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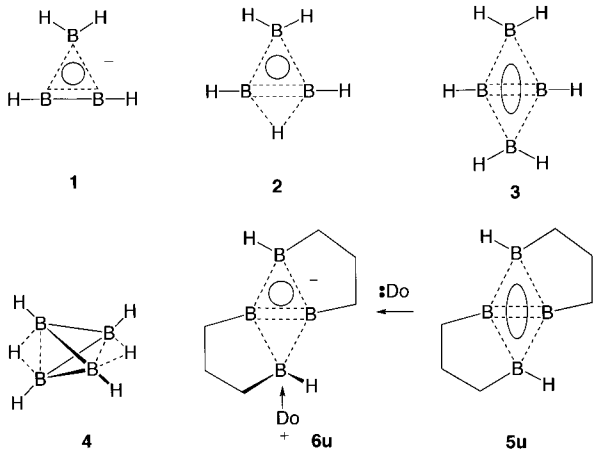
Aromatic Boranes with Planar-Tetracoordinate Boron Atoms and Very Short B–B Distances**

Carsten Präsang, Matthias Hofmann, Gertraud Geiseler, Werner Massa, and Armin Berndt*

Dedicated to Professor Anton Meller on the occasion of his 70th birthday

Boranes with planar-tetracoordinate boron atoms have until now only been studied by computations.[1–3] The prototype of such compounds is anion **1** (Scheme 1), whose planar-tetracoordinate boron atom forms a three-center, two-electron (3c2e) σ bond as well as a 3c2e π bond with the two other boron atoms.[2] Thus **1** is one of the simplest double



Scheme 1. Borane prototypes **1**–**3**, **5u**, and **6u** with planar-tetracoordinate boron atoms. Solid lines symbolize 2c2e bonds, triangles drawn with dashed lines 3c2e σ bonds, circles 3c2e π bonds, and ellipsoids 4c2e π bonds. In the distorted tetrahedral **4** the four connecting lines between the boron atoms are drawn to indicate the spatial relationships. In **4** there are ten electrons available to connect the boron atoms. In contrast, in the isomer **3** as well as in **5u** and **6u** there are only six electrons each.

aromatics.[4] Upon protonation the classical B–B bond in **1** is transformed into a 3c2e B-H-B bond in **2**. However, the double aromatic electronic structure of **1** is retained in **2**. In tetraborane(6) **3**[5] the hydrogen bond in **2** is replaced by a planar BH_2 bridge.[6, 7] Known tetraboranes(6) are derivatives of the distorted tetrahedral isomer **4**, which according to computations at the MP2/6-31G* level is 9.2 kcal mol^{-1} lower in energy than **3**.[5] Here we present **5a** and **6a** (Scheme 2), the first derivatives of the prototypes **5u** and **6u**; both represent

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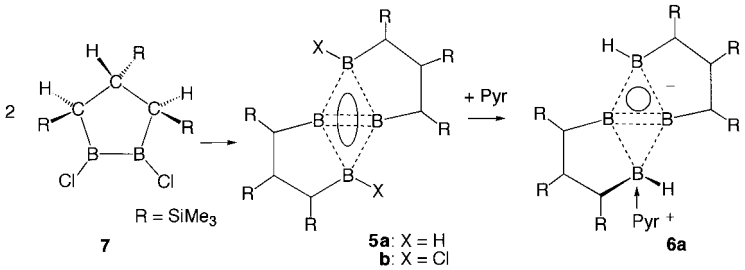

Scheme 2. Synthesis of the tetraboranes(6) **5a**, **b** from **7** and of the pyridine adduct **6a** from **5a**; Pyr = 4-*tert*-butylpyridine.

two-electron aromatics. In **6a** one of three boron π centers is planar-tetracoordinate, in **5a** all four are.

The dichlorotetraborane(6) **5b** is formed along with KCl as the sole product upon treatment of 1,2-dichloro-1,2-diborolane **7**[8] with K/Na alloy in pentane. The tetraborane(6) **5a** results from the reaction of **5b** with two equivalents of $NaBEt_3H$. The adduct **6a** crystallizes at −30 °C from a solution of **5a** and two equivalents of 4-*tert*-butylpyridine in pentane (Scheme 2). Figure 1 shows the structures of **5a** and **6a** in the crystal.[9] Table 1 compares relevant structural data experimentally observed for **5a** and **6a** with those computed at the B3LYP level[10] for **5u** and **3** as well as for the adduct **3** · NH_3 (as a model for **6a**). The NMR data for **5a**, **5b**, and **6a** are presented in Table 2.

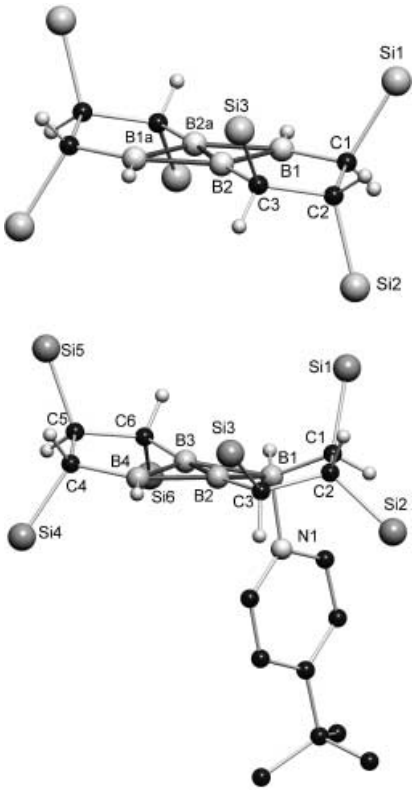

Figure 1. Structures of **5a** (top) and **6a** (bottom) in the crystal; for reasons of clarity the methyl groups of the trimethylsilyl substituents are omitted. Selected bond lengths [pm] and angles [°] (supplementing Table 1): **5a**: B1−H 112.3(17), B1−C1 155.8(2), B2−C3 157.8(2), C1−C2 156.3(2), C2−C3 156.4(2); H-B1-C1 117.7(9), B2-B1-B2A 51.7(1), B1-B2a-B2 64.4(1), B1-B2-B2a 63.9(1), B1-B2-B1a 128.3(1), B1-B2-C3 109.1(1), B2-B1-C1 99.8(1); **6a**: B1−N1 164.9(3).

The boron atoms in **5a** form a diamond with a very short diagonal length of 152.4(3) pm. In the slightly folded (12.8°) pyridine adduct **6a** the corresponding distance is only 151.1(3) pm and thus represents the shortest distance ever measured between two boron atoms.[11, 12] Even more unusual is the geometry at the corner of the diamond in **5a** and at the noncoordinated corner in **6a**: Both B1 and B1a in **5a** as well as B4 in **6a** have four neighboring atoms in one plane (torsional angles in **5a**: H,B1,B2,B2a 4.3(16)°, C1,B1,B2,B2A 179.4(2)°; in **6a**: H04,B4,B2,B3 2.7(11)°, C4,B4,B3,B2 173.9(2)°).[13] It is also remarkable that despite the presence of two equivalents of 4-*tert*-butylpyridine, only the monoadduct is formed. Diboranes(4) with four donor substitutents (OR or SR) easily add two molecules of 4-methylpyridine.[14] While the addition of one molecule of 4-methylpyridine to diborane(4) only leads to a modest increase in the B−B distance (by 2.8 pm), the B−B distance in the "pyridine-coordinated" boron triangle B1,B2,B3 of **6a** increases by about 13 pm. In the "non-

Table 1. Selected structural data for **5a** and **6a** (experimental) as well as for **5u**, **3**, and **3** · NH_3 (calcd).[a]

	5a	**5u**	**3**	**6a**	**3** · NH_3
B1−B2	175.2(2)	176.3	174.4	188.6(3)	187.0
B2−B1A	174.5(3)	173.3	174.4		
B2−B4				169.7(3)	168.1
B1A−B2A	175.2(2)	176.3	174.4		
B4−B3				169.1(3)	168.1
B2A−B1	174.5(2)	173.3	174.4		
B3−B1				187.4(3)	187.0
B2−B2A	152.4(3)	152.0	153.0		
B2−B3				151.1(3)	150.9
B1,B2,B2A,B1A	180.0	166.4	180.0		
B1,B2,B3,B4				167.2(2)	167.0
B2A-B2-C3	172.9(1)	169.0	–		
B3-B2-C3				171.3(2)	–

[a] Bond length [pm], bond angles [°]; see Figure 1 for the numbering of the atoms.

Table 2. Selected physical and spectroscopic properties of **5a**, **5b**, and **6a**.

5a: Yellow solid, m.p. 165 °C (no decomp), yield 60 %; ^{1}H NMR (300 MHz, C_6D_6, 27 °C): δ = 7.00 (br. s, 2H; BH), 2.31 (s, 2H; (B_2H)BC*H*Si), 2.03 (d, ^3J(H,H) = 4.2 Hz, 2H; B_3BCHSi), 1.78 (pseudo triplet, ^3J(H,H) = 3.5 Hz, 2H; CHSi), 0.28, 0.20, 0.08 (each s, each 18H; $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): δ = 41.4 (br. d, ^1J(C,H) = 111 Hz; (B_2H)BCHSi), 28.8 (d, ^1J(C,H) = 122 Hz; CHSi), 27.2 (br. d, overlapping, B_3BCHSi), 0.6, 0.2, −3.7 (each q; $SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): δ = 50, 26.

5b: Yellow solid, m.p. 102 °C (decomp), yield 96 %; ^{1}H NMR (300 MHz, C_6D_6, 27 °C): δ = 2.40 (d, ^3J(H,H) = 3.2 Hz, 2H; B_3BCHSi), 2.37 (d, ^3J(H,H) = 2.9 Hz, 2H; (B_2Cl)BCHSi), 1.53 (pseudo triplet, ^3J(H,H) = 2.9 Hz, 2H; CHSi), 0.29, 0.22, 0.08 (each s, each 18H; $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): δ = 48.3 (br. d, ^1J(C,H) = 110 Hz; (B_2Cl)BCHSi), 27.7 (br. d, ^1J(C,H) = 116 Hz; B_3BCHSi), 24.8 (d, ^1J(C,H) = 122 Hz; CHSi), 1.9, 0.3, −3.0 (each q; $SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): δ = 62, 28.

6a · 0.2 4-*tert*-butylpyridine: Yellow solid, m.p. 112 °C, yield 85 %; ^{1}H NMR (500 MHz, [D_8]Toluol, −50 °C): δ = 8.67 (br. s, 2H; coord. Pyr), 8.59 (s; Pyr), 7.13 (br. s, 1H; BH), 6.74 (s; Pyr), 6.40 (s, 2H; coord. Pyr), 4.45 (br. s, 1H; BH), 2.38 (m, 1H; CHSi), 2.22 (d, 1H; CHSi), 1.92–1.86 (m, 2H; CHSi), 1.84 (d, 1H; CHSi), 1.02 (s; Pyr), 0.83 (s, 9H; coord. Pyr), 0.75 (m, 1H; CHSi), 0.55, 0.53, 0.38, 0.33, −0.06, −0.34 (each s, each 9H; $SiMe_3$); at 27 °C the ^{1}H NMR spectrum displays one broad signal at 6.28 instead of two broad signals at 7.13 and 4.45.

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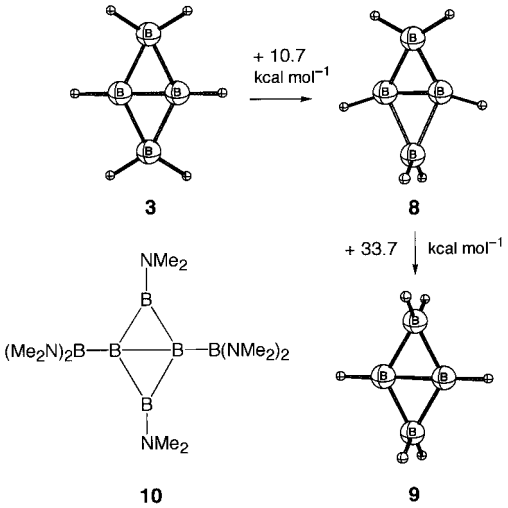
coordinated" boron triangle B2,B3,B4 the distances shorten by ca. 5 pm upon addition of pyridine.

These unusual properties can be explained by the fact that **5a** and **6a** (just as **1**, **2**, and **3**) are two-electron aromatics. The cyclic delocalization of two π electrons over four boron centers in **5a** and over three boron centers in **6a** is only possible when the axes of the p orbitals of the boron atoms at the corners of the diamond in **5a** or at the noncoordinated corner in **6a** are perpendicular to the plane formed by the boron triangle. For this to occur, the four neighboring atoms of these particular boron atoms must lie in one plane. The addition of one pyridine molecule to **5a** transforms the 4c2e aromatic **5a** into the 3c2e aromatic **6a**, in which the two π electrons are delocalized over the boron triangle without coordinated pyridine. The B···B distances are intermediate between those in the negatively charged prototype **1** and those in the hydrogen-bridged **2** (Scheme 1). The bridging hydrogen bond in **2** corresponds to the BHR·pyridine bridge in **6a**. Addition of a second pyridine molecule to **6a** would result in loss of the cyclic delocalization of the two π electrons and thus in loss of the aromaticity. Density functional calculations[10] show that the transformation of the 4c aromatic **3** into the 3c aromatic **8** requires about 11 kcal mol^{-1}. In contrast, the transformation of **8** into **9** with loss of aromaticity requires almost 34 kcal mol^{-1} (Scheme 3).



Scheme 3. Computed[10] energies required for the transformation of **3** into **8** and of **8** into **9**. In both cases a planar-tetracoordinate boron atom is transformed into a tetrahedrally coordinated one.

The remarkably short B2···B2a distance in **5a** is a result of low ring strain and strong 1,3-π overlap[15] along the short diagonal. The distortion of a four-membered ring with four 2c2e σ bonds to form a diamond would lead to significant ring strain, owing to smaller angles between two electron pairs. In the four-membered rings described here only four electrons are available for the σ framework to form two B-B-B 3c2e σ bonds, as shown by a natural bond orbital (NBO) analysis for **3**. The bonding 1,3-interaction is further strengthened by a 4c2e π bond, whose electrons according to the NBO analysis are preferentially (36% each) localized on the boron centers of the short diagonal. In contrast, additional σ electrons must occupy molecular orbitals with 1,3-antibonding character.[16] This explanation is supported by the fact that the B···B distance in **9** (165.2 pm) with six σ framework electrons is significantly longer than in **8** and **3** (150.9 and 153.0 pm, respectively) with four σ framework electrons each. In addition, the B···B distance of 163.3 pm for the short diagonal in **10**,[16] which has six electrons available for the σ framework, is similar to that in **9**.

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[11] To our knowledge, the shortest B–B distance measured previously (156.5(4) pm) was observed in an anionic derivative of **4**.[5] A length of 146.9 pm was calculated for the B–B triple bond in $Li_2B_2H_2$,[12] and the HB–BH distance in **1** and **2** was computed to be 147[1]/148.0[2] and 152.7 pm, respectively.[2]

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[13] In **5a** the planar nature of the B_4 unit is implied by the presence of a symmetry center; deviations from the plane: C1 1.5(2) pm, H −5(2) pm. The "normal", nearly spherical displacement ellipsoids of the B atoms (U_{ii}(max.) = $0.045(1) \times 10^{-20}$ m^2) show that this is not a result of disorder. In contrast to the experimental planarity of the diamond in **5a**, calculations for the diamond in **5u** show a slight folding (166.6°). Apparently the folding in **5u** is induced by the two trimethylene bridges, and this effect is removed in the presence of the sterically bulky trimethylsilyl substituents in **5a**. In **6a** the deviations from the plane B2-B3-B4 are as follows: C4 −16.4(2), H04 5(2) pm.

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[16] A. Maier, M. Hofmann, H. Pritzkow, W. Siebert, *Angew. Chem.* **2002**, *114*, 1600; *Angew. Chem. Int. Ed.* **2002**, *41*, 1529. Attempts to synthesize tris(dimethylamino)cyclotriborane from 1,3-dichloro-1,2,3-tris(dimethylamino)triborane(5)[17] with K/Na alloy in pentane or with lithium naphthalenide in THF resulted in the formation of **10** in 40–50% yield.[18] **10**: colorless crystals, m.p. 105 °C (no decomp), ^{11}B NMR (96 MHz, C_6D_6, 25 °C): $\delta = 63, 41, 6$; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 3.4$ (s, 12H; NMe_2), 3.0 (s, 24H; NMe_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 44.4$ (q, 4C, NMe_2), 42.0 (q, 8C, NMe_2).

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A Planar, Aromatic *bicyclo*-Tetraborane(4)**

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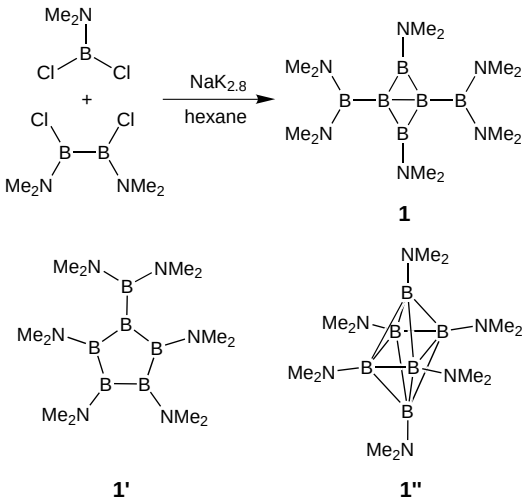
Dedicated to Professor Philipp Gütlich

Recently we demonstrated that the dehalogenation of bis(dialkylamino)dichlorodiboranes(4) provides colorful tetraborane(4) derivatives $(BR)_4$. The blue diisopropylamino derivative displays a folded B_4 ring, whereas a yellow tetrabora-tetrahedrane is formed with the larger 2,2′,6,6′-tetramethylpiperidino substituents.[1] The existence of planar[2] $(BNMe_2)_4$ could not be confirmed.[3] We report here on the *bicyclo*-tetraborane(4) **1**, whose boron atoms form a planar B_4 diamond (Scheme 1).



Scheme 1.

The reaction of a mixture of Me_2NBCl_2 and $(Me_2N)_2B_2Cl_2$[4] with $NaK_{2.8}$ alloy in hexane produced neither the anticipated B_3 nor a B_5 ring. Instead a colorless compound of the composition $B_6(NMe_2)_6$ (EI-MS, m/z 330) was formed in addition to oily products of unknown structure. This new compound is a constitutional isomer of the orange *cyclo*-$(BNMe_2)_6$, a chair-shaped compound that was first obtained in low yields by Nöth and Pommerening[5] upon dehalogenation of $(Me_2N)_2BCl$. The colorless $B_6(NMe_2)_6$ displays three ^{11}B NMR signals at $\delta = 6$, 41, and 63.[6] The pattern of the signals corresponds to a four-membered ring with two different substituents. The isomers **1′** and **1″** can therefore be excluded.

The crystal-structure analysis[7] of **1** displays a planar, diamond-shaped B_4 ring. The short distance across the diagonal (1.633(2) Å) indicates the presence of a B–B bond

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