroscopy experiments. Compound **9** displays three signals for the trimethylsilyl groups (ratio: 2:1:2) and two for the methylene groups (2:1; d and t). Formation of the isomeric 1-methylene-2,6-diboracyclohexane, i.e., the product of the often observed 1,1-diborylation of bis(trimethylsilyl)ethyne,[15,16] was ruled out by $^{13}C\{^{11}B\}$ NMR spectroscopy experiments. The signals of the boron-bound carbon atoms at $\delta = 181.2$ and 34.8 ppm sharpened considerably, but no sharp signal appears for a tricoordinated carbon atom that is not bound to boron atoms (i.e., for an $Si_2C{=}CB_2$ moiety). Similar 1,2-diborylations of ethynes are known to occur from 1,2-diamino-1,2-diborolanes, which, however, require $BF_3{\cdot}OEt_2$ as catalyst and elevated temperatures.[1]

One or both chlorine atoms in **1b** can be exchanged with amino groups by adding stoichiometric amounts of silylamines. In this way, we synthesized the monoaminodiborolanes **10a**,**b** and the diaminodiborolanes **2c**,**e**,**f**. Reaction of **10a** with lithium powder in diethyl ether did not yield a tetraborane(6) by dimerization,[5] but gave the 1,2-diborolan-3-ide **7b**, as proven by its X-ray structural analysis. This transformation, like that of **6a** to **7a**, requires the 1,2-migration of a trimethylsilyl substituent (here to a neighboring boron atom) and the generation of a boron-stabilized carbanion. The NMR spectroscopic data of **7b** are similar to those of **7a**, but some of the chemical shifts differ distinctly. The stronger acceptor in **7b** [$B(SiMe_3)$], when compared to $B(NMe_2)$ in **7a**, causes a downfield shift of the signals of the sp^2-hybridized carbon atom and its proton relative to those signals for **7a** (^{13}C: $\delta = 149.2$ vs. 109.0 ppm; ^{1}H: $\delta = 6.57$ vs. 4.58 ppm). The boron atom bearing the trimethylsilyl group, however, is more shielded ($\delta = 33$ vs. 38 ppm), even though it lacks a second π-donating group. Attempts to let **7b** react with electrophiles (MeI, Me_3SiCl, Me_3SnCl) to yield a *B*-trimethylsilyldiborolane were unsuccessful. The mixtures of products obtained obviously contained no compounds featuring a $B{-}B(SiMe_3)C$ moiety, which would result in a ^{11}B NMR signal for a strongly deshielded boron center.[17]

Reactions of **1b** with $K_{2.8}Na$ in *n*-pentane at room temperature yielded the nonclassical dichlorotetraborane(6) *cis*-**11** (Scheme 4).[5,18,19] As seen from its classical isomer **11***, there are only six electrons to connect the four centers of the B_4 ring of *cis*-**11**. Four of them are used for two three-center two-electron (3c2e) σ-bonds and the remaining two for a 4c2e π-bond.[5] Thus, *cis*-**11** is a 2e-aromatic system having a nonclassical σ-skeleton. Computations for model molecules show the energetic advantage of 2e-aromatic compounds of type **11** over orthogonal classical isomers, which benefit only from twofold B−B hyperconjugation (see below). The aromatic tetraborane(4) *cis*-**12** was obtained by reaction of *cis*-**11** with 2 equiv. of lithium naphthalenide at low temperatures.[6] Reduction of *cis*-**12** to its



Scheme 4

dianion and a subsequent reaction with either HCl or methyl iodide leads to the tetraborane(6) *cis*-**13** or *cis*-**14**, respectively.[20] Surprisingly, the stereoisomer *trans*-**13** was obtained by exchange of the Cl atoms of *cis*-**11** for hydrogen by use of sodium triethylhydroborate.[5] A reasonable mechanism for this stereoisomerization is presented below.

Crystal Structures

The lithium cations of all the derivatives of allyllithium analyzed by crystal structure determination so far are coordinated by ligands like TMEDA or diethyl ether.[14,21−24] The structure of **5b·Li** is the first one of a solvent-free allyllithium derivative. Attempts to obtain single crystals of **5a·Li** were unsuccessful: it is insoluble, even in boiling *para*-xylene, and it decomposed in boiling mesitylene.

The **5b·Li** complex exhibits a polymeric structure in the solid state with two independent spiral Li−allyl−Li chains parallel to the *c* axis (Figure 1). According to the space group $I4_1$, one spiral chain with Li1 turns around clockwise (4_1 screw axis at 1/4, 1/4, *z*, 90° rotation of subsequent allyl groups); the second one with Li2 turns anticlockwise (4_3 screw axis at 3/4, 1/4, *z*). By the twofold axis in 0.5,0.5,*z*, a second pair of equivalent chains is generated in 3/4,1/4,*z* (Li2) and 3/4,3/4,*z* (Li1) leading to a tetragonal chain packing of alternating 4_1 and 4_3 spirals (Figure 2). Figure 1 displays a section of the Li1 chain that indicates the η^3-connection of the allyl moieties; the C_3 planes are located at an angle of 60.4(3)° [61.7(3)° for the Li2 chain] with respect to the chain axis. In contrast, the structure of (1,3-diphenylallyl)lithium·OEt$_2$ [22] possesses chains having 2_1-symmetry (180° rotation of subsequent allyl groups); the inclination of the allyl planes to the chain axis is similar (60°).

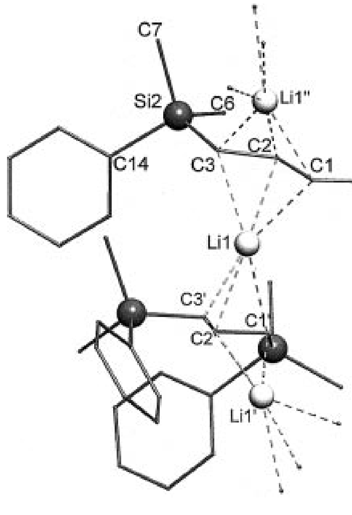


Figure 1. Section of the spiral chain with Li1 in the crystal structure of **5b·Li**; selected bond lengths [pm] and angles [°], the corresponding values for the second spiral chain with Li2 are provided in brackets (same e.s.d.s): C1−C2 140.6(4) [140.2], C2−C3 140.0(4) [139.9], C1−Li1 231.4(6) [233.9], C2−Li1 215.8(6) [215.6], C3−Li1 231.8(6) [228.7], C1′−Li1 228.8(6) [229.7], C2′−Li1 219.3(6) [216.2], C3′−Li1 235.3(6) [229.7]; C1−C2−C3 129.9(3) [128.9], C2−C1−Si1 123.2(2) [124.4], C2−C3−Si2 123.8(2) [123.5], Si1−C1−C2−C3 −176.1(2) [177.9]

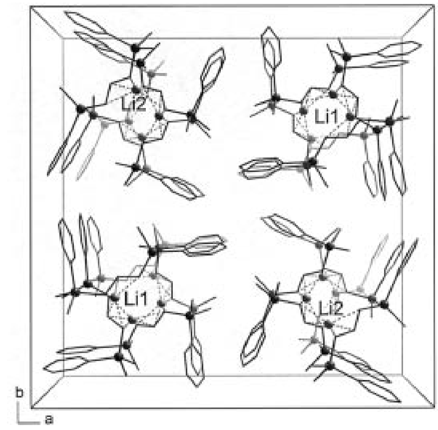


Figure 2. Perspective view along the *c* axis of the unit cell of **5b·Li** having alternating clockwise (Li1) and anticlockwise (Li2) spiral chains

While the differences in the C_3 moieties are not worth mentioning, the absence of an additional ligand coordinating the cation in **5b·Li** has a distinct effect, unsurprisingly, on the C−Li distances. In (1,3-diphenylallyl)lithium·OEt$_2$, the cation is ca. 10 to 20 pm more remote from the carbon atoms [C−Li: 230(3), 232(3), 248(3), 240(3), 250(3), 252(3) pm].

Compound **7a**·Li[THF]$_2$ forms a contact ion pair; the cation is coordinated by N1, B1−C1, C1−H1, and two molecules of THF, one of which shows disorder. The bond B1−C1 [146.6(3) pm] is significantly shorter than the B2−C3 bond [160.8(3) pm] because of its double bond character. This situation results in a long N1−B1 bond [153.1(2) pm] while the N2−B2 distance [140.8(2) pm] is in the typical range of N−B bonds having a strong π-interaction.

Like **7a**·Li[THF]$_2$, compound **7b**·Li[Et$_2$O]$_2$ forms a contact ion pair: the cation is coordinated by C1−B1 and two molecules of diethyl ether in this case. The unit cell contains two independent molecules of **7b**·Li[Et$_2$O]$_2$ with only slightly different bond lengths and bond angles (the second set of data is given in brackets in the following discussion). Complexes **7a**·Li[THF]$_2$ and **7b**·Li[Et$_2$O]$_2$ are similar with regard to their B_2C_3 rings (see Figures 3 and 4); while the Li cation of the latter is placed approximately above the C−B double bond {B1−Li1: 238.9(5) pm [238.3(4)]; C1−Li1: 239.7(5) pm [243.1(4)]; B2−B1−C1−Li1: 101.9(2)° [101.0(2)°]}, the cation in **7a**·Li[THF]$_2$ is located nearer to the ring plain because of the coordination to the amino group [Li1−C1−B1−B2 146.5 (2)].

In the structure of **1b** (Figure 5), the B−B [169.2(4) pm] and B−Cl [175.9(3), 176.0(3) pm] bond lengths are quite similar to those found in 1,2-dichloro-1,2-dimesityldiborane(4)[25] [168.0(6), 177.0(5) and 177.4(4) pm, respectively]. Compound **1b** deviates from C_s symmetry in the solid state mainly because the orientations of the SiMe$_3$ groups at C1 and C3 break the symmetry of a mirror plane, but also because of slight nonplanarity around the B−B moiety [Cl1−B1−B2−Cl2: 5.8(3)°] and the inequivalent B−C and

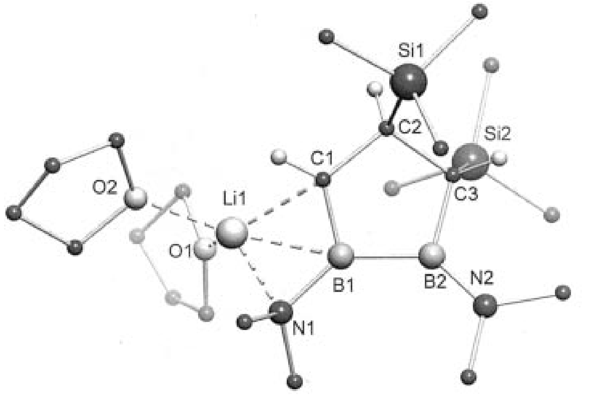


Figure 3. Structure of **7a**·Li[THF]$_2$ in the crystal (most H atoms have been omitted for clarity); selected bond lengths [pm] and angles [°]: B1−B2 169.1(3), B1−C1 146.6(3), B2−C3 160.8(3), C1−C2 152.4(2), C2−C3 156.8(3), N1−Li1 203.3(4), B1−Li1 230.2(4), C1−Li1 223.6(4); C1−B1−B2 103.1(2), C3−B2−B1 105.1(2), C2−C1−B1 115.4(2), C2−C3−B2 104.9(2), sum of angles (without Li1) C1 359.6, N1 344.7, N2 359.8

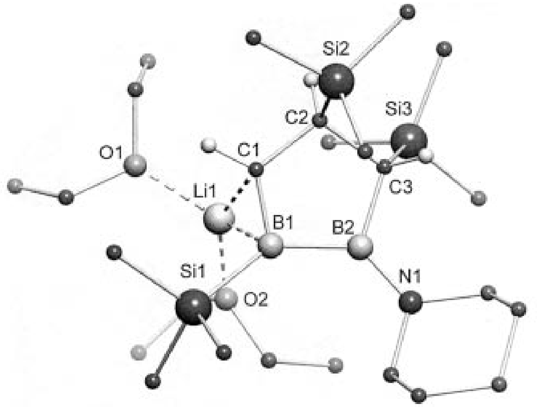


Figure 4. Structure of **7b**·Li[Et$_2$O]$_2$ in the crystal; selected bond lengths [pm] and angles [°], the corresponding values for the second independent ion pair are provided in brackets: B1−B2 171.3(3) [170.0(4)], B1−C1 146.1(3), B2−C3 160.1(3), C1−C2 151.9(3) [152.3(3)], C2−C3 157.4(3) [156.2(3)], B1−Si1 200.9(2) [201.2(2)], B1−Li1 238.9(5) [238.3(4)], C1−Li1 239.7(5) [243.1(4)]; C1−B1−B2 101.4(2) [101.8(2)], C3−B2−B1 107.2(2) [106.9(2)], C2−C1−B1 117.2(2) [116.9(2)], C2−C3−B2 105.1(2) [104.9(2)]; sum of angles (without Li1) C1 359.6 [359.2], N1 359.1 [359.3]

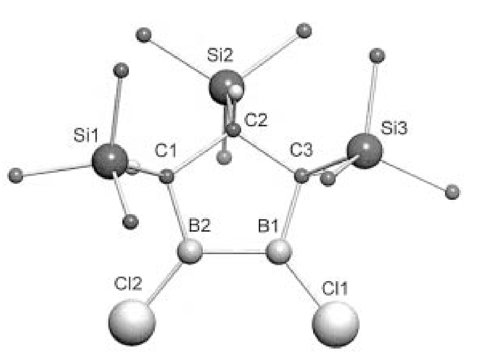


Figure 5. Structure of **1b** in the crystal; selected bond lengths [pm] and angles [°]: B1−B2 169.2(4), B2−C1 150.1(4), C1−C2 156.0(3), C2−C3 157.7(3), C3−B1 151.6(3), B1−Cl1 176.0(3), B2−Cl2 175.9(3), C1−Si1 193.0(2), C2−Si2 189.9(2), C3−Si3 192.5(2); B1−B2−C1 107.2(2), B1−B2−Cl2 128.3(2), B2−B1−C3 106.4(2), B2−B1−Cl1 128.3(2), B1−C3−C2 107.4(2), C3−C2−C1 109.8(2), C2−C1−B2 107.5(2), C1−B2−B1−C3 4.5(2)

C−C bond lengths (see caption to Figure 5). The short B−C [B2−C1: 150.1(4) pm; B1−C3: 151.6(3) pm; usually 158−160 pm] and long C−Si bonds [C1−Si1 193.0(2) pm; C3−Si3 192.5(2) pm; usually 186−187 pm] are mainly the result of C−Si hyperconjugation of the boron atoms with the C−Si bonds.

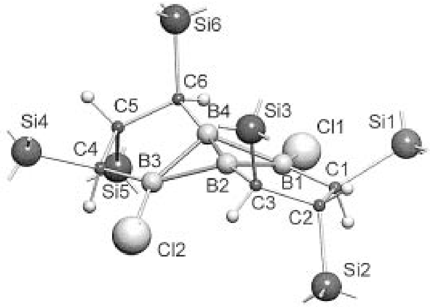


Figure 6. Structure of *cis*-**11** in the crystal; selected bond lengths [pm] and angles [°]: B1−B2 182.6(2), B2−B3 186.3(2), B3−B4 182.2(2), B4−B1 186.0(2), B2−B4 150.2(2), B1−Cl1 179.8(2), B3−Cl2 179.8(2), B1−C1 157.1(2), C1−C2 155.6(2), C2−C3 157.1(2), C3−B2 156.4(2); Cl1−B1−C1 112.1(1), Cl2−B3−C4 112.0(1), C3−B2−B4 169.4(1), C6−B4−B2 170.1(1), B1−B2−B4−B3 135.2(1)

Compound *cis*-**11** (Figure 6) possesses a folded [135.2(1)°] diamond-like structure that has a remarkably short diagonal of only 150.2(2) pm. The edges of this diamond are considerably longer [182.2(2) to 186.3(2) pm] than the B−B bond in **1b** [169.2(4) pm], which indicates multicenter bonding. The boron centers that carry chloro substituents show an approximately planar surrounding by their four neighbors [Cl1−B1−B4−B2: 174.1(1)°; Cl2−B3−B2−B4: 176.7(1)°]. All trimethylsilyl substituents at carbon atoms bound to boron atoms lie on the same side of the B$_4$ ring. We refer to this stereochemistry as "*cis*" in this text.

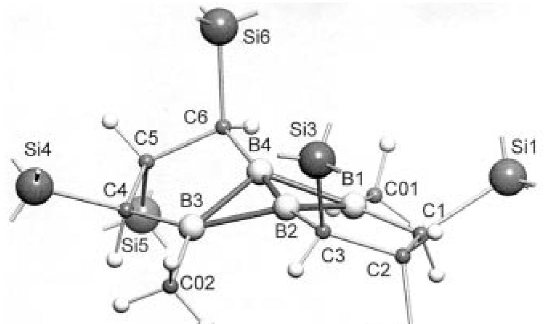
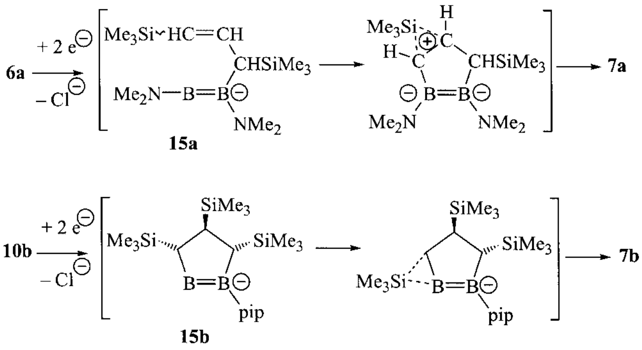


Figure 7. Structure of *cis*-**14** in the crystal; selected bond lengths [pm] and angles [°]: B1−B2 179.9(3) B2−B3 183.0(3), B3−B4 180.2(3), B4−B1 183.5(3), B2−B4 150.1(3), B1−C01 164.8(3), B3−C02 160.9(3), B1−C1 159.6(2), C1−C2 156.1(2), C2−C3 157.0(2), C3−B2 158.0(2); C01−B1−C1 112.0(2), C02−B3−C4 113.0(2), C3−B2−B4 169.4(2), C6−B4−B2 170.1(2), B1−B2−B4−B3 140.2(1)

Compound *cis*-**14** (Figure 7) is isostructural to *cis*-**11** and has a similar folding angle of 140.2(1)° for the B$_4$ diamond. Its diagonal is short [150.1(3) pm], and the edges of the diamond are a bit shorter [179.9(3) to 183.5(3) pm] than those in *cis*-**11**. The boron centers that carry methyl substituents are almost planar-tetracoordinate (max. deviations from best planes: B1,B2,B4,C01,C1, 9.9(2) pm; B2,B3,B4,C02,C4, 5.3(2) pm].

Discussion

The ring closure, accompanied by an 1,2-migration of a trimethylsilyl group, which takes place upon reaction of **6a** with lithium metal and leads to the boron-stabilized carbanion **7a**, is unprecedented to the best of our knowledge. It may be explained, however, by analogy to reactions of carbon electrophiles with allylsilanes,[26] by invoking the borylborenate **15a** as an intermediate (Scheme 5). Since borylborenates are isoelectronic with methyleneboranes[27] and vinyl cations, their dicoordinate boron center can be expected to react intramolecularly as a strong electrophile with the allylsilane moiety to generate a carbocation in the β-position relative to a silyl substituent. 1,2-Migration of silyl substituents in cations of this type are well-known processes in the chemistry of allylsilanes.[26]



Scheme 5

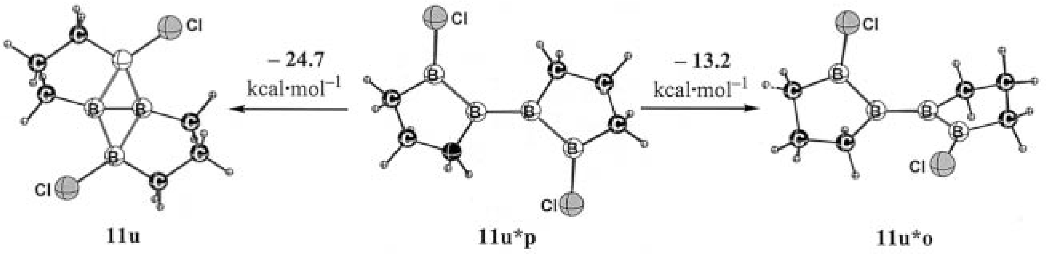
By analogy, the formation of the boron-stabilized carbanion **7b** upon reaction of **10b** with lithium metal can be rationalized by assuming that the borylborenate **15b** is the intermediate. In this case, the silyl substituent migrates to the neighboring electrophilic dicoordinate boron center.

Obviously, the first 1,2-dichloro-1,2-diborolane, **1b**, owes its persistence to the trimethylsilyl substituents at all of the carbon atoms. All attempts to generate a derivative lacking this substituent next to one of the boron centers were unsuccessful. This result explains the failure of earlier efforts to prepare **1a** lacking any substituents.[2]

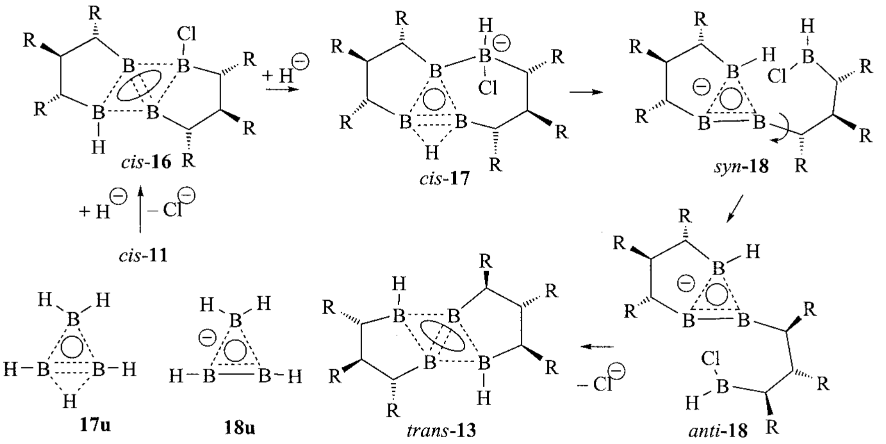
So far, reaction of metals with 1,2-dichloro-1,2-diboranes(4) having appropriate substituents, like sterically demanding amino or *tert*-butyl substituents, have led to the elimination of both chlorine atoms and generation of folded or tetrahedral tetraboranes(4).[28,29] The reductive dimerization of **1b** to *cis*-**11** is the first example where only one chlorine atom of each 1,2-dichloro-1,2-diborane(4) is eliminated. The dichlorotetraborane(6) *cis*-**11** is a 2e-aromatic tetraborane(6) that has a nonclassical σ-skeleton. Computations (B3LYP/6-311+G**//B3LYP/6-31G*+ZPE)[30] of model molecules lacking silyl substituents show that the aromatic folded diamond **11u** is preferred over the classical planar **11u*p** by 24.7 kcal·mol^{-1}. The orthogonal **11u*o** (Scheme 6), which benefits from twofold B–B hyperconjugation, is only 13.2 kcal·mol^{-1} lower in energy than **11u*p**.

While the *cis* configuration is retained during the transformations of *cis*-**11** to *cis*-**13** and *cis*-**14** via *cis*-**12** and its dianion,[20] the stereoisomer *trans*-**13** is obtained upon reaction of *cis*-**11** with 2 equiv. of sodium triethylhydroborate. All transformations leading to *cis*-**13** occur with conservation of 2e-aromaticity and retention of the stereochemistry in the four-membered rings. The inversion of the stereochemistry of three adjacent centers during the formation of *trans*-**13** requires opening of one ring and then reclosure after inversion at these three centers. This process is possible without loss of 2e-aromaticity by formation of three-membered aromatic systems as intermediates. The initially formed *cis*-**17** can open to *syn*-**18** with conservation of 2e-aromaticity. Rotation about the B–C bond marked with a curved arrow in Scheme 7 in *syn*-**18** leads to *anti*-**18** in which three trimethylsilyl substituents pointing in opposite directions relative to those in *syn*-**18**. This stereochemistry is locked by the reaction to form *trans*-**13**; thus, the transformation of *cis*-**11** into *trans*-**13** occurs with conservation of 2e-aromaticity in all steps. Our mechanism is supported by computations that show that the prototype molecules **17u** and **18u** are low-energy minima.[31] In addition, attack of electrophiles at the 2c2e B–B bond of triboracyclopropanates **18**, like that which occurs during the transformation of *anti*-**18** into *trans*-**13**, are well known experimentally.[7]

Our assumption that the stereoisomerization does not take place during the substitution of the *first* chloride by



Scheme 6



Scheme 7

hydride, but requires a hydrogen atom for the transformation *cis*-**17** → *syn*-**18** to be easy, is supported by the following observation. Substitution of one chloride in *cis*-**11** for CH_2SiMe_3, by reaction with $LiCH_2SiMe_3$, occurs with conservation of the *cis* configuration, as is evidenced by the X-ray structure determination of the obtained monochlorotetraborane(6).[32]

Transformation of the versatile **1b** into 1,2-diorganyl-1,2-diborolanes and their spontaneous and thermally induced reactions will be described in a forthcoming paper.

Experimental Section

General: All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with argon. Glassware was dried using a heat gun under high vacuum. ^1H, ^{11}B, and ^{13}C NMR: Bruker ARX 300 and AMX 500 spectrometers. NMR references: Me_4Si, $BF_3{\cdot}OEt_2$.

(*E*)-1,3-Bis[dimethyl(phenyl)silyl]propene (4b): *n*-Butyllithium solution (1.6 N in hexanes, 73.1 mL 117 mmol) was added to a solution of 3-(dimethylphenylsilyl)propene (20.6 g, 116.9 mmol) in *n*-pentane/diethyl ether (1:1, 100 mL) at 0 °C within 2 h. After the solution had been stirred at room temperature for 3 d, chlorodimethyl(phenyl)silane (20.5 g, 120 mmol) was added at −78 °C and the mixture was warmed to room temperature. The organic layer was washed with water (2 × 200 mL), dried with $MgSO_4$, and distilled at 1×10^{-3} mbar. Yield: 29.8 g (82%); colorless oil (b.p. 98 °C). For spectroscopic data, see ref.[10]

[1,3-Bis(trimethylsilyl)allyl]lithium (5a·Li): *n*-Butyllithium solution (1.6 N in hexanes, 45 mL 72 mmol) was added at 0 °C to a solution of **4a** (11.9 g, 64.0 mmol) in *n*-pentane/diethyl ether (1:1, 100 mL). After the solution had been stirred at room temperature for 8 d, all volatile components were evaporated in vacuo and the residue was suspended in *n*-pentane (100 mL) and stirred for 2 h. Insoluble **5a·Li** was separated using a reverse glass frit and washed with *n*-pentane (2 × 30 mL). Yield: 9.6 g (78%); colorless, pyrophoric powder. ^1H NMR (200 MHz, [D$_8$]THF, 300 K): $\delta = -0.11$ (s, 18 H, $SiMe_3$), 2.64 (d, $^3J_{H,H} = 16$ Hz, 2 H, CHSi), 6.57 (t, $^3J_{H,H} = 16$ Hz, 1 H, C_2CH) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF, 300 K): $\delta = 2.1$ (q, $SiMe_3$), 67.3 (d, $^1J_{C,H} = 128$ Hz, CHSi), 154.3 (d, $^1J_{C,H} = 137$ Hz, C_2CH) ppm.

1,3-Bis[dimethyl(phenyl)silyl]allyllithium (5b·Li): In a similar reaction to the preparation of **5a·Li**, **4b** (12.0 g, 38.6 mmol) was treated with *n*-butyllithium solution (1.6 N in hexanes, 26.3 mL 42.1 mmol) for 4 d. After workup, **5b·Li** (8.56 g, 70%) was obtained as a slightly yellow, pyrophoric powder. ^1H NMR (300 MHz, [D$_8$]THF, 300 K): $\delta = 0.20$ (s, 12 H, SiMe), 2.95 (d, $^3J_{H,H} = 16$ Hz, 2 H, CHSi), 6.77 (t, $^3J_{H,H} = 16$ Hz, 1 H, C_2CH), 7.15−7.65 (m, 10 H, Ph) ppm.

(*E*/*Z*)-1-[1,3-Bis(trimethylsilyl)allyl]-2-chloro-1,2-bis(dimethylamino)diborane(4) (6a): 1,2-Dichloro-1,2-bis(dimethylamino)diborane(4) (**3**)[33] (17.2 g, 95.0 mmol) was added dropwise to a solution of [1,3-bis(trimethylsilyl)allyl]lithium (**5a·Li**) (18.0 g, 93.6 mmol) in diethyl ether (150 mL) at −78 °C. The mixture was warmed to room temperature and all volatile compounds were evaporated in vacuo. After filtration and washing the residue with *n*-pentane (2 × 50 mL), the filtrate was distilled at 1×10^{-1} mbar to yield allyldiborane(4) (*E*/*Z*)-**6a** (29.4 g, 95% relative to **3**; 85:15) as a colorless oil (b.p. 68−72 °C). **(*E*)-6a:** ^1H NMR (300 MHz, $CDCl_3$, 300 K): $\delta = -0.01$, 0.02 (each s, each 9 H, $SiMe_3$), 2.00 (d, $^3J_{H,H} = 11$ Hz, 1 H, BCHSi), 2.68, 2.69, 2.77, 2.88 (each s, each 3 H, NMe), 5.20 (d, $^3J_{H,H} = 18$ Hz, 1 H, C=CHSi), 6.09 (dd, $^3J_{H,H} = 18$, 11 Hz, 1 H, C*H*=CHSi) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): $\delta = 42$, 46 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): $\delta = -1.1$, −0.8 (each q, $SiMe_3$), 41.2 (br. d, $^1J_{C,H} = 94$ Hz, BCHSi), 37.6, 39.3, 42.2, 44.6 (each q, NMe), 123.3 (d, $^1J_{C,H} = 132$ Hz, CH=*C*HSi), 149.3 (d, $^1J_{C,H} = 148$ Hz, *C*H=CHSi) ppm.

(*E*/*Z*)-1-{1,3-Bis[dimethyl(phenyl)silyl]allyl}-2-chloro-1,2-bis(dimethylamino)diborane(4) (6b): (*E*/*Z*)-**6b** was synthesized by a similar procedure to that of (*E*/*Z*)-**6a** from **3** (4.42 g, 24.44 mmol) and {1,3-bis[dimethyl(phenyl)silyl]allyl}lithium (**5b·Li**, 6.9 g, 22.2 mmol). Distillation at 1×10^{-3} mbar yielded (*E*/*Z*)-**6b** (8.29 g, 82% relative to **3**; 9:1) as a colorless oil (b.p. 105−110 °C). **(*E*)-6b:** ^1H NMR (300 MHz, $CDCl_3$, 300 K): $\delta = 0.27$, 0.29, 0.37 (each s, total 12 H, SiMe), 2.28 (d, $^3J_{H,H} = 11$ Hz, 1 H, BCHSi), 2.35, 2.62, 2.71, 2.85 (each s, each 3 H, NMe), 5.29 (d, $^3J_{H,H} = 18$ Hz, 1 H, CH=C*H*Si), 6.24 (dd, $^3J_{H,H} = 18$, 11 Hz, 1 H, C*H*=CHSi), 7.25−7.60 (m, 10 H, Ph) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): $\delta = 42$ ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): $\delta = -3.4$, −2.5, −2.2, −2.1 (each q, SiMe), 40.9 (br. d, $^1J_{C,H} = 126$ Hz, BCHSi), 37.6, 39.0, 42.1, 44.5 (each q, NMe), 122.2 (d, $^1J_{C,H} = 136$ Hz, CH=*C*HSi), 127.3, 127.6, 128.6, 128.6, 133.8, 134.0 (each d, *o*-, *m*-, *p*-C), 139.6, 139.9 (each s, *i*-C), 150.9 (d, $^1J_{C,H} = 150$ Hz, *C*H=CHSi) ppm.

Lithium 1,2-Bis(dimethylamino)-4,5-bis(trimethylsilyl)diborolan-3-ide (7a·Li): Naphthalene (ca. 10 mg) was added to a mixture of lithium powder (600 mg, 86.4 mmol) in THF (150 mL) and then the suspension was stirred until it turned dark-green (5−30 min). The flask was then placed in a big water bath and allyldiborane(4) **6a** (12.0 g, 36.3 mmol) was added within 2 min. After the mixture had been stirred overnight, all volatile compounds were evaporated in vacuo and the residue was suspended in *n*-pentane (150 mL). After filtration, a stable solution of **7a** was obtained, which was used for further syntheses. Crystallization from *n*-pentane at −30 °C yielded **7a**·Li[THF]$_2$ (8.76 g, 50%) as colorless crystals (m.p. 43 °C). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 0.31, 0.33 (each s, each 9 H, $SiMe_3$), 1.20 (s, 1 H, BCHSi), 1.41 (m, 8 H, THF), 2.08 (d, $^3J_{H,H}$ = 3 Hz, 1 H, C_2CHSi), 2.78, 3.03, 3.25 (each s, total 12 H, NMe), 3.48 (m, 8 H, THF), 4.58 (d, $^3J_{H,H}$ = 3 Hz, 1 H, B=CH) ppm. ^{11}B NMR (96 MHz, C_6D_6, 300 K): δ = 38, 52 ppm. ^{13}C NMR (75 MHz, C_6D_6, 300 K): δ = −2.5, 0.8 (each q, $SiMe_3$), 25.4 (t, THF), 30.4 (br. d, $^1J_{C,H}$ = 109 Hz, BCHSi), 33.6 (d, $^1J_{C,H}$ = 115 Hz, C_2*C*HSi), 42.5, 46.5, 46.8 (each q, NMe), 68.5 (t, THF), 109.0 (br. d, $^1J_{C,H}$ = 118 Hz, B=CH) ppm.

3,4-Bis(dimethylamino)-5-(trimethylsilyl)-3,4-diboracyclopentene (8): 1,1,1-Trifluoro-2-iodoethane (8.19 g, 39.0 mmol) was added to a solution of **7a** (prepared from 12.9 g **6a**) in diethyl ether (100 mL) at −78 °C. The mixture was warmed to room temperature within 10 min by using a water bath and then distilled at 20 mbar to yield **8** (4.33 g) as colorless liquid (b.p. 60−62 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.08 (s, 9 H, $SiMe_3$), 1.45 (d, $^3J_{H,H}$ = 3 Hz, 1 H, BCHSi), 2.78, 2.87, 2.95, 2.99 (each s, each 3 H, NMe), 6.13 (d, $^3J_{H,H}$ = 9 Hz, 1 H, BCH), 7.01 (dd, $^3J_{H,H}$ = 9, 3 Hz, 1 H, C_2CH) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 46, 51 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −1.3 (q, $SiMe_3$), 34.4 (br. d, $^1J_{C,H}$ = 112 Hz, BCHSi), 41.2, 41.4, 44.9, 45.5 (each q, NMe), 137.1 (br. d, $^1J_{C,H}$ = 149 Hz, BCH), 159.5 (d, $^1J_{C,H}$ = 152 Hz, C_2*C*H) ppm.

1,2-Bis(dimethylamino)-3,4,5-tris(trimethylsilyl)-1,2-diborolane (2c): A solution of **7a·Li** [prepared from **6a** (12.0 g, 36.3 mmol)] in *n*-pentane/diethyl ether (2:1, 150 mL) was cooled to −78 °C and mixed with 1.1 equiv. of chlorotrimethylsilane (4.34 g, 39.9 mmol). After warming to room temperature, all volatile components were evaporated in vacuo and the residue was suspended in *n*-pentane (100 mL). Filtration and evaporation of the solvent yielded **2c** (12.43 g, 93% relative to **6a**) as a highly viscous oil that crystallized overnight (m.p. 42 °C). Usually, the *n*-pentane solutions were used for the synthesis of **1b** without further workup. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.15, 0.04 (each s, total 27 H, $SiMe_3$), 0.64 (d, $^3J_{H,H}$ = 3 Hz, 2 H, BCHSi), 1.46 (t, $^3J_{H,H}$ = 3 Hz, 1 H, C_2CHSi), 2.82, 2.90 (each s, each 6 H, NMe) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 54 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −3.3, 1.5 (each s, $SiMe_3$), 23.6 (br. d, $^1J_{C,H}$ = 123 Hz, BCHSi; d, $^1J_{C,H}$ = 123 Hz, C_2*C*HSi), 42.7, 45.5 (each q, NMe) ppm.

1,2-Bis(dimethylamino)-3,4-bis(trimethylsilyl)-1,2-diborolane (2d): Starting from **6a** (12.2 g), **2d** was synthesized by a similar procedure to that of **2c** from **7a** and 6 N HCl (1 equiv., diethyl ether). Distillation (10 mbar, 65−70 °C) yielded **2d** (8.53 g, 78%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.15, 0.13 (each s, each 9 H, $SiMe_3$), 0.76 (s, 1 H, BCHSi), 0.77 (dd, $^2J_{H,H}$ = 17, $^3J_{H,H}$ = 4 Hz, 1 H, BCH*H′*), 1.05 (dd, $^2J_{H,H}$ = 17, $^3J_{H,H}$ = 10 Hz, 1 H, BC*H*H′), 1.17 (dd, $^3J_{H,H}$ = 10, 4 Hz, 1 H, C_2CHSi), 2.75, 2.79, 2.89, 2.91 (each s, each 3 H, NMe) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 53 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −3.3, −0.9 (each q, $SiMe_3$), 20.5 (br. pseudo t, $^1J_{C,H}$ = 117 Hz, BCH_2), 20.9 (d, $^1J_{C,H}$ = 120 Hz, C_2*C*HSi), 27.0 (br. d, $^1J_{C,H}$ = 109 Hz, BCHSi), 40.7, 40.9, 45.1, 45.6 (each q, NMe) ppm.

1,2-Dichloro-3,4,5-tris(trimethylsilyl)-1,2-diborolane (1b): A solution of **2c** (6.8 g, 18.5 mmol) in *n*-pentane (150 mL) was mixed with neat BCl_3 (8.67 g, 74 mmol, 4.4 equiv.) at −78 °C and then warmed to 0 °C within 3 h. All volatile components were evaporated at this temperature and then the residue was warmed to room temperature in vacuo and evacuation was continued for 2 h. The residue was treated with *n*-pentane (50 mL) and the insoluble byproducts were filtered off. Evaporation of the solvent yielded **1b** (6.2 g, 96%) as a highly viscous oil, which was essentially pure based on its ^{1}H NMR spectra. Crystallization from *n*-pentane (necessary for reactions starting with more than 10 g of **2c**) at −30 °C gave light-yellow crystals [68%; m.p. 44 °C (decomposition)]. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.15, 0.16 (each s, total 27 H, $SiMe_3$), 1.92 (t, $^3J_{H,H}$ = 1 Hz, 1 H, C_2CHSi), 2.13 (d, $^3J_{H,H}$ = 2 Hz, 2 H, BCHSi) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 84 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −3.4, 1.0 (each q, $SiMe_3$), 28.4 (d, $^1J_{C,H}$ = 124 Hz, C_2*C*HSi), 53.2 (br. d, $^1J_{C,H}$ = 117 Hz, BCHSi) ppm.

3,7-Dichloro-1,2,4,5,6-pentakis(trimethylsilyl)-3,7-diboracycloheptene (9): 1b (ca. 4.5 g, 12.8 mmol) dissolved in *n*-pentane (50 mL) was treated with bis(trimethylsilyl)ethyne (3.27 g, 19.2 mmol, 1.5 equiv.) at 0 °C. After warming to room temperature, all volatile components were evaporated in vacuo, to yield **9** (6.35 g, 95%) as a highly viscous oil that contained some minor impurities. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 0.10, 0.18, 0.33 (each s, total 45 H, $SiMe_3$), 1.26 (t, $^3J_{H,H}$ = 7 Hz, 1 H, C_2CHSi), 1.43 (d, $^3J_{H,H}$ = 7 Hz, 2 H, BCHSi) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 67 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 0.7, 1.6, 3.0 (each q, $SiMe_3$), 18.4 (d, $^1J_{C,H}$ = 127 Hz, C_2*C*HSi), 34.8 (br. d, $^1J_{C,H}$ = 112 Hz, BCHSi), 181.2 (br. s, BCSi) ppm.

1,2-Dipiperidino-3,4,5-tris(trimethylsilyl)-1,2-diborolane (2e): *N*-(Trimethylsilyl)piperidine (ca. 4 equiv.) was added to a stirred solution of **2c** (2.2 g, 6.27 mmol) in *n*-pentane (50 mL) at room temperature. After 24 h, all volatile components were evaporated in vacuo to yield **2e** (2.64 g, 94%) as a slightly yellow solid. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 0.26, 0.43 (each s, total 27 H, $SiMe_3$), 1.00 (d, $^3J_{H,H}$ = 5 Hz, 2 H, BCHSi), 1.5−1.7 (m, 12 H, pip), 1.91 (t, $^3J_{H,H}$ = 5 Hz, 1 H, C_2*C*HSi), 3.3−3.5 (m, 8 H, pip) ppm. ^{11}B NMR (96 MHz, C_6D_6, 300 K): δ = 53 ppm. ^{13}C NMR (75 MHz, C_6D_6, 300 K): δ = −2.6, 2.0 ($SiMe_3$), 22.7 (br., BCHSi), 24.3 (C_2*C*HSi), 25.3, 27.8, 28.2, 51.9, 53.9 (pip) ppm.

1,2-Bis(diethylamino)-3,4,5-tris(trimethylsilyl)-1,2-diborolane (2f): By a procedure analogous to that for the preparation of **2e**, **2f** was synthesized from **2c** (4.0 g, 11.39 mmol) and diethyl(trimethylsilyl)amine (4 equiv.) to yield **2f** (4.59 g, 95%) as a slightly yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.14, 0.03 (each s, total 27 H, $SiMe_3$), 0.65 (d, $^3J_{H,H}$ = 3 Hz, 2 H, BCHSi), 1.05 (t, 12 H, NCH_2CH_3), 1.47 (t, $^3J_{H,H}$ = 3 Hz, 1 H, C_2CHSi), 3.22 (q, 8 H, NCH_2CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 54 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −2.8, 1.5 (each q, $SiMe_3$), 14.6, 15.0 (each q, NCH_2CH_3), 22.8 (br. d, $^1J_{C,H}$ = 110 Hz, BCHSi), 23.8 (d, $^1J_{C,H}$ = 122 Hz, C_2*C*HSi), 43.2, 45.8 (each t, NCH_2CH_3) ppm.

1-Chloro-2-(dimethylamino)-3,4,5-tris(trimethylsilyl)-1,2-diborolane (10a): Dimethyl(trimethylsilyl)amine (530 mg, 4.52 mmol) was added to a solution of **1b** (1.6 g, 4.56 mmol) in *n*-pentane (50 mL) at room temperature. After the mixture had been stirred overnight, all the volatile components were evaporated in vacuo and the residue was treated with *n*-pentane (25 mL) and filtered. Crystallization from *n*-pentane (5 mL) at −30 °C yielded **10a** (990 mg, 60%) as slightly yellow crystals [m.p. 52 °C (some decomposition)]. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = −0.05, 0.25, 0.31 (each s, each 9 H, $SiMe_3$), 1.29 (s, 1 H, NBCHSi), 1.67 (d, $^3J_{H,H}$ = 2 Hz, 1 H, ClBCHSi), 1.79 (d, $^3J_{H,H}$ = 2 Hz, 1 H, C_2CHSi), 2.62, 3.04 (each s, each 3 H, NMe) ppm. ^{11}B NMR (96 MHz, C_6D_6, 300 K): δ = 48, 91 ppm. ^{13}C NMR (75 MHz, C_6D_6, 300 K): δ = −4.6, 0.1, 0.2 ($SiMe_3$), 24.4 (C_2CHSi), 27.9 (br., NBCHSi), 40.7, 41.4 (NMe), 46.8 (br., ClBCHSi) ppm.

1-Chloro-2-piperidino-3,4,5-tris(trimethylsilyl)-1,2-diborolane (10b): *N*-(Trimethylsilyl)piperidine (2.62 g, 16.7 mmol) was added to a solution of **1b** (5.85 g, 16.7 mmol) in *n*-pentane (50 mL) at −78 °C. After warming to room temperature, the mixture was stirred for an additional 18 h and then all the volatile components were evaporated in vacuo. Crystallization of the residue from *n*-pentane (15 mL) at −30 °C yielded **10b** (4.86 g, 73%) as colorless crystals [m.p. 72 °C (some decomposition)]. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = −0.15, 0.01, 0.13 (each s, each 9 H, $SiMe_3$), 1.21 (d, $^3J_{H,H}$ = 2 Hz, 1 H, BCHSi), 1.43 (d, $^3J_{H,H}$ = 2 Hz, 1 H, BCHSi), 1.62 (dd, $^3J_{H,H}$ = 3, 2 Hz, 1 H, C_2CHSi), 1.32−1.75 [m, 6 H, $N(CH_2)_5$], 3.06, 3.29, 3.95 [each m, total 4 H, $N(CH_2)_5$] ppm. ^{11}B NMR (96 MHz, $CDCl_3$, 300 K): δ = 47, 92 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = −3.4, 1.1, 1.3 (each q, $SiMe_3$), 25.1 (d, $^1J_{C,H}$ = 123 Hz, $C_2\mathit{C}HSi$), 27.9 (br. d, $^1J_{C,H}$ = 123 Hz, NBCHSi), 47.3 (br. d, $^1J_{C,H}$ = 104 Hz, ClBCHSi), 25.1, 28.1, 28.6, 51.1, 51.7 [each d, $N(CH_2)_5$] ppm.

Lithium 1-Piperidino-2,4,5-tris(trimethylsilyl)-1,2-diborolan-3-ide (7b·Li): A solution of **10b** (2.42 g, 6.1 mmol) in diethyl ether (25 mL) was added to a suspension of lithium powder (ca. 500 mg) in diethyl ether (25 mL) at room temperature. After the mixture had been stirred for 2 h, all the volatile components were evaporated in vacuo. The residue was treated with *n*-pentane (50 mL) and the excess lithium powder and LiCl were filtered off. Crystallization from *n*-pentane (20 mL) at −30 °C yielded **7b**·Li$[Et_2O]_2$ (1.67 g, 62%) as colorless crystals (m.p. 93 °C). ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 0.15, 0.23, 0.45 (each s, each 9 H, $SiMe_3$), 0.86 (t, 6 H, Et_2O), 1.26 (s, 1 H, BCHSi), 1.55−1.87 [m, 6 H, $N(CH_2)_5$], 2.33 (d, $^3J_{H,H}$ = 3 Hz, 1 H, C_2CHSi), 3.01 (q, 4 H, Et_2O), 3.13, 3.42, 3.66, 4.21 [each m, each 1 H, $N(CH_2)_5$], 6.57 (d, $^3J_{H,H}$ = 3 Hz, 1 H, BCH) ppm. ^{11}B NMR (96 MHz, C_6D_6, 300 K): δ = 33, 58 ppm. ^{13}C NMR (75 MHz, C_6D_6, 300 K): δ = −2.5, 0.3, 3.2 (each q, $SiMe_3$), 14.4 (q, Et_2O), 27.5 (br., BCHSi), 26.3, 28.8, 29.3, [each t, $N(CH_2)_5$], 42.3 (d, $^1J_{C,H}$ = 119 Hz, $C_2\mathit{C}HSi$), 51.8, 56.2 [each t, $N(CH_2)_5$], 66.1 (t, Et_2O), 149.2 (br. d, $^1J_{C,H}$ = 122 Hz, BCH) ppm.

Dichlorotetraborane(6) (*cis*-11): $K_{2.8}Na$ (3 mL) was added to a solution of **1b** (5.92 g, 16.9 mmol) in *n*-pentane (150 mL; water bath, reflux condensor) at room temperature. After the reaction started (reflux, precipitation of a deep-blue salt), the mixture was stirred for an additional 30 min. The insoluble components were filtered off and washed with *n*-pentane (3 × 50 mL). Removal of the solvent yielded *cis*-**11** (5.11 g, 96%) as a yellow solid, essentially pure based on its ^{1}H NMR spectra. The use of larger quantities (> 10 g) of **1b** in this reaction caused the formation of some impurities. In this case, crystallization from *n*-pentane at −30 °C yielded **1b** (ca. 75%) as yellow crystals. Spectroscopic data: see ref.[5]

Tetraborane(6) (*trans*-13): $NaBEt_3H$ solution (1.0 N in toluene, 6 mL, 6 mmol) was added to a solution of *cis*-**11** (1.9 g, 3 mmol) in diethyl ether (50 mL) at −78 °C. The mixture was warmed slowly (12 h) to room temperature and then all the volatile components were evaporated in vacuo. The residue was treated with *n*-pentane (50 mL) and then the solution was separated from the solids using a pipette. After washing the solids with additional *n*-pentane (25 mL), the combined solutions were reduced to a volume of 20 mL. Crystallization at −30 °C yielded *trans*-**13** (1.02 g, 60%) in three fractions. Spectroscopic data: see ref.[5]

Tetraborane(4) (*cis*-12): Lithium naphthalenide solution (1.0 N, 26.7 mL, 26.7 mmol) was added to a suspension of *cis*-**11** (8.4 g, 13.3 mmol) in diethyl ether (150 mL) at −100 °C. After warming to room temperature, all of the volatile components were evaporated in vacuo and the naphthalene was sublimed (60 °C/1 × 10^{-3} mbar). The residue was treated with *n*-pentane (120 mL) and the insoluble solids were filtered off. Crystallization at −30 °C yielded *cis*-**12** (7.08 g, 95%) as a yellow solid. Spectroscopic data: see ref.[6]

Dimethyltetraborane(6) (*cis*-14): A solution of *cis*-**12** (1.9 g, 3.39 mmol) in THF (25 mL) was treated with lithium naphthalenide (2 equiv.), followed by iodomethane (0.95 g, 6.79 mmol), at −100 °C. After warming to room temperature, all of the volatile compounds were evaporated in vacuo, the residue was treated with *n*-pentane, and the insoluble material was filtered off. Crystallization from *n*-pentane (10 mL) at −30 °C yielded *cis*-**14** (1.60 g, 80%) as yellow crystals [m.p. 125 °C (decomposition)]. Spectroscopic data: see ref.[20]

Tetraborane(6) (*cis*-13): A solution of *cis*-**12** (1.1 g, 1.96 mmol) in THF (25 mL) was treated with lithium naphthalenide (2 equiv.) followed by HCl solution (2 N in diethyl ether, 0.99 mL, 1.98 mmol). After warming to room temperature and evaporation of the volatile compounds in vacuo, the naphthalene was separated by sublimation (60 °C/1 × 10^{-3} mbar). The residue was treated with *n*-pentane and the insoluble compounds were filtered off. *cis*-**13** of only 95% parity was obtained by crystallization from *n*-pentane at −30 °C. Yield (^{1}H NMR spectroscopy): 90%. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 0.07, 0.24, 0.28 (each s, each 18 H, $SiMe_3$), 1.74 (pseudo t, $^3J_{H,H}$ = 4 Hz, 2 H, C_2CHSi), 1.93 (d, $^3J_{H,H}$ = 4 Hz, 2 H, B_3BCHSi), 2.23 (m, 2 H, $HBC\mathit{H}Si$), 7.01 (very br. s, 2 H, BH) ppm. ^{11}B NMR (96 MHz, C_6D_6, 300 K): δ = 27, 51 ppm. ^{13}C NMR (75 MHz, C_6D_6, 300 K): δ = −3.6, 0.4, 0.5 ($SiMe_3$), 28.9 (d, $^1J_{C,H}$ = 123 Hz, $C_2\mathit{C}HSi$), 30 (br., BCHSi), 41.6 (br. d, $^1J_{C,H}$ = 110 Hz, BCHSi) ppm.

Crystal Structure Determinations: All single-crystal diffraction experiments were performed with an image plate area detector system (IPDS, Stoe) using an Mo-K_α radiation source equipped with a graphite monochromator. Crystals were selected from dry inert paraffin oil, mounted on top of a quartz capillary, and measured with φ scans. All crystal and experimental data of the six structure determinations are listed in Table 1. The structures were all solved by direct methods using the SHELXS program[34] and refined by the full-matrix least-squares method against all F^2 data.[35] "Interesting" hydrogen atoms at the nuclei of the structures were localized from difference Fourier maps and refined using individual isotropic displacement parameters; those of peripheral moieties, like the $SiMe_3$ groups, were treated as riding on idealized calculated positions. Their displacement parameters were fixed to 1.2- or (for methyl groups) 1.5-times the U_{eq} values of their bonding partners. All heavier atoms were refined using anisotropic displacement parameters. Images of the structure were drawn using DIAMOND.[36] Crystals of **1b** suitable for X-ray analysis were grown from an *n*-pentane solution at −30 °C. Single crystals of **5b·Li** were obtained by dissolving **5b·Li** (ca. 2 g) in boiling toluene (80 mL) and then keeping the solution at 95 °C for 18 h. The diffraction pattern of the very sensitive crystal showed weak powder rings, which probably caused the somewhat reduced quality of the results, especially

Table 1. Crystal data and experimental details of the crystal structure determinations; all crystals were measured at T = 193(1) K

	1b	**5b**·**Li**	**7a**·**Li[THF]$_2$**	**7b**·**Li[Et$_2$O]$_2$**	*cis*-**11**	*cis*-**14**
Empirical formula	$C_{12}H_{30}B_2Cl_2Si_3$	$C_{19}H_{25}Li_1Si_2$	$C_{21}H_{49}B_2LiN_2O_2Si_3$	$C_{25}H_{60}B_2LiN_2O_2Si_3$	$C_{24}H_{60}B_4Cl_2Si_6$	$C_{26}H_{66}B_4Si_6$
Formula mass	351.15	316.51	446.36	519.57	631.40	590.57
Crystal system	monoclinic	tetragonal	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	$I4_1$ ($I4_3$)	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell [pm, °]	a = 909.6(1)	2447.8(1)	973.2(1)	1011.5(1)	1015.6(1)	1014.5(1)
	b = 1762.4(1)	2447.8(1)	1126.0(1)	1768.5(2)	1273.5(1)	1280.6(1)
	c = 1325.3(1)	1289.8(1)	1426.2(1)	1986.4(2)	1652.0(1)	1643.9(1)
	α = 90	90	94.46(1)	83.09(1)	103.10(1)	103.40(1)
	β = 90.650(10)	90	98.76(1)	90.00(1)	90.28(1)	90.05(1)
	γ = 90	90	104.04(1)	81.67(1)	109.30(1)	108.69(1)
V [Å^3]	2124.4(3)	7728.1(7)	1487.7(2)	3489.8(6)	1956.7(3)	1961.4(3)
Z	4	16	2	4	2	2
Calculated density [g·cm^{-3}]	1.098	1.088	0.996	0.989	1.072	1.000
Absorption coefficent [mm^{-1}]	0.462	0.177	0.136	0.155	0.363	0.227
F(000)	752	2720	492	1152	684	652
Crystal size [mm]	0.12 × 0.10 × 0.03	0.65 × 0.30 × 0.25	0.45 × 0.30 × 0.30	0.55 × 0.45 × 0.30	0.45 × 0.40 × 0.40	0.35 × 0.30 × 0.30
$\Theta_{max.}$ [°]	26.13	25.90	25.92	25.93	25.91	25.92
Index range	$-11 < h < 11$,	$-29 < h < 29$	$-11 < h < 11$	$-12 < h < 12$	$-12 < h < 12$	$-12 < h < 11$
	$-21 < k < 21$	$-29 < k < 30$	$-13 < k < 13$	$-21 < k < 21$,	$-15 < k < 15$,	$-15 < k < 15$
	$-16 < l < 15$	$-15 < l < 15$	$-17 < l < 17$	$-24 < l < 24$	$-20 < l < 20$	$-20 < l < 20$
Scan type	φ scans	φ scans	φ scans	φ scans	φ scans	φ scans
No. of reflections	16576	22589	16018	34646	17996	11838
Unique reflections (R_{int})	4133 (0.061)	7427 (0.0511)	5411 (0.0490)	12717 (0.0718)	7099 (0.0289)	7067 (0.0306)
Observed reflections [$I > 2\sigma(I)$]	2472	6331	3349	7402	5674	5125
Parameters, data/param. ratio	193, 21	430, 17	303, 18	655, 19	367, 19	371, 19
Goodness-of-fit (F^2)	0.818	1.023	0.885	0.827	0.966	0.947
R [$I > 2\sigma(I)$]	0.0327	0.0463	0.0427	0.0427	0.0298	0.0348
wR_2 (all refl.)	0.0648	0.1236	0.1156	0.0974	0.0770	0.0878
Largest diff. peak/hole [e·Å^{-3}]	+0.221/−0.261	+0.690/−0.220	+0.329/−0.238	+0.419/−0.285	+0.286/−0.225	+0.340/−0.252

the relatively high residual electron density of 0.69 e/Å^3. The absolute structure could not be determined clearly because of the absence of suitably strong anomalous scatters [Flack parameter x = 0.21(11)]. Possible twinning by merohedry could be excluded. Crystals of **7a**·Li[THF]$_2$ suitable for X-ray analysis were grown from an *n*-pentane solution at −30 °C. In its structure, one of the THF molecules coordinated to lithium shows disorder: C15 has two alternative positions (1:1) above and below the plane of the remaining atoms. A single crystal of **7b**·Li[Et$_2$O]$_2$ was obtained from an *n*-pentane/diethyl ether (1:1) solution at −30 °C. Crystals of the isostructural compounds *cis*-**11** and *cis*-**14** were grown from an *n*-pentane solution at −30 °C. CCDC-225331 (**1b**), -225332 (**5b·Li**), -225333 (**7a·Li[THF]$_2$**), -225334 (**7a·Li[Et$_2$O]$_2$**), -225335 (*cis*-**11**), and -225336 (*cis*-**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm Polyeder) and the Fonds der Chemischen Industrie.

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Received January 30, 2004
Early View Article
Published Online May 25, 2004