

FULL PAPER

Two-Electron Aromatics with Classical and Non-Classical Homobridges

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Received: 18 October 1999/ Accepted: 18 January 2000/ Published: 28 February 2000

Abstract Bishomotriborirane anions with a B-H-B bridge, **7**, have been synthesized by a) protonation and b) methylation of bishomodianions, **3**, as well as by c) hydride addition to 1,2,4-triboracyclopentanes, **15**. Compounds **7** were characterized by ¹H, ¹³C and ¹¹B NMR spectroscopy and X-ray diffraction analyses. The suggested mechanism for the formation of **7** is supported by MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* computations on [C₂B₃H₈]⁻ model compounds. Classical 1,2-dibora-4-boratacyclopentane intermediates **16** undergo an intramolecular hydrogen shift to the B-B unit in their envelope conformation to give intermediates **17**, which easily isomerize to **7**. Relative energies for the parent compounds, **16u**, **17u**, **7u** and the transition structures, **TS-16/17u** and **TS-7/17u** are predicted to be 30.7, 14.5, 0.0, 32.6 and 23.5 kcal mol⁻¹, respectively. The terms classical and non-classical homobridges are suggested for methylene and hydrogen bridges in **7** and in related compounds on the grounds of common building principles. The strength of homoaromaticity in **7u** was estimated to be at least 23.5 kcal mol⁻¹, neglecting the much higher strain in **7u** compared to **TS-7/17u** without a 3c2e bond.

Keywords *Ab initio*, Boron compounds, Crystal structure, Homoaromatics, Three center two electron bond

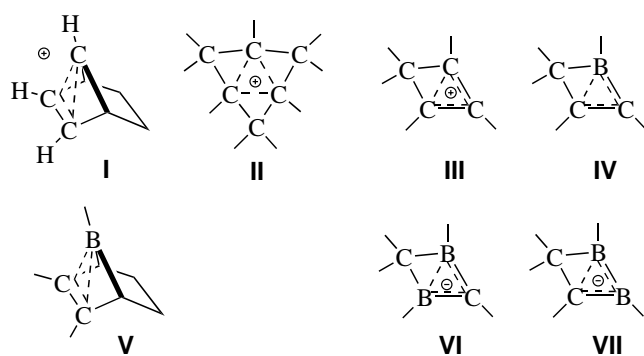
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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

Introduction

Cyclic delocalization of (4n+2)π electrons, the characteristic feature of aromatics [1], is retained in homoaromatics [2], although some or all of the centers of this delocalization are no longer directly connected by σ-bonds. The concept of homoaromaticity was introduced by Roberts [3] and Winstein [4] for bis-homocyclopropenyl cation **I** [3a], tris-homocyclopropenyl cation **II** [4c,d] and (mono-)homocyclopropenyl cation **III** [3b] (Scheme 1) between 1956 and 1962. However, until 1984 only carbocations like **I-III** were demonstrated to be homoaromatics beyond any doubt.



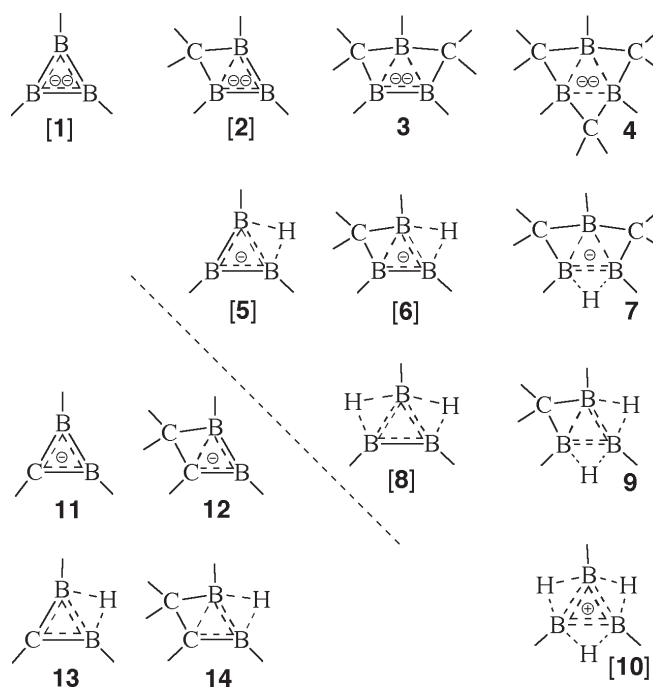
Scheme 1 Cationic, neutral and anionic two-electron homoaromatic species

Derivatives of **IV** [5] and **V** [6] as well as of **VI** [7] and **VII** [8] are examples of neutral and anionic (hetero-) homoaromatics, respectively, the cyclic delocalization of which is definitely proven by NMR-, X-ray and *ab initio* studies.

All molecular skeletons shown in Scheme 2 (like those in Scheme 1) have two electrons delocalized in a cyclic array over three centers: three boron atoms in **1-10**; two boron atoms and one carbon atom in **11-14**, which are isoelectronic with **1**, **2**, **5**, and **6**, respectively. Compounds of type **1** and **11** are aromatic, those of type **2** and **12** monohomoaromatic, of type **3** and **4** bishomoaromatic and trishomoaromatic, respectively. Derivatives of **3** [9], **4** [10], and **9** [11], the diprotonated form of **2**, as well as those of **11-14** [8,12-14] are known experimentally, the prototypes of **1** [15], **2** [8], **5** [15], **6**, and **8** [15] as well as of **10** [16] and **11** [17] by computations. According to calculations, the aromaticity of the dianion **1** [15] is neither destroyed by protonation to **5**, nor by diprotonation to **8**, nor by triprotonation to **10** [16]. We present here experimental evidence that protonation of bishomoaromatic **3** [9] leads to bishomoaromatic **7**. [a] Derivatives of **7** are also obtained by reaction of derivatives of **3** with methyl iodide as well as by addition of hydride to derivatives of **15** [9], the uncharged precursor of **3**.

Model compounds were computed by *ab initio* methods to estimate the strength of the homoaromaticity of anions of type **7** and to elucidate the reaction mechanisms for formation of anions **7**, which require migration of hydrogen atoms from the boron atom between the carbon atoms to the B-B unit. Classical five-membered ring structures of type **16** and **17** were identified as plausible intermediates. The term “nonclassical” homobridges is suggested for B-H-B bridges

[a] Based on results reported in this work we suggest the term non-classical homobridge for the hydrogen bridge in **7**. However, in order to avoid confusion, we suggest to continue naming the structures according to the number of classical homobridges. Hence, structure **7** is a bishomoaromatic with one non-classical homobridge (and two classical homobridges).

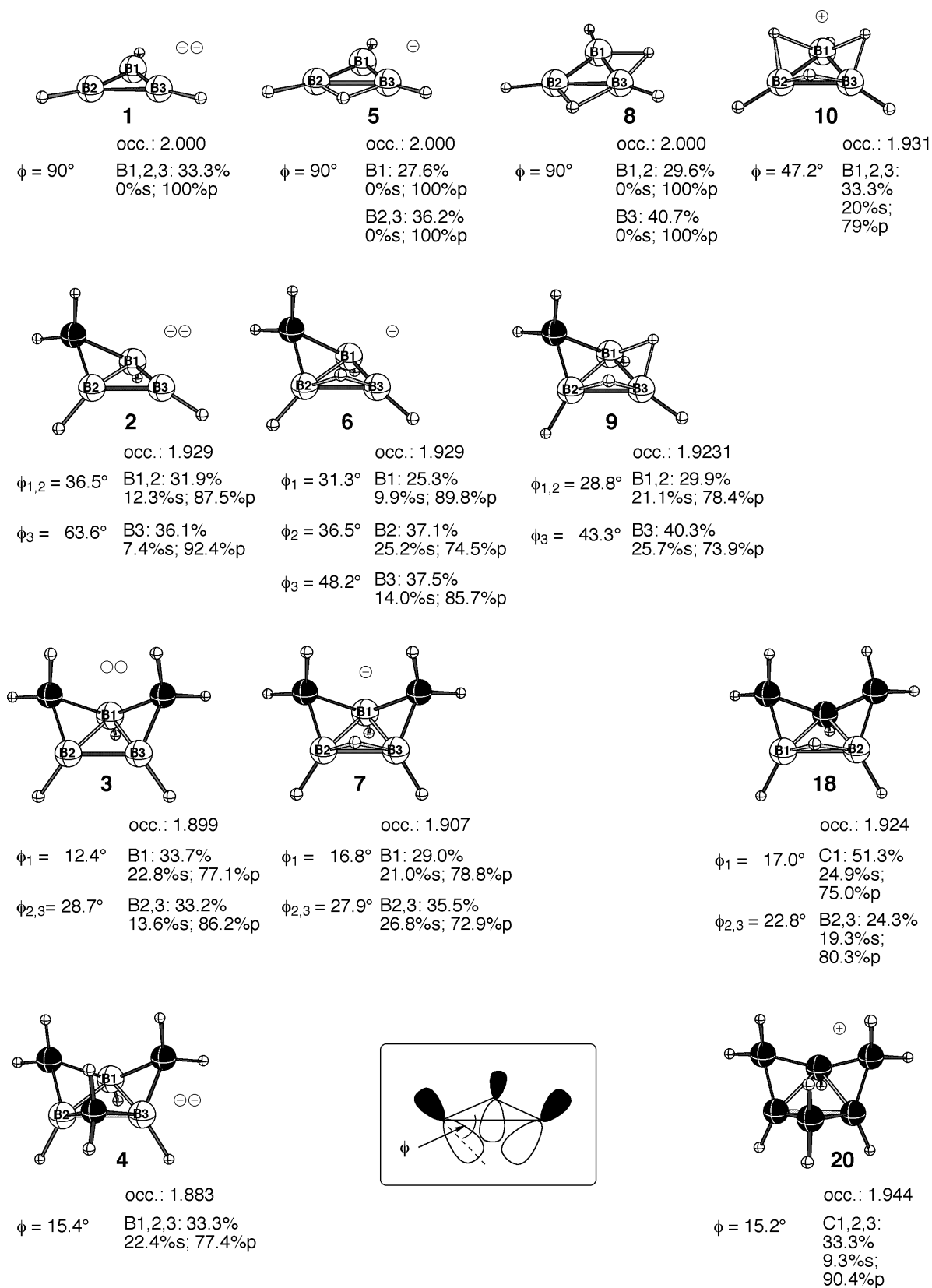


Scheme 2 Skeletons of aromatic and homoaromatic species all having two electrons delocalized in a cyclic array over three centers: three boron atoms in **1-10**, two boron and one carbon atoms in **11-14**. Derivatives are known experimentally unless for skeletons with numbers included in brackets. Prototypes for the latter are known from *ab initio* calculations

of homoaromatics (like **6**, **7**, **9** and **14**) since they underlie the same building principle as “classical” homobridges.

Computational details

All structures were fully optimized in the given symmetry point group unless stated otherwise. Electron correlation was accounted for by a Møller-Plesset perturbation theory treatment truncated after second order (MP2) and making use of the frozen core (fc) approximation. Diffuse functions as included in the 6-31+G* basis set are important for an accurate theoretical treatment of anions [18]. The HF/6-31G*, MP2(fc)/6-31G* and MP2(fc)/6-31+G* methods were applied consecutively for geometry optimizations and final results reported in the text correspond to the MP2(fc)/6-31+G* level unless stated otherwise. Benchmark calculations for **7u**, **TS-7/17u** and **17u** up to the CCSD(T)/6-311++G**//MP2(fc)/6-311++G** level (listed in Table 1) suggest that MP2(fc)/6-31+G* is sufficient for geometries: relative energies from MP2/6-311++G** single points for geometries optimized at the MP2(fc)/6-31+G* or at the MP2(fc)/6-311++G** level are basically the same. Selected distances optimized at different levels are compared in Scheme 4. Changes beyond the



Scheme 3 The orbital out-of-plane angle ϕ , occupation of the $3c2e$ bond and distribution of the delocalized electrons over the boron centers for aromatic **1** and homoaromatics **2** to **10** as well as for **18** and trishomocyclopropenylium cation **20**

Table 1 Relative Energies [kcal mol⁻¹] for **7u**, **TS-7/17u**, and **17u** computed at different levels of theory

| | 7u | TS-7/17u | 17u |
|--|-----------|-----------------|------------|
| MP2(fc)/6-31+G* [a] | 0.0 | 29.6 | 19.0 |
| MP2(fc)/6-311++G**//MP2(fc)/6-31+G* [a] | 0.0 | 26.4 | 16.3 |
| MP2(fc)/6-311++G** [a] | 0.0 | 26.4 | 16.4 |
| MP4SDQ/6-311++G**//MP2(fc)/6-31+G* [a] | 0.0 | 21.3 | 13.6 |
| MP4SDQ/6-311++G**//MP2(fc)/6-311++G** [a] | 0.0 | 21.0 | 13.7 |
| MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* [a] | 0.0 | 23.5 | 14.5 |
| CCSD/6-311++G**//MP2(fc)/6-311++G** [a] | 0.0 | 21.3 | 13.5 |
| CCSD(T)/6-311++G**//MP2(fc)/6-311++G** [a] | 0.0 | 22.8 | 14.0 |
| B3LYP/6-31+G* [b] | 0.0 | 20.4 | 13.7 |
| B3LYP/6-311++G**//B3LYP/6-31+G* [b] | 0.0 | 19.3 | 13.2 |
| B3LYP/6-311++G** [b] | 0.0 | 19.3 | 13.2 |
| MP4SDQ/6-311++G**//B3LYP/6-31+G* [b] | 0.0 | 21.2 | 13.9 |
| MP4SDTQ/6-311++G**//B3LYP/6-31+G* [b] | 0.0 | 23.3 | 15.0 |
| CCSSD/6-311++G**//B3LYP/6-31+G* [b] | 0.0 | 21.0 | 13.8 |
| CCSSD(T)/6-311++G**//B3LYP/6-31+G* [b] | 0.0 | 22.5 | 14.4 |

[a] Corrected by scaled (0.89) zero point vibrational energies from frequency calculations at the HF/6-31G* level

[b] Corrected by zero point vibrational energies from frequency calculations at the B3LYP/6-31G* level

MP4SDQ/6-311++G**//MP2(fc)/6-311++G** level are small, suggesting that MP4SDQ/6-311++G** gives reliable energies. When possible full MP4/6-311++G** single point energies were computed for other molecules, if not, triples were left out (MP4SDQ/6-311++G**). All relative energies were corrected for scaled (0.89) [19] zero point vibrational energies (ZPE) from HF/6-31G* analytical frequency calculations. Due to their size, the phenyl derivatives, **7uPh**, **TS-7/17uPh** and **17uPh**, were treated by more economical density functional theory levels: Geometries were optimized at

B3LYP/6-31G* and B3LYP/6-31+G*; frequencies were obtained at B3LYP/6-31G*. NMR chemical shifts were computed at the GIAO-SCF level [20] applying the 6-311+G** basis set. The Gaussian94 [21] program package was used throughout this work. The NBO 4.M program [22] was employed together with Gaussian 94 to perform NBO analyses [23]. The orbital out-of-plane angles in Scheme 3 were calculated from the hybrids involved in the occupied natural bond orbitals (NBO's) localized for the 3c2e bonds. All three p contributions (which arise from the use of the 6-31+G* basis

Scheme 4 Selected geometric parameters for **7u**, **TS-7/17u**, and **17u** optimized at MP2(fc)/6-31+G*, MP2(fc)/6-311++G**, and B3LYP/6-31+G* levels of theory. For relative energies computed at various levels see Table 1

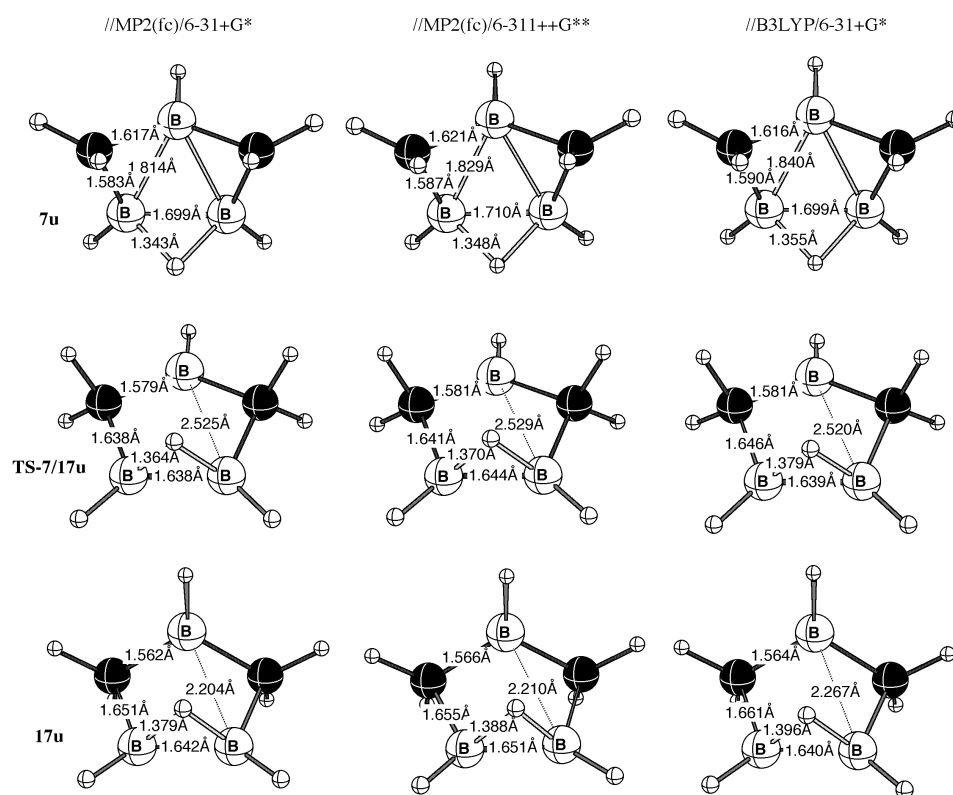


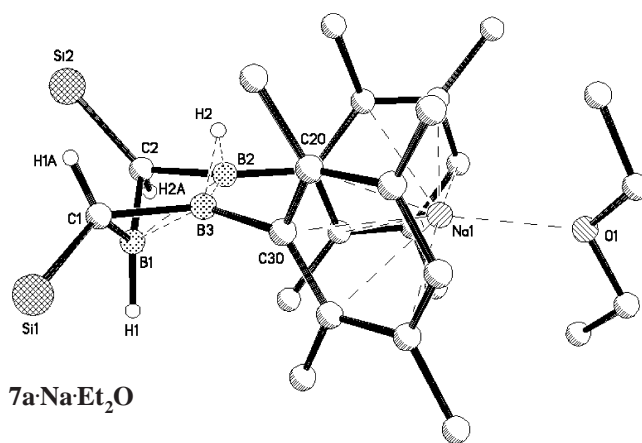
Figure 1 (right column) Crystal structures of **7a·Na·Et₂O**, **7b·Na·Et₂O** and **7c·Na·4 Et₂O**. Methyl substituents at Si1 and Si2 as well as most of the hydrogen atoms have been omitted for clarity. The cation Na(Et₂O)₄ of **7c** is not shown. Selected bonding distances (completing Table 3) [pm] and -angles [°]. **7a**: B1-C1 160.4(3), B1-C2 161.4(3), C1-B3 159.9(3), C2-B2 159.4(2); C1-B1-C2 116.69(16), B1-C2-B2 70.46(12), C2-B2-B3 109.35(14), B2-B3-C1 107.99(13), B3-C1-B1 70.27(12); **7b**: B1-C1 161.7(3), B1-C2 161.9(3), C1-B3 159.3(2), C2-B2 160.3(2); C1-B1-C2 114.41(14), B1-C2-B2 72.81(12), C2-B2-B3 108.04(13), B2-B3-C1 108.60(14), B3-C1-B1 73.65(12). **7c**: B1-C1 161.5(5), B1-C2 160.4(6), C1-B3 161.5(5), C2-B2 160.6(5); C1-B1-C2 114.5(3), B1-C2-B2 73.0(2), C2-B2-B3 107.9(3), B2-B3-C1 108.0(3), B3-C1-B1 72.8(2)

set) of the same orientation (e.g. those labeled 2p_x, 3p_x and 4p_x) were summed up to determine the orientation of the hybrids.

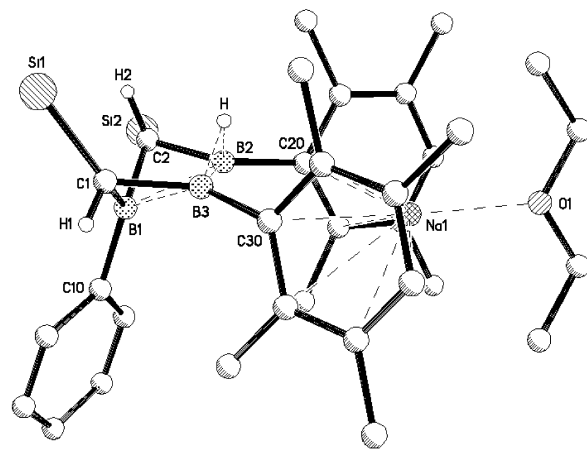
Crystal structure determinations

7a·Na·Et₂O: a colorless plate-sized crystal (0.40 x 0.20 x 0.10 mm³) was measured on a Stoe IPDS diffractometer at -80°C using MoK_α radiation. - C₃₂H₅₈B₃NaOSi₂, monoclinic, space group P2₁/n, Z = 4, a = 968.5(1) pm, b = 2183.2(1) pm, c = 1730.0(1) pm, β = 100.69(1)°, V = 3594.5(5) x 10⁻³⁰ m³, ρ_{ber} = 1.054 g cm⁻³; a total of 28022 reflections were recorded in the range of 2.25° < θ < 25.97°, resulting in 6989 independent reflections of which 4426 were observed (F₀ > 4σ(F₀)). All 6989 reflections were used for subsequent calculations, no absorption correction was applied (μ = 1.33 cm⁻¹). The structure was solved by direct methods and refined against F₀² with full matrix. Non-hydrogen atoms were refined using anisotropic displacement factors. The protons attached to C1, C2 and B1 and the bridging proton between B2 and B3 were refined, the other protons were kept on calculated positions. For those 1.2 or 1.5 (CH₃) times the equivalent isotropic U values of the corresponding C atom were used as displacement factors. The refinement converged at wR₂ = 0.0973 for all reflections, corresponding to a conventional R = 0.0385 for the observed reflections.

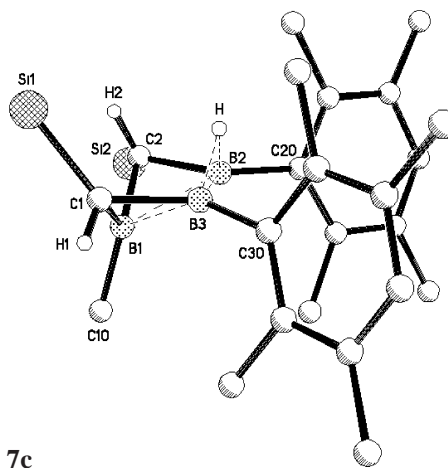
7b·Na·Et₂O: a pale yellow plate-sized crystal (0.75 x 0.60 x 0.15 mm³) was measured on a Stoe IPDS diffractometer at -80°C using MoK_α radiation. - C₃₈H₆₂B₃NaOSi₂, monoclinic, space group P2₁/n, Z = 4, a = 1436.4(1) pm, b = 1526.9(1) pm, c = 1884.7(1) pm, β = 97.68(1)°, V = 4096.5(4) x 10⁻³⁰ m³, ρ_{ber} = 1.048 g cm⁻³; a total of 29541 reflections were recorded in the range of 1.91° < θ < 24.92°, resulting in 7063 independent reflections of which 4963 were observed (F₀ > 4σ(F₀)). All 7063 reflections were used for subsequent calculations, no absorption correction was applied (μ = 1.23 cm⁻¹). The structure was solved by direct methods and refined against F₀² with full matrix. Non-hydrogen atoms were



7a·Na·Et₂O



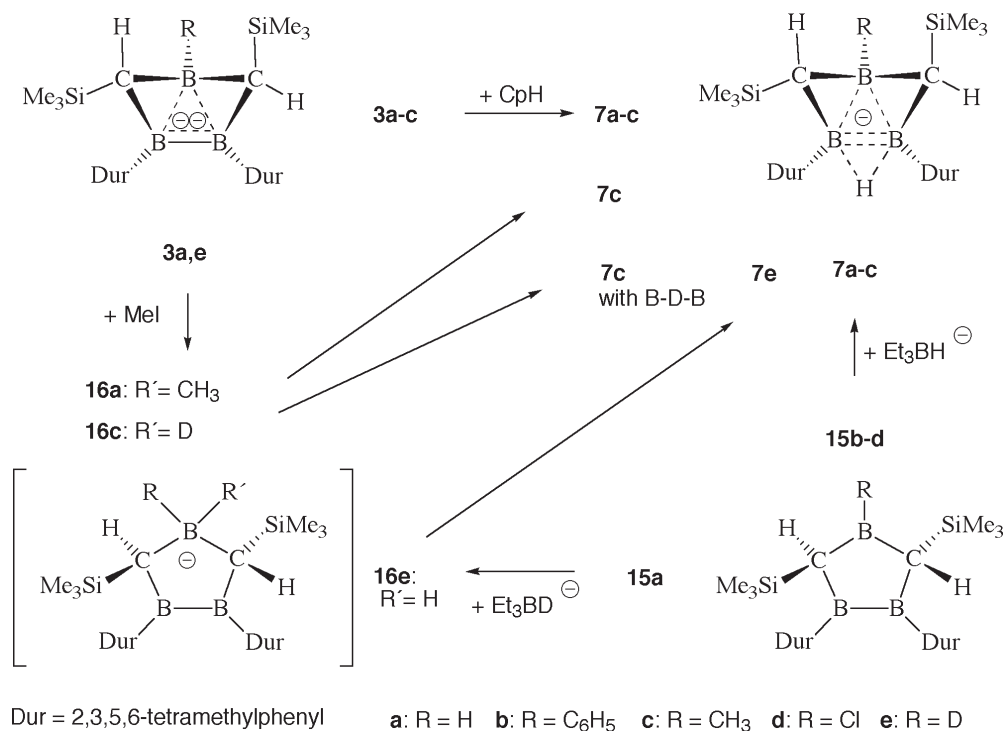
7b·Na·Et₂O



7c

refined using anisotropic displacement factors. The protons attached to C1 and C2 and the bridging proton between B2 and B3 were refined, the other protons were kept on calculated positions. For those 1.2 or 1.5 (CH₃) times the equivalent isotropic U values of the corresponding C atom were used as displacement factors. The refinement converged at

Scheme 5 Different synthetic approaches leading to compounds of type **7** and experiments using deuterated reactants



$wR_2 = 0.1054$ for all reflections, corresponding to a conventional $R = 0.0398$ for the observed reflections.

7c·Na·4 Et₂O: a colorless block-sized crystal (0.40 x 0.18 x 0.18 mm³) was measured on a Stoe IPDS diffractometer at -80°C using Mo_{Kα} radiation. - C₄₅H₉₀B₃NaO₄Si₂, monoclinic, space group P2₁/c, Z = 4, a = 1658.7(1) pm, b = 1641.0(1) pm, c = 1933.7(1) pm, β = 91.82(1)°, V = 5260.7(5) x 10⁻³⁰ m³, ρ_{ber} = 1.017 g cm⁻³; a total of 33490 reflections were recorded in the range of 1.75 < θ < 24.07°, resulting in 7942 independent reflections of which 3752 were observed (F₀ > 4σ(F₀)). All 7942 reflections were used for subsequent calculations, no absorption correction was applied (μ = 1.11 cm⁻¹). The structure was solved by direct methods and refined against F₀² with full matrix. Non-hydrogen atoms were refined using anisotropic displacement factors. The protons attached to C1 and C2 and the bridging proton between B2 and B3 were refined, the other protons were kept on calculated positions. For those 1.2 or 1.5 (CH₃) times the equivalent isotropic U values of the corresponding C atom were used as displacement factors. The refinement converged at $wR_2 = 0.1558$ for all reflections, corresponding to a conventional $R = 0.0586$ for the observed reflections.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications nos. CCDC-135300 (**7a·Na·Et₂O**), CCDC-135299 (**7b·Na·Et₂O**) and CCDC-135951 (**7c·Na·4 Et₂O**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results

Monoprotonation of dianions **3a-c** [9] by cyclopentadiene (CpH) yields monoanions **7a-c**. The latter are also obtained by reacting 1,2,4-triboracyclopentanes **15b-d** [9] with triethylboron hydride (Scheme 5). During the formation of **7a** from **15d** and two equivalents of this hydride, **15a** is probably formed *in situ*. The short-lived **15a** can be prepared by oxidation of **3a** with 2,3-dibromo-2,3-dimethylbutane. Reaction of **15a** with triethylboron deuteride yields mainly **7e** and only small amounts of the isomer with a B-D-B-bridge. The latter is, however, the only product when **3a** is treated with D₂O. The reaction of **3a** with methyl iodide leads to **7c** (ca. 50 - 70%) in addition to **7a** (ca. 50 - 30%). With trideuteromethyl iodide only **7c** with R = CD₃ instead of R = CH₃ is formed. The reaction of **3e** with methyl iodide gives **7c**, which has a B-D-B-bridge, in addition to **7e**. The structures of the novel compounds **7a-c** in solution were deduced from their ¹¹B-, ¹H- and ¹³C-NMR-data (Experimental section); their crystal structures (Figure 1) were determined by X-ray diffraction analyses. Analysis of deuterated products was accomplished by deuterium NMR spectroscopy.

The ¹¹B-NMR chemical shifts of **7a-c** resemble those of the corresponding dianions of type **3** and thus indicate bishomoaromatic structures for **7a-c**. The protons attached to the skeleton carbon atoms of **7a-c** show negative ¹H-NMR chemical shifts as observed before in bishomoaromatic dianions **3**. For the protons of the B-H-B bridges of **7a-c** broad signals between -1.2 and -2.0 are found, which sharpen on ¹¹B decoupling using the frequency of the neighboring boron

Scheme 6 Computed (MP2/6-31+G*) geometries and relative energies (MP4SDQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31G*)) for homoaromatics **7**, “classical” isomers **17**, and the connecting transition structures **TS-7/17** with (a) H (**u**), (b) methyl (**uMe**), (c) phenyl (**uPh**), (d) hydroxy (**uOH**) and (e) amino (**uNH₂**) substituents at B1. Results for the phenyl derivatives correspond to the B3LYP/6-311++G**//B3LYP/6-31+G* + ZPE(B3LYP/6-31G* DFT level of theory

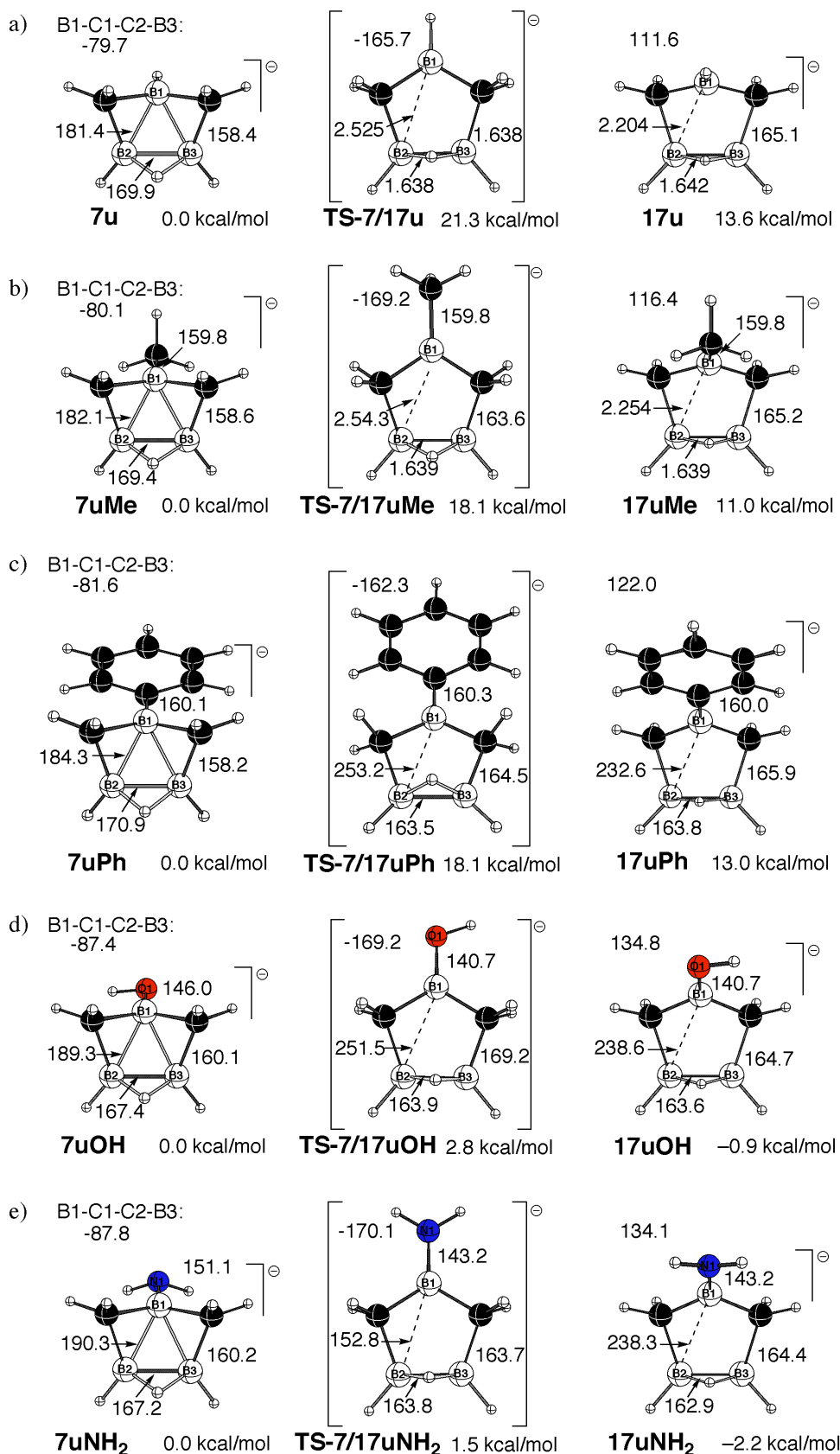


Table 2 Selected bond distances [pm] and interplanar angle [°] of **7a·Na·Et₂O**, **7b·Na·Et₂O** and **7c·Na·4 Et₂O** (crystal structures) and corresponding values computed for models

| | B1··B2 | B1··B3 | B2-B3 | C1B2B3C2/ C1B1C2 [a] | δ ¹¹ B B1 | δ ¹¹ B B2,B3 |
|--------------------------------|----------|----------|----------|-------------------------|-------------------------|----------------------------|
| 7a·Na·Et₂O | 185.1(3) | 184.4(3) | 171.7(3) | 82.7(2) | -25 | 17 |
| 7u [b] | 181.4 | 181.4 | 169.9 | 79.7 | -38.0 | 13.9 |
| 7b·Na·Et₂O | 191.2(3) | 192.4(3) | 171.5(3) | 87.3(2) | -14 | 20 |
| 7uPh [c] | 184.3 | 184.3 | 170.9 | 81.8 | -29.8 | 15.7 |
| 7c·Na·4 Et₂O | 191.0(5) | 191.6(5) | 171.7(5) | 86.1(3) | -14 | 18 |
| 7uMe [b] | 182.1 | 182.1 | 169.4 | 80.1 | -29.7 | 16.6 |
| 7uOH [b] | 189.3 | 189.3 | 167.4 | 87.4 | -6.7 | 19.1, 16.0 |
| 7uNH₂ [b] | 190.3 | 190.3 | 167.2 | 87.8 | -11.4 | 17.9 |

[a] interplanar angle

[b] Computed at the GIAO-SCF/6-311+G**//MP2(fc)/6-31+G* level of theory.

7u, **7uMe**, **7uOH**, **7uNH₂** (//MP2/6-31+G*) and **7uPh** (//B3LYP/6-31+G*). ¹¹B NMR chemical shifts for these [ppm] are also given.

[c] Computed at the GIAO-SCF/6-311+G**//B3LYP/6-31+G* level of theory.

atoms. In the crystal, the anions **7a** and **7b** form contact ion pairs with sodium ions, coordinated to the *ipso*- and *ortho*-C atoms of the duryl (2,3,5,6-tetramethylphenyl) rings as well as to one additional ether molecule each. Compound **7c**, however, is a solvent separated ion pair. Monoanions **7a** to **7c** have an extra B-H-B bridge compared to dianions **3**, but all share five-membered ring distortions which are typical for two-electron bishomoaromatics [6,24]: short transannular distances (here B··B) and small interplanar angles (here between the C1,B2,B3,C2 and the C1,B1,C2 planes). Table 2 compares values measured for **7a,b·Na·Et₂O** and **7c·Na·4 Et₂O** to those computed for models **7u**, **7uPh**, **7uMe**, **7uOH** and **7uNH₂**. Important geometrical parameters of the former and of their classical isomers **17** as well as the connecting transition states **TS-7/17** are also shown in Scheme 6.

Structure and strength of homoaromaticity of anions of type 7

The transannular B··B distances in **7b** (191.2(3) and 192.4(3) pm) and in **7c** (191.0(5) and 191.6(5) pm) are significantly longer than those in **7a** (184.4(3) and 185.1(3) pm) and those computed for **7u** (181.4 pm) and **7uPh** (184.3 pm). Correspondingly, the interplanar angles in **7b** (87.3(2)°) and **7c** (86.1(3)°) are larger than those in **7a** (82.7(2)°) and **7u** (79.7°). The geometric effect of the phenyl substituent is larger in monoanionic **7** than in dianionic **3** [9]. The additional proton in **7** reduces the total charge and hence lowers the orbital energies of the 3c2e bond which makes the conjugation between the 3c2e bond and the phenyl group more effective. This interaction involves a formally empty 3c2e bond orbital that is antibonding between B1 and both B2 and B3 and bonding between B2 and B3. Therefore, donation into this orbital leads to elongated B1-B2,3 and shortened B2-B3 distances. The geometrical changes become more pronounced as the

donor ability of the B1 substituent increases in the series **7u**, **7uMe**, **7uPh**, **7uOH**, **7uNH₂** (compare Scheme 6). Another way to explain this trend is to imagine a classical Lewis formula where the empty P-orbital at B1 can interact with a protonated B2=B3 double bond (cyclic conjugation leading to a 3c2e bond), but B1 also can conjugate with a potentially π-donating substituent. The stronger the donation from the substituent, the weaker is the 3c2e bond.

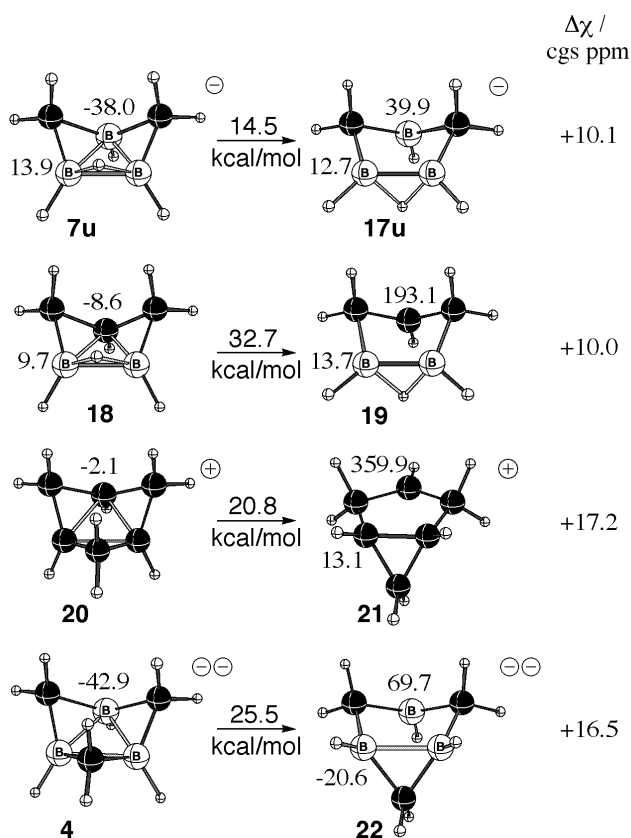
The strength of homoaromaticity is hard to estimate accurately, as has been pointed out before [2,25]. The transition structures **TS-7/17** for ring inversion between compounds **7** with BBB 3c2e bonds and isomers **17**, where B1 faces the B2-B3 unit at the H-bridged side, have classical five-membered ring structures (with one non-classical B-H-B bridge). The ring inversion barrier for the parent **7u** via **TS-7/17u** is 23.5 kcal mol⁻¹ at the MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31G*) level (21.3 kcal mol⁻¹ with MP4SDQ). However, this value is only a lower estimate for the 3c2e bond energy of homoaromatic **7u** because the considerable ring strain of **7u** is largely released in **TS-7/17u**. Hyperconjugation (**7uMe**) and conjugation (**7uPh**, **7uOH**, **7uNH₂**) are more important when a p-orbital (B1 in **TS-7/17**) is involved instead of a 3c2e bond orbital (in **7**). Therefore, the inversion barriers are lower with better donor substituents.

Consequences of placing bridges on the “wrong” side of the plane of centers of cyclic delocalization

Structure **17u**, which has the B-H-B bridge on the opposite side compared to **7u**, is predicted to lie 14.5 kcal mol⁻¹ higher in energy than **7u** (at the MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31*) level, for other levels of theory see Table 1). The five-membered ring of **17u** is slightly distorted by C-B hyperconjugation - as seen from long C-

B(B) bonds (165.1 pm) and small B-C-B angles (86.6°). However, there is *no 3c,2e bond between the three boron atoms*, which means that **17u** is *not homoaromatic*. The neutral molecule **18** [14], which is the bishomo form of **13**, is isoelectronic to **7u** and also has a 3c2e bond though a B-C-B one. Placing the hydrogen bridge at the other side of the ring, however, destroys the 3c2e bond in **18** and gives the zwitterionic isomer **19** which is 32.7 kcal mol⁻¹ higher in energy than **18**. 3c2e bonding not only has geometric and energetic, but also magnetic effects: The atoms which are pentacoordinate in the homoaromatic systems are considerably more shielded than the corresponding tricoordinate atoms in the classical isomers. In addition, 3c2e bonds lead to increased *diamagnetic* susceptibilities χ (= more negative values, compare Scheme 7), another magnetic criterion for aromaticity [1b,2b].

Molecules with B-H-B bridges must have the hydrogen bridge and the homobridges on the same side of the centers of cyclic delocalization to be homoaromatics. All experimentally known bis- and tris-homoaromatics without B-H-B bridges, e.g. dianions of type **3** [9] as well as the



Scheme 7 Effect of the loss of 3c2e bonding upon stabilization (MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31G*)), NMR chemical shifts and magnetic susceptibility, $\Delta\chi$, (GIAO-SCF/6-311+G**//MP2(fc)/6-31+G*) in homoaromatics **7u**, **18**, **20**, and **4** in comparison to non-homoaromatic **17u**, **19**, **21** and **22** respectively

trishomocyclopropenyl cation **20** [4,25] and Siebert's dianion of type **4** [10], have the homobridges on the same side. The isomer **21** [25] of **20** was computed at the MP4SDQ/6-31G*/MP2/6-31G* + ZPE(HF/6-31G*) level by Cremer's group to be 16.8 kcal mol⁻¹ higher in energy than **20** (20.8 kcal mol⁻¹ at MP4SDTQ/6-311+G**//MP2(fc)/6-31G* + 0.89 ZPE(HF/6-31G*)). Here we show that the energy difference between **4** and **22** is even greater (25.5 kcal mol⁻¹ at MP4SDTQ/6-311++G**//MP2/6-31+G* + 0.89 ZPE(HF/6-31G*)). Both B-H-B bridges and the methylene bridge are on the same side in Paetzold's derivative of **9** [11]. The three B-H-B bridges of **10**, which was computed by Jemmis et al. [16], also lie on the same side of the B₃-plane. Attempts to estimate the energy of isomers of **9** and of **10**, with the H-bridges on opposite sides, have been unsuccessful.[b]

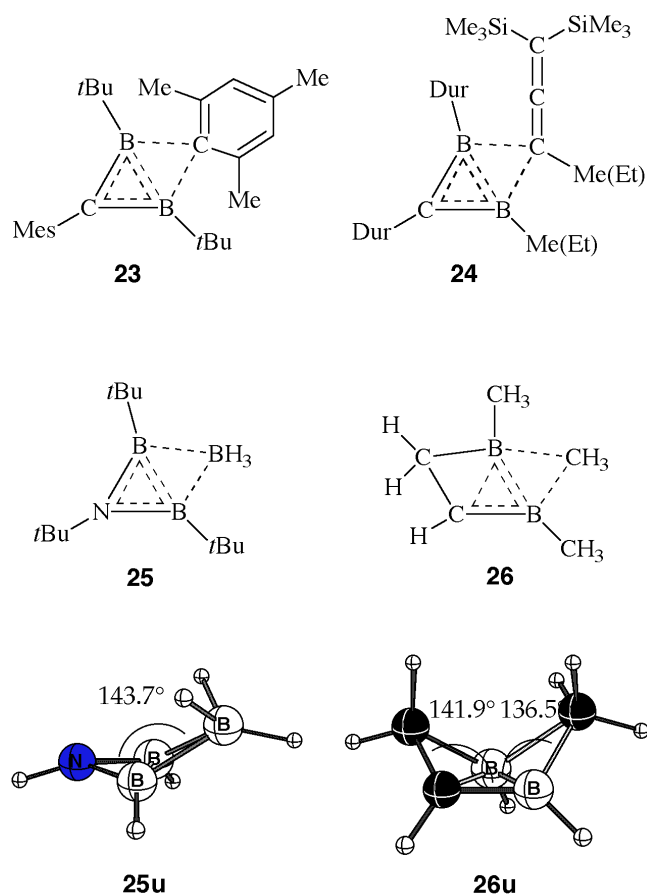
Nonclassical homobridges

Obviously, the B-H-B bridges in homoaromatics underlie the same building principles as the "classical" homobridges. Therefore, we suggest the term "non-classical homobridges" for these B-H-B bridges in homoaromatics. However, in order to avoid confusion, we also suggest to continue to name homoaromatics according to the number of classical homobridges. Cation **10** has three nonclassical homobridges, Paetzold's derivative of monohomoaromatic **9** has one classical and *two* non-classical homobridges, and monoanions of type **7** are bishomoaromatic with two classical and *one* non-classical homobridges. Homoaromatics with non-classical homobridges are between aromatics and homoaromatics with classical homobridges in character: in unbridged aromatics like **1** and **11** the atoms participating in the aromatic systems are held together by additional 2c2e bonds. In contrast, for some (**2**, **3**, **12**) or all (**4**, **20**) pairs of atoms participating in the aromatic system of a homoaromatic compound there is *no* direct extra bonding. Non-classical homobridges provide *partial* bonding for pairs of atoms of the aromatic system by involving them in 3c2e bonds (**5** - **10**, **13**, **14**, **18**).

Classical homobridges always lie outside the plane of the centers of cyclic delocalization. However, non-classical homobridges like those in **5**, **8** and in **13** may as well lie in the plane. This is experimentally realized in derivatives [13] of **13**, which is isoelectronic with **5**. Only the presence of three H-bridges simultaneously (i.e. **10**) cause distortion from planarity for steric reasons [16].

Non-classical homobridges discussed so far consist of a protonated B-B bond. Other Lewis acids may also be suitable for 3c2e bond formation. Non-classical homobridges other than H are realized in **23** [26] and **24** [27] as well as in **25** [28] which have BCB and BBB 3c2e bonds, respectively (compare Scheme 8). Structure **26** [29] with a classical meth-

[b] Optimizations of starting geometries with one or two bridge hydrogen atoms mirrored to the opposite side of the BBB plane converged to the homoaromatic structures.



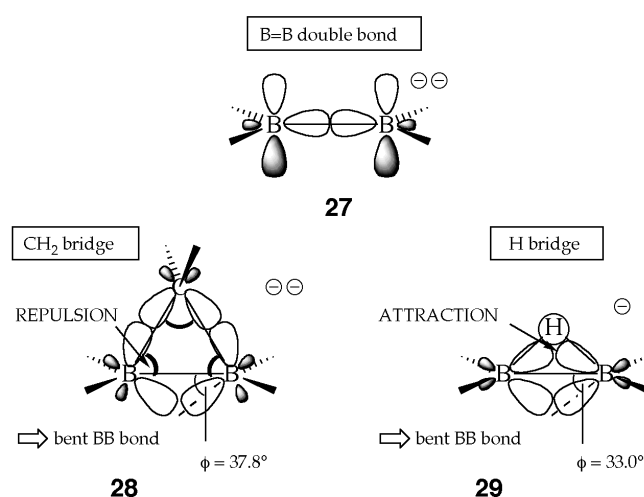
Scheme 8 Compounds with nonclassical homobridges other than hydrogen

ylene and a nonclassical methyl bridge was computed for C-dimethylboryl-B-methylborirane at MP2/6-31G*.

σ - Versus π -character of the $3c2e$ bonds

Basic features of the methylene and hydrogen bridges can be deduced when they are incorporated into the diborane(4) dianion **27** [30], the simplest molecule with a BB double bond. A classical homobridge causes considerable strain due to the three-membered ring formation. As a consequence, the $2c2e$ BB bond becomes considerably bent (compare angles ϕ for **28** in Scheme 9). The additional proton in **29** engages two boron hybrids in a BHB $3c2e$ bond and leads to rehybridization of the BB $2c2e$ -bond, which can be considered between π and σ in character. Both methylene and hydrogen bridges cause bent BB bonds that are good donors and therefore excellent building blocks for $3c2e$ bonds.

The concept of classical and non-classical homobridges is further supported by the similarities with respect to overlap, hybridization and bending of orbitals relative to the plane of the centers in the cyclic array. In unbridged π -aromatics, the atomic orbitals forming the aromatic system are perpendicular to the plane spanned by the ring of atoms. Compounds



Scheme 9 Bent $2c2e$ BB bonds as a consequence of a classical methylene (**28**) and of a non-classical hydrogen bridge (**29**). The bending angle ϕ was obtained from an NBO analysis [23]

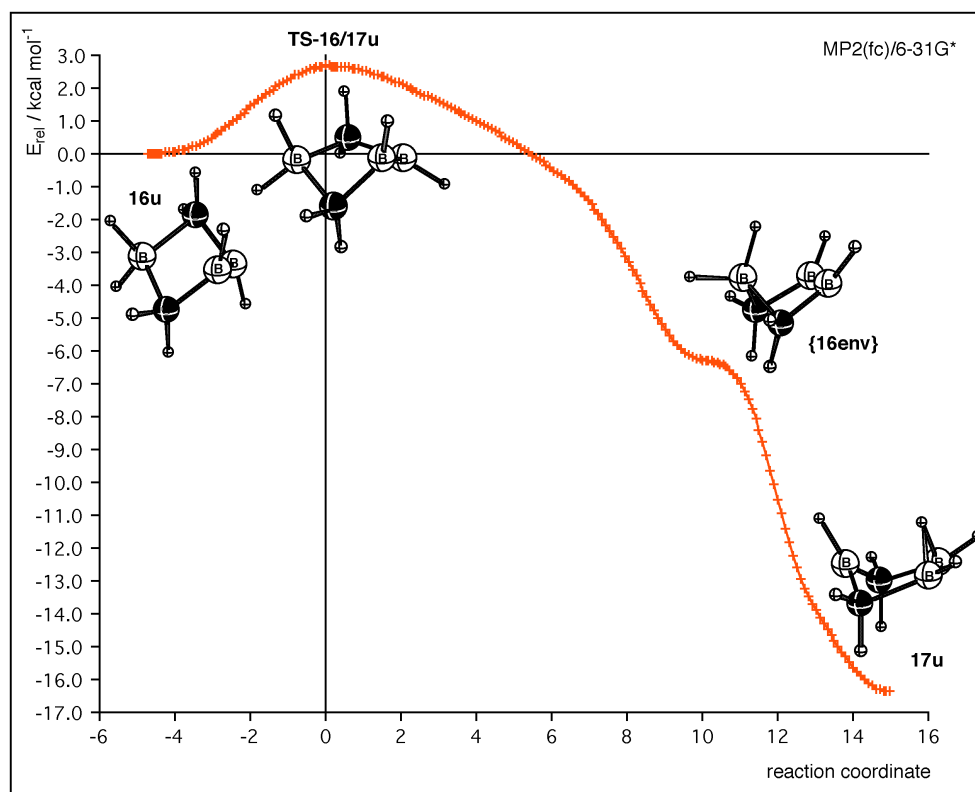
with overlap in the plane of atoms and the appropriate number of electrons may be called “ σ -aromatics” [31]. We computed various (homo)aromatics shown in Scheme 3 to investigate how classical and non-classical homobridges change the π -character of the BBB $3c2e$ bond.

The $3c2e$ bond was localized by the NBO procedure [23], and the angle ϕ between the three contributing hybrids and the BBB plane was determined. Of course, planar compounds **5** and **8** have $\phi = 90^\circ$, since they are true π -aromatics, and the in plane H-bridges only polarize the π -system towards the B atoms participating in the BHB bridges (compare the percentages given in Scheme 3). The three H-bridges of **10**, however, reduce ϕ to 47.2° , which is approximately halfway between π - ($\phi = 90^\circ$) and σ -overlap ($\phi = 0^\circ$). Loss of planarity also allows considerable s/p-hybridization, which further maximizes overlap on one end [32]. A single CH_2 bridge in **2** bends the hybrids of the boron atoms it is attached to even further ($\phi = 36.5^\circ$). The B3 hybrid also twists ($\phi = 63.6$) to maximize overlap. Generally, more bridges change the character towards σ -aromaticity. Classical bridges have a stronger effect than non-classical ones; e.g. in **7u** ϕ is 16.8° for B1 (between the two classical homobridges), but $\phi = 27.9^\circ$ for B2,3, which are both involved in the H-bridge. In the trishomoaromatic **4** the orbital out-of-plane angle is just 15.4° , which is basically the same as for the trishomocyclopropenyl cation, **20**. Hence, all-homoaromatics are much closer to σ - than to π -aromatics.

Formation of homoaromatic anions **7** via migration of hydrogen atoms: nonaromatic isomers **17** as intermediates

In **3a** and **3e** the boron between two carbon atoms has a terminal hydrogen and deuterium atom, respectively. After the

Scheme 10 The intrinsic reaction coordinate for transition structure **TS-7/17u**, connecting minima **16u** and **17u** by an intramolecular hydrogen transfer. No minimum but only a flat region is found at MP2(fc)/6-31G* for the envelope conformation {**16env**}



reaction with methyl iodide, however, this boron atom carries the methyl group and the H or D occupies the B-B bridging position. Likewise, in the reaction of **15a** with triethylboron deuteride, the boron bound hydrogen atom of **15a** is replaced by the incoming deuterium and moves to the B-H-B bridge position. These observations can be explained by postulating intermediates **16a** and **16c** as well as **16e** (Scheme 5), respectively, which represent classical isomers of **7c** and **7e**, respectively. A planar C_{2v} symmetric model, **16u***, however, is characterized by two imaginary frequencies at the HF/6-31G* level. A geometry optimization of a distorted **16u*** geometry without imposing symmetry constraints converged to a 14.9 kcal mol⁻¹ more stable and strongly distorted C_2 symmetric five-membered ring structure **16u** with the two methylene groups placed on opposite sides of the B_3 -plane. A C_s symmetric envelope conformation {**16env**} was characterized as a minimum at the HF/6-31G* level of theory. Re-optimization of the geometry at correlated levels (MP2/6-31G* and B3LYP/6-31G*) converged to **7u**. Likewise the transition structure for hydrogen transfer from B1 to the B2-B3 bridging position, {**TS-16Hshift**}, could not be refined at the MP2/6-31G* level. This suggests that neither {**16env**} nor the transition structure {**TS-16Hshift**} exist as stationary points. However, we finally succeeded in locating a transition structure, **TS-16/17u**, for the conformational change that brings one methylene bridge in **16** to the other side of the B_3 plane. Once **16u** transforms to an envelope like conformation, which involves a small 3.0 kcal mol⁻¹ barrier, the endo-H at B1 will be transferred to B2/B3. [c] Transition structure **TS-16/17u** was confirmed by computing the intrinsic reac-

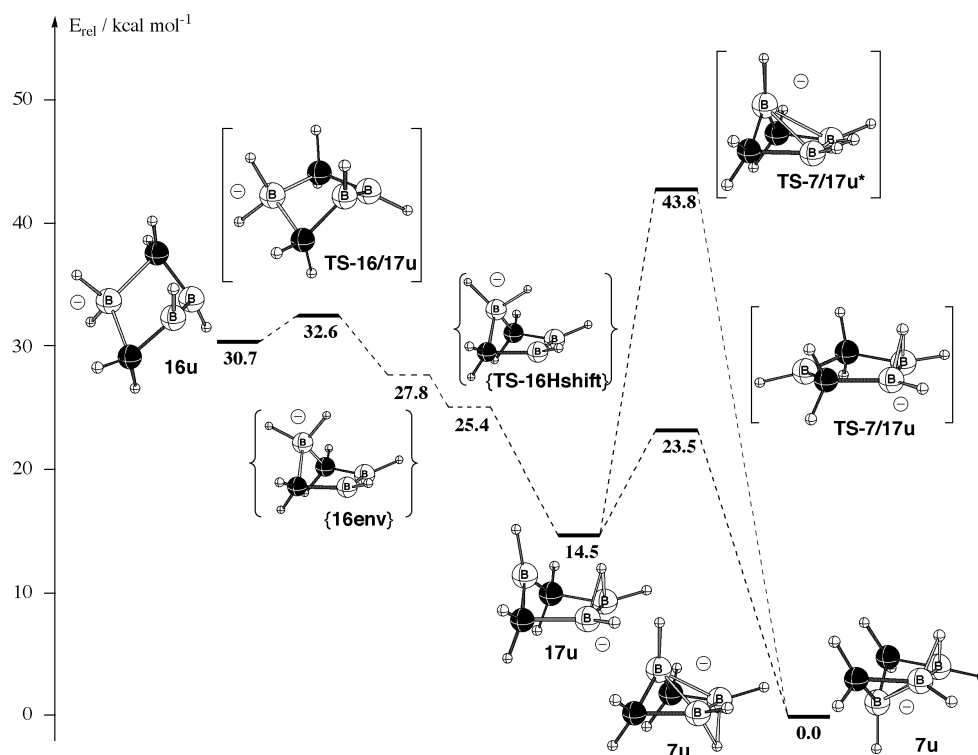
tion coordinate at the MP2(fc)/6-31G* level to connect **16u** and **17u** directly. A flat region along the coordinate corresponds to the {**16env**} conformation (see Scheme 10).

“Classical” **16u** is 30.7 kcal mol⁻¹ higher in energy than **7u**, which has both methylene groups and the hydrogen bridge on the same side of the B_3 -plane. In order to bring B1 to the unbridged side of the B2-B3 unit, either the hydrogen bridge has to move or the HB1 group. In the transition state for the hydrogen rearrangement, the bridge-H lies basically in the HBBH plane, which is also the nodal plane of the B2B3 π -bond. The transition state, **TS-7/17u***, thus has a protonated σ - instead of a protonated π -bond and the B2-B3 p,p- π bond is developing the 3c2e bond with B1. It is 29.3 kcal mol⁻¹ higher in energy than **17u** (see Scheme 11). The alternative ring flipping via **TS-7/17u** has a barrier of only 9.0 kcal mol⁻¹. The high energy of **TS-7/17u*** in spite of its two 3c2e bonds is remarkable and reminiscent of the high energy of the D_{3h} symmetric transition state of **10** (42.0 kcal mol⁻¹ above **10** at MP2/6-31G*) [16] in spite of four 3c2e bonds as in **10**.

Dianions of type **3** might be protonated at the bridging position between B2 and B3 giving monoanions of type **7**

[c] At HF/6-31G* the barrier for the H-shift in {**16env**} via {**TS-16Hshift**} is only 0.2 kcal mol⁻¹. So, regardless whether {**16env**} and {**TS-16Hshift**} are stationary points on the potential energy surface or not, the conclusion remains the same: the hydrogen shift occurs readily from the envelope conformation.

Scheme 11 Relative energies (MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31G*)) of $[C_2B_3H_8]^-$ model structures and transition states involved in the formation of homoaromatic **7u** via **16u** and **17u**. Transition structures **TS-7/17u** and **TS-7/17u*** are for moving of B1-H and for moving of the B-H-B hydrogen to the opposite side of the B_3 plane, respectively. Energies for {**16env**} and {**TS-16Hshift**} correspond to MP4SDTQ/6-311++G**//HF/6-31G* + 0.89 ZPE(HF/6-31G*) as these structures only exist at the HF/6-31G* but not at correlated levels (see Text for details)



directly, or protonation of the BBB face might first lead to **17** which in turn can isomerize to **7** via **TS-7/17**. Electrophilic attack at the 3c2e bond in **3** by a methyl group probably leads to a structure of type **16** (or {**16env**}) because an alkyl bridge is disfavored. Nucleophilic attack of **15** by a hydride occurs at B1 also leading to **16**. With small substituents R (H, D) the nucleophilic attack is likely to occur in an envelope like conformation (compare {**16env**}) with R at the endo position for steric reasons. This prepares R = H, D for the migration to the B2B3 bridge position to give **17**. With larger R's, more conformational changes are required to transform structures **16** to **17**, but these are not expected to involve large barriers. Further isomerization to **7** is easy because the barrier between **17** and **7** is less than the energy that is gained from the **16** → **17** step.

The C_2 conformation of **16u** is the consequence of very strong hyperconjugation of the empty P-orbitals of the neighboring boron atoms with the C-BH₂ σ-bonds leading to very long C-BH₂ (182.4 pm) and short C-B(B) bonds (150.6 pm) and to small B-C-B angles (79.0°). Hyperconjugation is considerably weaker in the corresponding uncharged **15u** as seen from the smaller energy difference between the planar C_{2v} symmetric **15u*** (also a second order stationary point) and the corresponding C_2 minimum, **15u**, (7.5 kcal mol⁻¹) as well as from the smaller geometric changes (compare Scheme 12).

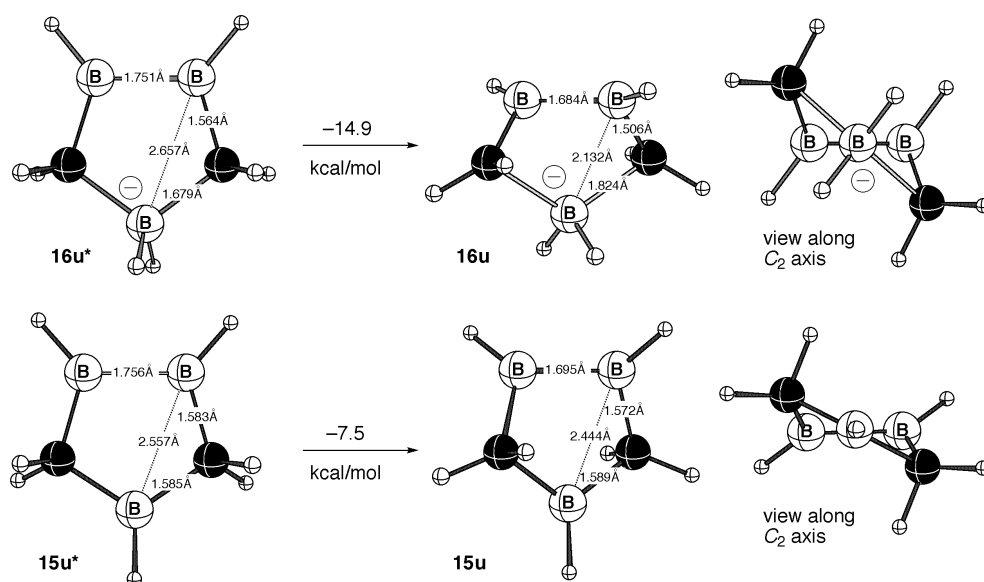
Comparison of **16u** and **15u** demonstrates impressively the effect of the higher donor ability of the C-BH₂ σ-bonds due to their higher p-character and due to the formal negative charge at boron (reducing the electronegativity of that

boron) on the strength of hyperconjugation with electron deficient centers. Experimentally we have observed this effect recently for bicyclic 1,2-diboryl-boratiranes and corresponding boriranes [33].

Summary

Homoaromatic anions **7** containing two electrons delocalized over three boron atoms can be synthesized by electrophilic and nucleophilic additions to **3** and **15**, respectively. Use of different reactants and deuterium labeling experiments demonstrate that the formation of anions **7** involves migration of hydrogen atoms from the boron atom between carbon atoms to the B-B-moiety (at least in most cases). *Ab initio* computations of the relevant region of the $[C_2B_3H_8]^-$ potential energy surface reveal details of the mechanism. Addition of a nucleophile probably initially leads to classical anions **16**, which readily undergo intramolecular H-shift reactions once they adopt an envelope like conformation. This transformation results in isomers **17**, which are non-aromatic because the hydrogen bridge is on the opposite side of the B_3 plane as the methylene groups, in contrast to homoaromatic anions **7**, where it is found on the same side of the B_3 plane as the two methylene homobridges. The rearrangement from **7u** to **17u** has a 9.0 kcal mol⁻¹ barrier and occurs *via* transition structure **TS-7/17u** with a quasi planar five-membered ring. Its 23.5 kcal mol⁻¹ higher energy relative to **7u** is used as a lower estimate for the strength of homoaromaticity in **7u** - neglect-

Scheme 12 Distortion and stabilization by hyperconjugation of **16u** and **15u** relative to planar **16u*** and **15u***, respectively (geometries and energies at the MP2(fc)/6-31+G* and MP4SDTQ/6-311++G**//MP2(fc)/6-31+G* + 0.89 ZPE(HF/6-31G*) levels, respectively)



ing the much higher strain of **7u**. B-H-B bridges in **7** and other BBB homoaromatics are recognized to underlie the same building principle as more conventional “classical” methylene homobridges and therefore are suggested to be designated “nonclassical homobridges”. 3c2e homoaromatic bonds are further characterized by short transannular distances (**7u**: $d(\text{B}\cdots\text{B}) = 181.4$ pm), enhanced diamagnetic susceptibilities and considerably shielded pentacoordinate atoms as compared to the corresponding tricoordinate atoms of classical isomers.

Outlook

The concept of nonclassical homobridges should stimulate further synthetic and computational efforts. Some questions to be answered are: Can derivatives of **8** with two B-H-B bridges in the plane of the cyclic array, be prepared? These products would have a planar pentacoordinate boron atom in addition to two planar tetracoordinate boron atoms [13]. May nonclassical bridges other than hydrogen be forced into the plane of the cyclic array? Protonated 1,2-diboratabenzene is one of the simplest candidates for six-electron aromatics with nonclassical homobridges, which, to our knowledge, are unknown. Highly negatively charged aromatic compounds suffer from large destabilizing Coulomb repulsion but may be stabilized by non-classical homobridges, which may reduce the total charge (as e.g. a proton) or at least accept considerable partial charges (neutral Lewis acids). Thus, diprotonated 1,2,4,5-tetraboratabenzene may be accessible. Even triprotonated hexaboratabenzenes may be stable since three negative charges in a six membered ring should be a smaller problem than in a five-membered ring, which we prepared recently [34]. The concept of classical and non-classical homobridges might even be applied to three dimensional aromatics [35,36]: *nido*-polyboranes and *nido*-carboranes with B-H-B-bridges could be regarded as three-dimensional aro-

matics with nonclassical homobridges. The structural relationship between boranes, carboranes and carbocations was recognized by Williams [37]. The hetero- μ -bridges of several pentaboranes(9) [38] could be considered as nonclassical hetero homobridges.

Experimental section

Physical and spectroscopic properties of **7a-c** and **15a**.

7a: white solid, mp. > 200°C, yields: from **3a** 99% (NMR), from **15a** 99% (NMR), from **15d** 85% (isolated); $^1\text{H}\{^{11}\text{B}\}$ -NMR (500 MHz, $[\text{D}_8]$ -THF, 25°C): $\delta = 6.41, 6.30$ (each s, each 1H, Dur-H), 3.37 (q, Et_2O), 2.38, 2.16, 2.07, 2.06, 2.02, 1.95, 1.93, 1.88 (each s, in total 24H, Dur- CH_3), 1.31 (s, 1H, C_2BH), 1.11 (t, Et_2O), $-0.03, -0.38$ (each s, each 9H, SiMe_3), $-0.45, -0.58$ (each s, each 1H, BCH), -2.04 (s, 1H, B_2H); $^{13}\text{C}\{^{11}\text{B}\}$ -NMR (125 MHz, $[\text{D}_8]$ -THF, 25°C): $\delta = 153.9, 149.6$ (each s, Dur-*i*-C), 138.2, 138.1, 134.9, 134.8, 131.2, 131.0, 130.5, 130.4 (each s, Dur-*o*- und *m*-C), 128.7, 127.4 (each d, Dur-*p*-C), 66.5 (t, Et_2O), 21.6, 21.03, 20.98, 20.5, 20.0, 19.4, 19.2 (each q, Dur- CH_3), 15.9 (q, Et_2O), 14.2 (d, $^1J(\text{C-H}) = 114$ Hz, BCH), 11.6 (d, $^1J(\text{C-H}) = 124$ Hz, BCH), 3.7, 1.7 (each q, SiMe_3); ^{11}B -NMR (96 MHz, $[\text{D}_8]$ -THF, 25°C): $\delta = 17, -23$.

7b: pale-yellow crystals, yields: from **3b** 99% (NMR), from **15b** 65% (isolated); $^1\text{H}\{^{11}\text{B}\}$ -NMR (500 MHz, $[\text{D}_8]$ -THF, 25°C): $\delta = 7.55$ (d, 2H, Ph-*o*-H), 6.90 (pseudo-t, 2H, Ph-*m*-H), 6.79 (t, 1H, Ph-*p*-H), 6.53, 6.31 (each s, each 1H, Dur-H), 3.37 (t, Et_2O), 2.52, 2.14, 2.06, 1.97, 1.95, 1.93, 1.50 (each s, in total 24H, Dur- CH_3), 1.10 (t, Et_2O), 0.08, -0.55 (each s, each 9H, SiMe_3), $-0.06, -0.19$ (each s, each 1H, BCH), -1.17 (s, 1H, B_2H); $^{13}\text{C}\{^{11}\text{B}\}$ -NMR (125 MHz, $[\text{D}_8]$ -

THF, 25°C): δ = 157.0 (s, Ph-*i*-C), 153.7, 148.8 (each s, Dur-*i*-C), 138.5, 138.3, 135.5 (br.), 134.8 (br.), 131.3, 130.6, 130.2 (br.) (each s, Dur-*o*- und *m*-C), 128.8, 127.3 (each d, Dur-*p*-C), 136.9, 125.6, 122.8 (each d, Ph-C), 66.2 (t, Et₂O), 22.2, 21.4 (br.), 21.0, 20.7 (br.), 20.5, 20.0, 19.6 (br.), 18.8 (br.) (each q, Dur-CH₃), 15.6 (q, Et₂O), 14.6 (d, 2C, ¹J(C-H) = 123 Hz, BCH), 3.6, 2.8 (each q, SiMe₃); ¹¹B-NMR (96 MHz, [D₈]-THF, 25°C): δ = 20, -14.

7c: white solid, yields from **3a** 50-70% (NMR), from **3c** 47% (isolated); ¹H{¹¹B}-NMR (500 MHz, [D₈]-THF, 25°C): δ = 6.43, 6.34 (each s, each 1H, Dur-H), 3.41 (t, Et₂O), 2.40, 2.13, 2.10, 2.06, 1.98, 1.95 (each s, in total 24H, Dur-CH₃), 1.14 (t, Et₂O), 0.33 (s, 3H, B-Me), -0.01, -0.33 (each s, each 9H, SiMe₃), -0.36, -0.77 (each s, each 1H, BCH), -1.61 (s, 1H, B₂H); ¹³C{¹¹B}-NMR (125 MHz, [D₈]-THF, 25°C): δ = 154.8, 151.0 (each s, Dur-*i*-C), 137.5, 135.0, 134.7, 130.5, 130.4, 130.3 (each s, Dur-*o*- und *m*-C), 128.1, 127.1 (each d, Dur-*p*-C), 66.2 (t, Et₂O), 21.5, 20.8, 20.7, 20.6, 20.5, 20.1, 19.9, 19.3 (each q, Dur-CH₃), 17.5 (d, ¹J(C-H) = 112 Hz, BCH), 15.6 (q, Et₂O), 11.9 (d, ¹J(C-H) = 119 Hz, BCH), 8.1 (br.q, ¹J(C-H) = 116 Hz, B-Me), 3.6, 2.8 (each q, SiMe₃); ¹¹B-NMR (96 MHz, [D₈]-THF, 25°C): δ = 19, -13.

15a: yellow solid, yield from **3a** 85% (NMR); ¹H{¹¹B}-NMR (500 MHz, CDCl₃, 25°C): δ = 7.45 (s, 1H, BH), 6.86 (s, 2H, Dur-H), 3.74 (s, 2H, BCH), 2.30 - 2.10 (in total 24H, Dur-CH₃), 0.15 (s, 18H, SiMe₃); ¹³C{¹¹B}-NMR (125 MHz, CDCl₃, 25°C): δ = 149.2 (s, Dur-*i*-C), 132.7, 131.4 (each s, Dur-*o*- und *m*-C), 130.3 (d, Dur-*p*-C), 67.1 (d, ¹J(C-H) = 108 Hz, BCH), 20.2, 19.4 (each q, Dur-CH₃), 2.8 (q, SiMe₃); ¹¹B-NMR (96 MHz, CDCl₃, 25°C): δ = 99, 86.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm Polyeder) and the Fonds der Chemischen Industrie. MH gratefully acknowledges a postdoctoral fellowship by the Deutscher Akademischer Austauschdienst. Research at the University of Georgia was supported by the U.S. National Science Foundation.

Supplementary material Cartesian coordinates in XYZ format together with absolute energies for optimized structures discussed in the text are provided.

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