Boron Compounds

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A Radical Tricationic Rhomboid Tetraborane(4) with Four-Center, Five-Electron Bonding

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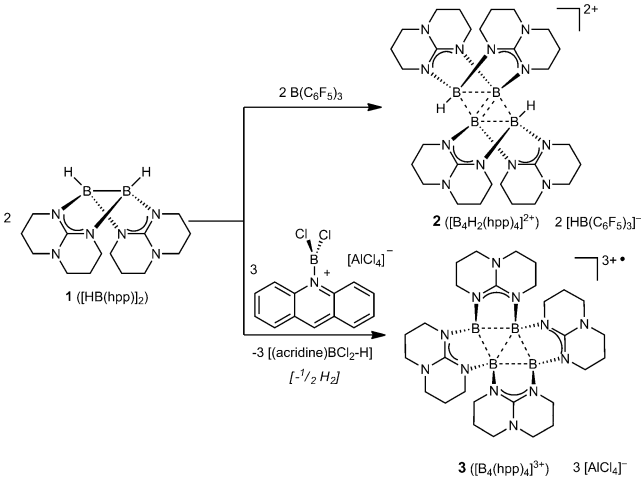
Abstract: *The red-colored tetraborane(4) $[B_4(hpp)_4]^{3+\bullet}$ (**3**; hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinate) with a rhomboid B_4 skeleton stabilized by four N donors, was synthesized by the reaction of the strong hydride abstraction reagent $[(acridine)BCl_2][AlCl_4]$ with the electron-rich diborane(4) $[HB(hpp)]_2$ (**1**). The salt $\mathbf{3}[AlCl_4]_3$ was structurally characterized and the presence of unpaired electrons proven by EPR measurements. The unprecedented radical tricationic **3** is distinguished by a high positive charge and boron atoms in a low oxidation state (less than two).*

The development of element–element coupling reactions, which assemble small building blocks to useful compounds, is one of the key concerns of synthetic chemistry. In boron chemistry, new boron–boron coupling strategies might pave the way for the long-sought directed construction of oligomeric and polymeric boron compounds.[1] However, only a handful of boron–boron coupling routes, namely reductive coupling of haloboranes, catalytic dehydrocoupling, borylene coupling, and hydroboration of diborenes, are known, often requiring special boron compounds and conditions. Therefore the scope of synthetic possibilities is very limited to date. Hydride abstraction, being frequently employed to generate highly Lewis acidic cationic boron compounds for a variety of applications,[2] is not known for inducing boron–boron coupling reactions. Nevertheless, we recently reported a singular hydride abstraction from the electron-rich, doubly base-stabilized diborane(4) $[HB(hpp)]_2$ (**1**; hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidinate) with $B(C_6F_5)_3$ (Scheme 1).[3] The postulated intermediate $[HB(hpp)_2B]^+$ $(\mathbf{1}-H^-)^+$ dimerized to the tetraborane(6) dication $[B_4H_2(hpp)_4]^{2+}$ (**2**) with four-center, four-electron (4c,4e) bonding in the central rhomboid B_4 unit. In the presence of a suitable Lewis base L (for example, L = PCy_3, P(allyl)$_3$, $PHCy_2$, P*i*Pr$_3$, or N-heterocyclic carbenes; NHCs), the intermediate monocation $(\mathbf{1}-H^-)^+$ was captured as $[(\mathbf{1}-H^-)\text{-}L]^+$.[4] The abstraction of the remaining hydrogen atoms from **2** might open up the possibility to link-up the rhomboid B_4 units (see the discussion of polymer materials composed of rhomboid building blocks in Ref. [5]).

We now report on experiments aimed at the abstraction of both hydrides from $[HB(hpp)]_2$ (**1**) by use of the stronger hydride abstraction reagent $[(acridine)BCl_2]^+$.[6,7] When **1** was reacted with $[(acridine)BCl_2][AlCl_4]$, the reaction mixture turned intense red within seconds. Indeed, both hydrides of **1** were abstracted, followed by dimerization of $(\mathbf{1}-2H^-)^{2+}$, but surprisingly the product of the reaction was the red-colored radical trication $[B_4(hpp)_4]^{3+\bullet}$ (**3**; see Scheme 1). The electron required for the reduction of the cationic intermediates is most likely transferred from the electron-rich boron hydride **1**, during or at the end of the reaction. Several experiments with varying reactant stoichiometry indicated that the highest yield (60% with respect to the applied $AlCl_4^-$) is obtained with an equimolar ratio of the two reactants.



Scheme 1. Hydride abstraction from **1** with $B(C_6F_5)_3$ leads to **2** and with $[(acridine)BCl_2][AlCl_4]$ to **3**.

In the IR spectra of **3**, the absence of any band in the region 2500–1800 cm^{-1} characteristic for stretching modes ν(B–H) (cf. 2396 cm^{-1} for **2** and 2272/2249 cm^{-1} for **1**) confirmed removal of all B–H hydrogen atoms (Supporting Information, Figure S1). Relatively strong bands in the region 1650–1500 cm^{-1} appear which are characteristic for stretching modes ν(CN) of intact hpp units. The UV/Vis spectra (Supporting Information, Figure S2) showed a strong and relatively broad absorption centered at 536 nm, which is responsible for the red color. Owing to the presence of an unpaired electron in **3**, the NMR spectra showed no clear signature. An EPR spectrum (X-band) of the clean solid product (Supporting Information, Figure S3) confirmed the presence of unpaired electrons. A relatively broad (due to unresolved hyperfine coupling) and intense signal was detected ($g = 2.006$).

Deep-red crystals of $\mathbf{3}[AlCl_4]_3$ were grown from a concentrated CH_2Cl_2 solution. The structure of **3** is visualized in Figure 1. Similar to the dication **2** ($[B_4H_2(hpp)_4]^{2+}$), the trication **3** ($[B_4(hpp)_4]^{3+\bullet}$) exhibits a rhomboid B_4 skeleton. The B–B bond distances vary between 1.7910(5) for B2–B3 and 1.9367(3) Å for B1–B2. **3** has five skeletal electrons in the

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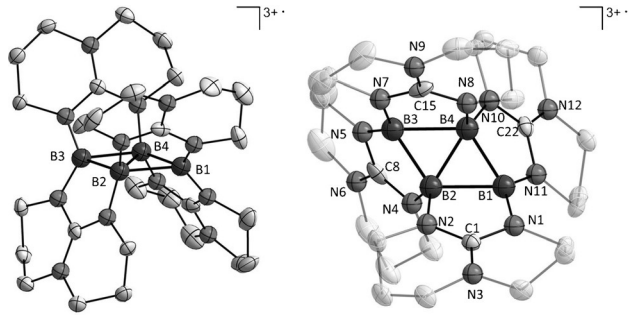
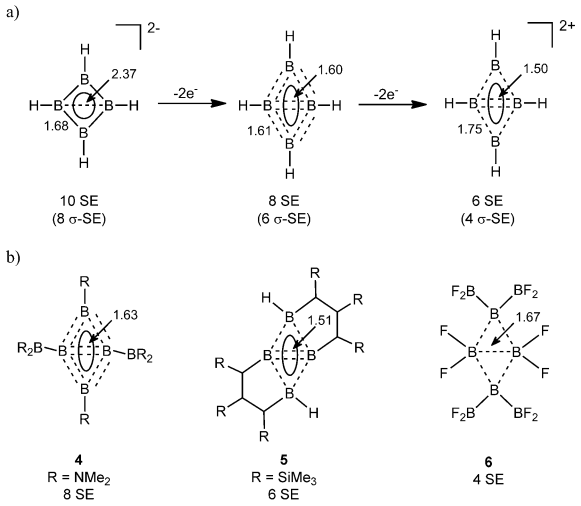


Figure 1. Structure of the $[B_4(hpp)_4]^{3+\cdot}$ trication in $[B_4(hpp)_4][AlCl_4]_3 \cdot 2.5\,CH_2Cl_2$ from two perspectives. Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [°]: B1–B2 1.9367(3), B2–B3 1.7910(5), B3–B4 1.8906(3), B4–B1 1.8006(5), B2–B4 1.7987(3), B1–N1 1.4141(5), B2–N2 1.5143(5), N1–C1 1.3635(3), N2–C1 1.3329(3), C1–N3 1.3320(4), B2–N4 1.4867(3), B3–N5 1.4538(3), N4–C8 1.3561(4), N5–C8 1.3786(2), C8–N6 1.3098(3), B3–N7 1.4347(2), B4–N8 1.4924(3), N7–C15 1.3617(2), N8–C15 1.3515(2), C15–N9 1.3273(3), B4–N10 1.4872(3), B1–N11 1.4468(2), N10–C22 1.3212(2), N11–C22 1.3928(6), C22–N12 1.3415(2); B1-B2-B3 121.020(14), B2-B3-B4 58.416(12), B3-B4-B1 123.087(15), B4-B1-B2 57.400(12).



Scheme 2. a) Lewis structures to highlight the electronic structures of $[B_4H_4]^z$ compounds ($z = -2$, 0, or 2). The number of skeletal electrons (SE) are given below each structure. The calculated transannular B–B distances (in Å, calculated with B3LYP/6-31G*; see Ref. [9]) are given. b) Lewis structures of the tetraboranes **4**–**6**.

B_4 unit (4c,5e bonding), and **2** has four skeletal electrons (4c,4e bonding). The different charge and number of skeletal electrons (SE) lead to differences in the structural parameters. In particular, the B–B distances in $[B_4(hpp)_4]^{3+\cdot}$ (**3**) are longer than in $[B_4H_2(hpp)_4]^{2+}$ (**2**). The transannular B–B bond distance measures 1.7987(3) Å in **3** and 1.703(4) Å in **2**. The dication **2** and the trication **3** also vary in the arrangement of the hpp substituents. In **2**, two opposite edges of the B_4 unit are bridged by two hpp substituents, while the other two edges are not bridged, whereas in **3**, all edges are bridged by one hpp substituent.

Compounds with a rhomboid B_4 skeleton or related rhomboid structures are rare, but not unprecedented, and interestingly stable with distinct SE, and their general importance has been pointed out in an article by Balakrishnarajan and Hoffmann.[5] The interplay between stabilization through σ- and π-delocalization is responsible for this striking stability. Scheme 2 shows the Lewis structures of $[B_4H_4]^z$ compounds ($z = -2$, 0, $+2$). The unknown dianionic tetraborane(4) $[B_4H_4]^{2-}$ (SE = 10) is isoelectronic to the dication $[C_4H_4]^{2+}$, for which Schleyer et al. postulated a folded structure,[8] and also to the 1,3-dihydro-1,3-diboret $B_2C_2H_4$. Derivatives of $B_2C_2H_4$, namely $[\{C(tBu)\}_2\{B(NMe_2)_2\}_2]$[9] and $[(CH)_2\{B(NiPr_2)_2\}_2]$,[10] were synthesized and shown to exhibit a folded structure. Formal removal of two electrons leads to the neutral tetraborane(4) B_4H_4 with SE = 8. The derivative bicyclotetraborane(4) $[B(NMe_2)]_2[B\{B(NMe_2)_2\}_2]$ (**4**; see Scheme 2)[11] with a transannular B–B bond distance of 1.633(1) Å was synthesized and structurally characterized. While dicationic tetraborane(4) $[B_4H_4]^{2+}$ (SE = 6) or derivatives are unknown, the tetraborane(6) **5** (also with SE = 6, see Scheme 2) was synthesized and is the rhomboid tetraborane with the shortest experimentally verified transannular B–B bond (1.511(3) Å).[12,13] Quantum-chemical calculations predict a decrease of the transannular B–B distance with decreasing SE ($SE \geq 6$). The tetracation $[B_4H_4]^{4+}$ (SE = 4) seems to be not stable according to quantum chemical calculations, but the highly reactive tetraborane(8) $B_4(BF_2)_4F_4$ (**6**) with a folded structure and SE = 4 was prepared.[14] The remarkably stable tetraborane(6) **2**, which is water-stable, also exhibits an SE of 4, but in a planar rhomboid B_4 unit. Formal addition of four NH_3 molecules to $[B_4H_4]^{4+}$ gives $[B_4H_4(NH_3)_4]^{4+}$, again calculated to be stable with rhomboid B_4 skeleton (see the Supporting Information). The hypothetical product of double hydride abstraction from **1** followed by dimerization (**7** ($[B_4(hpp)_4]^{4+}$) with a transannular B–B bond of 1.76 Å), is isoelectronic to $[B_4H_4(NH_3)_4]^{4+}$ (each hpp group is replaced by (H,NH_3)). One-electron reduction of **7** finally leads to the radical trication **3**, the first compound with rhomboid B_4 unit and uneven SE. Calculations (B3LYP/SVP) indicated that **7** ($[B_4(hpp)_4]^{4+}$; see the Supporting Information for details) exhibits an extremely high electron affinity ($E_A = -13.5$ eV). An inspection of the frontier orbitals shows that the LUMO of **7** is almost identical with the SOMO of **3** (see the Supporting Information). Boron-containing radicals have attracted considerable attention in the last decades,[15] but only a few cationic boron-centered radicals have been reported, for example, a mononuclear radical cationic boron hydride that is persistent for several hours at room temperature,[16] and monocations obtained by one-electron oxidation of electron-rich diborenes.[17]

Further experiments showed that $[B_4(hpp)_4]^{3+\cdot}$ (**3**) could not be synthesized upon reaction of **2**$[HB(C_6F_5)_3]_2$ with $[(acridine)BCl_2][AlCl_4]$. Instead of hydride abstraction from **2**, the hydride abstraction took place from the anion $[HB(C_6F_5)_3]^-$, and crystals of the salt **2**$[AlCl_4]_2$ were isolated from the reaction mixture (see the structural characterization in Figure S4 of the Supporting Information). Presumably, hydride abstraction from **2** is sterically prohibited, so that hydride abstraction takes place only from the $[HB(C_6F_5)_3]^-$ anions even when a large excess of $[(acridine)BCl_2][AlCl_4]$ is used. From this result it may be concluded that **2** is not likely to be the direct precursor to **3**.

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The solid salt **3**$[AlCl_4]_3$ is stable for several month when air contact is strictly avoided. On the other hand, decoloration of the solid is observed within minutes when brought in contact with dioxygen. We are currently studying the reactivity of the new radical trication $[B_4(hpp)_4]^{3+\cdot}$ (**3**), which combines a high charge with a radical character and boron atoms in a formal oxidation state less than two. This work shows that hydride abstraction from electron-rich base-stabilized diboranes(4) is a boron–boron coupling option. We are currently exploring the possibility to stabilize such rhomboid B_4 units with other diazaallyl-type substituents (for example, bicyclic amidinates).

Experimental Section

The reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. All solvents were rigorously dried by applying standard procedures (with a solvent purification system MBraun SPS 800 Manual) and stored over molecular sieves (4 Å) prior to their use. The syntheses of $[HB(hpp)]_2$[18–20] and [(acridine)BCl_2]-$[AlCl_4]$[6] were accomplished according to previously reported procedures. Acridine (purified by sublimation) and $AlCl_3$ were delivered from Sigma Aldrich and stored in a glove box (MBraun LABmaster dp, MB-20-G) under argon. BCl_3 solution (1.0 M in dichloromethane) was obtained from Sigma Aldrich. IR spectra were recorded on a BIORAD Excalibur FTS 3000. A BRUKER Avance II 400 or BRUKER Avance III 600 machine was used for NMR spectroscopy. C,H,N analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. UV/Vis measurements were carried out with a Cary 5000 spectrometer. EPR spectra (X-band) were recorded with a Bruker ESP 300 E spectrometer.

3$[AlCl_4]_3$: A solution of $[HB(hpp)]_2$ (90 mg, 0.30 mmol) in dichloromethane (2 mL) was slowly added to a solution of [(acridine)BCl_2]-$[AlCl_4]$ (129 mg, 0.30 mmol) in dichloromethane (2 mL). After stirring at room temperature for 12 h, the solvent was removed and the residue was washed several times with dichloromethane (8 mL) and *n*-hexane (5 mL) to give a red solid in 60 % yield with respect to the used aluminium (62 mg, 0.06 mmol). Crystals suitable for X-ray diffraction were obtained from a concentrated dichloromethane solution. C,H,N analysis ($C_{28}H_{48}Al_3B_4Cl_{12}N_{12}$, MW: 1102.39 g mol^{-1}, %): calcd C 30.51, H 4.39, N 15.25; found C 30.99, H 4.63, N 15.04. IR (KBr): $\tilde{\nu}$ = 2965 (w, C–H val.), 2881 (w, C–H val.), 1636 (m), 1558 (w), 1521 (m), 1508 (m), 1449 (m), 1443 (m), 1405 (m), 1391 (m), 1361 (w), 1324 (m), 1283 (w), 1262 (w), 1235 (w), 1204 (w), 1134 (w), 1116 (w), 1069 (m), 1022 (w), 960 (w), 942 (w), 904 (w), 864 (w), 799 (m), 746 (w), 726 (w), 718 (w), 697 (w), 675 (w), 606 (w), 588 (w), 491 cm^{-1} (s, $[AlCl_4]^-$). Crystal data for **3**$[AlCl_4]_3 \cdot 2.5\,CH_2Cl_2$: $C_{30.5}H_{53}Al_3B_4Cl_{17}N_{12}$, M_r = 1314.68, 0.50 × 0.40 × 0.40 mm, monoclinic, space group $P2_1/n$, a = 24.917(5), b = 13.467(3), c = 37.038(7) Å, α = 90, β = 109.56(3), γ = 90°, V = 11711(4) Å^3, Z = 8, ρ_{calcd} = 1.491 Mg m^{-3}, MoK_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ = 1.93–30.08°. Reflections measured 117259, independent 34212, R_{int} = 0.1279. Final R indices $R1$ = 0.0947, w$R2$ = 0.2207.

CCDC 1442000 (**3**$[AlCl_4]_3$), 1442001 (**2**$[AlCl_4]_2$), and 1442002 (**2**$[HB(C_6F_5)_3]_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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