Trishomoaromatic Dianions of 1,3,5-Triboracyclohexanes**

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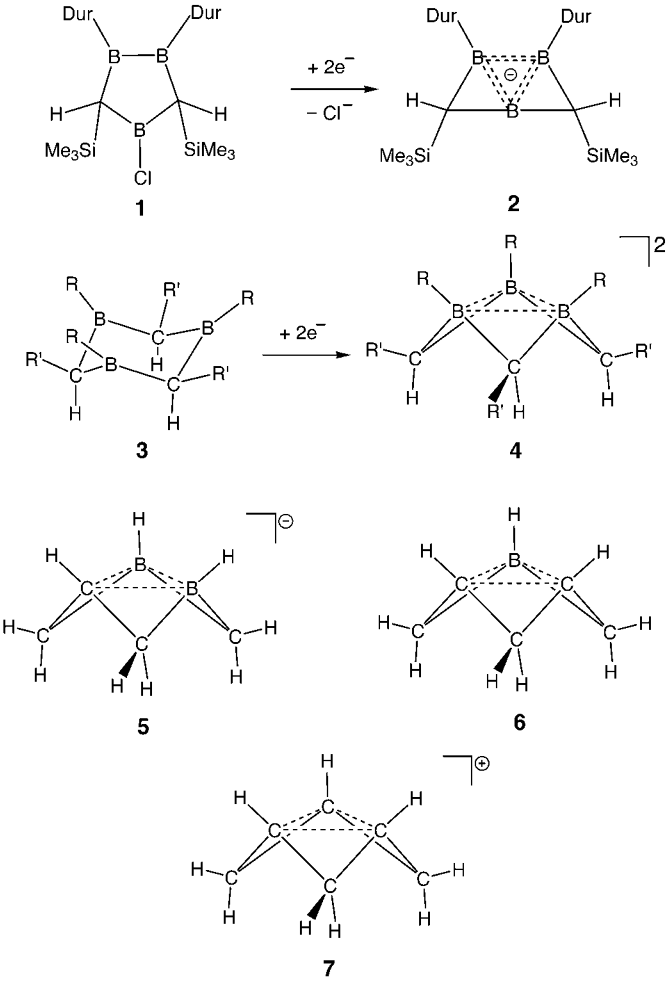
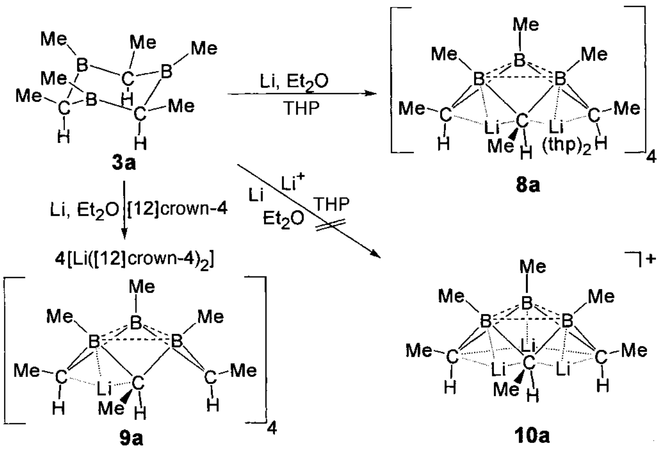
Dedicated to Professor Dirk Walther
on the occasion of his 60th birthday

Reductions of boron-containing heterocycles in donor solvents by alkaline metals lead to aromatic anions.[1] A remarkable example was obtained by Berndt et al.[2] from the organoborane **1** (Scheme 1): the monoanion **2** is both bishomo- and doubly aromatic, because it possesses two three-center, two-electron bonds, one with π and the other with σ symmetry (dashed B_3 triangles). The three empty p orbitals of the related trifunctional Lewis acidic 1,3,5-triboracyclohexanes **3**[3] should also accept two electrons and form the trishomoaromatic dianions **4**, which are isoelectronic with the trishomocyclopropenylium cations.[4] We report here on the unusual structure of reduced **3a** ($R = R' =$ Me) together with computational results on the stabilization and nucleus-independent chemical shifts (NICS)[5] of the isoelectronic, all-hydrogen-substituted trishomoaromatic set **4**–**7** ($R = R' = H$; Scheme 1).



Scheme 1. Dur = 2,3,5,6-Tetramethylphenyl.

While **3a** reacted with Li powder at 0 °C in both Et_2O and THF (Scheme 2) to give yellow-orange solutions after filtration, only amorphous residues resulted after solvent removal.



Scheme 2. Synthesis of **8a** and **9a**.

In [D_8]THF solution, the reduction product obtained initially exhibited two broad ^1H NMR signals at $\delta = -3.2$ and -3.4, which were assigned to methine protons. Three B-Me and two C-Me signals indicated the presence of a mixture of isomers with axial/equatorial orientations of the C-Me substituents, as has been found for $(MeCH)_3(ClB)_3$, the precursor of **3a**.[3] The ^{11}B NMR signal of these products at $\delta = -29.2$ was at extremely high fields (**3a**: $\delta = 84.3$) and indicated multiple connectivities at the boron atoms. IGLO calculations[5, 6] of the ^{11}B NMR shift of the C_{3v} model compound $[(CH_2)_3(BH)_3Li_3]^+$ (Figure 1) gave $\delta = -31.8$, in very good agreement with the experimental value, as well as NICS values[5] of $\delta = -28.5$ at the center of all the C and B atoms and $\delta = -42.3$ at the center of the three boron atoms. These

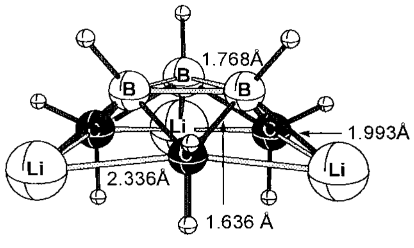


Figure 1. Structure of $[(CH_2)_3(BH)_3Li_3]^+$ (C_{3v}) optimized at the B3LYP/6-311+G** density functional level.

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data indicate pronounced homoaromatic character (see below).

Crystals were obtained by adding tetrahydropyran (THP) or the crown ether [12]crown-4 to the THF solutions after reduction. Surprisingly, the X-ray structure analyses revealed tetrameric aggregates for both **8a** and **9a**. While disorder of the THP ligands severely reduced the quality of the X-ray analysis of **8a**, the structure of **9a** was ligand-free and refined well[7] (Figure 2). The low solubility of both these crystals precluded spectroscopic characterization. Even the reduction of **3a** in the presence of LiCl (in the hope that $[(\mathrm{MeCH})_3(\mathrm{MeB})_3\mathrm{Li}_3]^+$, **10a**, might form) failed to give a monomeric product and to prevent aggregation.

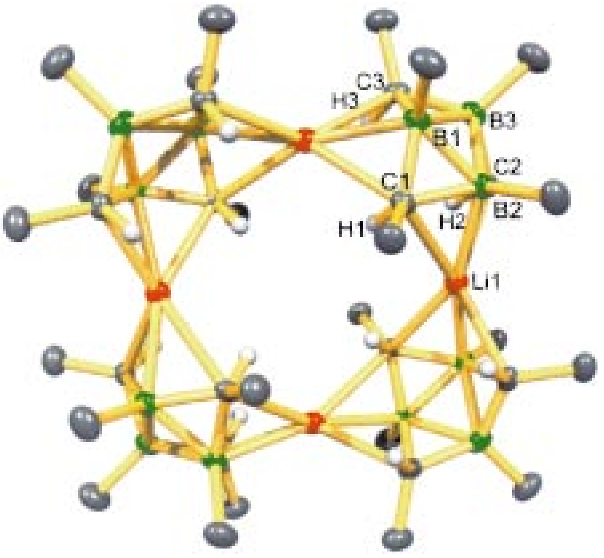

Figure 2. Molecular structure of **9a** in the crystal. Selected distances [Å] and angles [°]: B1-B2 1.825(5), B1-B3 1.851(5), B2-B3 1.848(5), Li1-C1 2.456(6), Li1′-C1 2.354(6), Li1′-C3 2.285(6), Li1-C2 2.247(6), Li1′-B1 2.239(6), Li1-B1 2.251(6); B2-B1-B3 60.4(2), B1-B2-B3 60.5(2), B1-B3-B2 59.1(2), B1-C1-B2 68.6(2), B2-C2-B3 70.0(2), B1-C3-B3 69.8(3).

The four $(\mathrm{MeCH})_3(\mathrm{MeB})_3\mathrm{Li}$ units in the ringlike arrangement of **9a** are connected by Lewis acidic Li centers. The transannular boron–boron distances in the $\mathrm{C}_3\mathrm{B}_3$ ring are short and differ somewhat (1.825(5) Å, when both B atoms coordinate to Li atoms, as well as 1.851(5) and 1.848(5) Å, when only one B coordinates to Li)). The Li⋯B contacts are long (2.239(6), 2.251(6) Å), the B–C bond lengths are normal for a single bond (between 1.603(5) and 1.632(4) Å). Each $\mathrm{C}_3\mathrm{B}_3$ unit has three axial C-H and three equatorial C-Me groups.

Comprehensive computations on the various possible minima of monomeric $[(\mathrm{CH}_2)_3(\mathrm{BH})_3\mathrm{Li}_3]^+$, $(\mathrm{CH}_2)_3(\mathrm{BH})_3\mathrm{Li}_2$, and $[(\mathrm{CH}_2)_3(\mathrm{BH})_3\mathrm{Li}]^-$ reveal that the B_3 face is preferred over the $\mathrm{C}_2\mathrm{B}$ face attachment of Li in all cases. The lithium bonding is predominantly electrostatic, but minor covalent interactions between the Li^+ centers and nearby H, B, and C atoms are present. The $\mathrm{C}_2\mathrm{B}$ face coordination observed experimentally for **8a** and **9a** may be attributed to the combined effects of the sterically active methyl groups at the B_3 face and to the electrostatic energetic advantages on the tetrameric association.

Most surprising is the remarkable homoaromatic stabilization energy[8] of the $[(\mathrm{CH}_2)_3(\mathrm{BH})_3]^{2-}$ dianion (**4**, R = R′ = H), which is larger than all three of the isoelectronic counterparts **5**–**7**. Stabilization energies, evaluated by two different methods, are given in Table 1.

Table 1. Stabilization energies [kcal mol^{-1}] (//B3LYP/6-311 + G**) and NICS values (PW91/IGLO III)[4b] for the trishomoaromatic systems **4**–**7** (R = R′ = H).

Trishomoaromatic system	Isodesmic reaction[a]	Difference to open form[b]	NICS(0)	NICS(rc)
$[(\mathrm{CH}_2)_3(\mathrm{BH})_3]^{2-}$ **4**	−41.05	−32.35	−35.4	−22.5
$[(\mathrm{CH}_2)_3(\mathrm{CH})(\mathrm{BH})_2]^{-}$ **5**	−19.63	−16.11	−37.1	−21.4
$[(\mathrm{CH}_2)_3(\mathrm{CH})_2(\mathrm{BH})]$ **6**	+5.55	+6.63	−34.8	−16.7
$[(\mathrm{CH}_2)_3(\mathrm{CH})_3]^{+}$ **7**	−8.73	−12.54	−46.4	−22.7

[a] The isoelectronic equations involve cyclohexane and **4**–**7** as product pairs. The reactions are valid for the cyclohexyl cation (for **7**) and boracyclohexane (for **4**–**6**) as well as for bicyclo[3.1.0]hexane (for **6** and **7**) and its 1-(B^-) (for **5**) and 1,5-$(\mathrm{B}^-)_2$ (for **4**) counterparts. [b] Energy differences between **4**–**7** and their chair-form conformers which lack 3c,2e bonding (see ref. [5f] for a prior use of this method).

The NICS(0) values, based on total NMR shieldings, and the NICS(rc; 3c,2e) ring current (rc) contributions (see Table 1) are computed at the centers of the ring 1,3,5-atoms with Malkin's implementation[5b] of Kutzelnigg's IGLO program.[6] IGLO provides a detailed breakdown of the total shieldings in terms of all the localized orbital contributions.

Of greatest interest are the diatropic effects due to the cyclic electron delocalization (i.e., the magnetic evaluation of the 3c,2e "aromatic" bonding given by NICS(rc)). These values are augmented by the local diatropic shielding contributions of nearby C–C, C–H, and B–H bonds. Hence, the NICS(0) values are displaced further upfield. (The local induced circulations of the sigma C–C bonds in benzene, in contrast, are paratropic and reduce the NICS(0) value to about −10.) The benzene NICS (rc, i.e. π value), which is about −22 at the ring center, is quite similar to the 3c,2e data above.

Our results show that the reaction of **3a** with lithium leads to the trishomoaromatic compounds **8a** and **9a** as tetrameric aggregates. The expected monomeric dianion **4a** (R = R′ = Me) and the cation **10a** as electronic analogues to the trishomocyclopropenylium cation **7**[4] could not be isolated. Alternatively the monomeric unit **10a** with two donor molecules at each of the three Li centers may be described as a *hypho* cluster with 26 skeleton electrons.[9]

Experimental Section

To a suspension of freshly purified lithium powder (50 mg, 350 mmol) in diethyl ether (20 mL), hexamethyl-1,3,5-triboracyclohexane (**3a**; 200 mg, 1.23 mmol) was added at 0 °C. The reaction mixture was allowed to warm to 20 °C while stirring overnight. Separation of excess alkaline metal by using a glass filter (G III porosity) led to a clear yellow-orange solution, which was reduced to 2 mL by vacuum evaporation. For crystallization [12]crown-4 (0.2 mL) was added to yield **9a** (12 mg; 2.9 %).

NMR data of the initial reduction product: ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = -3.42$ (q, ca. 2 H, $^3J(\mathrm{H,H}) = 3$ Hz, CH_{ax}), −3.23 (m, br., ca. 1 H, CH_{ax}), −0.59 (s, br., 9 H, BCH_3), −0.52 (s, br., 6 H, BCH_3), −0.45 (s, br., 3 H, BCH_3), 1.23 (d, 6 H, $^3J(\mathrm{H,H}) = 3$ Hz, CCH_3), 1.35 (d, 12 H, $^3J(\mathrm{H,H}) = 3$ Hz,

CCH_3); ^{13}C NMR (50 MHz, [D_8]THF): $\delta = 38.6$ (CCH_3), 39.1 (CCH_3); ^{11}B NMR (64 MHz, [D_8]THF): $\delta = -29.2$.

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[7] Crystal Structures: **8a**: monoclinic, spacegroup $C2/c$, $a = 31.846(11)$, $b = 16.305(11)$, $c = 23.787(14)$ Å, $\beta = 112.91(4)^\circ$, $Z = 4$. Because of the poor quality of the crystals (few observed reflections, disorder of the THP ligands) no accurate bond lengths and angles could be obtained. **9a**: $C_{36}H_{84}B_{12}Li_4 \cdot 4\,C_{16}H_{32}LiO_8$ tetragonal, space group $P4_2/n$, $a = 20.156(11)$, $c = 14.937(8)$ Å, $V = 6068(6)$ Å^3, $Z = 2$. Data were collected with a four-circle diffractometer ($Mo_{K\alpha}$ radiation, ω scan, $-70\,^\circ C$). A total of 5341 independent reflections were collected ($\theta_{max} = 25^\circ$), solution of the structure with direct methods (SHELXS 86), structure refinement with all reflections versus F^2 (SHELXL 97), non-hydrogen atoms anisotropic (364 parameters), $R1 = 0.059$, $wR2 = 0.173$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133326 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] In the preceding publication (D. Scheschkewitz, A. Ghaffari, P. Amseis, M. Unverzagt, G. Subramanian, M. Hofmann, P. von R. Schleyer, H. F. Schaefer III, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2000**, *112*, 1332; *Angew. Chem. Int. Ed.* **2000**, *39*, 1275) a bishomoaromatic dianion of 1,2,4-triboracyclopentane is reported, which also shows a remarkable aromatic stabilization energy (39.0 kcal mol^{-1}).

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