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

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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, 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(organyloxy)diboranes(4), $B_2(OR)_4$: Upon addition of suitable Lewis bases, monoadducts are formed in which the $B(sp^3)−B(sp^2)$ bond is polarized in such a way as to render the sp^2 boryl unit a masked nucleophilic $[B(OR)_2]^-$ equivalent.[2–4] The combined $−I$ and $+M$ 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 $B_2(OR)_4$/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 $Li[BH_2(PCy_3)]$ (Cy = cyclohexyl), an iso-electronic analogue of the well-known phosphonium ylides.[11] A related N-heterocyclic carbene adduct, $Li[BH_2(NHC)]$, 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, $[B(CN)_3]^{2-}$.[1] Here, the flow of negative charge from the doubly occupied boron p_z orbital into the antibonding CN orbitals counterbalances the electropositive character of the boron center.[14]

Despite recent progress in the field of boryl nucleophiles, examples of diarylboryl anions ($[BAr_2]^-$), 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 $Na[BPh_4]$ generated $[BPh_2]^-$ 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 $[B(oTol)_2]^-$.[18] One year earlier, our group had postulated the intermediate formation of compound $[\mathbf{A}]^-$ (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]

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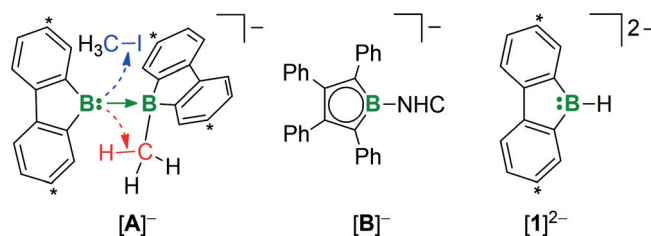https://doi.org/10.1002/anie.201914219.

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 tBu substituents.

In both instances, the actual reactive species would be the 9-borafluorenyl anion, [BFlu]⁻, a cyclized derivative of [BPh₂]⁻ (consider the conceptual relationship between [A]⁻ and the above-mentioned B₂(OR)₄/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_z orbital with a suitable Lewis base. Precedence exists in the form of Braunschweig's tetraphenylborolyl–NHC 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 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 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 9*H*-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, ¹¹B, and ¹³C{¹H} 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 Na₂[2][26] as the major product (Figure 2b, bottom). Precedence exists for an analogous *intra*molecular reductive B−B coupling reaction between two methylene-bridged borafluorene moieties.[27] In a first control experiment, we confirmed that also an *inter*molecular variant is possible by mixing equimolar amounts of Na₂[1] and 1·THF at −78°C (Scheme 1).
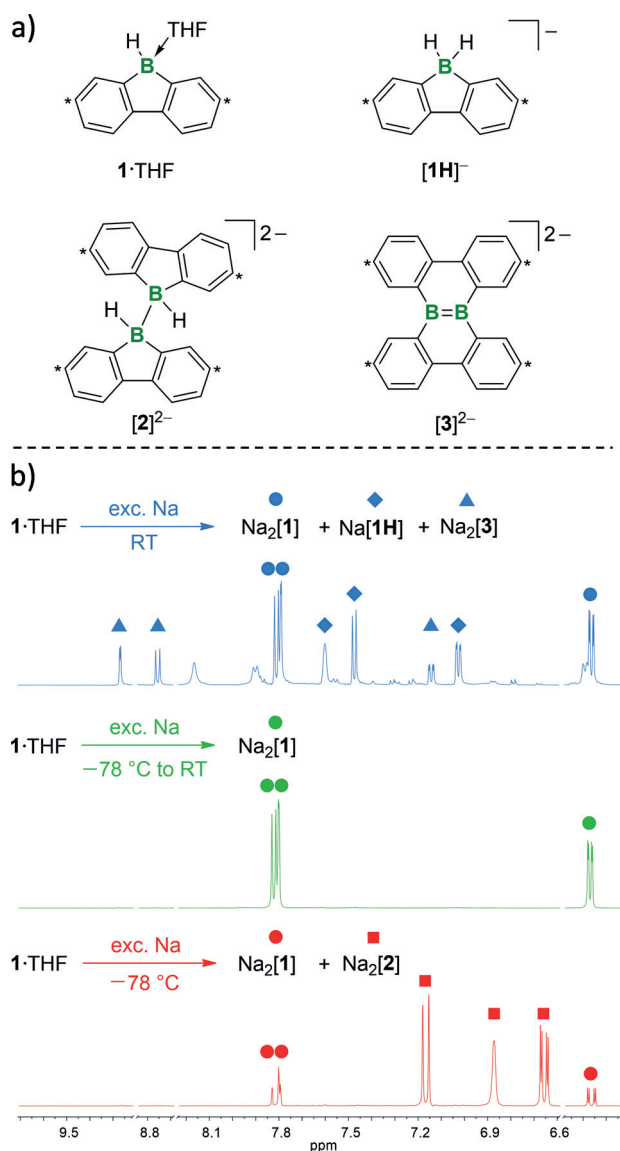
Figure 2. a) The neutral THF adduct 1·THF and the anions [1H]⁻, [2]²⁻, and [3]²⁻. b) ¹H NMR spectra ([D₈]THF) of the reaction products obtained from mixtures of 1·THF and excess sodium metal at room temperature (top), at −78°C (1 h)→room temperature (1 d; middle), and at −78°C (1 h; bottom). Carbon atoms marked with asterisks bear *t*Bu substituents.

NMR spectroscopy subsequently revealed the quantitative conversion into Na₂[2],[28] which was isolated in 98% yield and structurally characterized by X-ray crystallography (see the Supporting Information). In a second control experiment, Na₂[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 Na₂[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, Na₂[2] was treated at room temperature with a substoichiometric amount of the masked Lewis acid 1·THF. The mixture subsequently contained two new components: Na[1H] and Na[3H]
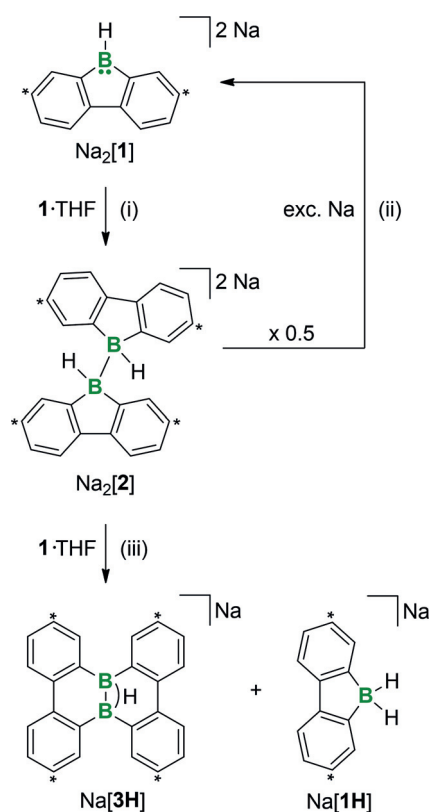
Scheme 1. Synthesis of Na₂[**2**] from Na₂[**1**] and **1**·THF; reductive cleavage of Na₂[**2**] to give Na₂[**1**]; hydride abstraction from Na₂[**2**] with **1**·THF and skeletal rearrangement to furnish Na[**3H**] and Na[**1H**]. Carbon atoms marked with asterisks bear *t*Bu substituents. Conditions: i) THF, −78 °C, 1 h; ii) [D₈]THF, room temperature, 21 h; iii) [D₈]THF, room temperature, 1 h.

Figure 3. a) Molecular structure of [Na(thf)₃][Na(thf)][**1**] in the solid state. Hydrogen atoms (except B*H*) and *t*Bu groups are omitted for clarity. b) Differences between selected (averaged) bond lengths [Å] of [Na(thf)₃][Na(thf)][**1**] and **1ᶜ**. c) LUMO of **1ᶜ** in two different orientations. d) ¹¹B NMR shifts of Na₂[**1**] and **BrBFlu** (green); differences between selected ¹³C NMR shifts [ppm] of Na₂[**1**] ([D₈]THF) and **BrBFlu** (C₆D₆). Carbon atoms marked with asterisks bear *t*Bu 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 2 a).[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 9*H*-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**]).[20] In lieu of the experimentally inaccessible monomeric **1**,[22,23] we will rely on the computed structure **1ᶜ** (B3LYP/TZVP) for comparison with the (averaged) bond lengths of Na₂[**1**] (Figure 3 a). Two-electron injection into neutral 9*H*-9-borafluorene significantly changes its heavy-atom scaffold (Figure 3 b). The pattern of bond-length elongations and contractions matches perfectly with the nodal structure of the LUMO of **1ᶜ**, which becomes doubly
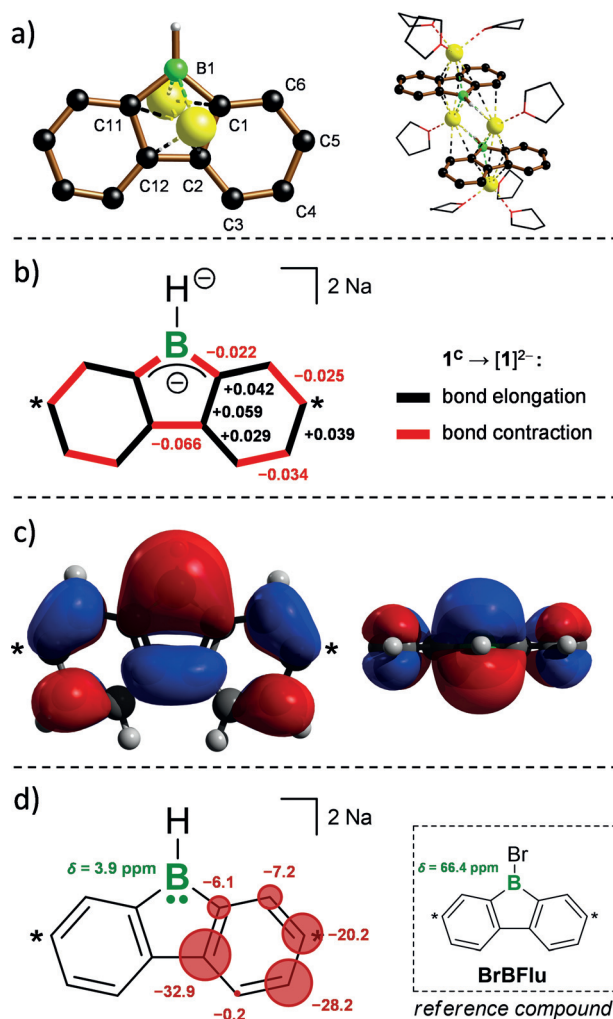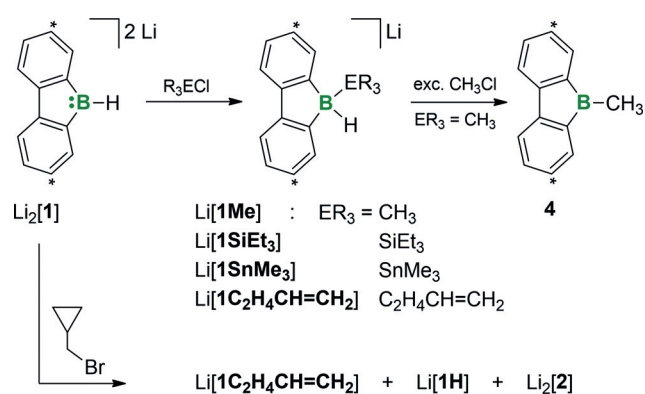
occupied upon reduction (Figure 3 c): 1) Na₂[**1**] shows enhanced bond-length alternations within its benzene rings; specifically, the peripheral rims adopt a butadiene-like character. 2) The B−C bonds in Na₂[**1**] (avg. 1.537 Å) are shorter by 0.022 Å than those of **1ᶜ**, which is consistent with 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 Δ = −0.059 Å in Na₂[**1**] and +0.066 Å in **1ᶜ**. 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 Na₂[**1**]. Somewhat surprisingly in view of the aromatic character of [**B**]⁻ (Figure 1),[20] the bond-length alternation in the central C₄B 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 Na$_2$[**1**] also becomes evident from the ^{13}C NMR spectrum, which shows that all except one of the C(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}C{^{1}H} NMR data have been recorded in a non-donor solvent (C$_6$D$_6$) and fully assigned.[23]

Notwithstanding the evidence of charge delocalization in Na$_2$[**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, [**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 Na$_2$[**1**] and **1**·THF furnishes the B(sp^3)−B(sp^3) species Na$_2$[**2**] in quantitative yield (see above). Conceptually related examples of targeted B−B bond-forming reactions are scarce and restricted to hetero-atom-stabilized boryl nucleophiles, such as Nozaki's and Yamashita's boryllithium[32,33] or (in situ generated) pinacolatoboryl anions,[34] and [B(CN)$_3$]$^{2-}$.[35] B−B coupling between Na$_2$[**1**] and **1**·THF can take place either in a closed-shell fashion (as for Finze's K$_2$[B(CN)$_3$]/K[FB(CN)$_3$] system)[35] or by comproportionation within an encounter complex constituted by the electron-rich [**1**]$^{2-}$ and the electron-poor **1** (see Power's claim in a related case).[36] In fact, the Na$_2$[**2**] species transiently generated during the synthesis of Na$_2$[**1**] may also result from the dimerization of two boranyl radicals Na[**1**].

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

take this as a proof of principle that [**1**]$^{2-}$ can indeed be used as a [BFlu]$^-$ equivalent in the synthesis of triorganoboranes. The stannylated hydroborate Li[**1SnMe$_3$**] was formed to approximately 80%, together with Li[**1H**] and Sn$_2$Me$_6$ (Scheme 2). These side products raise the question as to whether the apparent nucleophilicity of [**1**]$^{2-}$ is, at least in part, a consequence of radical reactivity (as has been observed for the system [**B**]$^-$/Me$_3$SnCl[21]): Single-electron transfer from [**1**]$^{2-}$ to Me$_3$SnCl yields the [**1**]$^{·-}$ and [Me$_3$Sn]$^·$ radicals, which can either recombine in the solvent cage to generate Li[**1SnMe$_3$**] or undergo radical-pair separation with subsequent homocoupling (Sn$_2$Me$_6$) and H-atom abstraction (Li[**1H**]).

The assumption of a possible radical pathway gains further support from the observation that the reaction of Li$_2$[**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 Li$_2$[**1**] with 1 equiv of the fast radical clock (bromomethyl)cyclopropane gave mainly the ring-opened olefin Li[**1C$_2$H$_4$CH=CH$_2$**] together with Li$_2$[**2**] and small amounts of Li[**1H**], with all three products indicating radical intermediates.[38] An authentic sample of Li[**1C$_2$H$_4$CH=CH$_2$**] was synthesized from Li$_2$[**1**] and 4-X-1-butene (X = Cl, Br); similar to the case of MeX, only the organochloride gave a high conversion into Li[**1C$_2$H$_4$CH= CH$_2$**] (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**]$^{2-}$). The steric hindrance of the boron center is minimal, and [**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 [**1Me**]$^-$ can be easily abstracted, thus rendering [**1**]$^{2-}$ a true surrogate of the elusive [BFlu]$^-$ nucleophile. The extent of closed-shell versus open-shell reactivity of [**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.

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

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