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[15] The steric influences of the dendrons are also mirrored in the long reaction times: The mixtures had to be stirred for up to four weeks before all of the starting materials had reacted while usually the reaction is complete after a few days. Furthermore, between 77% (in case of **9b**) and 94% (in case of **10b**) of the free axles were formed here.

[16] To make sure that under these severe conditions the spectral changes were caused by mechanical deslipping and not by chemical decomposition, we exposed the free components of the rotaxanes, that is the tetralactam **1** and the axles, to the same conditions. Indeed, there was a slow color change of the solutions and slight changes in the spectra were observed, however, these processes were significantly slower than the changes observed in the spectra of the rotaxanes.

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Bishomoaromatic 1,2,4-Triboracyclopentane Dianions: Strong Three-Center, Two-Electron Bonds between Three Boron Atoms**

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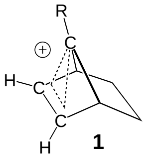
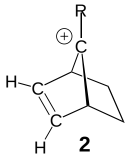
Markus Unverzagt, Govindan Subramanian,
Matthias Hofmann, Paul von Ragué Schleyer,
Henry F. Schaefer III, Gertraud Geiseler,
Werner Massa, and Armin Berndt*

The three-center, two-electron (3c,2e) bonding of bishomoaromatic cations of type **1**[1–4] are known to be weakened by $R = C_6H_5$[2b, 3a] and displaced by $R = p\text{-MeOC}_6H_4$ and R = OH.[4] Evidently, cations **1** are stabilized by the 3c,2e bonds, whereas cations **2** are stabilized by donor substituents R. According to computational estimates, **1u** (R = H) is more stable than **2u** (R = H) by 15 kcal mol^{-1}.[2a] The energy difference between the prototypes **3u** and **4u**, neither of which is known experimentally, is only 10.1 kcal mol^{-1}.[5]



1



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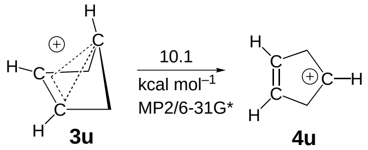
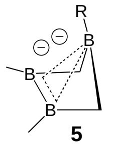


3u **4u**



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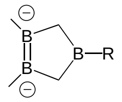

6

We now report on bishomoaromatic dianions **5** of 1,2,4-triboracyclopentanes that have skeletons isoelectronic to that of **3u**.[6, 7] The 3c,2e bonds of dianions of type **5** remain intact even in the presence of strong donor substituents like $R = NR_2$. Hence, the energy difference between **5** and **6** must be larger than the 26 kcal mol^{-1} stabilization afforded to a tricoordinate boron atom by a dialkylamino substituent.[8] Calculations at the MP2/6-31+G* level[9] confirm this conclusion.

The dianions **5a–c** (Dur = 2,3,5,6-tetramethylphenyl) are obtained by reduction of **7a–c** with lithium in diethyl ether.

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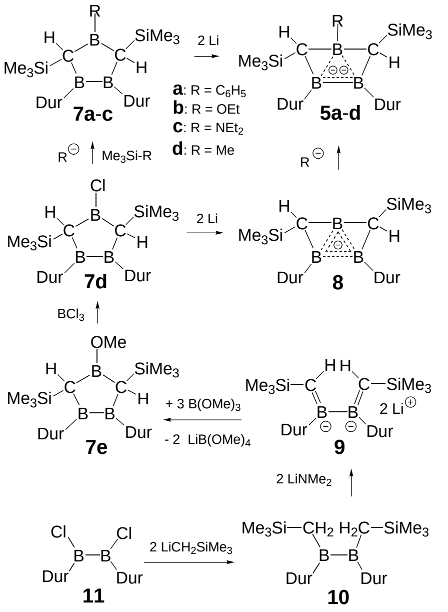


The reaction of **8** with phenyllithium and methyllithium yields **5a** and **5d**, respectively. Compounds **7a–c** and **8** were obtained from **7d**, which can be synthesized from **11**[10] via **10**, **9**, and **7e**. The structures of the new compounds are deduced from their ^{11}B, ^{1}H, and ^{13}C NMR spectra (Tables 1 and 2). Similarities of the NMR data with those of the known[11] isomers with *cis*-trimethylsilyl substituents allows identification of **7d**, **7e**, and **8**. The crystal structures[12] of $\mathbf{5a}\cdot 2Li\cdot 2Et_2O$ and $\mathbf{5b}\cdot 2Li\cdot 3Et_2O$ are shown in Figure 1, their relevant spectroscopic and physical data and that of $\mathbf{5c}\cdot 2Li\cdot 2Et_2O$ are included in Table 2.

Dianions **5a** and **5b** form contact triple ions with two lithium cations, which, in addition, are coordinated to diethyl ether molecules. Li1 is η^2-coordinated to the B2–B3 σ bond and to the *ipso*- and *ortho*-C atoms of the duryl substituents.[13] Li2 in **5a** exibits a remarkably short distance to B1 (211 pm) as well as contacts to C1 and C2 (230 pm).

The five-membered rings of **5a–c** feature distortions characteristic of two-electron bishomoaromatics:[3] short transannular distances (e.g. between B1 and B2,3) as well as

Table 1. Selected physical and spectroscopic properties of **5a–c**, **7a–e**, and **8–10**.

5a: yellow solid, yield 98 %; ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 7.92$ (d, 2H, Ph-*o*-H), 7.20 (m, 2H, Ph-*m*-H), 7.04 (t, 1H, Ph-*p*-H), 6.71, 6.68 (each s, each 1H, Dur-H), 2.93, 2.82, 2.45, 2.22, 2.18, 2.12, 2.08 (each s, total of 24H, Dur-CH_3), 2.64 (br., 8H, Et_2O), 0.59 (br., 12H, Et_2O), 0.46, 0.15 (each s, each 9H, $SiMe_3$), 0.02, –0.43 (each s, each 1H, BCH); $^{13}C\{^{11}B\}$ NMR (125 MHz, C_6D_6, 25 °C): $\delta = 156.2$ (s, Ph-*i*-C), 152.2, 151.7 (each s, Dur-*i*-C), 139.5, 138.6, 138.2, 137.1, 133.8, 133.7, 133.5, 133.2 (each s, Dur-*o*- and *m*-C), 136.0 (d, Ph-*o*-C), 129.62, 129.57 (each d, Dur-*p*-C), 126.8 (d, Ph-*m*-C), 123.7 (d, Ph-*p*-C), 65.1 (t, Et_2O), 22.4, 22.1, 21.3, 21.0, 20.9, 20.8 (each q, Dur-CH_3), 18.0 (d, ^{1}J(C,H) = 111 Hz, BCH), 14.0 (q, Et_2O), 4.3, 3.8 (each q, $SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 25 °C): see Table 2

5b: orange-red solid, yield 97 %; ^{1}H NMR (500 MHz, C_6D_6, 25 °C): $\delta =$ 6.70, 6.65 (each s, each 1H, Dur-H), 3.95 (q, 2H, OEt), 2.79, 2.68, 2.64, 2.21, 2.15 (each s, total of 24H, Dur-CH_3), 2.70 (br., 8H, Et_2O), 1.22 (t, 3H, OEt), 0.64 (br., 12H, Et_2O), 0.45, 0.14 (each s, each 9H, $SiMe_3$), –0.07, –0.98 (each s, each 1H, BCH); $^{13}C\{^{11}B\}$ NMR (125 MHz, C_6D_6, 25 °C): $\delta =$ 155.1, 152.6 (each s, *i*-C), 139.2, 136.9, 136.2, 133.5, 132.8, 132.4 (each s, *o*- and *m*-C), 128.9, 128.8 (each d, *p*-C), 65.5 (t, Et_2O), 61.4 (t, OEt), 24.0, 21.3, 21.1, 20.9, 20.5 (each q, Dur-CH_3), 18.7 (q, OEt), 18.0 (d, ^{1}J(C,H) = 107 Hz, BCH), 14.2 (q, Et_2O), 12.1 (d, ^{1}J(C,H) = 113 Hz, BCH), 3.8, 3.7 (each q, $SiMe_3$); ^{11}B NMR (160 MHz, C_6D_6, 25 °C): see Table 2

5c: orange-red solid, yield 95 %; ^{1}H NMR (500 MHz, $[D_{10}]Et_2O$, –30 °C): $\delta = 6.65$ (s, 2H, Dur-H), 3.38 (q, Et_2O), 2.68, 2.54, 2.50, 2.49, 2.12, 2.11, 2.09 (each s, total of 24H, Dur-CH_3), 1.13 (t, Et_2O), 0.14, –0.31 (each s, each 9H, $SiMe_3$), BCH and NEt_2 not observed; $^{13}C\{^{11}B\}$ NMR (125 MHz, $[D_{10}]Et_2O$, –30 °C): $\delta = 153.0$, 152.2 (each s, *i*-C), 140.5, 137.3, 136.8, 134.8, 133.6, 133.5, 133.1 (each s, *o*- and *m*-C), 129.14, 129.10 (each d, *p*-C), 66.2 (t, Et_2O), 51.5, 49.0 (t, NEt_2), 23.1, 22.4, 21.3, 21.2, 21.1, 20.9, 20.7, 20.0 (each q, Dur-CH_3), 18.2, 17.2 (q, NEt_2), 15.6 (q, Et_2O), 4.3, 3.7 (each q, $SiMe_3$), BCH not observed; ^{11}B NMR (160 MHz, C_6D_6, 25 °C): see Table 2

7a: yellow solid, m.p. 98 °C, yield 99 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.76$ (m, 2H, Ph-H), 7.53 (m, 3H, Ph-H), 6.98 (s, 2H, Dur-H), 3.98 (s, 2H, BCH), 2.25 (s, 12H, Dur-CH_3), 2.1 (br. s, 12H, Dur-CH_3), –0.08 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.5$ (br. s, Dur-*i*-C), 146.2 (br. s, Ph-*i*-C), 133.0, 132.5 (each s, Dur-*o*- and *m*-C), 131.7 (d, Ph-*m*-C), 130.7 (d, Dur-*p*-C), 129.9 (d, Ph-*p*-C), 127.5 (d, Ph-*o*-*C*), 65.0 (d, ^{1}J(C,H) = 108 Hz, BCH), 20.9, 19.6 (each q, Dur-CH_3), 3.0 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 101$, 82 (2:1)

7b: yellow oil, yield 99 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.86$ (s, 2H, Dur-H), 4.20 (m, 2H, OEt), 2.80 (s, 2H, BCH), 2.25, 2.20 (each s, each 12H, Dur-CH_3), 1.43 (t, 3H, OEt), 0.12 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.5$ (br. s, *i*-C), 132.8, 131.1 (each br. s, *o*- and *m*-C), 130.2 (d, *p*-C), 62.9 (t, OEt), 53.3 (d, ^{1}J(C,H) = 101 Hz, BCH), 20.4, 19.7, 19.0 (each br. q, Dur-CH_3), 17.6 (q, OEt), 2.7 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 96$, 53 (2:1).

7c: yellow solid, m.p. 128 °C, yield 98 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.91$ (s, 2H, Dur-H), 3.51, 3.01 (each q, each 2H, NEt_2), 3.01 (s, 2H, BCH), ca. 2.2 (br. s, 24H, Dur-CH_3), 1.19 (t, 6H, NEt_2), 0.02 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.8$ (br. s, *i*-C), 133.3, 133.1 (each s, *o*- and *m*-C), 130.9 (d, *p*-C), 52.5 (d, ^{1}J(C,H) = 107 Hz, BCH), 42.9 (t, NEt_2), 21.6, 19.8 (each q, Dur-CH_3), 15.8 (q, NEt_2), 3.5 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 97$, 49 (2:1)

7d: yellow solid, m.p. 133 °C, yield 75 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.85$ (s, 2H, Dur-H), 3.37 (s, 2H, BCH), 2.12 (s, 12H, Dur-CH_3), ca. 1.9 (br. s, 12H, Dur-CH_3), 0.13 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 148.4$ (br. s, *i*-C), 133.1, 131.8 (each s, *o*- and *m*-C), 130.8 (d, *p*-C), 63.8 (d, ^{1}J(C,H) = 111 Hz, BCH), 20.6, 19.4 (each q, Dur-CH_3), 2.6 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 97$, 74 (2:1)

7e: yellow oil, yield 99 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.82$ (s, 2H, Dur-H), 3.89 (s, 3H, OMe), 2.82 (s, 2H, BCH), 2.16 to 1.58 (br. s, total of 24H, Dur-CH_3), 0.01 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.5$ (br. s, *i*-C), 132.8, 131.3 (each s, *o*- and *m*-C), 130.2 (d, *p*-C), 54.7 (q, OMe), 53.2 (d, ^{1}J(C,H) = 104 Hz, BCH), 20.3, 19.2 (each q, Dur-CH_3), 2.6 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 97$, 53 (2:1)

8: yellowish solid, yield 59 %; ^{1}H NMR (500 MHz, $[D_8]THF$, –80 °C): $\delta =$ 6.34 (s, 2H, Dur-H), 3.35 (Et_2O), 2.10, 1.80, 1.63 (each s, total of 24H, Dur-CH_3), 1.11 (Et_2O), 0.05 (s, 2H, BCH), –0.28 (s, 18H, $SiMe_3$); ^{13}C NMR (125 MHz, $[D_8]THF$, –80 °C): $\delta = 153.6$ (br. s, *i*-C), 132.8, 135.0, 134.5, 130.6, 130.1 (each s, *o*- and *m*-C), 126.9 (d, *p*-C), 66.8 (Et_2O), 21.4, 20.2 (each q, Dur-CH_3), 2.9 (d, ^{1}J(C,H) = 129 Hz, BCH), 2.2 (q, $SiMe_3$); ^{11}B NMR (96 MHz, Et_2O, 25 °C): $\delta = 24$, 20 (2:1)

9: colorless solid, m.p. 118 °C, yield 85 %; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.67$ (s, 2H, Dur-H), 3.25 (q, 8H, Et_2O), 3.24 (s, 2H, BCH), 2.23, 2.16 (each s, each 12H, Dur-CH_3), 1.01 (t, 12H, Et_2O), 0.08 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 155.7$ (br. s, *i*-C), 132.2, 131.4 (each s, *o*- and *m*-C), 128.0 (d, *p*-C), 83.7 (d, ^{1}J(C,H) = 90 Hz, BCH), 66.1 (t, Et_2O), 22.2, 20.6 (each q, Dur-CH_3), 3.2 (q, $SiMe_3$); ^{11}B NMR (96 MHz, C_6D_6, 25 °C): $\delta = 51$

10: greenish, fluorescent solid, m.p. 134 °C, yield 98 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.80$ (s, 2H, Dur-H), 2.16, 1.90 (each s, each 12H, Dur-CH_3), 1.79 (s, 4H, BCH_2), 0.06 (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.6$ (br. s, *i*-C), 133.0, 129.5 (each s, *o*- and *m*-C), 129.3 (d, *p*-C), 28.6 (t, ^{1}J(C,H) = 113 Hz, BCH_2), 20.3, 19.3 (each q, Dur-CH_3), 1.7 (q, $SiMe_3$); ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 97$

Table 2. Selected distances [pm] and interplanar angles [°] of **5a**$\cdot$2Li$\cdot$2Et$_2$O, **5b**$\cdot$2Li$\cdot$3Et$_2$O, and **5c**$\cdot$2Li$\cdot$2Et$_2$O (crystal structures) as well as of model compounds **5u**-R (R = H, Me, Ph, OH, NH$_2$) (//MP2/6-31 + G*); ^{11}B NMR chemical shifts [ppm] are also given.

	B1⋯B2	B1⋯B3	B2-B3	C1-B2-B3-C2/ C1-B1-C2[a]	δ(B1)	δ(B2), δ(B3)
5a$\cdot$2Li$\cdot$2Et$_2$O	185.7(6)	184.1(6)	163.7(6)	80.0(4)	−20	15, 18
5u-Ph[b]	185.8	185.8	166.4	82.4	−35.6	20.8
5b$\cdot$2Li$\cdot$3Et$_2$O	186.5(4)	187.8(4)	163.0(4)	82.7(3)	−2	13, 15
5u-OH[b]	184.7	184.7	165.3	81.8	−7.1	20.5
5c$\cdot$2Li$\cdot$2Et$_2$O	192.7(6)	190.8(5)	165.0(6)	85.1(4)	−4	7, 21
5u-NH$_2$[b]	183.6	183.6	165.5	80.2	−17.2	21.6, 19.7
5d					−21	13, 16
5u-Me[b]	184.6	184.6	165.4	81.4	−28.5	20.0
5u-H[b]	184.8	184.8	165.5	81.7	−47.8	9.2

[a] Interplanar angle. [b] NMR chemical shifts were computed at GIAO-SCF/6-311+G**//MP2(fc)/6-31+G*.

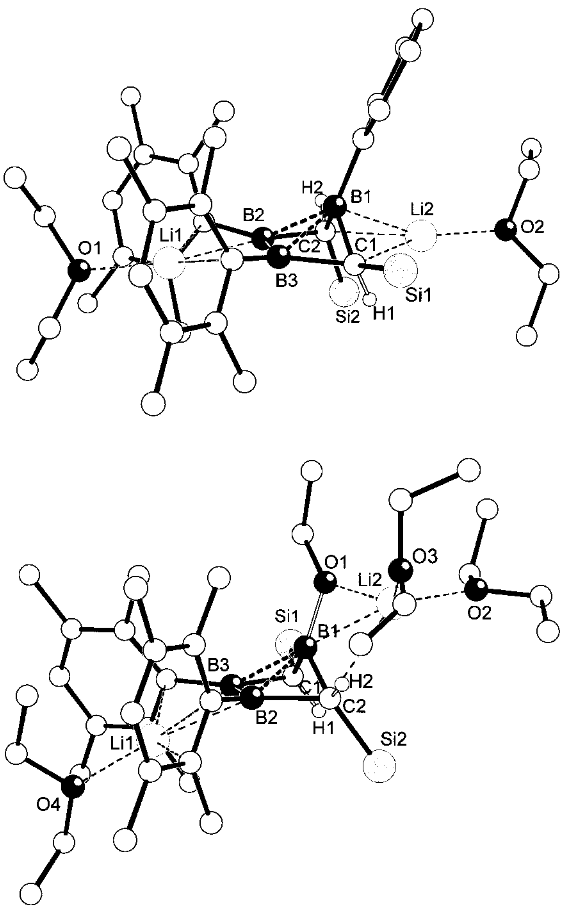
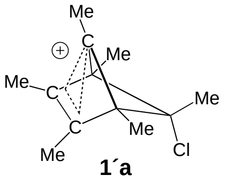


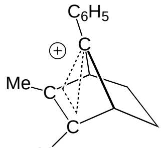
Figure 1. Structures of **5a**$\cdot$2Li$\cdot$2Et$_2$O (top) and **5b**$\cdot$2Li$_2\cdot$3Et$_2$O (bottom) in the crystal, the methyl substituents at Si1 and Si2 as well as most of the H atoms are omitted for clarity. Selected bond lengths (in addition to those in Table 2) [pm] and bond angles [°]. **5a**: B1-C1 165.1(5), B1-C2 163.6(5), C1-B3 162.3(5), C2-B2 163.3(5); C1-B1-C2 110.1(3), B1-C2-B2 69.2(2), C2-B2-B3 108.9(3), B2-B3-C1 109.0(3), B3-C1-B1 68.4(2); **5b**: B1-C1 161.4(4), B1-C2 162.7(4), C1-B3 164.1(4), C2-B2 164.4(4); C1-B1-C2 113.7(2), B1-C2-B2 69.5(2), C2-B2-B3 109.3(2), B2-B3-C1 109.1(2), B3-C1-B1 70.5(2).

small interplanar angles (here between the C1-B3-B2-C2 and C1-B1-C2 planes). The experimental data are compared to values computed for the model compounds **5u**-R (R = H, Me, Ph, OH, NH$_2$) in Table 2.

The strong donors OEt, OH, NEt$_2$, and NH$_2$ distort bishomoaromatics of type **5** to a small extent (Table 2). For the bishomoaromatic cations of type **1**, even the relatively weak phenyl donor substituent at C7 leads to a considerable elongation of the transannular C–C distance from 172.1 pm[14] in **1u** (R = H) to 190.1 pm in **1a** (R = C$_6$H$_5$). The interplanar angle also is increased (from 81.3 to 93.6°, //MP2(fc)/6-31G*).[2b] Similar geometries are found in the X-ray structures of **1′a**[3b] and **1a**-Me$_2$.[3a]



1´a



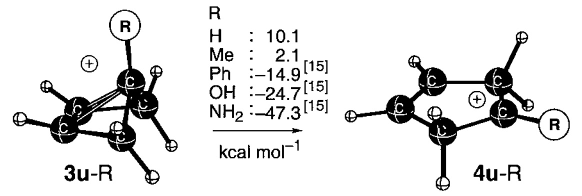
1a-Me$_2$

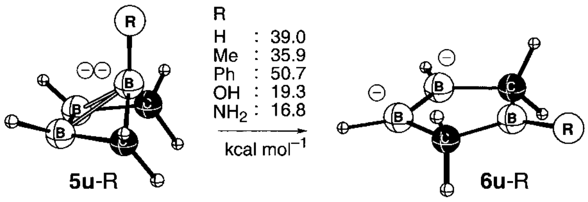
The monocyclic cation **3u**-Me (with a transannular distance of 182.1 pm) is only 2.1 kcal mol^{-1} higher in energy than the classical 4-methyl-4-cyclopentenyl cation, **4u**-Me, and no local minima of the **3u** type could be localized when effective π- or n-donors like phenyl or OH and NH$_2$ were present. These structures must be much less stable than the corresponding classical cations **4u**-Ph, **4u**-OH, and **4u**-NH$_2$.[15]

Likewise, strong donors influence the NMR chemical shifts of the pentacoordinate boron atoms of dianions **5** (Table 2) to a lesser extent than the shifts of the pentacoordinate C atoms of **1**. Replacing R = Me in the nonclassical **1** by OH gives the classical **2b** (R = OH), as indicated by the deshielding of C7 by 153 ppm (δ^{13}C = 72 → 225). An analogous exchange of substituents in the dianions **5** (**5d** → **5b**) leads to a ^{11}B deshielding of only 19 ppm.[16, 17]

The ineffectiveness of the donor substituents is expressed most impressively in the geometries characterizing the 3c,2e bonds of the bishomoaromatics **5a**–**c**: these parameters, like those in **5u**-Ph, **5u**-OH, and **5u**-NH$_2$, are almost identical (Table 2).

Hence, the 3c,2e bonding in bishomoaromatic dianions **5** is much stronger than those of the isoelectronic cations of type **1**. A quantitative measure for the 3c,2e bond strengths is given by the computed energy differences between bishomoaromatic **5u**-R and classic **6u**-R. At the MP2/6-31+G* + 0.89 ZPE(HF/6-31G*) level **5u**-H is more stable than **6u**-H by 39.0 kcal mol^{-1}; this is about 30 kcal mol^{-1} greater than the difference between the isoelectronic **3u** and **4u** . The difference between nonclassical and classical forms is only about





10 kcal mol^{-1} smaller (29.6 kcal mol^{-1}) for the monoanionic prototypes which result from protonating the B–B bond in dianions of type **5**.[18]

In conclusion, both the statement, based on results for homoaromatic cations and neutral compounds, that "the very existence of homoaromaticity is a matter of a few kcal mol^{-1}"[19] as well as the one that anionic homoaromaticity is "either quite insignificant or nonexistent altogether"[20] are not valid any longer.

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[6] The following communication[7] describes a trishomoaromatic 1,3,5-triboracyclohexane dianion, a system isoelectronic with the trishomocyclopropenylium cation.

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[9] The geometries of the dianions were optimized at the MP2(fc)/6-31+G* level, while MP2(fc)/6-31G* was applied for the cations. Relative energies were corrected for scaled (0.89) zero-point vibrational energies from HF/6-31G* frequency calculations. Chemical shifts were computed at the GIAO-SCF/6-311+G** level employing the optimized geometries. The Gaussian 94 program was used for all computations: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian 94 Revision C.3, Gaussian, Inc., Pittsburgh PA, **1995**.

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[12] Crystal structure determination: **5a**·2Li·2Et$_2$O: A yellow plateletlike crystal ($0.4 \times 0.35 \times 0.05$ mm^3) was measured on a Stoe IPDS diffractometer at $-80\,^{\circ}$C using Mo$_{K\alpha}$ radiation. $C_{42}H_{70}B_3Li_2O_2Si_2$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 1022.0(1)$, $b = 1970.0(2)$, $c = 2267.2(3)$ pm, $\beta = 100.02(2)^{\circ}$, $V = 4495.0(9) \times 10^{-30}$ m^3, $\rho_{\text{calcd}} = 1.048$ g cm^{-3}; a total of 30705 reflections were recorded in the range $1.82^{\circ} < \theta < 24.91^{\circ}$, resulting in 7636 independent reflections from which 3397 with $F_o > 4\sigma(F_o)$ were observed. All 7636 independent reflections were used for subsequent calculations; no absorption correction was applied ($\mu = 1.1$ cm^{-1}). The structure was solved with direct methods and refined against F_o^2 with full matrix. Non-hydrogen atoms were refined using anisotropic displacement factors. The H atoms at C1 and C2 were refined; the remaining H atoms were kept at calculated positions, and 1.2 or 1.5 times (CH$_3$) the equivalent isotropic U value of the corresponding C atom was used as displacement factors. The refinement converged at $wR_2 = 0.1534$ for all reflections, corresponding to a conventional $R = 0.0632$ for 3397 reflections with $F_o > 4\sigma(F_o)$. **5b**·2Li·3Et$_2$O: A yellow plateletlike crystal ($0.6 \times 0.2 \times 0.06$ mm^3) was measured on a Stoe IPDS diffractometer at $-80\,^{\circ}$C using Mo$_{K\alpha}$ radiation. $C_{42}H_{80}B_3Li_2O_4Si_2$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 2355.0(2)$, $b = 1107.2(1)$, $c = 1899.6(1)$ pm, $\beta = 96.30(1)^{\circ}$, $V = 4923.2(7) \times 10^{-30}$ m^3, $\rho_{\text{calcd}} = 1.014$ g cm^{-3}; a total of 38176 reflections was observed in the range $1.74^{\circ} < \theta < 24.11^{\circ}$, resulting in 7734 independent reflections from which 3283 with $F_o > 4\sigma(F_o)$ were observed. All 7734 reflections were used for the subsequent calculations; no absorption correction ($\mu = 1.06$ cm^{-1}) was applied. The structure was solved by direct methods and refined against F_o^2 with full matrix as described above. The refinement converged at $wR_2 = 0.0785$ for all reflections, corresponding to a conventional $R = 0.0406$ for 3283 reflections with $F_o > 4\sigma(F_o)$. 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-133560 (**5a**·2Li·2Et$_2$O) and CCDC-133561 (**5b**·2Li·3Et$_2$O). 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).

[13] Similar lithium cation coordinations were found recently for 1,2-diboratacyclopentadienides: D. Scheschkewitz, M. Hofmann, P. von R. Schleyer, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **1999**, *111*, 3116; *Angew. Chem. Int. Ed.* **1999**, *38*, 2936.

[14] Quantum Chemistry Archive, Computer Chemie Centrum, Universität Erlangen-Nürnberg.

[15] Without symmetry constraints the geometry optimizations of **3u**-OH, **3u**-NH$_2$, and **3u**-Ph converge to the planar five-membered ring structures **4u**-OH, **4u**-NH$_2$, and **4u**-Ph. However, the transition states **3u**-Ph and **3u**-OH as well as a second-order stationary point for **3u**-NH$_2$ (with planar amino group) can be obtained by choosing conformations that exclude effective conjugation between substituent R and the cationic center in **3u**-R. The energies of **3u**-Ph, **3u**-OH, and **3u**-NH$_2$ are 14.9, 24.7, and 47.3 kcal mol^{-1} (MP2(fc)/6-31G* + 0.89 ZPE(HF/6-31G*)) relative to the corresponding classical structures **4u**-R.

[16] Application of the Nöth–Wrackmeyer relation,[17] which correlates ^{13}C and ^{11}B chemical shifts of isoelectronic carbocations and boron compounds, gives $\delta^{11}B = 43.6$ for a boron compound corresponding to **2b**; however, $\delta^{11}B = -2$ is observed experimentally for **5b**.

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