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Boron–Carbon Clusters

# Extensive Structural Rearrangements upon Reduction of 9*H*-9-Borafluorene**

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**Abstract:** *Common wisdom has it that organoboranes are readily oxidized. Described herein is that also their reduction can result in remarkable chemistry. Treatment of dimeric 9H-9-borafluorene with Li metal in toluene yields two strikingly different classes of compounds. One part of the sample reacts in a way similar to $B_2H_6$, thus affording an aryl(hydro)borane cluster reminiscent of the $[B_3H_8]^-$ anion. The other part furnishes a dianionic boron-doped graphene flake devoid of hydrogen substituents at the boron centers and featuring a central B=B bond. A change in the solvent to THF allows an isolation of this dibenzo[g,p]chrysene analogue in good yields.*

The targeted manipulation of covalent bonding is the essence of molecular chemistry. Underlying valence electron redistributions can be studied in their purest form when individual electrons, without accompanying atomic nuclei, are added to a molecule to witness it rearrange its scaffold or aggregate with its congeners. In this respect, boron-containing species are particularly well-suited objects of investigation, because the boron atom possesses only three valence electrons, thereby rendering covalent, three-coordinated boron compounds inherently electron deficient. As a result, monoborane does not exist as the monomeric compound $BH_3$, but forms the dimer $B_2H_6$ featuring two B-H-B two-electron three-center (2e3c) bonds. The fundamental question thus arises as to whether electrons, supplied from an external source, can be injected into $B_2H_6$ to prepare a dianion $[H_3B{-}BH_3]^{2-}$, which contains an electron-precise B−B σ bond and is isoelectronic with the hydrocarbon ethane.[1] Already Alfred Stock, the pioneer of hydroborane chemistry, treated $B_2H_6$ with Na/Hg amalgam and indeed obtained a salt with the empirical composition $Na_2B_2H_6$.[2] The reaction was later revisited to unequivocally identify $Na[BH_4]$ and $Na[B_3H_8]$ as the ultimate reduction products [Eq. (1)].[3]

$$2\,B_2H_6 + 2\,Na \rightarrow Na[BH_4] + Na[B_3H_8] \qquad (1)$$

Shore claimed $^{11}$B NMR evidence for the generation of $[H_3B{-}BH_3]^{2-}$ as an intermediate during the reduction of $B_2H_6$ with alkali metal naphthalides (MNaph) in THF.[4] Introduction of steric bulk and the application of a related reduction protocol finally allowed Matsuo and Tamao et al. to isolate the derivative $[\mathbf{A}]^{2-}$ of $[H_3B{-}BH_3]^{2-}$ (Figure 1).[5]

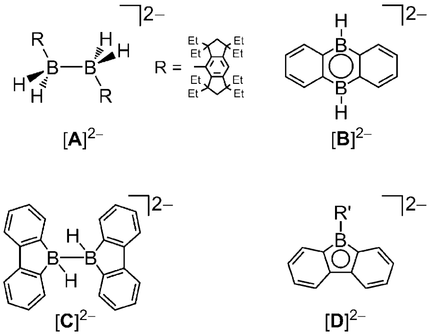

*Figure 1.* The isolable $[H_3B{-}BH_3]^{2-}$ derivative $[\mathbf{A}]^{2-}$, the π-delocalized 9,10-diborataanthracene $[\mathbf{B}]^{2-}$, and their 9-borafluorene analogues $[\mathbf{C}]^{2-}$ and $[\mathbf{D}]^{2-}$, respectively.

Another focus of current research in boron redox chemistry is on the ability of extended boron-doped π-conjugated molecules to accept electrons into their delocalized π systems. Important issues here are investigations of electron affinities, radical–radical interactions, and the charge-carrier transport in thin layers, with the aim to develop novel n-type materials for optoelectronic applications.[6] Particularly promising results have been achieved once the boron atoms are embedded into cyclic structures,[7] such as 9,10-dihydro-9,10-diboraanthracenes[8,9] or boroles,[10] to optimize π overlap by minimizing the degree of conformational freedom.

Hence, whenever arylboranes are used as substrates, two reduction scenarios will inevitably be competing with each other: 1) B−B σ bond coupling or 2) formation of discrete anions with π-delocalized electrons. The level of competition should be rather well balanced in the case of aryl(hydro)boranes, because hydrogen atoms pose a minimal steric hindrance on B−B coupling. As examples illustrating the two conceivable reaction outcomes, we again refer to compound $[\mathbf{A}]^{2-}$ and to the dianionic anthracene analogue $[\mathbf{B}]^{2-}$ (Figure 1),[9] which was synthesized by treatment of the polymeric parent 9,10-dihydro-9,10-diboraanthracene (**B**)[11] with lithium metal.

Our group is currently investigating the chemical behavior of pristine 9*H*-9-borafluorene (dibenzoborole).[12–14] In spite of its close formal relationship to **B**, 9*H*-9-borafluorene shows distinctly different structural features and reactivity: 1) The

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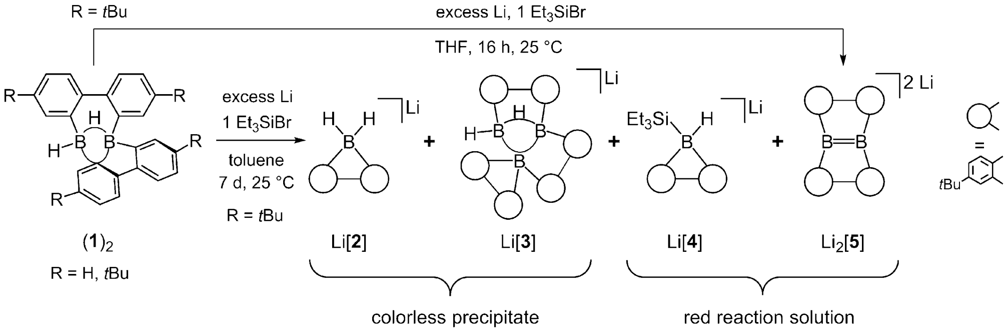

***Scheme 1.*** Lithium reduction of the 9*H*-9-borafluorene dimer (**1**)$_2$ (R = *t*Bu), prepared in situ from 9-Br-9-borafluorene and Et$_3$SiH: When using toluene as the reaction solvent the colorless precipitate consisted of the 9,9-dihydrido-9-boratafluorene Li[**2**] and the trinuclear cluster Li[**3**]. The burgundy red supernatant contained the 9-silyl-9-hydrido-boratafluorene Li[**4**] and the boron-doped graphene flake Li$_2$[**5**]. Targeted synthesis of Li$_2$[**5**] from (**1**)$_2$ in THF.

compound exists as a $C_1$-symmetric dimer with a B–B bridging phenylene ring, both in solution and in the solid state [(**1**)$_2$; Scheme 1].[13] 2) The parent dimer (R = H) is not stable in solution over a long time period (contrary to its derivative R = *t*Bu), but undergoes a ring-opening oligomerization reaction.[12] Herein, we will show that the very peculiar character of (**1**)$_2$ extends further into the area of its redox chemistry. Upon treatment of (**1**)$_2$ (R = *t*Bu) with lithium metal neither of the two a priori expected products, that is, an electron-precise diborate [**C**]$^{2-}$ or a discrete dianion [**D**]$^{2-}$ (R′ = H; Figure 1), is obtained.[15] The reaction in toluene furnishes the lithium 9,9-dihydrido-9-boratafluorene Li[**2**] accompanied by the trinuclear aggregate Li[**3**] (Scheme 1). Apart from the surprising similarities between the reactivities of (**1**)$_2$ and $B_2H_6$, we note the appearance of two other remarkable products, namely Li[**4**] and the boron-doped graphene flake Li$_2$[**5**]. Given the current interest in boron-containing polyaromatics, the serendipitous finding of Li$_2$[**5**] led us to develop also a protocol for its targeted synthesis.

To exclude the potential influence of a Lewis basic solvent on the structural integrity of (**1**)$_2$,[12,13,16] we used toluene rather than THF in the initial reduction experiments [from now on, (**1**)$_2$ refers exclusively to the derivative R = *t*Bu]. Following the standard protocol, the compound was prepared from 9-Br-2,7-di-*t*Bu-9-borafluorene and excess Et$_3$SiH.[13] For a quick workup, the mixture was evaporated under reduced pressure to remove the unreacted Et$_3$SiH and roughly half of the Et$_3$SiBr byproduct. The subsequent addition of lithium granules to a solution of (**1**)$_2$ in toluene resulted in the gradual formation of a colorless precipitate and in a color change of the supernatant from yellow-green to burgundy red (7 d at room temperature). An NMR spectroscopic investigation of the colorless precipitate in [D$_8$]THF revealed only two constituents: the mononuclear Li[**2**] and the trinuclear cluster Li[**3**] (Scheme 1), which can be separated from each other by recrystallization of the solid material from THF.

The parent lithium 9,9-dihydrido-9-boratafluorene without *t*Bu substituents is known.[17] Moreover, we have prepared an authentic sample of Li[**2**] from its corresponding 9-methoxyborane and Li[AlH$_4$] and found a perfect match of all NMR resonances (see the Supporting Information for details). In the $^{11}$B{$^1$H} NMR spectrum of the trinuclear cluster Li[**3**], two resonances are visible at $\delta = 18.9$ ppm ($h_{1/2} =$ 700 Hz) and −9.7 ppm ($h_{1/2}$=250 Hz). All $^1$H NMR, as well as the $^{13}$C NMR resonances could be assigned to three magnetically inequivalent di-*t*Bu-biphenyl fragments constituting an overall $C_1$-symmetric scaffold (see the Supporting Information for more details and plots of the spectra). A closer inspection of the chemical shift values reveals that proton signals of two biphenyl fragments are comparatively deshielded (i.e., $\delta =$ 8.1–7.4 ppm), whereas the third biphenyl unit gives rise to resonances in the upfield region of the spectrum (i.e., $\delta = 6.7$–6.3 ppm). From our experience,[12,13,16] low-field $^1$H NMR signals usually suggest the presence of ring-opened 9-borafluorenes (blue parts of Li[**3**] in Figure 2 a), whereas high-field signals are indicative of an intact 9-borafluorene framework (red part of Li[**3**] in Figure 2 a).

The molecular structure of [**3**]$^-$ was finally determined by X-ray crystallography on the solvate complex [Li(thf)$_4$]-[**3**]·2 THF (Figure 2 c; see the Supporting Information for full details). Formally, the molecule can be viewed as the insertion product of a singlet carbene-analogous 9-borafluorene anion ([**6**]$^-$) into the B-C-B bridge of (**1**)$_2$ (Figure 2 a; red and blue parts, respectively). In the dimer (**1**)$_2$ the bridging phenylene ring contributes a C(sp$^2$)-hybrid orbital and one electron pair to a B-C-B 2e3c bond, and the aromaticity of the phenylene bridge remains largely unperturbed.[13] The core connectivity within [**3**]$^-$ can be rationalized by assuming that the electron lone pair on carbon has left the B–B bridging position and instead interacts with the vacant p$_z$ orbital of the borate(I) [**6**]$^-$ (see B1−C51; Figure 2 c). In turn, the two nonbonding electrons residing on B1 have been placed into the space formerly occupied by the carbon lone pair to establish a B2-B1-B3 2e3c bond. Yet, there is a second way to interpret the bonding situation in [**3**]$^-$: If we replace all carbon atoms attached to boron by hydrogen atoms (red dots in Figure 2 b), the molecule obtained would be the well-known octahydrotriborate cluster [$B_3H_8$]$^-$.

Independent of the counterion, all published solid-state structures of the octahydrotriborate anion show distorted isosceles triangles of approximate $C_{2v}$ symmetry. The molecular framework is composed of three BH$_2$ groups and two hydrogen bridges (Figure 2 b).[18] According to quantum-chemical calculations,[19] the $C_{2v}$ form is only slightly more stable than an alternative $C_s$ form. Indeed, [$B_3H_8$]$^-$ was found to be highly fluxional in solution on the NMR time scale.[20] Thus, at the borderline between classical organoboron and cluster chemistry, the molecular scaffold of [**3**]$^-$ resembles the transition-state structure of the [$B_3H_8$]$^-$ scrambling process. In

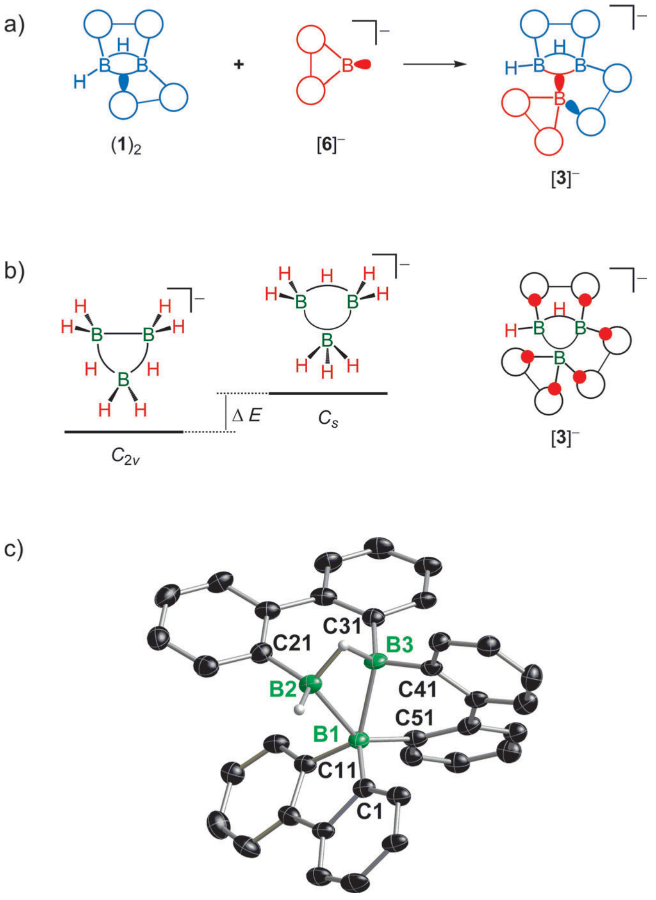

**Figure 2.** a) Drawing of [**3**]$^-$ as a formal insertion product of a singlet 9-borafluorene anion [**6**]$^-$ (red) and (**1**)$_2$ (blue). b) According to quantum-chemical calculations, the [B$_3$H$_8$]$^-$ ground state with $C_{2v}$ symmetry is energetically only slightly more favorable than the $C_s$ structure. The solid-state structure of [**3**]$^-$ resembles the $C_s$ form of [B$_3$H$_8$]$^-$. c) Molecular structure of [**3**]$^-$ in the crystal lattice (C*H* atoms and *t*Bu groups are omitted for clarity. The compound crystallizes as [Li(thf)$_4$][**3**]·2THF). Selected bond lengths [Å]: B1-B2 = 2.019(8), B1-B3 = 1.998(8), B2···B3 = 1.721(8), B1-C51 = 1.668(7).[23]

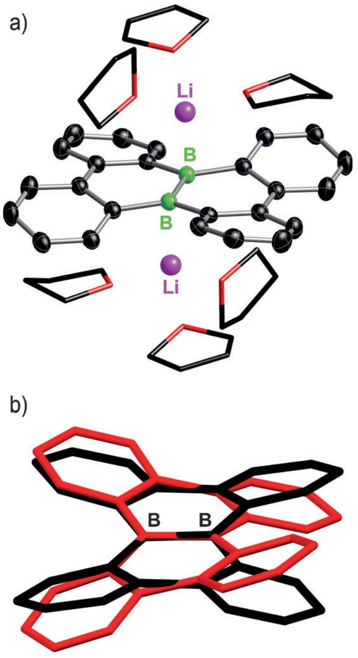

**Figure 3.** a) Solid-state structure of [Li(thf)$_3$]$_2$[**5**] (C*H* atoms and *t*Bu groups are omitted for clarity). Selected bond lengths [Å] and atom···atom distances [Å]: B−B = 1.608(4); B···Li = 2.567(4), 2.564(4). b) Overlay of the molecular structures of [**5**]$^{2-}$ in [Li(thf)$_3$]$_2$[**5**] (black) and [{Li(**4**)}$_2$Li$_2$(**5**)·2C$_6$H$_6$] (red).[23]

the same manner as [**3**]$^-$ relates to [B$_3$H$_8$]$^-$, the 9,9-dihydrido-9-boratafluorene [**2**]$^-$ can be considered as an organyl derivative of the [BH$_4$]$^-$ anion. Thus, striking parallels become obvious between the reduction reactions of (**1**)$_2$ and B$_2$H$_6$ [Eq. (1)]. As a distinct difference, however, we note that [BH$_4$]$^-$ and [B$_3$H$_8$]$^-$ form in equimolar quantities, whereas the product ratio [**2**]$^-$/[**3**]$^-$ is typically about 5:1.

NMR spectroscopy on the red mother liquor proved the complete precipitation of both species, but also the presence of two more major products. The two compounds cocrystallized upon storage of the red reaction solution at −35 °C and the material was subsequently recrystallized from C$_6$H$_6$ to improve the crystal quality. An X-ray analysis allowed the unambiguous identification of the two components as 9-silyl-9-hydrido-boratafluorene [**4**]$^-$ and the dianionic, boron-doped graphene flake [**5**]$^{2-}$ (Scheme 1, Figure 3). The stoichiometric ratio of 2:1 in the solid-state structure [{Li(**4**)}$_2$Li$_2$(**5**)·2C$_6$H$_6$] reflects, in good approximation, the relative distribution of the two compounds in the red solution according to $^1$H NMR spectroscopy (see the Supporting Information). As anticipated, the nature of the solvent has a pronounced influence on the reduction outcome. Upon switching from toluene to THF, no precipitate is observed anymore and the signatures of Li[**2**] and Li[**3**] are now absent in the NMR spectra of the crude reaction mixtures. Instead, Li$_2$[**5**] appears as major reaction product [$\delta(^{11}$B) = 32 ppm] and was isolated as single-crystalline thf solvate [Li(thf)$_3$]$_2$[**5**] in 43 % yield. According to X-ray crystallography, the compound forms contact ion pairs in the solid state, with the two Li$^+$ ions located above and below the midpoint of the B−B bond (Figure 3a). The B–B distances in [Li(thf)$_3$]$_2$[**5**] and in the cocrystal [{Li(**4**)}$_2$Li$_2$(**5**)·2C$_6$H$_6$] are identical [i.e. 1.608(4) Å and 1.611(3) Å, respectively]. These values are also very similar to the B=B bond length in Power's diborane(4) dianion [Li(OEt$_2$)]$_2$[Mes$_2$B=B(Mes)Ph][21] [1.636(11) Å], even though the polycyclic architecture of [**5**]$^{2-}$ enforces a much better conjugation of the boron p$_z$ orbitals with the sp$^2$-hybridized carbon atoms. As a result of steric repulsion between *ortho*-H atoms of adjacent phenylene rings, the anions [**5**]$^{2-}$ in [Li(thf)$_3$]$_2$[**5**] and [{Li(**4**)}$_2$Li$_2$(**5**)·2C$_6$H$_6$] deviate from planarity. The nature of the structural deformation is, however, different in both species. While the central C−C bonds of the two biphenyl fragments are parallel in [Li(thf)$_3$]$_2$[**5**] (black structure in Figure 3b), the corresponding C−C bonds in the cocrystal form a pair of skewed lines, mutually oriented at an angle of 28° (red structure in Figure 3b). An analogous twist is also observed in the solid-state structures of the isoelectronic and isostructural congeners 4b-aza-12b-boradibenzo-

[*g*,*p*]chrysene[22] and dibenzo[*g*,*p*]chrysene[22] with angles between the skew C–C bonds of 39° and 37°, respectively.

To rationalize the formation of Li[**4**], one has to take into account that the starting material $(\mathbf{1})_2$ still contains appreciable amounts of $Et_3SiBr$. Initially, we considered the bromosilane as an innocent bystander which will at most react to give $Si_2Et_6$ by slow reductive Si–Si coupling under the reaction conditions applied. Later, after the identification of the 9,9-dihydrido-9-boratafluorene Li[**2**], we recognized that $Et_3SiBr$ might even perform as a useful additive for the in situ recycling of Li[**2**] to $(\mathbf{1})_2$, thereby increasing the yields of Li[**3**], Li[**4**], and $Li_2$[**5**]. Indeed, only from the in situ prepared mixture $(\mathbf{1})_2/Et_3SiBr$, we have so far been able to generate a product palette of manageable complexity and to isolate the individual constituents. Our current working hypothesis is that $Et_3SiBr$ also facilitates the hydride abstraction from primary reaction intermediates and thereby assists the system to funnel into a specific number of thermodynamic sinks. A comprehensive assessment of the overall mechanistic scenario, which requires much more detailed scrutiny, is subject of ongoing work beyond the scope of this communication.

In summary, the reduction of the pristine 9*H*-9-borafluorene dimer with elemental lithium leads to a number of remarkable species. Among them, the trinuclear molecule Li[**3**] combines facets of the worlds of borohydride clusters and classical organoboranes. Graphene flakes such as $Li_2$[**5**], which is available on a preparative scale, are the focus of current research devoted to the development of novel organic optoelectronic materials.

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[23] CCDC-1006266 ($[Li(thf)_4][\mathbf{3}]\cdot 2\,THF$), 1006267 ($[\{Li(\mathbf{4})\}_2Li_2(\mathbf{5})\cdot 2\,C_6H_6]$), 1011480 ($[Li(thf)_3]_2[\mathbf{5}]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The Supporting Information of this publication contains all experimental procedures together with further crystallographic and spectroscopic details.