The 9H-9-Borafluorene Dianion: A Surrogate for Elusive Diarylboryl Anion Nucleophiles

Jannik Gilmer+, Hendrik Budy+, Thomas Kaese, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

Abstract: Double reduction of the THF adduct of 9H-9-borafluorene (1·THF) with excess alkali metal affords the dianion salts M₂[1] in essentially quantitative yields (M = 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, Et₃SiCl, Me₃SnCl) 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, hypervalent boron compounds are electrophiles. Polarity inversion can, in principle, be achieved through the addition of two electrons into the vacant boron p 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 tetracoordinated diboranes(4), B₂(O),₄: Upon addition of suitable Lewis bases, monoadducts are formed in which the B(sp³)–B(sp³) bond is polarized in such a way as to render the sp³ boryl unit a masked nucleophile [B(OR)₂]⁻ equivalent.[2–4] The combined −I and + E effects of the oxygen atoms decisively stabilize the [B(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 B₂(O)/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 Li[BH₂(PCy₃)] (Cy = cyclohexyl), an isoelectronic analogue of the well-known phosphonium ylides.[11] A related N-heterocyclic carbene adduct, Li[BH₂(NHC)], was described by Lacôte and co-workers,[12] while the Bertrand group reported on a cyclic-(alkyl)(amino)carbene-supported dicyanoboryl anion, [B(CN)₂(CAAC)]⁻.[13] Willner and Finze recently isolated alkali metal salts of the nucleophilic tricyanoborate dianion, [B(CN)₃]₂⁻.[14] Here, the flow of negative charge from the doubly occupied boron p orbital into the antibonding CN orbitals counterbalances the electronegative character of the boron center.[14]

Despite recent progress in the field of boryl nucleophiles, examples of diarylboryl anions ([BAr₂]⁻), 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 Na[BPh₂] generated [BPh₂]⁻ 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(ortho-tolyl)diborane(4) dianion behaves as a dimer of [B(o-Tol)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]

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 fBu substituents.

* M. Sc. J. Gilmer,[1] M. Sc. H. Budy,[1] Dr. T. Kaese, Dr. M. Bolte, Dr. H.-W. Lerner, Prof. Dr. M. Wagner
Institut für Anorganische Chemie
Goethe-Universität Frankfurt
Max-von-Labes-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.
In both instances, the actual reactive species would be the 9-borafluorenyl anion, [BFlu]−, a cyclized derivative of [BPh3]− (consider the conceptual relationship between [A]− and the above-mentioned B{(OR)}3/Lewis base system). In compound [A]−, the [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, [BFlu]− could be tamed through adduct formation of its boron p orbital with a suitable Lewis base. Precedence exists in the form of Braunschweig’s tetrphenylborolyl-NH complex [B]− (37% yield),[20,21] and we thus wondered whether the 9-borafluorenyl dianion [1]2− (Figure 1), a formal hydride adduct of [BFlu]−, can also be made accessible on a preparative scale. We envisage two advantages of [1]2− over [B]− as a nucleophile 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 EL−X, the hydride substituent should be easily removable from the primary intermediate [EL(H)BFlu]− to generate three-coordinate ELBFlu, thereby rendering [1]2− a true synthetic equivalent of the thus far elusive [BFlu]−.

Herein, we report high-yielding syntheses of M2[1] salts (M = Li, Na, 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 M2[1].

The synthesis of M2[1] is based on the two-electron reduction of parent 9H-9-borafluorene (1), which is stable in monomeric form as its THF adduct 1·THF (Figure 2a).[22–24] Treatment of 1·THF in THF with excess alkali metal M for one to two days led to a color change from pale yellow to dark green (M = Li, Na) or dark red (M = K). The isolation of the corresponding salts M2[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, 13C, and 11B NMR spectroscopy; Li2[1] (Supporting Information) and Na2[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 [1H]− and [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 Na2[1], together with the B−B-bonded dimer Na3[2][26] as the major product (Figure 2b, bottom). Precedence exists for an analogous intramolecular reductive B−B coupling reaction between two methylene-bridged borafluorenyl moieties.[27] In a first control experiment, we confirmed that also an intermolecular variant is possible by mixing equimolar amounts of Na2[1] and 1·THF at −78 °C (Scheme 1).

NMR spectroscopy subsequently revealed the quantitative conversion into Na3[2],[28] which was isolated in 98% yield and structurally characterized by X-ray crystallography (see the Supporting Information). In a second control experiment, Na3[2] was stirred in a glovebox with sodium metal in [D8]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 Na2[1], which unveils the role of Na3[2] as the key intermediate on the way from 1·THF to Na2[1] (see the work of Kinjo[29] for a comparable B−B bond cleavage reaction). In a third control experiment, Na3[2] was treated at room temperature with a stoichiometric amount of the masked Lewis acid 1·THF. The mixture subsequently contained two new components: Na[1H] and Na[3H].
It has been shown previously that M[3H] reacts with alkali metals M to afford the diborene M₂[3] (see Figure 2a). We therefore propose that the hydride transfer between Na₂[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 Na₂[2] is kinetically prohibited.

With the doubly reduced 9H-9-borafluorene [1][2] in hand, we were then able to tackle long-standing questions regarding the electronic structure of the central C₄B ring in its dianionic (formally aromatic) and neutral (formally antiaromatic) states. 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 K[B][2][19]). In lieu of the experimentally inaccessible monomeric 1[2], we will rely on the computed structure 1C (B3LYP/TZVP) for comparison with the (averaged) bond lengths of Na₃H and BrB Flu (green); differences between selected ¹³C NMR shifts [ppm] of Na₂[1] ([D₈]THF) and BrB Flu (C₆D₆). Carbon atoms marked with asterisks bear tBu substituents.

(Scheme 1)[26] It has been shown previously that M[3H] reacts with alkali metals M to afford the diborene M₂[3] (see Figure 2a).[24,30] We therefore propose that the hydride transfer between Na₂[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 Na₂[2] is kinetically prohibited.

With the doubly reduced 9H-9-borafluorene [1][2] in hand, we were then able to tackle long-standing questions regarding the electronic structure of the central C₄B 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 K[B][2][19]). In lieu of the experimentally inaccessible monomeric 1[2], we will rely on the computed structure 1C (B3LYP/TZVP) for comparison with the (averaged) bond lengths of Na₃H and BrB Flu (green); differences between selected ¹³C NMR shifts [ppm] of Na₂[1] ([D₈]THF) and BrB Flu (C₆D₆). Carbon atoms marked with asterisks bear tBu substituents.
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 Na2[1] also becomes evident from the 13C NMR spectrum, which shows that all except one of the C(sp²) 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 trilateral-planar 2,7-di-tert-butyl-9-borafluorene, for which 13C{1H} NMR data have been recorded in a non-tert fashion (as for Finze/C29’s K2[B(CN)3]/K[FB(CN)3] system) [35] or transiently generated during the synthesis of Na2[1H][Me3SnCl][21]: Single-electron transfer from [1]2− to MeSnCl yields the [1]− and [MeSn]− radicals, which can either recombine in the solvent cage to generate Li[1SnMe3] or undergo radical-pair separation with subsequent homocoupling (SnMe3) and H-atom abstraction (Li[1H]).

The assumption of a possible radical pathway gains further support from the observation that the reaction of Li2[1] with MeI (30% conversion into Li[1Me]) is far less selective than that with MeCl; for MeI, radical reactivity has been reported.[37] Moreover, treatment of Li2[1] with 1 equiv of the fast radical clock (bromomethyl)cyclopropane gave mainly the ring-opened olefin Li[1C2H4CH=CMe3]+ and small amounts of Li[1H], with all three products indicating radical intermediates.[38] An authentic sample of Li[1C2H4CH=CH2] was synthesized from Li2[1] and 4-X-1-butene (X = Cl, Br); similar to the case of MeX, only the organochloride gave a high conversion into Li[1C2H4CH=CH2] (75% by NMR analysis).

In summary, we have disclosed the first example of a fully conjugated diarylboryl ([BFlu]+) anion, stabilized by a hydride ligand ([1]−). The steric hindrance of the boron center is minimal, and [1]− 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 [1Me]− can be easily abstracted, thus rendering [1]− a true surrogate of the elusive [BFlu]+ nucleophile. The extent of closed-shell versus open-shell reactivity of [1]− 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

[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, L. A. I. Mkalid, 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.
Manuscript received: November 7, 2019
Accepted manuscript online: December 13, 2019
Version of record online: January 22, 2020