A Highly Reactive Triboracyclobutane and Its Dianion: Two-Electron Homoaromatics with Nonclassical and Classical σ Skeletons[†]

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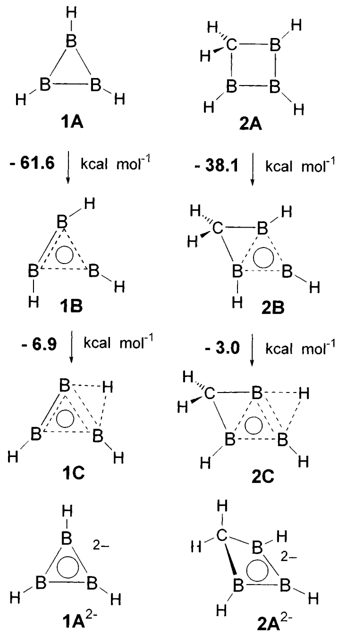
Summary: The first triboracyclobutane, **2c**, *a two-electron homoaromatic having a nonclassical σ skeleton, was generated at −80 °C and stabilized as its dianion* $\mathbf{2a}^{2-}$, *which was characterized by the crystal structure determination of its dilithium salt and which possesses a classical σ skeleton.*

The classical D_{3h} structure of triboracyclopropane (triborirane; **1A**) (Scheme 1), with three 2c−2e B−B bonds, is much less stable (61.6 kcal mol^{-1} at the MP2/6-31G* level) than its alternative aromatic state **1B**, which has lower (C_{2v}) symmetry and two cyclically delocalized π electrons (symbolized by a circle).[1] One pair of BB electrons in **1A** is transformed into the 3c−2e π electrons of **1B** and a second pair into a 3c−2e σ bond (drawn as a dashed triangle).[2] Thus, **1B** has a nonclassical σ skeleton like the global minimum **1C**, which is further stabilized by 6.9 kcal mol^{-1} due to the formation of an additional BHB bridge. A classical σ skeleton as in **1A** is to be expected only for the dianion $\mathbf{1A}^{2-}$.[1] Our own DFT computations[3] revealed triboracyclobutane (triboretane) to be the homoform of triboracyclopropane: the two-electron homoaromatic **2B** containing a 3c−2e σ bond and a 3c−2e π bond between the three boron centers is considerably lower in energy than planar **2A** with two classical 2c−2e B−B σ bonds. The global minimum **2C** is slightly more stable due to an additional BHB bridge. The homoaromaticity of the dianion $\mathbf{2A}^{2-}$ with two classical 2c−2e B−B bonds was discussed already on the basis of computations.[4] Here we present the generation and NMR characterization of the triboracyclobutane **2c** (Scheme 2), which possesses, aside from substituents, an aryl bridge instead of the hydrogen bridge in **2C**.

Scheme 1. Computed Energy Differences for Nonaromatic (1A, 2A) and Aromatic (1B, 2B, 1C, 2C) Structures of Triboracyclopropane and Triboracyclobutane[a]



[a] A dashed triangle symbolizes a cyclic three-center−two-electron (3c−2e) σ bond and a circle a cyclic 3c−2e π bond.

The highly reactive triboracyclobutane **2c** is obtained when the borenate **3**[5] is protonated with HCl in diethyl ether at −80 °C. When the temperature is raised to −60 °C, the deep red solution turns yellow within about 40 min. This indicates the formation of **4**, which can be

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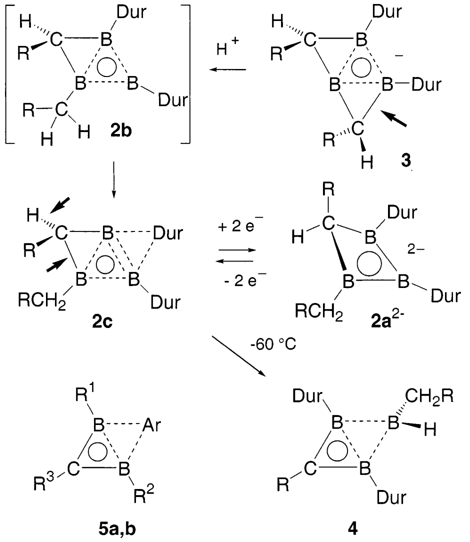
Scheme 2. Generation of the Highly Reactive Triboracyclobutane 2c, Stabilization of 2c as Its Dianion $2a^{2-}$, and Reoxidation of $2a^{2-}$ to 2c[a]



[a] During the formation of **2c** from **3**, the C−B bond of **3** marked with an arrow is cleaved by protonation. The rearrangement of **2c** into **4** requires activation (cleavage) of the C−H and C−B bonds of **2c**, marked with arrows. During all these transformations, the two-electron aromaticity is retained. Legend: R = $SiMe_3$, Dur = 2,3,5,6-tetramethylphenyl; for **5a**, R^1 = 1-neopentyl-3,3-bis(trimethylsilyl)allenyl, R^2 = neopentyl, R^3 = Ar = Dur; for **5b**, R^1 = R^2 = *t*-Bu, R^3 = Ar = 2,4,6-trimethylphenyl.

isolated in 70% yield after warming and crystallization.[6] At −100 to −80 °C, **2c** can be stabilized as its dianion $\mathbf{2a}^{2-}$ by reaction with 2 equiv of Li naphthalenide in THF.[7]

After the bulk (about 90%) of naphthalene is removed by sublimation under high vacuum, the red dilithium salt of $\mathbf{2a}^{2-}$ was obtained by crystallization from pentane. The crystal structure of $(\mathbf{2a})Li_2{\cdot}3THF{\cdot}0.5C_5H_{12}$[8] is shown in Figure 1.

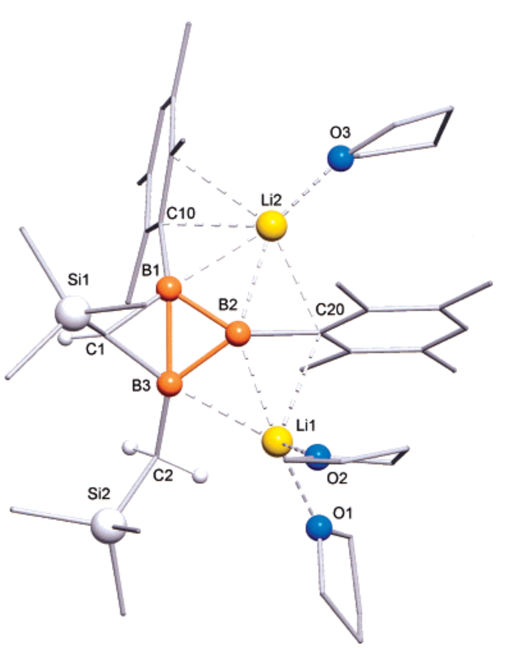


Figure 1. Structure of $(\mathbf{2a})Li_2{\cdot}3THF{\cdot}0.5C_5H_{12}$.[12] The solvent molecule and most of the hydrogen atoms are omitted for clarity. Selected bond distances (pm) and angles (deg): B1−B2 = 162.5(4), B2−B3 = 163.1(3), B1−B3 = 182.8(4), C1−B1 = 162.3(3), C1−B3 = 161.5(3), B1−C10 = 161.5(3), B2−C20 = 160.2(3), B3−C2 = 161.6(4), C1−Si1 = 182.3(2), Li1−B2 = 232.3(5), Li1−B3 = 252.9(5), Li2−B1 = 230.9(5), Li2−B2 = 222.0(5), Li1−O1 = 199.8(5), Li1−O2 = 198.2(5), Li2−O3 = 190.8(5), Li1−C20 = 247.2(5), Li2−C20 = 225.4(5), Li2−C10 = 230.7(5), Li2−C21 = 273.1(5); B1−B2−B3 = 68.3(2), B2−B1−C1 = 104.0(2), B2−B3−C1 = 104.1(2), B1−C1−B3 = 68.8(2); C1−B1−B3−B2 = −145.0(2).

The dianion $\mathbf{2a}^{2-}$ forms a triple contact ion with two lithium cations which coordinate one (Li2) or two (Li1) additional THF molecules. Neither of the two Li cations is located above or below the dianion, as found for the dilithium salt of the dianion of tetrakis(trimethylsilyl)cyclobutadiene by Sekiguchi,[10] but both are coordinated side-on to the B−B bonds almost within the plane of the boron atoms (Li1−B2−B3−B1 = 170.2°, Li2−B1−B2−B3 = −168.7°).[11] In solution, NMR signals for both stereoisomers of $(\mathbf{2a})Li_2$ are observed, one having the

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[6] A solution of HCl in Et_2O (3.15 mL, 6.3 mmol) was added to a solution of 3.5 g (6.3 mmol) of **3** in 80 mL of Et_2O at −80 °C. After 30 min of stirring at −80 °C followed by warming to room temperature, all volatile components were removed. The residue was digested with 50 mL of pentane, and LiCl was separated by a G4 reversed frit and washed with 10 mL of pentane. After the volume was reduced to 30 mL and the solution cooled to −30 °C, 2.2 g (70%) of **4** was obtained as colorless crystals, mp 109−110°C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ −0.54 (s, 9H, $SiMe_3$), 0.04 (s, 9H, $SiMe_3$), 0.42 (d, 2H, $^3J(H,H)$ = 6 Hz, CH_2Si), 2.21 (s, 24H, *o*-, *m*-CH_3), 6.2 (br, 1H, BH), 6.94 (s, 2H, *p*-H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ −0.3 (q, $SiMe_3$), 0.3 (q, $SiMe_3$), 13.9 (t, $^3J(C,H)$ = 105 Hz, CH_2Si), 19.7, 20.1, 21.1 (each q, *o*-, *m*-CH_3), 129.7 (s, *i*-C), 131.4 (s, CB_2), 132.6 (d, *p*-C), 133.3, 134.2, 138.0, 138.8 (each s, *o*-, *m*-C). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): δ 37 (2B), 62.

[7] A solution of HCl in Et_2O (3.38 mL, 6.75 mmol) was added to a solution of 3.75 g (6.75 mmol) of **3** in 80 mL of Et_2O at −100 °C. After 30 min of stirring at −100 °C, a freshly prepared and precooled solution of lithium naphthalenide in THF (15 mL, 13.5 mmol) was added within 5 min using a syringe. After 1 h the solution was warmed to room temperature and all volatile components were removed. The residue was digested with pentane, and LiCl was separated by a reversed frit. After the solvent was removed, the bulk of naphthalene was separated by sublimation under high vacuum. Cooling a pentane solution of the mixture obtained to −30 °C led to red crystals of $(\mathbf{2a})Li_2{\cdot}3THF{\cdot}0.5C_5H_{12}$, mp >165 °C. ^1H NMR (500 MHz, $[D_8]THF$, 25 °C): δ −0.03 (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 0.27 (br, 1H, SiCH), 0.34, 0.40 (each br, each 1H, diastereotopic CH_2Si), 2.08, 2.09, 2.37, 2.41 (br) (each s, together 24H, *o*-, *m*-CH_3), 6.36, 6.47 (each s, each 1H, *p*-H). ^{13}C NMR (125 MHz, $[D_8]THF$, 25 °C): δ 2.8, 3.3 (each br, $SiMe_3$) 14.9 (br, CH_2Si), 20.4, 21.0, 21.6 (*o*-, *m*-CH_3), 32.6 (br, CHSi), 125.8, 127.3 (each d, *p*-C), 132.0, 132.3, 134.2, 136.2 (each br, *o*-, *m*-C), 156, 158 (each br s, *i*-C). ^{11}B NMR (160 MHz, $[D_8]$toluene): −80 °C, δ 10, 13, 16, 21, 40, 51; 25 °C, δ 14, 22, 42, 54; 65 °C, δ 16, 24, 48.

[8] Crystal structure determination for $(\mathbf{2a})Li_2{\cdot}3THF{\cdot}0.5C_5H_{12}$: red crystal from pentane, 0.25 × 0.20 × 0.15 mm: $C_{42.5}H_{77}B_3Li_2O_3Si_2$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 1146.5(1)$ pm, $b = 1302.6(1)$ pm, $c = 1792.0(2)$ pm, $\alpha = 76.65(1)°$, $\beta = 81.43(1)°$, $\gamma = 64.29(1)°$, $V = 2342.4(4) \times 10^{-30}$ m^3, $\rho = 1.047$ Mg m^{-3}. Data collection was carried out on a Stoe IPDS area detector system, with $T = -80$ °C. A total of 37 137 reflections were measured up to $\theta = 24.9°$; there were 8199 unique reflections ($R_{int} = 0.0832$) and 5137 with $I > 2\sigma(I)$. The structure was solved using direct and Fourier methods[9] and refined by full matrix least-squares methods (based on F_o^2, SHELXL-97[9]); anisotropic displacement parameters were used for all non-H atoms in the final cycles, and H atoms were treated by a mixture of independent (H1, H2a, H2b) and constrained refinement. R1 = 0.0523 ($I > 2\sigma(I)$), and wR2 = 0.1489 (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-175173. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code + 44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk).

[9] Sheldrick, G. M. SHELX-97, Programs for the Solution and Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

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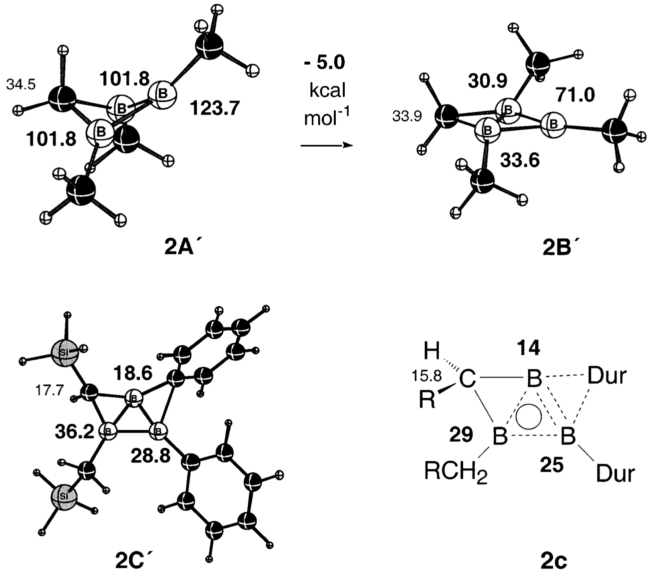
skeleton $SiMe_3$ substituent in an endo position as found in the solid state and the other in an exo position. Coalescence of the room-temperature ^{11}B signals (δ 42 and 54) at 65 °C indicates a barrier of 14 kcal mol^{-1} for the exchange of the stereoisomers of (**2a**)Li_2 by ring inversion. Computations for the unsubstituted prototype **2A**$^{2-}$ (without gegenions) led to barriers of 15.5 (MP2/6-31G*) and 11.2 kcal mol^{-1} (B3LYP/6-311+G**).[4]

The unsymmetrical substitution pattern of **2c** is retained in the dianion **2a**$^{2-}$: the ring carbon atom has boron neighbors with different substituents, is tetracoordinate, and is still connected to a hydrogen atom. Compound **4**, which was also characterized by a crystal structure determination, however, shows a symmetrical pattern of substituents: the ring carbon is tricoordinate, and the hydrogen atom bound to the ring carbon in **2c** is found at the CH_2SiMe_3-substituted boron atom in **4**. During the conversion of **2c** into **4**, a C−H and a C−B bond have to be cleaved under very mild conditions. This can be understood as the consequence of strong electron deficiency in **2c** due to three adjacent boron centers without strong donor substituents.

Compound **2c** was definitely characterized by analyses of its ^1H, ^{13}C, and ^{11}B NMR spectra,[13] which had to be measured below −80 °C because of the easy rearrangement of **2c** into **4**. Suitable solutions of **2c** in [D_{10}]diethyl ether or [D_8]toluene were obtained by oxidation of (**2a**)Li_2·3THF with 1,2-dibromoethane at −90 °C directly in NMR tubes.[13] The presence of a bridging aryl substituent is indicated by ^{13}C NMR signals for two deshielded and one shielded carbon atom at $\delta(^{13}C)$ 156, 155, and 118 ppm, respectively. Deshielding of ortho and shielding of ipso carbon atoms is characteristic for aryl substituents bridging the B−B bond of two-electron aromatics: for **5a** and **5b** similar chemical shifts ($\delta(^{13}C)$ 151, 124 and $\delta(^{13}C)$ 160, 113 ppm, respectively) were observed.[14] Convincing evidence for the aromatic nature of **2c** comes from its ^{11}B NMR chemical shifts in comparison to those computed for model molecules **2A′**, **2B′**, and **2C′** (Scheme 3).

Scheme 3. Chemical Shifts of Skeleton Atoms As Computed[3] for Model Molecules 2A′, 2B′, and 2C′ and Experimentally Determined for 2c[a]



[a] Legend: R = $SiMe_3$, Dur = 2,3,5,6-tetramethylphenyl.

For classical **2A′**, which is folded to benefit from hyperconjugation, strongly deshielded boron atoms are predicted—as is to be expected for tricoordinate boron centers connected to further boron atoms. 1,2,4-Triboracyclopentanes, for example, are characterized by $\delta(^{11}B)$ 97−101 for the B−B moiety.[5] In the aromatic species **2B′** without an aryl bridge, all boron centers are shielded as compared to those in **2A′**. Only the two tetracoordinate boron atoms of **2B′** show chemical shifts comparable to two centers of **2c**. In contrast, all the experimental ^{11}B chemical shifts for **2c** agree well with those computed for the two-electron aromatic model **2C′** with a phenyl bridge (see Scheme 3).

Thus, triboracyclobutane **2c** is a two-electron homoaromatic containing a nonclassical σ skeleton: i.e., a homotriboracyclopropane. In contrast, the homoform of benzene, cycloheptatriene, is not a homoaromatic species: a homo bridge interrupts the cyclic delocalization of six electrons but not that of two electrons. This is due to the considerably larger aromatic stabilization energy of two-electron aromatics as compared to that of six-electron aromatics. Schleyer has repeatedly pointed out this fact.[15]

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Supporting Information Available: Figures and tables giving details of the crystal structure determination and the DFT computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) "Side-on" coordination two lithium cations to B−B σ bonds was computed to be preferred for the triple contact ion of **1A**$^{2-}$ over π coordination.[1]

(12) Brandenburg, K. DIAMOND 2.1c; Crystal Impact GbR, Bonn, Germany, 1999.

(13) A 2-fold excess of 1,2-dibromoethane was added to an NMR sample of (**2a**)Li_2·3THF (about 100 mg, 0.6 mL of [D_{10}]Et_2O or [D_8]toluene) at −110 °C. The tube was transferred to the spectrometer as fast as possible, warmed to −90 °C inside the magnet, and cooled again. **2c**: ^1H NMR (500 MHz, [D_{10}]Et_2O, −100 °C) δ 0.05 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$), 0.91 (s, 1H, SiCH), 1.1 (hidden by solvent, localized by H,H correlation), 1.52 (each d, each 1H, ^2J(H,H) = 10 Hz, diastereotopic CH_2Si), 1.45, 1.94, 2.03, 2.16, 2.28, 2.45, 2.49 (each s, together 24H, *o*-, *m*-CH_3), 6.79, 7.16 (each s, each 1H, *p*-H); ^{13}C NMR (125 MHz, [D_{10}]Et_2O, −100 °C) δ 0.9, 1.3 ($SiMe_3$), 11.8 (br, CH_2Si), 20.4, 20.5, 20.6, 20.9, 21.0, 21.6, 22.3 (*o*-, *m*-CH_3), 118.4, 135.8 (each br s, *i*-C), 132.7, 138.3 (each d, *p*-C), 132.3, 132.8, 134.0, 134.6, 139.4, 139.5, 155.0, 155.6 (each s, *o*-, *m*-C), the signal of BCHSi is hidden by the solvent and in [D_8]toluene it can be unambiguously localized at δ 15.8; ^{11}B NMR (160 MHz, [D_8]toluene, −105 °C) δ 14, 25, 29.

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(15) Budzelaar, P. H. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3967, and literature cited therein.