# Reactions of Diboratetrahalides(4) with Boriranylideneboranes − Formation, Reactivity, and Structures of Cyclic Tetraborylmethanes and Isomeric Diborylmethyleneborane Derivatives

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*Dedicated to Prof. Dr. Günter Helmchen on the occasion of his 60th birthday*

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Reaction of the boriranylideneboranes **1a**,**b**,**c** with tetrahalogenodiboranes(4) leads to two types of products. In the case of **1a** the cyclic tetraborylmethane derivatives **2a**,**a′** are formed in high yield, whereas **1b**,**c** yield the isomeric linear diborylmethyleneboranes **3b**,**c**. Compound **2a** reacts with diethylamine, (dimethylamino)trimethylsilane, and lithium pyrrolidinide to give the 1,3-diboretanes **4a**,**b**,**c**. The composition of the products was determined from spectroscopic data and X-ray structure analyses of **2a**, **3c**, **4a**, and **4c**.

## Introduction

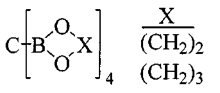
In 1969 the first synthesis of tetraborylmethane derivatives was reported. Stone et al.[1] obtained the tetrakis(dichloroboryl)methane (**A**), which was characterized by mass spectrometry, in a co-condensation reaction of carbon and borontrichloride. At the same time, Matteson et al. synthesized the oxygen-substituted derivatives **B** and **C**.[2−5] These compounds are widely used in organic synthesis.

$C(BCl_2)_4$

**A**

$C[B(OMe)_2]_4$

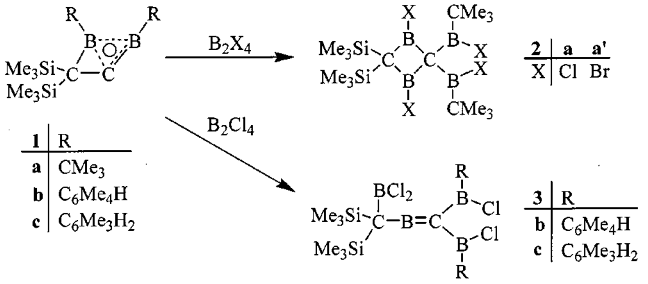
**B**



**C**

Tetraborylmethane [$C(BH_2)_4$] has been the subject of theoretical studies. Schleyer et al. calculated the energy differences between the tetrahedral and the planar structure of methane derivatives.[6] It was found that electropositive substituents like lithium or boron should stabilize the planar tetracoordinate configuration by reducing the energy difference of 630 kJ/mol between tetrahedral and planar methane. For nonclassical (planar) methane, boron and lithium should act as σ-donor and π-acceptor substituents. The formation of a three-center, two-electron bond means that all substituents must lie in the same plane. Recently, the X-ray structure analysis of $C[B(OMe)_2]_4$ revealed, as expected, that it has the classical tetrahedral structure.[7]

We present here reactions of the nonclassical boriranylideneboranes **1a**,**b**,**c**, first prepared by Berndt et al. in the early 1980s,[8,9] with tetrahalogenodiboranes(4). In the case of the *tert*-butyl-substituted compound **1a**, the addition of $B_2X_4$ (X = Cl, Br) leads to **2a**,**a′**, which are the first tetraborylmethane derivatives with two different substituents at the central carbon atom (Scheme 1). In contrast, **1b**,**c** and $B_2Cl_4$ form the linear products **3b**,**c** in good yields. To our surprise the reactivity of **2a**,**a′** is rather weak. Substitutions to form definite products occur with amines to give **4a**,**b**,**c**.



Scheme 1

## Results and Discussion

### Synthesis and Reactivity

The tetraborylmethanes **2a** and **2a′** are formed in excellent yields upon addition of $B_2X_4$ (X = Cl, Br) to a solution of **1a** in hexane at low temperature. The spectroscopic data of **2a**,**a′** are similar; **2a** is a colorless, low melting, crystalline solid, which shows only one $^{11}B$ NMR signal at δ = 69 for all boron atoms. In the $^1H$ NMR spectrum the expected signals for $SiMe_3$ and $CMe_3$ are observed. The $^{13}C$ NMR spectrum of **2a** exhibits the resonances of the methyl groups of the trimethylsilyl and *tert*-butyl substituents at δ = 3.7 and 29.6, respectively. The quaternary carbon atoms of $CMe_3$ and $Si_2CB_2$ give broad signals at δ = 31 and 58, respectively. A low-field temperature-dependent signal at δ = 79 is detected for the central carbon atom of $CB_4$.

Compound **2a′** is less stable than **2a**. Decomposition of freshly prepared, colorless **2a′** is visible by the increase of a

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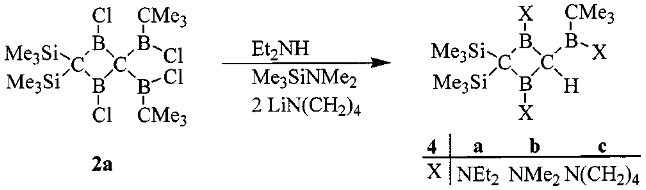
brown color. The CI mass spectra of **2a′** exhibits the molecular ion peak [$M^+$] at *m*/*z* = 648 with an intensity of 2%.

The reaction of $B_2Cl_4$ with the aryl-substituted compounds **1b**,**c** yields slightly yellow crystals of **3b**,**c** with a molecular mass of 622 and 594, respectively. The $^{11}B$ NMR spectra show, for both compounds, one broad signal, which splits at higher temperature into two peaks with a 1:1 intensity. The signal at lower field belongs to the two equivalent boron atoms, the second signal is formed by superposition of signals for the remaining boron centers. The expected signals appear in the $^1H$ and the $^{13}C$ NMR spectra of **3b**,**c**, the signals for $CB_3$ are broad and located at $\delta = 95$ and 96, respectively.

In an attempt to substitute the four chlorine atoms at boron by amino substituents, compound **4a** was synthesized by treating **2a** with an excess of diethylamine in hexane (Scheme 2). This type of compound is already known in the literature and was first prepared by Berndt et al.[10,11] It is obtained as a colorless solid in good yield. During the reaction, one of the carbon−boron bonds is cleaved with protonation of the carbon atom by the amine. The $^{11}B$ NMR spectrum of **4a** shows only one signal at $\delta = 45$ for all three boron atoms. For the methylene protons of the diethylamine groups of the ring, an $ABX_3$ system appears due to the prochiral carbon ring atom. The resonance for the proton at $HCB_3$ is located at $\delta = 0.37$, as indicated by a two-dimensional $^1H$, $^{13}C$ NMR study. The remaining signals of **4a** are in the expected areas. In the $^{13}C$ NMR spectrum the $CB_3$ signal is located at $\delta = 28$.



Scheme 2

In another attempt to synthesize a tetraborylmethane derivative with four amino groups, compound **2a** was treated with four equivalents of (dimethylamino)trimethylsilane. The only product isolated in this reaction is **4b**, an analog of **4a**. The origin of the hydrogen in **4b** is not known, although it might come from the *tert*-butyl group of the cleaved boryl group. However, the expected cleavage product, a (dimethylamino)boracyclopropane, was not detected. Compound **4b** was characterized by $^1H$, $^{13}C$ and $^{11}B$ NMR spectroscopy. A CI mass spectrum of **4b** shows the molecular ion peak [$M^+ + 1$] at *m*/*z* = 394 as the base peak.

To obtain further information on the reactivity of **2a**, attempts were made to substitute only two of the four chlorine atoms at boron by amino substituents. When **2a** is treated with two equivalents of lithium pyrrolidinide, the formation of **4c** is observed. Its composition was determined by NMR and MS spectroscopy and an X-ray structure analysis.

## Crystal Structures

Single crystals of **2a** were grown from a hexane solution at −20 °C. Figure 1 shows a molecule of **2a**. The torsion angle C1−B1−B2−C2 is very small (4.5°) so that the four-membered ring is almost planar. The bond lengths C1−B1 and C1−B2 are 1.555 and 1.547 Å, which are shortened in comparison to C2−B1 and C2−B2 (1.605 and 1.606 Å). The bond lengths C1−Si1 and C1−Si2 (1.912 and 1.914 Å) are longer than the corresponding distances in **4a** and **4c**. We explain these data by C−Si hyperconjugation of the ring boron atoms with the C1−Si1 and C1−Si2 bonds in **2a**. Tetracoordinate C2 is not a planar carbon center, it has a normal tetrahedral environment of four boron atoms.

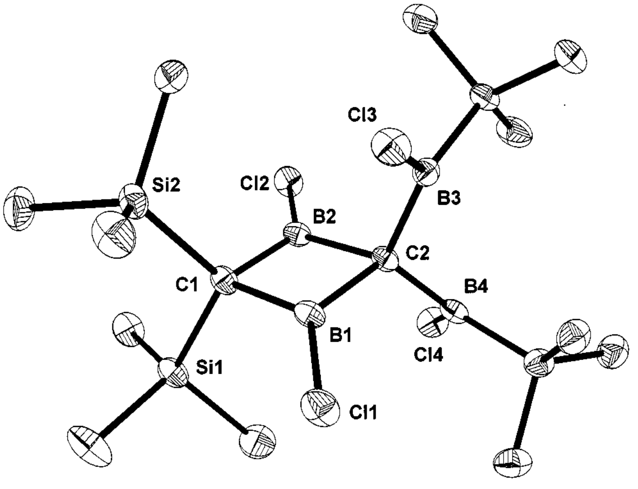


Figure 1. Structure of **2a** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.555(3), B1−C2 1.605(3), B2−C1 1.547(3), B2−C2 1.606(3), C2−B3 1.575(2), C2−B4 1.573(3), C1−Si1 1.912(2), C1−Si2 1.914(2); B1−C1−B2 80.4(1), B1−C2−B2 77.2(1), C1−B1−C2 101.0(1), C1−B2−C2 101.2(1), B3−C2−B4 113.4(1), torsion angle C1−B1−B2−C2 4.5(2)

Crystals of the compounds **3b**,**c** suitable for X-ray structure analyses were obtained from hexane at −20 °C. Both structures are disordered in the crystal. Only the structure of **3c** (Figure 2) will be discussed here because of its better crystallographic data. The most prominent feature is the linear C1−B1=C2 unit. The short B1−C2 bond length of 1.416 Å is in the range of a C=B double bond, the bond length C1−B1 (1.472 Å) is in between that of a single and a double bond. The C1−B3 bond is, at 1.732 Å, very long. Most surprising is the small B1−C1−B3 angle of 101.0°, which is a large deviation from the normal tetrahedral angle. The observed lengthening of the C1−B3 bond length in connection with the decreased bond angle and the short C1−B1 bond is explained by hyperconjugation of the C1−B3 sigma bond with the empty orbital at B1.[8]

Crystals of **4a** were obtained from hexane, whereas **4c** formed crystals in a solution of toluene. Only the structure of **4a** is discussed here. Selected bond lengths and angles of both molecules are listed in the legend of Figure 3. The four-membered ring of **4a** is slightly folded (8.7°). The B−N distances (1.397−1.414 Å) are in the range of those in other aminoboranes. The angles in the ring are very similar to those of **2a**.

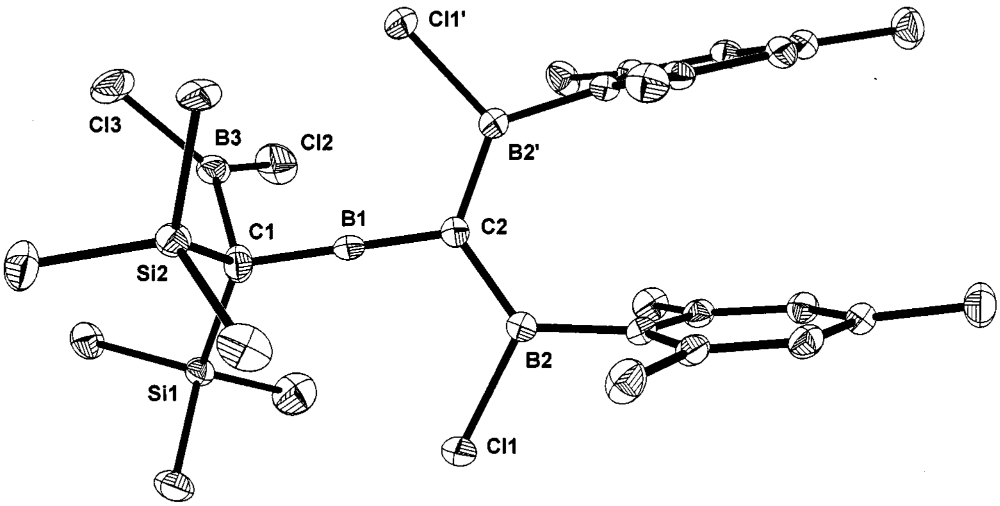


Figure 2. Structure of **3c** in the crystal; selected bond lengths [Å] and angles [°]: B1−C2 1.416(4), B1−C1 1.472(4), B2−C2 1.523(2), B3−C1 1.732(4), C1−Si1 1.878(1), C1−Si2 1.905(1); B1−C2−B2 117.5(1), B1−C1−B3 101.0(1), B1−C1−Si1 105.6(1), B1−C1−Si2 117.4(1), C2−B1−C1 180.00

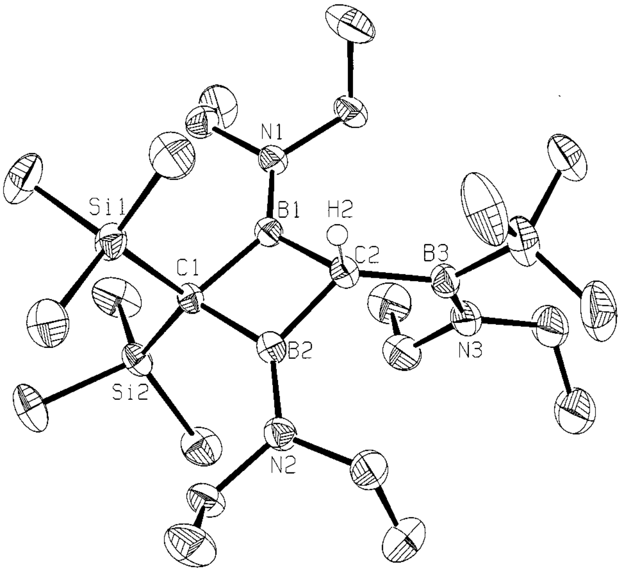


Figure 3. Structure of **4a** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.622(2), B1−C2 1.600(2), B2−C1 1.621(2), B2−C2 1.599(2), C2−B3 1.581(2), C1−Si1 1.881(1), C1−Si2 1.882(1), B1−N1 1.400(2), B2−N2 1.397(2), B3−N3 1.414(2);B1−C1−B2 79.5(1), B1−C2−B2 80.8(1), C1−B1−C2 99.2(1), C1−B2−C2 99.3(1), B2−C2−B3 129.6(1), B1−C2−B3 129.8(1), torsion angle C1−B1−B2−C2 8.7(2). − Selected bond lengths [Å] and angles [°] for **4c**: B1−C1 1.622(3), B1−C2 1.593(3), B2−C1 1.614(3), B2−C2 1.597(3), C2−B3 1.568(3), C1−Si1 1.879(2), C1−Si2 1.875(2), B1−N1 1.387(3), B2−N2 1.389(3), B3−N3 1.405(3); B1−C1−B2 78.1(2), B1−C2−B2 79.4(2), C1−B1−C2 99.2(2), C1−B2−C2 99.4(2), B2−C2−B3 129.7(2), B1−C2−B3 129.7(2), torsion angle C1−B1−B2−C2 14.8(2)

## Conclusion

Reaction of the boriranylideneboranes **1a**,**b**,**c** with tetrahalogenodiboranes(4) leads to the cyclic tetraborylmethane derivatives **2a**,**a′** or to the isomeric diborylmethyleneboranes **3b**,**c**. The substitution of the chlorine atoms of **2a** by amino groups yields the triamino derivatives **4a**,**b**,**c**, with unexpected cleavage of one of the exocyclic C−B bonds.

## Experimental Section

**General:** Reactions were carried out under dry argon or nitrogen, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. − $^1H$ and $^{13}C$ NMR: Bruker DRX 200 spectrometer and Bruker AC 500, $^{11}B$ NMR: Bruker DRX 200 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3{\cdot}Et_2O$. − Mass spectra were obtained with a ZAB-2F VH Micromass CTD spectrometer and high resolution mass spectra with a Joel MS Station JMS-700 spectrometer. − Melting points (uncorrected) were measured with a Büchi apparatus using capillaries which were filled under argon or nitrogen, and sealed.

**4,4-Bis(*tert*-butylchloroboryl)-1,3-dichloro-2,2-bis(trimethylsilyl)-1,3-diboretane (2a):** $B_2Cl_4$ (0.74 g, 4.50 mmol) was condensed into a solution of **1a** (1.33 g, 4.34 mmol) in 10 mL of hexane at −85 °C. The mixture was allowed to warm to room temperature. The solvent and all volatile components were removed under vacuum, and the colorless solid obtained was crystallized from hexane at −20 °C. Yield: 1.88 g (92%), m.p.: 78−81 °C. − $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.22 [s, 18 H, $Si(CH_3)_3$], 1.07 [s, 18 H, $C(CH_3)_3$]. − $^{11}B$ NMR (64 MHz, $CDCl_3$): δ = 69. − $^{13}C$ NMR (125 MHz, $CDCl_3$, 223 K): δ = 3.7 [q, $Si(CH_3)_3$], 29.6 [q, $C(CH_3)_3$], 31 [br. s, $C(CH_3)_3$], 58 (br. s, $CB_2$), 79 (br. s, $CB_4$). − CI-MS: *m/z* (%) = 470 (6) [$M^+$], 455 (13) [$M^+ - CH_3$], 433 (100) [$M^+ -$ Cl]. − HR-MS (CI): *m/z* = 433.1790 [$M^+ -$ Cl]; calcd. $^{12}C_{16}{}^1H_{36}{}^{35}Cl_3{}^{29}Si_2{}^{11}B_4$: 433.1794 (Δ*mm*: 0.4).

**1,3-Dibromo-4,4-bis(bromo-*tert*-butylboryl)-2,2-bis(trimethylsilyl)-1,3-diboretane (2a′):** $B_2Br_4$ (0.16 g, 0.31 mmol) was condensed into a solution of **1a** (0.10 g, 0.31 mmol) in 10 mL of hexane at −85 °C. The mixture was allowed to warm to room temperature. The solvent and all volatile components were removed under vacuum, and a colorless solid was obtained. Yield: 0.16 g (82%). − $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.32 [s, 18 H, $Si(CH_3)_3$], 1.21 [s, 18 H, $C(CH_3)_3$]. − $^{11}B$ NMR (64 MHz, $CDCl_3$): δ = 70. − $^{13}C$ NMR (125 MHz, $C_6D_6$): δ = 3.2 [q, $Si(CH_3)_3$], 29.4 [q, $C(CH_3)_3$], 32 [br. s, $C(CH_3)_3$], 61 (br. s, $CB_2$), 86 (br. s, $CB_4$). − CI-MS: *m/z* (%) = 648 (2) [$M^+$], 633 (3) [$M^+ - CH_3$], 567 (100) [$M^+ -$ Br].

**[Bis(trimethylsilyl)(dichloroboryl)methyl]-1,1-bis(chlorodurylboryl)-methyleneborane (3b):** $B_2Cl_4$ (1.11 g, 6.80 mmol) was condensed into a solution of **1b** (3.36 g, 6.80 mmol) in 45 mL of hexane at −85 °C. The mixture was allowed to warm to room temperature. The product was filtered and the colorless solid obtained was crystallized from hexane at −80 °C. Yield: 2.27 g (50%), m.p.: 189−191 °C (dec.). − $^{1}$H NMR (200 MHz, $CDCl_3$): δ = 0.65 [s, 18 H, $Si(CH_3)_3$], 1.91 (s, 12 H, *o*- and *m*-$CH_3$), 1.94 (s, 12 H, *o*- and *m*-$CH_3$), 6.54 (s, 2 H, *p*-H). − $^{11}$B NMR (96 MHz, $CDCl_3$): δ = 54, 62 (1:1). − $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 2.7 [q, $Si(CH_3)_3$], 18.9 (q, *o*- or *m*-$CH_3$), 19.5 (q, *o*- or *m*-$CH_3$), 130.8 (d, *p*-C), 131.4 (s, *o*- or *m*-C), 132.2 (s, *o*- or *m*-C), 142 (br. s, *i*-C). − $^{13}$C NMR(125 MHz, $CD_2Cl_2$, 183 K, additional signals): δ = 44 (br. s, $CB_2$), 95 (br. s, $CB_3$). − EI-MS: *m/z* (%) = 622 (44) [M$^+$], 512 (76) [M$^+$ − $Me_3SiCl$]. − HR-MS (EI): *m/z* = 620.2135 [M$^+$]; calcd. $^{12}C_{28}{}^{1}H_{44}{}^{35}Cl_4{}^{29}Si_2{}^{11}B_4$: 620.2162 (Δ*mm*: 2.7).

**[Bis(trimethylsilyl)(dichloroboryl)methyl]-1,1-bis(chloromesitylboryl)methyleneborane (3c):** $B_2Cl_4$ (1.22 g, 7.47 mmol) was condensed into a solution of **1c** (2.07 g,4.81 mmol) in 45 mL of hexane at −85 °C. The mixture was allowed to warm to room temperature, and then kept for 15 h at −20 °C to yield yellow crystals of **3c**. Yield: 0.94 g (33%), m.p.: 146−148 °C (dec.). − $^{1}$H NMR (200 MHz, $CDCl_3$): δ = 0.61 [s, 18 H, $Si(CH_3)_3$], 2.03 (s, 12 H, *o*-$CH_3$), 2.11 (s, 6 H, *p*-$CH_3$), 6.35 (s, 4 H, *m*-H). − $^{11}$B NMR (64 MHz, $CDCl_3$, 298 K): δ = 60. − $^{11}$B NMR (64 MHz, toluene, 333 K): δ = 57, 65. − $^{13}$C NMR (125 MHz, $CDCl_3$, 223 K): δ = 3.2 [q, $Si(CH_3)_3$], 22.0 (q, *p*-$CH_3$), 23.2 (q, *o*-$CH_3$), 45 (br. s, $CB_2$), 96 (br. s, $CB_3$), 126.8 (d, *m*-C), 136.5 (s, *o*-C), 137.5 (s, *p*-C), 140 (s, *i*-C). − CI-MS: *m/z* (%) = 594 (20) [M$^+$], 558 (60) [M$^+$ − Cl]. − HR-MS (EI): *m/z* = 592.1803 [M$^+$]; calcd. $^{12}C_{26}{}^{1}H_{40}{}^{35}Cl_4{}^{29}Si_2{}^{11}B_4$: 592.1811 (Δ*mm*: 0.8).

**4-(*tert*-Butyldiethylaminoboryl)-1,3-bis(diethylamino)-2,2-bis(trimethylsilyl)-1,3-diboretane (4a):** Compound **2a** (0.10 g, 0.21 mmol) was dissolved in 8 mL of hexane and diethylamine (0.12 g, 1.70 mmol) was added at −30 °C. The mixture was allowed to warm to room temperature and then was refluxed for three days. After filtration, part of the solvent was removed under vacuum, and the solution was cooled to −80 °C to give colorless crystals, m.p.: 230−233 °C. Yield: 0.04 g (42%). − $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 0.03 [s, 9 H, $Si(CH_3)_3$], 0.10 [s, 9 H, $Si(CH_3)_3$], 0.37 (s, 1 H, $B_3CH$), 0.89 (t, 3 H, $NCH_2CH_3$), 0.97 (t, 9 H, $NCH_2CH_3$), 0.98 [s, 9 H, $C(CH_3)_3$], 1.04 (t, 6 H, $NCH_2CH_3$), 2.71 (q, 2 H, $NCH_2CH_3$), 2.95 (dq, 2 H, $NCH_2CH_3$), 3.05−3.25 (m, 4 H, $NCH_2CH_3$), 2.22 (q, 2 H, $NCH_2CH_3$), 3.34 (dq, 2 H, $NCH_2CH_3$). − $^{11}$B NMR (64 MHz, $CDCl_3$): δ = 45. − $^{13}$C NMR (125 MHz, $CDCl_3$, 223 K): δ = 3.2 [q, $Si(CH_3)_3$], 4.9 [q, $Si(CH_3)_3$], 13.2 (q, $NCH_2CH_3$), 14.2 (q, $NCH_2CH_3$), 14.3 (q, $NCH_2CH_3$), 18 (br. s, $CB_2$), 22 [br. s, $C(CH_3)_3$], 28 (br. s, $CB_3$), 31.2 [q, $C(CH_3)_3$], 39.3 (t, $NCH_2CH_3$), 40.9 (t, $NCH_2CH_3$), 41.0 (t, $NCH_2CH_3$), 44.5 (t, $NCH_2CH_3$). − CI-MS: *m/z* (%) = 477 (5) [M$^+$], 420 (100) [M$^+$ − $C(CH_3)_3$]. − HR-MS (EI): *m/z* = 477.4482 [M$^+$]; calcd. $^{12}C_{24}{}^{1}H_{58}{}^{11}B_3{}^{14}N_3{}^{29}Si_2$: 477.4449 (Δ*mm*: 3.3).

**4-(*tert*-Butyldimethylaminoboryl)-1,3-bis(dimethylamino)-2,2-bis(trimethylsilyl)-1,3-diboretane (4b):** Compound **2a** (0.22 g, 0.47 mmol) was dissolved in 10 mL of toluene and (dimethylamino)trimethylsilane (0.22 g, 1.87 mmol) was added at −25 °C. The mixture was allowed to warm to room temperature and was then refluxed for two days. The solvent and volatile compounds were removed under vacuum to yield an orange solid. The crude product was sublimed to give 0.06 g (32%) of **4b**. − $^{1}$H NMR (200 MHz, $CDCl_3$): δ = 0.02 [s, 9 H, $Si(CH_3)_3$], 0.06 [s, 9 H, $Si(CH_3)_3$], 0.30 (s, 1 H, $B_3CH$), 0.97 [s, 9 H, $C(CH_3)_3$], 2.41 (s, 3 H, $NCH_3$), 2.64 (s, 6 H, $NCH_3$), 2.77 (s, 6 H, $NCH_3$), 2.80 (s, 3 H, $NCH_3$). − $^{11}$B NMR (64 MHz, $CDCl_3$): δ = 45. − $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 3.1 [q, $Si(CH_3)_3$], 4.7 [q, $Si(CH_3)_3$], 21 (br. s, $CB_2$), 23 [br. s, $C(CH_3)_3$], 28 (br. s, $CB_3$), 31.2 [q, $C(CH_3)_3$], 40.4 (q, $NCH_3$), 40.5 (q, $NCH_3$), 41.7 (q, $NCH_3$), 44.5 (q, $NCH_3$). − CI-MS: *m/z* (%) = 394 (100) [M$^+$ + 1]. − HR-MS (EI): *m/z* = 336.2820 [M$^+$ − $C(CH_3)_3$]; calcd. $^{12}C_{14}{}^{1}H_{37}{}^{11}B_3{}^{14}N_3{}^{29}Si_2$: 336.2835 (Δ*mm*: 1.5).

**4-(*tert*-Butylpyrrolidylboryl)-1,3-dipyrrolidyl-2,2-bis(trimethylsilyl)-1,3-diboretane (4c):** A suspension of lithium pyrrolidinide (0.09 g, 1.20 mmol) in 20mL of hexane was added dropwise to a solution

Table 1. Crystal data and structure refinement for **2a**, **3c**, **4a**, and **4c**

| | **2a** | **3c** | **4a** | **4c** |
|---|---|---|---|---|
| Empirical formula | $C_{16}H_{36}B_4Cl_4Si_2$ | $C_{26}H_{40}B_4Cl_4Si_2$ | $C_{24}H_{58}B_3N_3Si_2$ | $C_{24}H_{52}B_3N_3Si_2$ |
| Formula weight | 469.67 | 593.80 | 477.34 | 471.30 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *P*2$_1$/*n* | *C*2/*c* | *P*2$_1$/*n* | *P*2$_1$/*c* |
| Unit cell | | | | |
| *a* [Å] | 13.926(7) | 15.7018(10) | 12.1986(6) | 21.0269(4) |
| *b* [Å] | 11.899(6) | 14.7365(9) | 16.0124(8) | 17.5429(3) |
| *c* [Å] | 16.961(8) | 15.2120(10) | 16.9864(8) | 17.0373(4) |
| β [°] | 112.75(2) | 112.175(1) | 107.725(1) | 108.693(1) |
| *V* [Å$^3$] | 2592(2) | 3259.5(4) | 3160.4(3) | 5953.1(2) |
| *Z* | 4 | 4 | 4 | 8 |
| Calcd. density [g/cm$^3$] | 1.204 | 1.210 | 1.003 | 1.052 |
| Absorp. coeff. [mm$^{-1}$] | 0.550 | 0.452 | 0.128 | 0.135 |
| *F*(000) | 992 | 1248 | 1064 | 2080 |
| Crystal size [mm] | 0.65 × 0.60 × 0.50 | 0.51 × 0.27 × 0.23 | 0.54 × 0.38 × 0.29 | 0.46 × 0.38 × 0.20 |
| $\Theta_{max}$ [°] | 25.0 | 28.3 | 28.3 | 25.7 |
| Index ranges | −16/15, 0/14, 0/20 | −20/18, 0/19, 0/20 | −16/15, 0/21, 0/22 | −25/24, 0/21, 0/20 |
| No. of reflections | | | | |
| Unique | 4563 | 3960 | 7622 | 11316 |
| Observed [$I > 2\sigma(I)$] | 3982 | 2957 | 5819 | 8689 |
| Transmission | 0.954−1.000 | 0.739−0.894 | 0.788−0.894 | 0.761−0.894 |
| Parameters | 250 | 226 | 522 | 602 |
| Final *R* indices | | | | |
| *R*1 [$I > 2\sigma(I)$] | 0.0296 | 0.0444 | 0.0407 | 0.0566 |
| *wR*2 | 0.0801 | 0.1329 | 0.1147 | 0.1680 |
| Largest diff. peak/hole [e/Å$^3$] | +0.30 / −0.21 | +0.66 / −0.36 | +0.41 / −0.15 | +0.57 / −0.53 |

of **2a** (0.28 g, 0.60 mmol) in 10 mL of hexane at −55 °C. The mixture was allowed to warm to room temperature and then was refluxed overnight. The solvent and volatile compounds were removed under vacuum, and the crude orange product was crystallized from toluene to give orange **4c**. Yield: 0.14 g (48%). − $^{1}$H NMR (200 MHz, $C_6D_6$): δ = 0.28 [s, 9 H, $Si(CH_3)_3$], 0.34 [s, 9 H, $Si(CH_3)_3$], 1.24 [s, 9 H, $C(CH_3)_3$], 1.52 (m, 12 H, $NCH_2C\mathit{H}_2$), 2.76−3.52 (m, 12 H, $NC\mathit{H}_2$), signal for $B_3CH$ was not observed. − $^{11}$B NMR (64 MHz, $C_6D_6$): δ = 44. − $^{13}$C NMR (50 MHz, $C_6D_6$): δ = 3.7 [q, $Si(CH_3)_3$], 5.0 [q, $Si(CH_3)_3$], 24.1 (t, $NCH_2\mathit{C}H_2$), 25.7 (t, $NCH_2\mathit{C}H_2$), 27.0 (t, $NCH_2\mathit{C}H_2$), 28.9 (t, $NCH_2\mathit{C}H_2$), 31.0 [q, $C(\mathit{C}H_3)_3$], 44.3 (t, $NCH_2$), 48.8 (t, $NCH_2$), 50.0 (t, $NCH_2$), 52.3 (t, $NCH_2$), CB signals were not observed. − EI-MS: *m/z* (%) = 471 (1) [$M^+$], 414 (100) [$M^+ - C(CH_3)_3$]. − HR-MS (EI): *m/z* = 471.4000 [$M^+$]; calcd. $^{12}C_{24}{}^{1}H_{52}{}^{11}B_3{}^{14}N_3{}^{29}Si_2$: 471.3979 (Δ*mm*: 2.1).

**X-ray Structure Determinations of 2a, 3c, 4a, and 4c:** Crystal data and details of the structure determinations are listed in Table 1. Intensity data for **3c**, **4a**, and **4c** were collected at 173 K with a Bruker AXS Smart 1000 and for **2a** at 210 K with a Siemens Stoe AED2 diffractometer (Mo-$K_\alpha$ radiation, λ = 0.7107 Å, graphite monochromator, ω-scan). The structures were solved by direct methods and refined by least-squares methods based on $F^2$ with all measured reflections (SHELXTL NT5.1).[12] All non-hydrogen atoms were refined anisotropically. One of the two independent molecules in **4c** is disordered.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147172 (**2a**), CCDC-147173 (**3c**), CCDC-147174 (**4a**), CCDC-147175 (**4c**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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