

Boryl Anions

International Edition: DOI: 10.1002/anie.201914219

German Edition: DOI: 10.1002/ange.201914219

The 9*H*-9-Borafluorene Dianion: A Surrogate for Elusive Diarylboryl Anion NucleophilesJannik Gilmer[†], Hendrik Budy[†], Thomas Kaese, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

Abstract: Double reduction of the THF adduct of 9*H*-9-borafluorene (**1**·THF) with excess alkali metal affords the dianion salts $M_2[**1**]$ in essentially quantitative yields ($M = \text{Li-K}$). Even though the added charge is stabilized through π delocalization, $[**1**]²⁻$ acts as a formal boron nucleophile toward organoboron (**1**·THF) and tetrel halide electrophiles (MeCl , Et_3SiCl , Me_3SnCl) to form B–B/C/Si/Sn bonds. The substrate dependence of open-shell versus closed-shell pathways has been investigated.

The quest for boron-centered nucleophiles remains a major challenge, but is rewarded with fundamentally new opportunities for element-organic synthesis. Three-coordinate, hypovalent boron compounds are electrophiles. Polarity inversion can, in principle, be achieved through the addition of two electrons into the vacant boron p_z orbital to generate an electron lone pair. Yet, this approach is impeded by the low electronegativity of the boron atom.^[1] Thus far, the arguably most versatile strategy to circumvent this problem relies on the in situ generation of nucleophilic boron species from tetra(organoxo)diboranes(4), $\text{B}_2(\text{OR})_4$: Upon addition of suitable Lewis bases, monoadducts are formed in which the $\text{B}(\text{sp}^3)\text{--B}(\text{sp}^2)$ bond is polarized in such a way as to render the sp^2 boryl unit a masked nucleophilic $[\text{B}(\text{OR})_2]^-$ equivalent.^[2–4] The combined $-I$ and $+M$ effects of the oxygen atoms decisively stabilize the $[\text{B}(\text{OR})_2]^-$ fragment—ultimately to an extent that allowed for the structural characterization of the corresponding magnesium boryl complexes by Hill and co-workers.^[5] Until today, the system $\text{B}_2(\text{OR})_4/\text{Lewis base}$ has been developed into a broadly applicable tool for the preparation of boronic acid esters,^[6] which serve as key building blocks in organic synthesis.^[7]

Also the important field of organic optoelectronic materials increasingly demands for novel organoboranes, and specifically for boron-doped polycyclic aromatic hydrocarbons (B-PAHs) to be applied as electron acceptors or light emitters.^[8–10] Here, nucleophilic boron precursors would be equally desirable, but now they should be devoid of π -donating heteroatom substituents so that the boron atom can unfold its full capacity as an electronically perturbing element in the final products. The first firmly established, heteroatom-free boryl anion intermediate was the base-stabilized species $\text{Li}[\text{BH}_2(\text{PCy}_3)]$ ($\text{Cy} = \text{cyclohexyl}$), an iso-electronic analogue of the well-known phosphonium ylides.^[11] A related N-heterocyclic carbene adduct, $\text{Li}[\text{BH}_2(\text{NHC})]$, was described by Lacôte and co-workers,^[12] while the Bertrand group reported on a cyclic-(alkyl)(amino)carbene-supported dicyanoboryl anion, $[\text{B}(\text{CN})_2(\text{CAAC})]^-$.^[13] Willner and Finze recently isolated alkali metal salts of the nucleophilic tricyanoborate dianion, $[\text{B}(\text{CN})_3]^{2-}$.^[1] Here, the flow of negative charge from the doubly occupied boron p_z orbital into the antibonding CN orbitals counterbalances the electro-positive character of the boron center.^[14]

Despite recent progress in the field of boryl nucleophiles, examples of diarylboryl anions ($[\text{BAr}_2]^-$), which would be the building blocks of choice for the synthesis of B-PAHs, are still scarce: Eisch and co-workers claimed that UV irradiation of $\text{Na}[\text{BPh}_4]$ generated $[\text{BPh}_2]^-$ via the reductive elimination of biphenyl,^[15] but the existence of the free anion remains subject to debate.^[16,17] In 2019, Yamashita and co-workers disclosed that the tetra(*o*-tolyl)diborane(4) dianion behaves as a dimer of $[\text{B}(\textit{oTol})_2]^-$.^[18] One year earlier, our group had postulated the intermediate formation of compound **[A]**[−] (Figure 1), which, depending on the reaction conditions, either undergoes boron insertion into one of the methyl C–H bonds or nucleophilic substitution of MeI to afford 2 equiv of 9-methyl-9-borafluorene.^[19]

[*] M. Sc. J. Gilmer,^[†] M. Sc. H. Budy,^[†] Dr. T. Kaese, Dr. M. Bolte, Dr. H.-W. Lerner, Prof. Dr. M. Wagner
Institut für Anorganische Chemie
Goethe-Universität Frankfurt
Max-von-Laue-Strasse 7, 60438 Frankfurt (Main) (Germany)
E-mail: Matthias.Wagner@chemie.uni-frankfurt.de

[†] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201914219>.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial, and no modifications or adaptations are made.

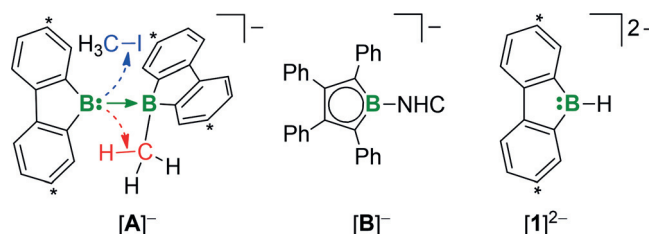


Figure 1. The postulated intermediate **[A]**[−] containing a Lewis-acid-stabilized boryl anion,^[19] the isolable anion **[B]**[−] with a boron-bonded NHC ligand,^[20] and the borafluorene dianion **[1]**^{2−} (this work). Carbon atoms marked with asterisks bear *t*Bu substituents.

In both instances, the actual reactive species would be the 9-borafluorenyl anion, $[\text{BFlu}]^-$, a cyclized derivative of $[\text{BPh}_2]^-$ (consider the conceptual relationship between $[\text{A}]^-$ and the above-mentioned $\text{B}_2(\text{OR})_4/\text{Lewis base}$ system). In compound $[\text{A}]^-$, the $[\text{BFlu}]^-$ moiety is stabilized through adduct formation of its electron lone pair with a Lewis acidic 9-methyl-9-borafluorene molecule. As an alternative option, $[\text{BFlu}]^-$ could be tamed through adduct formation of its boron p_z orbital with a suitable Lewis base. Precedence exists in the form of Braunschweig's tetraphenylborolyl-NHC complex $[\text{B}]^-$ (37% yield),^[20,21] and we thus wondered whether the 9-borafluorenyl dianion $[\mathbf{1}]^{2-}$ (Figure 1), a formal hydride adduct of $[\text{BFlu}]^-$, can also be made accessible on a preparative scale. We envisage two advantages of $[\mathbf{1}]^{2-}$ over $[\text{B}]^-$ as a nucleophilic building block: 1) Its molecular framework is fully conjugated, and the boron center is not sterically shielded, given that an H^- ion is the smallest possible ligand. 2) After reaction with an electrophile E^+-X , the hydride substituent should be easily removable from the primary intermediate $[\text{E}(\text{H})\text{BFlu}]^-$ to generate three-coordinate E^+BFlu , thereby rendering $[\mathbf{1}]^{2-}$ a true synthetic equivalent of the thus far elusive $[\text{BFlu}]^-$.

Herein, we report high-yielding syntheses of $\text{M}_2[\mathbf{1}]$ salts ($\text{M}=\text{Li}, \text{Na}, \text{K}$) and their use as boron nucleophiles for establishing B–B and B–C/Si/Sn bonds. We also investigated key mechanistic issues regarding the formation and closed-shell versus open-shell reactivity of $\text{M}_2[\mathbf{1}]$.

The synthesis of $\text{M}_2[\mathbf{1}]$ is based on the two-electron reduction of parent 9H-9-borafluorene ($\mathbf{1}$), which is stable in monomeric form as its THF adduct $\mathbf{1}\cdot\text{THF}$ (Figure 2a).^[22–24] Treatment of $\mathbf{1}\cdot\text{THF}$ in THF with excess alkali metal M for one to two days led to a color change from pale yellow to dark green ($\text{M}=\text{Li}, \text{Na}$) or dark red ($\text{M}=\text{K}$). The isolation of the corresponding salts $\text{M}_2[\mathbf{1}]$ was achieved through simple removal of unconsumed alkali metal and evaporation of the liquid phase under vacuum. The purity of the products, which were formed in essentially quantitative yields, was confirmed by ^1H , ^{11}B , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy; $\text{Li}_2[\mathbf{1}]$ (Supporting Information) and $\text{Na}_2[\mathbf{1}]$ (Figure 3a) were structurally characterized by X-ray crystallography.

The key to success is to maintain a temperature of -78°C during the first hour of the reaction in order to avoid the formation of unwanted side products, primarily $[\mathbf{1H}]^-$ and $[\mathbf{3}]^{2-}$ (Figure 2a and b, top vs. middle).^[25] Why is an initial low temperature of such critical importance, given that further stirring of the respective mixture at room temperature for a much longer time span is still required to drive the reaction to completion?

To answer this question, we will exemplarily refer to the sodium species. We first note that immediately after reaching room temperature, the reduction mixture already contains appreciable amounts of $\text{Na}_2[\mathbf{1}]$, together with the B–B-bonded dimer $\text{Na}_2[\mathbf{2}]$ ^[26] as the major product (Figure 2b, bottom). Precedence exists for an analogous *intramolecular* reductive B–B coupling reaction between two methylene-bridged borafluorene moieties.^[27] In a first control experiment, we confirmed that also an *intermolecular* variant is possible by mixing equimolar amounts of $\text{Na}_2[\mathbf{1}]$ and $\mathbf{1}\cdot\text{THF}$ at -78°C (Scheme 1).

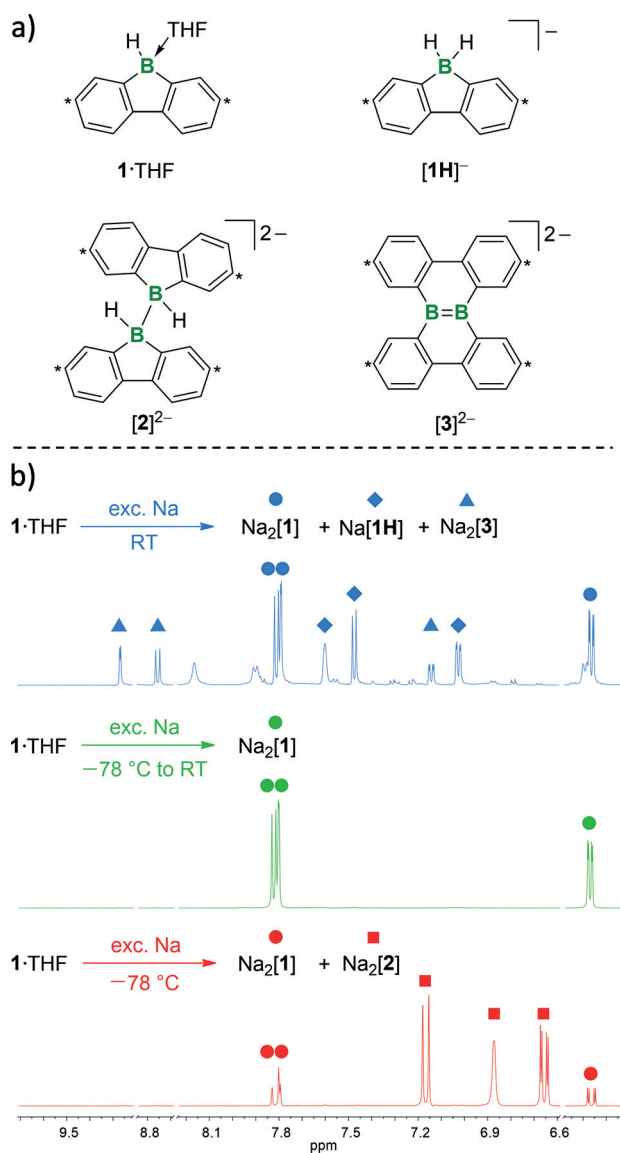
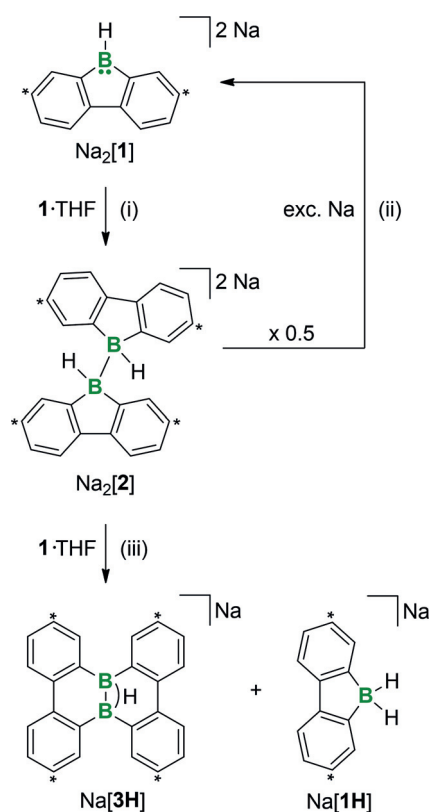


Figure 2. a) The neutral THF adduct $\mathbf{1}\cdot\text{THF}$ and the anions $[\mathbf{1H}]^-$, $[\mathbf{2}]^{2-}$, and $[\mathbf{3}]^{2-}$. b) ^1H NMR spectra ($[\text{D}_8]\text{THF}$) of the reaction products obtained from mixtures of $\mathbf{1}\cdot\text{THF}$ and excess sodium metal at room temperature (top), at -78°C (1 h) \rightarrow room temperature (1 d; middle), and at -78°C (1 h; bottom). Carbon atoms marked with asterisks bear *t*Bu substituents.

NMR spectroscopy subsequently revealed the quantitative conversion into $\text{Na}_2[\mathbf{2}]$,^[28] which was isolated in 98% yield and structurally characterized by X-ray crystallography (see the Supporting Information). In a second control experiment, $\text{Na}_2[\mathbf{2}]$ was stirred in a glovebox with sodium metal in $[\text{D}_8]\text{THF}$. NMR monitoring of the reaction progress over 21 h showed the gradual reductive cleavage of the B–B bond to ultimately furnish 2 equiv of $\text{Na}_2[\mathbf{1}]$, which unveils the role of $\text{Na}_2[\mathbf{2}]$ as the key intermediate on the way from $\mathbf{1}\cdot\text{THF}$ to $\text{Na}_2[\mathbf{1}]$ (see the work of Kinjo^[29] for a comparable B–B bond cleavage reaction). In a third control experiment, $\text{Na}_2[\mathbf{2}]$ was treated at room temperature with a substoichiometric amount of the masked Lewis acid $\mathbf{1}\cdot\text{THF}$. The mixture subsequently contained two new components: $\text{Na}[\mathbf{1H}]$ and $\text{Na}[\mathbf{3H}]$



Scheme 1. Synthesis of $\text{Na}_2[2]$ from $\text{Na}_2[1]$ and 1·THF; reductive cleavage of $\text{Na}_2[2]$ to give $\text{Na}_2[1]$; hydride abstraction from $\text{Na}_2[2]$ with 1·THF and skeletal rearrangement to furnish $\text{Na}[3H]$ and $\text{Na}[1H]$. Carbon atoms marked with asterisks bear *t*Bu substituents. Conditions: i) THF, -78°C , 1 h; ii) $[\text{D}_8]\text{THF}$, room temperature, 21 h; iii) $[\text{D}_8]\text{THF}$, room temperature, 1 h.

(Scheme 1).^[26] It has been shown previously that $\text{M}[3H]$ reacts with alkali metals M to afford the diborene $\text{M}_2[3]$ (see Figure 2a).^[24,30] We therefore propose that the hydride transfer between $\text{Na}_2[2]$ and 1·THF paves the way to the formation of the side products generated in the room-temperature reduction of 1·THF. The sole purpose of the low-temperature step is therefore to reductively quench the Lewis acidity of 1·THF under conditions where its reaction with $\text{Na}_2[2]$ is kinetically prohibited.

With the doubly reduced 9*H*-9-borafluorene $[1]^{2-}$ in hand, we were then able to tackle long-standing questions regarding the electronic structure of the central C_4B ring in its dianionic (formally aromatic) and neutral (formally antiaromatic) states.^[31] The pristine system is particularly valuable because here perturbations originating from steric or electronic influences of the boron-bonded substituent are not an issue (consider the π back-bonding contribution from B to NHC in $\text{K}[\text{B}]^{[20]}$). In lieu of the experimentally inaccessible monomeric $\mathbf{1}$,^[22,23] we will rely on the computed structure $\mathbf{1}^{\text{C}}$ (B3LYP/TZVP) for comparison with the (averaged) bond lengths of $\text{Na}_2[1]$ (Figure 3a). Two-electron injection into neutral 9*H*-9-borafluorene significantly changes its heavy-atom scaffold (Figure 3b). The pattern of bond-length elongations and contractions matches perfectly with the nodal structure of the LUMO of $\mathbf{1}^{\text{C}}$, which becomes doubly

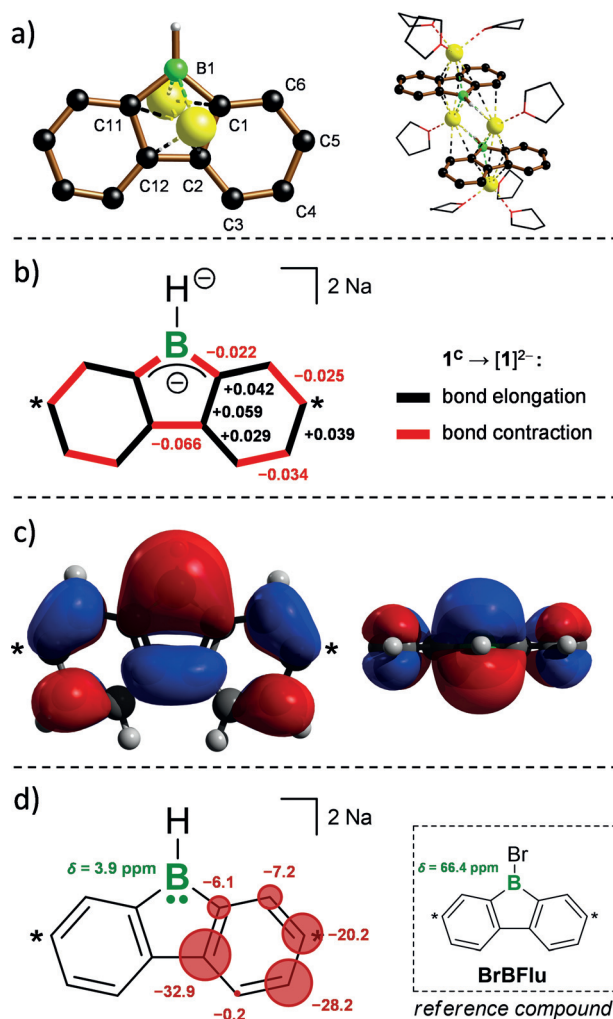


Figure 3. a) Molecular structure of $[\text{Na}(\text{thf})_3][\text{Na}(\text{thf})[1]]$ in the solid state. Hydrogen atoms (except BH) and *t*Bu groups are omitted for clarity. b) Differences between selected (averaged) bond lengths [Å] of $[\text{Na}(\text{thf})_3][\text{Na}(\text{thf})[1]]$ and $\mathbf{1}^{\text{C}}$. c) LUMO of $\mathbf{1}^{\text{C}}$ in two different orientations. d) ^{11}B NMR shifts of $\text{Na}_2[1]$ and BrBFlu (green); differences between selected ^{13}C NMR shifts [ppm] of $\text{Na}_2[1]$ ($[\text{D}_8]\text{THF}$) and BrBFlu (C_6D_6). Carbon atoms marked with asterisks bear *t*Bu substituents.

occupied upon reduction (Figure 3c): 1) $\text{Na}_2[1]$ shows enhanced bond-length alternations within its benzene rings; specifically, the peripheral rims adopt a butadiene-like character. 2) The B–C bonds in $\text{Na}_2[1]$ (avg. 1.537 Å) are shorter by 0.022 Å than those of $\mathbf{1}^{\text{C}}$, which is consistent with an increased double-bond character in the dianion. Moreover, the difference between the length of the C2–C12 bond minus the averaged C1–C2/C11–C12 bonds amounts to $\Delta = -0.059$ Å in $\text{Na}_2[1]$ and $+0.066$ Å in $\mathbf{1}^{\text{C}}$. The absolute values are similar, but the relative bond orders are inverted. Taken together, these structural features indicate that the two added electrons are not constrained to the boron p_z orbital, but to some extent distributed over the entire π -electron system of $\text{Na}_2[1]$. Somewhat surprisingly in view of the aromatic character of $[\text{B}]^-$ (Figure 1),^[20] the bond-length alternation in the central C_4B ring of $[1]^{2-}$ does not support the view of a cyclic delocalized “Clar sextet” within this substructure, but

rather points toward an allylic CBC fragment in combination with a C2–C12 bond of increased double-bond character. Accumulation of negative charge on the benzene rings of $\text{Na}_2[\mathbf{1}]$ also becomes evident from the ^{13}C NMR spectrum, which shows that all except one of the $\text{C}(\text{sp}^2)$ atoms are significantly shielded (Figure 3d). 2,7-Di-*tert*-butyl-9-bromo-9-borafluorene (**BrBFlu**) was used as a substitute for the uncharged reference system **1** because **BrBFlu** is the only derivative of trigonal-planar 2,7-di-*tert*-butyl-9-borafluorene, for which $^{13}\text{C}\{^1\text{H}\}$ NMR data have been recorded in a non-donor solvent (C_6D_6) and fully assigned.^[23]

Notwithstanding the evidence of charge delocalization in $\text{Na}_2[\mathbf{1}]$, an upfield-shifted ^{11}B NMR signal at 3.9 ppm suggests that considerable π -electron density remains accumulated at the boron center. Thus, $[\mathbf{1}]^{2-}$ has the potential of acting as a π nucleophile, and a first experiment in this direction has already proven that a mixture of $\text{Na}_2[\mathbf{1}]$ and **1**·THF furnishes the $\text{B}(\text{sp}^3)\text{--B}(\text{sp}^3)$ species $\text{Na}_2[\mathbf{2}]$ in quantitative yield (see above). Conceptually related examples of targeted B–B bond-forming reactions are scarce and restricted to heteroatom-stabilized boryl nucleophiles, such as Nozaki's and Yamashita's boryllithium^[32,33] or (in situ generated) pinacolatoboryl anions,^[34] and $[\text{B}(\text{CN})_3]^{2-}$.^[35] B–B coupling between $\text{Na}_2[\mathbf{1}]$ and **1**·THF can take place either in a closed-shell fashion (as for Finze's $\text{K}_2[\text{B}(\text{CN})_3]/\text{K}[\text{FB}(\text{CN})_3]$ system)^[35] or by comproportionation within an encounter complex constituted by the electron-rich $[\mathbf{1}]^{2-}$ and the electron-poor **1** (see Power's claim in a related case).^[36] In fact, the $\text{Na}_2[\mathbf{2}]$ species transiently generated during the synthesis of $\text{Na}_2[\mathbf{1}]$ may also result from the dimerization of two boranyl radicals $\text{Na}[\mathbf{1}]$.

In order to further assess the scope of $[\mathbf{1}]^{2-}$ as a surrogate of the nucleophilic boryl anion $[\text{BFlu}]^-$, reactions of $\text{Li}_2[\mathbf{1}]$ with MeCl, Et_3SiCl , and Me_3SnCl were performed (THF, room temperature). According to NMR analysis, quantitative conversion occurred to afford the B–Me- and B–SiEt₃-bonded species $\text{Li}[\mathbf{1Me}]$ and $\text{Li}[\mathbf{1SiEt}_3]$,^[25] respectively (Scheme 2). It was next confirmed that the hydride ligand of $\text{Li}[\mathbf{1Me}]$ can be easily abstracted with excess MeCl or Me_3SiCl in a one-pot reaction to furnish the free borane **4**. We

take this as a proof of principle that $[\mathbf{1}]^{2-}$ can indeed be used as a $[\text{BFlu}]^-$ equivalent in the synthesis of triorganoboranes. The stannylated hydroborate $\text{Li}[\mathbf{1SnMe}_3]$ was formed to approximately 80%, together with $\text{Li}[\mathbf{1H}]$ and Sn_2Me_6 (Scheme 2). These side products raise the question as to whether the apparent nucleophilicity of $[\mathbf{1}]^{2-}$ is, at least in part, a consequence of radical reactivity (as has been observed for the system $[\mathbf{B}]^-/\text{Me}_3\text{SnCl}^{[21]}$): Single-electron transfer from $[\mathbf{1}]^{2-}$ to Me_3SnCl yields the $[\mathbf{1}]^-$ and $[\text{Me}_3\text{Sn}]^\cdot$ radicals, which can either recombine in the solvent cage to generate $\text{Li}[\mathbf{1SnMe}_3]$ or undergo radical-pair separation with subsequent homocoupling (Sn_2Me_6) and H-atom abstraction ($\text{Li}[\mathbf{1H}]$).

The assumption of a possible radical pathway gains further support from the observation that the reaction of $\text{Li}_2[\mathbf{1}]$ with MeI (30% conversion into $\text{Li}[\mathbf{1Me}]$) is far less selective than that with MeCl; for MeI, radical reactivity has been reported.^[37] Moreover, treatment of $\text{Li}_2[\mathbf{1}]$ with 1 equiv of the fast radical clock (bromomethyl)cyclopropane gave mainly the ring-opened olefin $\text{Li}[\mathbf{1C}_2\text{H}_4\text{CH}=\text{CH}_2]$ together with $\text{Li}_2[\mathbf{2}]$ and small amounts of $\text{Li}[\mathbf{1H}]$, with all three products indicating radical intermediates.^[38] An authentic sample of $\text{Li}[\mathbf{1C}_2\text{H}_4\text{CH}=\text{CH}_2]$ was synthesized from $\text{Li}_2[\mathbf{1}]$ and 4-X-1-butene (X = Cl, Br); similar to the case of MeX, only the organochloride gave a high conversion into $\text{Li}[\mathbf{1C}_2\text{H}_4\text{CH}=\text{CH}_2]$ (75% by NMR analysis).

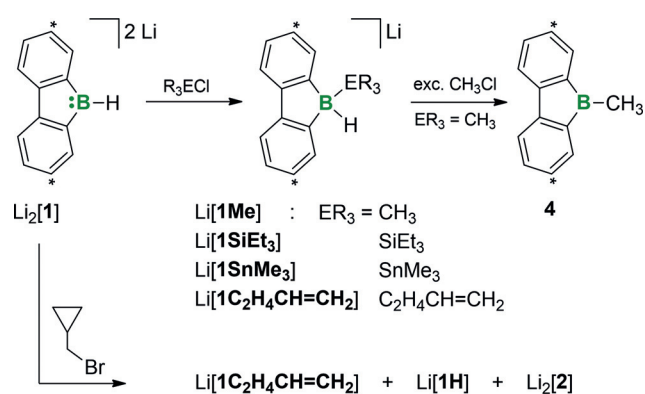
In summary, we have disclosed the first example of a fully conjugated diarylboryl ($[\text{BFlu}]^-$) anion, stabilized by a hydride ligand ($[\mathbf{1}]^{2-}$). The steric hindrance of the boron center is minimal, and $[\mathbf{1}]^{2-}$ straightforwardly reacts with organoboranes or tetrel halides to generate B–B/C/Si/Sn bonds. The hydride ligand of the thereby obtained methyl(hydro)borate $[\mathbf{1Me}]^-$ can be easily abstracted, thus rendering $[\mathbf{1}]^{2-}$ a true surrogate of the elusive $[\text{BFlu}]^-$ nucleophile. The extent of closed-shell versus open-shell reactivity of $[\mathbf{1}]^{2-}$ depends on the substrate: Evidence for radical intermediates has been found for the heavier halogen leaving groups (Br, I) and electrophilic tetrel centers (Sn).

Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · boryl anions · nucleophilic substitution · radical reactions · umpolung

How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 5621–5625
Angew. Chem. **2020**, *132*, 5670–5674



Scheme 2. Synthesis of $\text{Li}[\mathbf{1Me}]$, $\text{Li}[\mathbf{1SiEt}_3]$, $\text{Li}[\mathbf{1SnMe}_3]$, and $\text{Li}[\mathbf{1C}_2\text{H}_4\text{CH}=\text{CH}_2]$ from $\text{Li}_2[\mathbf{1}]$ and MeCl, Et_3SiCl , Me_3SnCl , and 4-chloro-1-butene, respectively; hydride abstraction from $\text{Li}[\mathbf{1Me}]$ to give the free borane **4**. Reaction of $\text{Li}_2[\mathbf{1}]$ with (bromomethyl)cyclopropane to form $\text{Li}[\mathbf{1C}_2\text{H}_4\text{CH}=\text{CH}_2]$. Carbon atoms marked with asterisks bear *t*Bu substituents.

[1] E. Bernhardt, V. Bernhardt-Pitchougina, H. Willner, N. Ignatiev, *Angew. Chem. Int. Ed.* **2011**, *50*, 12085–12088; *Angew. Chem.* **2011**, *123*, 12291–12294.

[2] E. C. Neeve, S. J. Geier, I. A. I. Mkhald, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091–9161.

[3] *Synthesis and Application of Organoboron Compounds* (Eds.: E. Fernández, A. Whiting), Springer International Publishing, Cham, **2015**.

[4] R. D. Dewhurst, E. C. Neeve, H. Braunschweig, T. B. Marder, *Chem. Commun.* **2015**, *51*, 9594–9607.

- [5] A. F. Pécharman, A. L. Colebatch, M. S. Hill, C. L. McMullin, M. F. Mahon, C. Weetman, *Nat. Commun.* **2017**, *8*, 15022. The field of heteroatom-stabilized boryl anions was pioneered by quantum-chemical calculations of Schleyer and co-workers and Nozaki's/Yamashita's preparation of a 1,3,2-diazaborole-derived boryllithium; see: a) M. Wagner, N. J. R. van Eikema Hommes, H. Nöth, P. v. R. Schleyer, *Inorg. Chem.* **1995**, *34*, 607–614; b) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115.
- [6] J. A. Schiffner, K. Müther, M. Oestreich, *Angew. Chem. Int. Ed.* **2010**, *49*, 1194–1196; *Angew. Chem.* **2010**, *122*, 1214–1216.
- [7] *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2011**.
- [8] E. von Grotthuss, A. John, T. Kaese, M. Wagner, *Asian J. Org. Chem.* **2018**, *7*, 37–53.
- [9] L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.* **2017**, *8*, 846–863.
- [10] A. Escande, M. J. Ingleson, *Chem. Commun.* **2015**, *51*, 6257–6274.
- [11] T. Imamoto, T. Hikosaka, *J. Org. Chem.* **1994**, *59*, 6753–6759.
- [12] J. Monot, A. Solov'yev, H. Bonin-Dubarle, É. Derat, D. P. Curran, M. Robert, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem. Int. Ed.* **2010**, *49*, 9166–9169; *Angew. Chem.* **2010**, *122*, 9352–9355.
- [13] D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 7590–7592; *Angew. Chem.* **2013**, *125*, 7739–7742.
- [14] J. Landmann, J. A. P. Sprenger, R. Bertermann, N. Ignat'ev, V. Bernhardt-Pitchougina, E. Bernhardt, H. Willner, M. Finze, *Chem. Commun.* **2015**, *51*, 4989–4992.
- [15] J. J. Eisch, K. Tamao, R. J. Wilcsek, *J. Am. Chem. Soc.* **1975**, *97*, 895–897.
- [16] J. D. Wilkey, G. B. Schuster, *J. Org. Chem.* **1987**, *52*, 2117–2122.
- [17] J. Radtke, S. K. Mellerup, M. Bolte, H. W. Lerner, S. Wang, M. Wagner, *Org. Lett.* **2018**, *20*, 3966–3970.
- [18] S. Akiyama, K. Yamada, M. Yamashita, *Angew. Chem. Int. Ed.* **2019**, *58*, 11806–11810; *Angew. Chem.* **2019**, *131*, 11932–11936.
- [19] T. Kaese, T. Trageser, H. Budy, M. Bolte, H. W. Lerner, M. Wagner, *Chem. Sci.* **2018**, *9*, 3881–3891.
- [20] H. Braunschweig, C. W. Chiu, K. Radacki, T. Kupfer, *Angew. Chem. Int. Ed.* **2010**, *49*, 2041–2044; *Angew. Chem.* **2010**, *122*, 2085–2088.
- [21] R. Bertermann, H. Braunschweig, R. D. Dewhurst, C. Hörl, T. Kramer, I. Krummenacher, *Angew. Chem. Int. Ed.* **2014**, *53*, 5453–5457; *Angew. Chem.* **2014**, *126*, 5557–5561.
- [22] A. Hübner, Z. W. Qu, U. Englert, M. Bolte, H. W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 4596–4609.
- [23] A. Hübner, M. Diefenbach, M. Bolte, H. W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2012**, *51*, 12514–12518; *Angew. Chem.* **2012**, *124*, 12682–12686.
- [24] T. Kaese, A. Hübner, M. Bolte, H. W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2016**, *138*, 6224–6233.
- [25] A. Hübner, M. Bolte, H. W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2014**, *53*, 10408–10411; *Angew. Chem.* **2014**, *126*, 10576–10579.
- [26] $\text{Li}_2[2]$, $\text{M}[1\text{H}]$, and $\text{M}[3\text{H}]$ ($\text{M}=\text{Li}, \text{K}$) are known; the NMR resonances of $\text{M}_2[2]$ ($\text{M}=\text{Na}, \text{K}$), $\text{Na}[1\text{H}]$, and $\text{Na}[3\text{H}]$ were assigned by analogy; see Refs. [24, 25].
- [27] A. Hübner, T. Kaese, M. Diefenbach, B. Endeward, M. Bolte, H. W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2015**, *137*, 3705–3714.
- [28] For practical reasons, the NMR spectra had to be recorded at room temperature. It can thus not be excluded that the actual B–B bond formation occurs not earlier than during warm-up.
- [29] L. Kong, W. Lu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2016**, *138*, 8623–8629.
- [30] T. Kaese, H. Budy, M. Bolte, H. W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2017**, *56*, 7546–7550; *Angew. Chem.* **2017**, *129*, 7654–7658.
- [31] A. Iida, S. Yamaguchi, *J. Am. Chem. Soc.* **2011**, *133*, 6952–6955.
- [32] K. Nozaki, Y. Aramaki, M. Yamashita, S. H. Ueng, M. Malacria, E. Lacôte, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 11449–11451.
- [33] Y. Hayashi, Y. Segawa, M. Yamashita, K. Nozaki, *Chem. Commun.* **2011**, *47*, 5880–5890.
- [34] A. F. Pécharman, M. S. Hill, C. L. McMullin, M. F. Mahon, *Angew. Chem. Int. Ed.* **2017**, *56*, 16363–16366; *Angew. Chem.* **2017**, *129*, 16581–16584.
- [35] J. Landmann, J. A. P. Sprenger, M. Hailmann, V. Bernhardt-Pitchougina, H. Willner, N. Ignat'ev, E. Bernhardt, M. Finze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11259–11264; *Angew. Chem.* **2015**, *127*, 11411–11416.
- [36] W. J. Grigsby, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 7981–7988.
- [37] L. M. Tolbert, J. Bedlek, M. Terapane, J. Kowalik, *J. Am. Chem. Soc.* **1997**, *119*, 2291–2292.
- [38] D. C. Nonhebel, *Chem. Soc. Rev.* **1993**, *22*, 347–359.

Manuscript received: November 7, 2019

Accepted manuscript online: December 13, 2019

Version of record online: January 22, 2020