6.8 Hz); 7.05 (d, $^3J = 9.2$ Hz, 2H); 6.62 (s, 2H); 3.53–3.49 (m, 4H); 2.87–2.86 (m, 2H); 2.64 (sept, $^3J = 8.6$ Hz, 2H); 2.13–2.10 (m, 2H); 1.90–1.87 (m, 2H); 1.32 (s, 9H); 1.29 (s, 9H); 1.08 ppm (d, $^3J = 8.6$ Hz, 12H); ^{13}C-NMR (500 MHz NMR, $C_2D_2Cl_4$, 313 K): $\delta = 185.41$ (C=O), 175.49 (C=O), 165.86 (C=O), 165.78 (C=O), 164.71 (C=O), 164.69 (C=O), 157.28, 155.35, 155.26, 150.55, 150.48, 148.06, 147.72, 142.29, 139.03, 137.79, 136.64, 136.61, 135.65, 134.77, 134.23, 133.58, 133.49, 133.44, 133.37, 133.21, 132.86, 132.41, 132.22, 132.12, 131.97, 131.53, 131.24, 131.15, 131.01, 130.59, 130.46, 130.33, 130.12, 130.04, 129.95, 129.74, 129.08, 128.29, 128.09, 126.69, 126,51, 125.51, 125.90, 125.27, 125.17, 125.12, 124.87, 124.26, 124.06, 121.85, 121.70, 117.78, 117.34, 45.10, 39.87, 37.28, 34.21, 32.08, 31.79, 31.44, 26.79, 24.66 ppm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 263 (60100), 272 (61300), 445 (4500), 651 (47800), 705 (89400) nm; field desorption (FD)-MS (8 kV): m/z (%): 1289.0 (100) [M^+]; anal. calcd for $C_{87}H_{73}N_3O_8$: C 81.10, H 5.71, N 3.26; found: C 81.23, H 5.79, N 3.22

The recombinant Lhcb1 mutants used in this work were derivatives of the clone D7f.3 coding for pea wild-type Lhcb1.[3,11] A single cysteine residue in position 79 of mutant C79S was exchanged with a serine residue, and mutant S3C carried the additional mutation of cysteine in place of serine in position 3.

BTI was covalently coupled to the N-proximal cysteine in the Lhcb1 mutant S3C. Lhcb1 (1 nmol) in buffer (25 μL; 1 g L^{-1} sodium dodecylsulfate, 10 g L^{-1} *n*-octyl-*β*-D-glucopyranoside and 20 mM sodium phosphate pH 7.0) was reduced for 15 min at 37 °C with 2 mM tris(2-cyanoethyl)phosphane and then mixed with BTI maleimide (12.5 nmol), dissolved in THF (2 μL). After 2 h incubation at 37 °C, the protein was precipitated with 80 % (v/v) acetone and 10 mM acetic acid. The protein pellet was dissolved in sodium dodecylsulfate (20 μL; 20 g L^{-1}), 100 mM Tris-HCl (Tris = tris(hydroxymethyl)aminomethane; pH 9.0), heated to 100 °C for 2 min and then centrifuged (5 min at 16000 g) to remove insoluble material.

In LHCIIb–BTI constructs, energy transfer from Chl *a* to the dye was calculated from the quenching of donor (Chl *a*) emission in the presence of the acceptor. Samples of LHCIIb with and without bound BTI were made up to the same Chl *a* absorption at 410 nm. The dye absorption was negligible at this wavelength. Energy transfer efficiency was estimated by comparing Chl *a* fluorescence emissions with and without energy transfer to the dye:

Energy transfer [%] = [1−(maximum Chl *a* emission in LHCIIb–BTI)/(maximum Chl *a* emission in LHCIIb)] 100.

Received: March 5, 2002
Revised: May 24, 2002 [Z18833]

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Triboracyclopropanates: Two-Electron Double Aromatic Compounds with Very Short B−B Distances**

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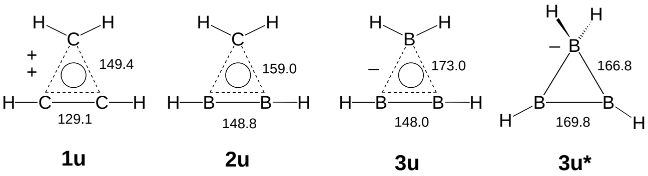
Dedicated to Professor Walter Siebert
on the occasion of his 65th birthday

According to computations, the isoelectronic, two-electron double aromatic compounds **1u**–**3u**[1–4] (Scheme 1) have one extremely short and two relatively long bonds in the ring. This results from the fact that all of the ring atoms are connected by one three-center, two-electron (3c–2e) π as well as one 3c–2e *σ* bond and that two ring atoms are connected by an additional 2c–2e *σ* bond. The planar compound **3u** is stabilized by 54.9 kcal mol^{-1} with respect to the classical structure **3u***.[3b] We present here the syntheses and crystal structures of **3a** and **3b** (see Scheme 2), the first derivatives of the triboracyclopropanate **3u**, as well as DFT computations[5] for model compounds **3c**–**f** (see Figure 2).



Scheme 1. Two-electron aromatic compounds, each containing a 3c–2e π (circles) and *σ* bond (dashed triangle). Solid lines symbolize a 2c–2e bond. The numbers indicate the distances in pm, computed at the MP2/6-31G* level.[1–3]

The monoanion **3a** is obtained from the reaction of two equivalents of lithium naphthalenide in THF with **4**, which forms upon treatment of **5**[6] with $(CH_3)_3SiCH_2Li$ (Scheme 2). The dianion **3b** results when **5** is treated with lithium in Et_2O at −80 °C.[7] Compounds **3a** and **3b** react with electrophiles to tetraboranes(6). Treatment of **3a** with hexachloroethane results in the regeneration of **4**, and **3b** reacts with methyl iodide[8] to form **6**, which spontaneously transforms into **7** in solution with elimination of 1,2-bis(trimethylsilyl)ethene. The constitutions of the new compounds are in agreement with their NMR data (Table 1), and the structures of **3a**, **3b**, and **6** have been confirmed by crystal structure analysis.[9]

The anion **3a** forms a contact ion pair with a lithium ion, which is coordinated to the B2−B3 bond as well as to two THF

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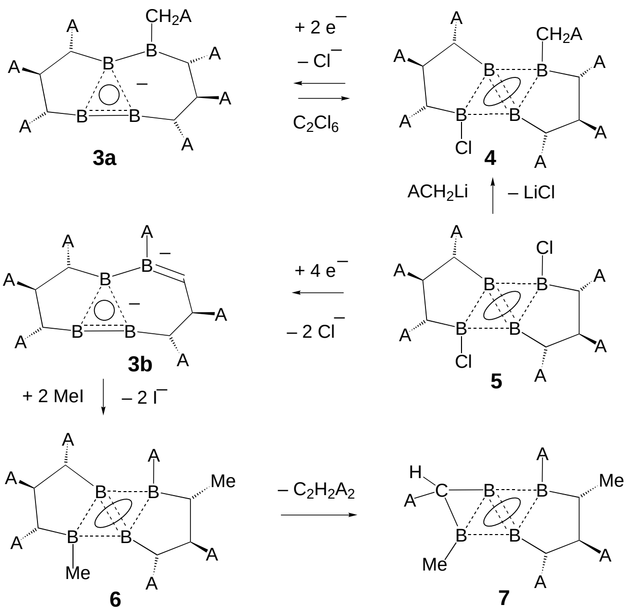
[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.



Scheme 2. Syntheses and reactions of the triboracyclopropanates **3a** and **3b.** All reactions proceed with retention of the two-electron aromaticity. A = $SiMe_3$.

Table 1. Selected physical and spectroscopic characteristics of **3a**, **3b**, **4**, **6**, and **7**.

3a: Yellow solid, m.p. 129 °C (decomp), yield 80 % (based on NMR spectroscopy); ^1H NMR (300 MHz, C_6D_6, 27 °C): $\delta = 3.49$, 1.37 (each m, each 8 H, THF), 2.78, 1.98 (each pseudo t, each 1 H, C_2CHSi), 2.64, 2.10, 1.56, 1.12 (each d, each 1 H, BCHSi), 1.70, 1.22 (each d, each 1 H, BCH_2Si), 0.47, 0.43, 0.37, 0.34, 0.24 (each s, in total 63 H, $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): $\delta = 68.8$, 25.3 (THF), 40.2, 26.9 (each d, C_2CHSi), 38.1, 36.3, 28.8, 19.7 (each br d, BCHSi), 23.7 (br pseudo t, BCH_2Si), 3.2, 2.7, 2.1, 1.2, 0.8, 0.3, –0.9 ($SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): $\delta = 59$, 46, 27 (2 B).

3b: Yellow solid, m.p. 114 °C (decomp), yield 60 %; ^1H NMR (400 MHz, C_6D_6, 27 °C): $\delta = 5.35$, (d, 1 H, BCHC), 3.26 (q, 8 H, Et_2O), 2.44 (dd, 1 H, C_2CHSi), 2.76, 1.61, 1.11 (each d, each 1 H, BCHSi), 1.23 (d, 1 H, C_2CHSi), 0.97 (t, 12 H, Et_2O), 0.45, 0.40, 0.26, 0.25, 0.22 (each s, in total 54 H, $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): $\delta = 121.9$ (br d, $J = 141$ Hz, B = CHC), 65.6, 14.5 (Et_2O), 36.8, 26.9, 15.0 (each br d, BCHSi), 35.6, 24.6 (each d, C_2CHSi), 5.2, 2.1, 1.6, 1.0, –0.3, –2.0 ($SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): $\delta = 69$, 59, 36 (2 B).

4: Light yellow crystals, m.p. 148 °C, yield 87 %; ^1H NMR (300 MHz, C_6D_6): $\delta = 2.55$, 2.49, 2.33, 2.09 (each d, each 1 H, BCHSi), 1.91, 1.67 (each pseudo t, each 1 H, C_2CHSi), 1.83, 1.56 (each d, each 1 H, BCH_2Si), 0.34, 0.29, 0.28, 0.26, 0.22, 0.21 (each s, in total 63 H, $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 27 °C): $\delta = 51.2$, 46.4, 31, 30 (each br d, BCHSi), 30.1, 23.6 (each d, C_2CHSi), 25.4 (br pseudo t, BCH_2Si), 2.4, 1.9, 1.8, 1.3, 0.7, 0.0, –1.6 ($SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): $\delta = 68$, 65, 34, 27.

6: Colorless solid, m.p. 99 °C (decomp), yield 89 %; ^1H NMR (300 MHz, C_6D_6, 27 °C): $\delta = 3.15$ (q, 1 H, BCHMe), 2.38 (d, 1 H, MeBCHSi), 2.28 (d, 1 H, B_3BCHSi), 1.82 (dd, 1 H, C_2CHSi), 1.74 (s, 1 H, B_3BCHSi), 1.68 (s, 1 H, C_2CHSi), 1.31 (d, 3 H, BCHMe), 1.24 (s, 3 H, BMe), 0.38, 0.27, 0.25, 0.21, 0.21, 0.14 (each s, each 9 H, $SiMe_3$); ^{13}C NMR (125 MHz, C_6D_6, 27 °C): $\delta =$ 50.9 (br d, MeBCHSi), 45.8 (br d, BCHMe), 44.2 (d, C_2CHSi), 31.4 (br d, B_3BCHSi), 29.2 (d, C_2CHSi), 27.5 (br d, B_3BCHSi), 24.0 (q, BCHMe), 17.7 (br q, BMe), 4.0, 2.8, 1.0, –0.2, –0.6, –2.4 (each q, $SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C): $\delta = 65$, 62, 43, 30.

7: Yellow oil, yield 90 % (based on NMR spectroscopy); ^1H NMR (300 MHz, C_6D_6, 27 °C): $\delta = 2.87$ (q, 1 H, BCHMe), 1.75 (s, 1 H, C_2CHSi), 1.61 (d, 1 H, BCHSi), 1.35 (s, 3 H, MeB), 1.32, (d, 3 H, BCHMe), 1.06 (s, 1 H, B_2CHSi), 0.39, 0.30, 0.18, 0.16 (each s, each 9 H, $SiMe_3$); ^{13}C NMR (125 MHz, C_6D_6, 27 °C): $\delta = 46.8$ (d, C_2CHSi), 38.9 (br, BCHMe), 24.6 (br, B_2CHSi and BCHSi), 24.0 (BCHMe), 7 (br, MeB), 1.6, 1.4, 1.1, 0.1 ($SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 27 °C) $\delta = 57$, 45 (2 B), 17.

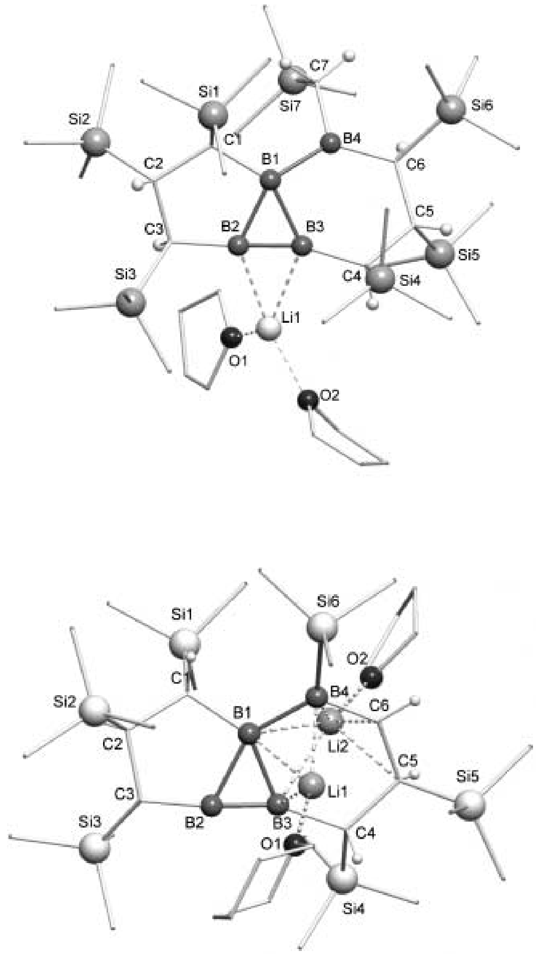
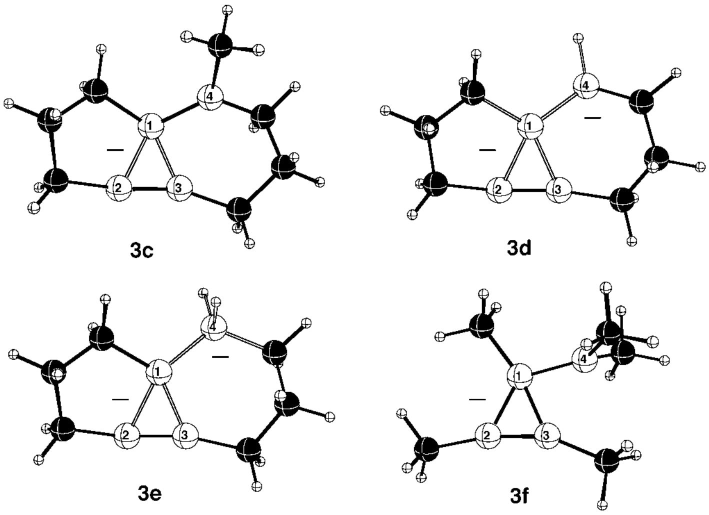


Figure 1. Structures of **3a**·Li(THF)$_2$ (top) and **3b**·Li(THF)·Li(THP) (bottom) in the crystal. Selected distances [pm] and angles [°] (see also Table 2): **3a**·Li(THF)$_2$: B2–Li1 234.9(6), B3–Li1 240.0(6); C1-B1-B4 119.7(2), C3-B2-B1 112.5(2), C4-B3-B1 130.2(2), B3-B1-B4 93.2(2). **3b**·Li(THF)·Li(THP): B1–Li1 248.0(13), B3–Li1 231.2(11) B1–Li2 245.3(12), B4–Li1 230.6(12), B3–Li2 250.1(13), B4–Li2 225.4(10); C1-B1-B4 117.1(4), C3-B2-B1 112.0(4), C4-B3-B1 130.7(2), B3-B1-B4 100.3(5).



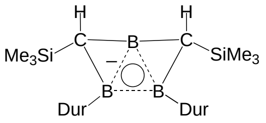
3c **3d** **3e** **3f**

Figure 2. Structures computed at the B3LYP/6-31G* level for **3c** and **3d**, which represent models for **3a** and **3b** without silyl substituents, and related compounds **3e** and **3f**, which contain planar-tetracoordinated boron atoms.

molecules (Figure 1). In the contact ion triple **3b**·Li(THF)·Li(THP) (THP = tetrahydropyrane) the two lithium ions are located above and below the six-membered ring and in addition are coordinated by a THP or a THF molecule. The B2–B3 distances in **3a** and **3b** are 148.3 and 148.0 pm, respectively, and thus the shortest ever observed between two boron atoms.[10] The B2–B3 and all the other B–B distances are in good agreement with those computed for **3u** and model compounds **3c** and **3d**, without silyl substituents (Figure 2, Table 2). The characteristics for three-membered, two-electron double aromatic compounds, namely, one very short and two relatively long distances, are thus experimentally realized in **3a** and **3b**. In contrast, the well-known bishomo double aromatic compound **8**[11] (Dur = 2,3,5,6-tetramethylphenyl) and the corresponding double aromatic compound **9**[3a] have one long B–B bond (168.8 and 183 pm, respectively), because they lack the 2c–2e σ bond between the basal boron atoms characteristic for double aromatic compounds of the type **1**–**3**: Compound **9** is the dehydro form of **3u.**

Table 2. Selected structural data for **3a**, **3b** (experimental), **3c**–**3f**, and **3u** (computed at the B3LYP/6-31G* level).

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3u**
B1–B2	173.2(4)	179.4(8)	175.8	177.1	178.1	167.6	172.9
B1–B3	172.5(4)	173.3(8)	171.8	174.2	172.8	166.6	172.9
B2–B3	148.3(4)	148.0(10)	148.7	147.3	147.2	149.9	146.8
B1–B4	172.1(4)	176.0(9)	166.1	174.1	177.9	167.4	–



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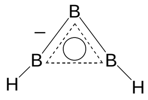

9

The boron atom at the apex of **3u** is surrounded by its four neighbors in a planar fashion. In **3a**, **3b**, **3c**, and **3d** the plane containing the B_3 triangle forms an angle of 22, 26, 14.6, and 2.1°, respectively, with the plane C-B1-B4 at the peak of the triangle; the boron atoms B1 are therefore almost planar-tetracoordinated. Complete planarity is prevented in **3a** and **3c** by the electron deficiency of the boron atom in the six-membered ring.[12] In the model compound **3e**, in which atom B4 is tetrahedrally coordinated, the angle between the two planes described is only 3.2°, and in **3d**, which contains a doubly bound, tricoordinated B4 atom, this angle is only 2.1°. The deviation from planarity is 24° greater in **3b** than in **3d** and results from the bulky trimethylsilyl group at B4. In the model compound **3f**, which does not contain methylene bridges, atom B1 is exactly planar-tetracoordinated. Therefore, the first triboracyclopropanates basically display the predicted structures.

Received: April 11, 2002 [Z19072]

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[7] The mechanism for the formation of **3b** from **5**, which has for the most part been clarified, will be described elsewhere.

[8] Attempts to synthesize a monomethylation product resulted in a mixture of **6** and unchanged **3b**: Therefore, the second methylation occurs more quickly than the first one.

[9] Crystal structure analyses: **3a**·Li(THF)$_2$: A yellow crystal (0.40 × 0.35 × 0.25 mm) was measured at 193 K on an IPDS area detector system (Stoe) with Mo$_{K\alpha}$ radiation. $C_{36}H_{87}B_4LiO_2Si_7$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 1274.9(1)$, $b = 1956.8(1)$, $c = 2135.1(1)$ pm, $\beta = 96.08(1)°$, $V = 5296.5(6) \times 10^{-30}$ m^3, $\rho_{calcd} = 1.002$ Mg m^{-3}. Of 41 406 reflections up to $\theta = 25.94°$, 10 047 were independent ($R_{int} = 0.0993$) and 5787 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined against all F^2 data with full matrix. The hydrogen atoms of the SiMe$_3$ groups and the THF molecules were refined as "riding" in calculated positions, and the remaining H-atoms were refined with isotropic displacement factors. One of the two THF molecules was disordered; $wR_2 = 0.1361$ for all reflections, $R = 0.0489$ for the observed reflections. **3b**·Li(THF)·Li(THP): Under similar conditions as for **3a**·Li(THF)$_2$, a yellow crystal (0.25 × 0.15 × 0.05 mm) was measured. $C_{33}H_{77}B_4Li_2O_2Si_6$, orthorhombic, space group $Pca2_1$, $Z = 4$, $a = 2021.4(1)$, $b = 1226.0(1)$, $c = 1979.3(2)$ pm, $V = 4905.2(7) \times 10^{-30}$ m^3, $\rho_{calcd} = 0.991$ Mg m^{-3}. Of 19 940 reflections up to $\theta = 25.96°$, 6927 were independent ($R_{int} = 0.0981$) and 3491 with $I > 2\sigma(I)$. The structure solution and refinement were analogous to that of **3a**·Li(THF)$_2$. Since only very thin crystal platelets could be obtained, the accuracy of the refinement with use of a non-centrosymmetric space group is much lower than for **3a**·Li(THF)$_2$. Nevertheless, the hydrogen atoms H1–H6 could be freely refined; $wR_2 = 0.1028$ for all reflections, $R = 0.0519$ for the observed reflections. The structure determination of **6** is of insufficient quality owing to the very weak data set but does confirm the constitution of **6**. CCDC-183545 (**3a**·Li(THF)$_2$) and CCDC-183544 (**3b**·Li(THF)·Li(THP)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[10] Recently, B–B distances of 152.4(3) and 151.1(3) pm were observed in derivatives of **5**.[6]

[11] M. Unverzagt, G. Subramanian, M. Hofmann, P. von R. Schleyer, S. Berger, K. Harms, W. Massa, A. Berndt, *Angew. Chem.* **1997**, *109*, 1567; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1469.

[12] An NBO analysis of **3c** provides the following occupation for the p orbitals: B1 0.67, B2 0.53, B3 0.68, B4 0.26. Conjugation with B4 decreases the π bond order between B1 and B2 or between B1 and B3. This facilitates rotation of the C-B1-B4 plane with respect to the B1-B2-B3 plane, as this does not influence the 3c–2e σ bond.

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