

Anionic Organoboranes | Very Important Paper |

VIP

Anionic Organoboranes: Delicate Flowers Worth Caring for

Hendrik Budy,^{[a][‡]} Jannik Gilmer,^{[a][‡]} Timo Trageser,^{[a][‡]} and Matthias Wagner*^[a]

Dedicated to the memory of Professor Malcolm L. H. Green

Abstract: Subvalent boron compounds contain boron atoms with oxidation numbers lower than +III. Over the last decades, the development of isolable derivatives has relied heavily on the use of specially designed ligands capable of stabilizing the electron-rich boron centers electronically or through steric protection. Herein, we are exclusively reviewing anionic organo-(hydro)boranes largely devoid of stabilizing ligands or heteroatom substituents. The restriction to these subvalent species is intended to minimize the risk of ligand artifacts being included when carving out the characteristic properties of the respective

boron centers, such as nucleophilic or carbenoid behavior. The scope of this review encompasses triorganoborane radical monoanions ($[\cdot\text{BR}_3]^-$) along with closed-shell dianions ($[\text{:BR}_3]^{2-}$), boryl anions ($[\text{:BR}_2]^-$), as well as B–B single-bonded diborane(6) dianions ($[\text{R}_3\text{B}-\text{BR}_3]^{2-}$) and diborane(5) monoanions ($[\text{R}_2\text{B}-\text{BR}_3]^-$), and finally B=B double-bonded diborane(4) dianions ($[\text{R}_2\text{B}=\text{BR}_2]^{2-}$). We are showing how these species are related to each other and comment on their bonding situations from an experimentalist's perspective.

Introduction

Main group chemistry is nowadays experiencing a vivid renaissance – after a period during which the p-block elements seemed dwarfed by the lustrous transition metals.^[1] Much of the credit for this turnaround goes to recent breakthroughs in the field of organoboranes, which are not only fundamentally interesting, but also play vital roles as building blocks in organic synthesis^[2] and materials for organic optoelectronic devices.^[3] In the form of “Frustrated Lewis Pairs” (FLPs)^[4] or highly reactive subvalent species^[5] they are also increasingly applied for the (catalytic) activation of small molecules.

Just what is it that makes boron compounds so different and appealing? The boron atom of tricoordinate boranes (BR_3) formally owns six valence electrons and a vacant p_z orbital, which renders it an archetypal electrophilic center and a Lewis acid. The energetically favorable valence-electron octet can be approached through σ electron-pair donation from a suitable Lewis base (cf. $\text{R}'_3\text{N} \rightarrow \text{BR}_3$), π electron-pair donation from a suitable heteroatom substituent (cf. $(\text{HO})\text{BR}_2$), or, in the case of hydroboranes, dimerization via the formation of B–H–B two-

electron–three-center (2e3c) bonds (cf. $\text{R}_2\text{B}(\mu\text{-H})_2\text{BR}_2$). Contrary to the hundreds of examples that exist for each of these saturation modes, a fourth option has only scarcely been investigated: the one- or two-electron reduction of the boron center. While neutral boranes, BR_3 , are isoelectronic to carbenium ions, the reduced species $[\text{BR}_3]^-$ and $[\text{BR}_3]^{2-}$ are analogues of alkyl radicals and anions, respectively. As a result of the lower electronegativity of B vs. C and the higher negative charge of the organoboron compared to the corresponding carbonaceous compounds, $[\text{BR}_3]^-$ and $[\text{BR}_3]^{2-}$ are generally even more reactive than their already highly reactive organic counterparts.

Scheme 1 summarizes selected conversions that can follow the one- or two-electron reduction of boranes **A** as well as **E** and illustrates how the products are interrelated. The observed scenario strongly depends on the nature of the boron-bonded substituents: If the boron atom bears aryl substituents or is directly embedded into a π -electron system the added electron(s) may be delocalized to such an extent that the primary products, $[\text{A}]^-$ and $[\text{A}]^{2-}$, are persistent enough to be isolated. The energy of an open-shell anion $[\text{A}]^-$ can also be lowered through delocalization of the odd electron into the vacant p_z orbital of a second (neutral) borane moiety such that a one-electron–two-center (1e2c) bond is created ($[\text{B}]^-$). Further one-electron reduction leads from $[\text{B}]^-$ to a diborane(6) dianion $[\text{C}]^{2-}$. Especially if $[\text{A}]^-$ features an electronically more innocent ligand sphere, it may dimerize with formation of an electron-precise B–B single bond to directly afford $[\text{C}]^{2-}$. The abstraction of an R^- group from $[\text{C}]^{2-}$ generates a still negatively charged $\text{B}(\text{sp}^2)\text{--B}(\text{sp}^3)$ diborane, which can be viewed as the adduct between a Lewis basic boryl anion, $[\text{:BR}_2]^-$, and a Lewis acidic borane, BR_3 . Some compounds of the type $[\text{R}_2\text{B}-\text{BR}_3]^-$ (**D**) indeed serve as sources of boron nucleophiles. Anions $[\text{R}_2\text{B}-\text{BR}_3]^-$ carrying a hydrogen substituent have been found to adopt symmetric

[a] H. Budy, J. Gilmer, T. Trageser, Prof. Dr. M. Wagner
Institut für Anorganische Chemie, Goethe-Universität Frankfurt,
Max-von-Laue-Str. 7, 60438 Frankfurt (Main), Germany
E-mail: Matthias.Wagner@chemie.uni-frankfurt.de

[‡] These authors contributed equally to this work.

ORCID(s) from the author(s) for this article is/are available on the WWW under <https://doi.org/10.1002/ejic.202000786>.

© 2020 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-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.

structures in which the electron-precise B–B bond is supported by a B–H–B 2e3c bond ($[\mathbf{D}]^{-}$). In certain cases, such compounds are also accessible through deprotonation of dimeric organyl-(hydro)boranes (\mathbf{A})₂ or via the two-electron reduction of (\mathbf{A})₂ and the concomitant transfer of one H[−] ion. An effective four-electron reduction of (\mathbf{A})₂, accompanied by the loss of two H[−] ions, has been successfully applied for the synthesis of B=B double-bonded species $[\mathbf{E}]^{2-}$. To complete the picture laid out in Scheme 1, the two-electron reduced borane $[\mathbf{A}]^{2-}$ can (formally) be transformed into a boryl anion $[\mathbf{F}]^{-}$ through the abstraction of one covalently bonded substituent R[−]. The dimerization of $[\mathbf{F}]^{-}$ would, in principle, produce the aforementioned diborene derivative $[\mathbf{E}]^{2-}$. A more practical approach to $[\mathbf{E}]^{2-}$ proceeds via the two-electron reduction of diboranes(4) \mathbf{E} .

Research on subvalent organoboron compounds of types $[\mathbf{A}]^{n-}$ – $[\mathbf{F}]^{-}$ equipped with σ -donating N-heterocyclic-/cyclic alkyl amino carbenes (NHCs/CAACs), electronically stabilizing π -donor substituents, or kinetically protecting bulky groups has pioneered the synthesis of isolable derivatives and paved the way for groundbreaking studies on their properties.^[6] As a downside, electronically or kinetically stabilizing substituents inevitably act by taming the innate properties of the low-valent boron center. In contrast to previous review articles,^[7] the present re-

view therefore puts its main focus on hydrogen- or organyl-substituted boron species as they allow key properties to be assessed in their purest form and largely unspoiled by ligand artifacts. We will discuss the rewards that can be earned in return for the challenges that come with the handling of such sensitive species by showing molecules that exhibit reversible redox switching, boron-centered nucleophilicity, carbene-type C–H insertion, transition metal-like element–element bond activation, or the ability to perform B–B-bond forming reactions. For the sake of clarity, the main text has been structured in three sections: section 1) compiles real existing compounds which correspond to the general formulae $[\mathbf{A}]^{n-}$ – $[\mathbf{F}]^{-}$ and explains how they are synthesized, section 2) deals with the reactivities of these species, and section 3) uses experimental observations augmented by quantum-chemical calculations to describe the electronic structures of the subvalent organoboranes. All ionic species have been numbered according to the following general scheme $[\mathbf{M}(\text{solv})]_n[\mathbf{X}]^{n-}$. Whenever appropriate we will only mention the anionic part $[\mathbf{X}]^{n-}$ or an abbreviated formula $\mathbf{M}_n[\mathbf{X}]$. The full formula is used when solid-state structures are discussed. Whenever a solvent molecule (THF, DME) serves as a ligand, its acronym is written in lower case letters (thf, dme).



Hendrik Budy, born in 1993, studied chemistry (B. Sc., M. Sc.) at the Goethe-Universität Frankfurt. Since 2019, he is conducting his Ph.D. studies in Prof. M. Wagner's group, where he carries out research on the synthesis and properties of reduced arylboranes, especially systems with unusual bonding situations.



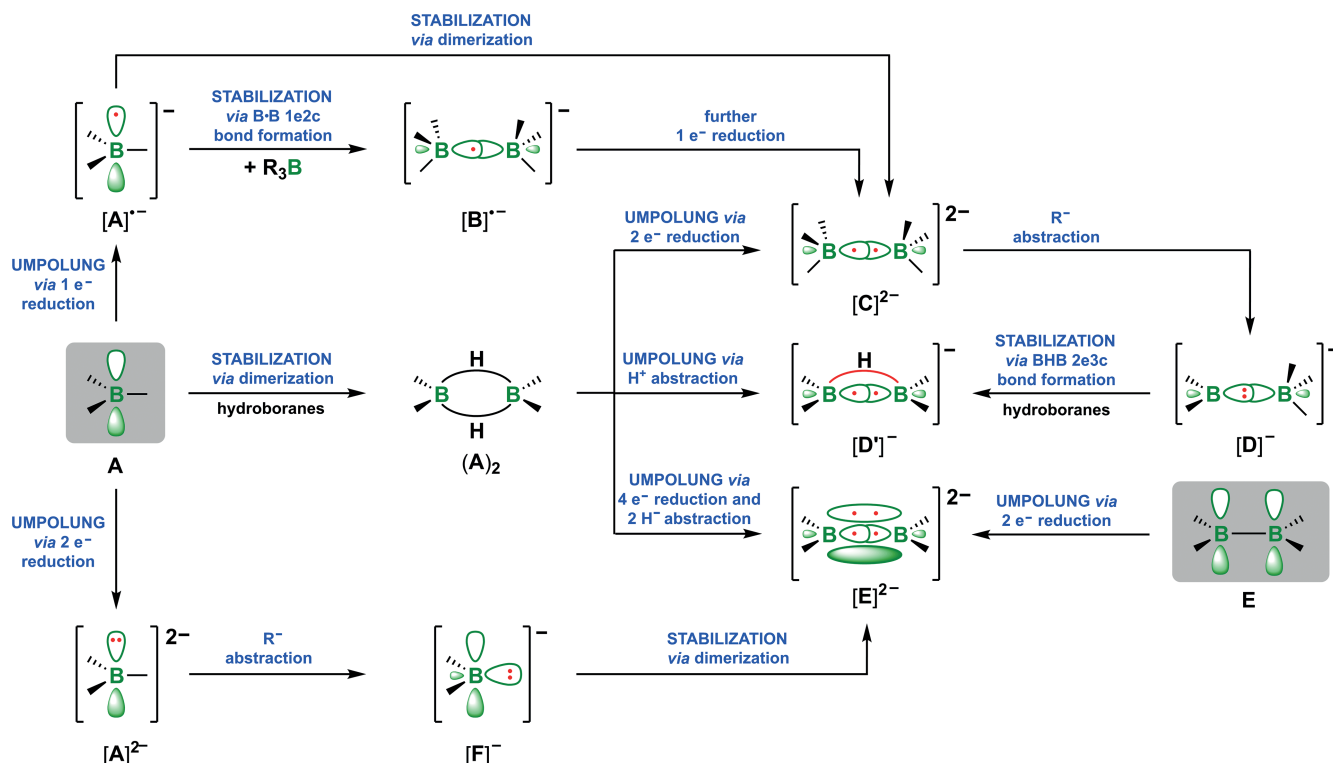
Jannik Gilmer, born in 1996, earned his B. Sc. and M. Sc. degrees in chemistry from the Goethe-Universität Frankfurt. He is currently working on his Ph.D. thesis in the group of Prof. M. Wagner. His research focuses on the reactivity of anionic aryl(hydro)boranes as well as hydride-substituted silyborates.



Timo Trageser, born in 1992, completed his chemistry studies at the Goethe-Universität Frankfurt. Since 2018, he is working on his Ph.D. thesis in Prof. M. Wagner's group. His research interests concentrate on the reactivity of B–B bonds in anionic aryl(hydro)boranes. He held scholarships of the Goethe-Universität ("Deutschlandstipendium") as well as the Fonds der Chemischen Industrie ("Kekulé grant").



Prof. Matthias Wagner obtained his Ph.D. with Prof. Nöth at the LMU München. He stayed for a postdoc position with Prof. Green at Oxford University and finished his Habilitation in 1997 at the TU München in the group of Prof. Herrmann. Since 1999, he holds the chair of Organometallic Chemistry at the Goethe-Universität Frankfurt. His current research interests are boron and silicon chemistry, the investigation of reactive intermediates, and organometallic catalysis directed toward materials synthesis.



Scheme 1. Relationship diagram showing the general types of anionic organoboranes covered in this review article.

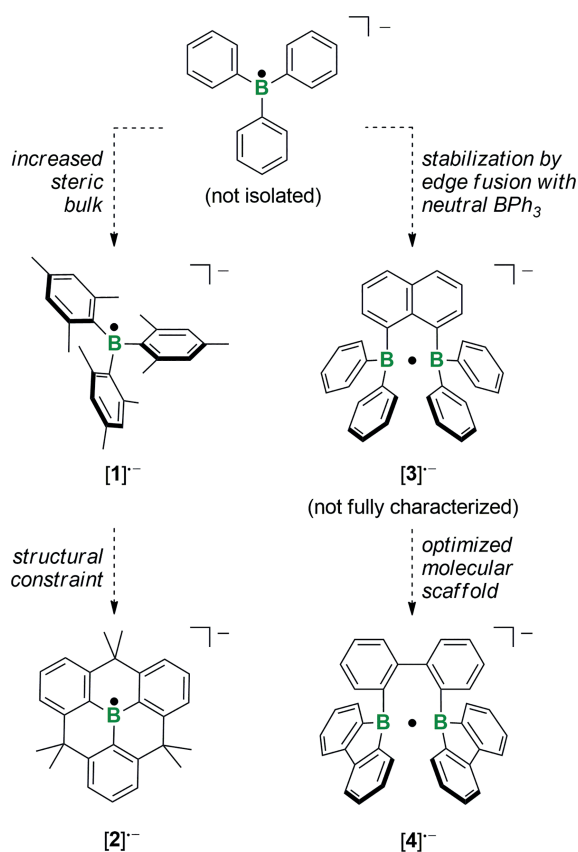
1. Synthetically Accessible Examples of Compounds Containing the General Structural Motifs [A]•− [F]•−

Structurally authenticated, mononuclear triorganoborane radicals [A]•− are rare. A sodium salt of the trimesitylborane anion, [BMe₃]^{•−} (Na[1]; Scheme 2), forms quantitatively upon single-electron reduction of **1** with 40 % Na/Hg in THF; the injection of a second electron to afford [1]^{2−} was not observed under the applied conditions.^[8] Power et al. performed an X-ray crystal structure determination of the 12-crown-4 ether solvate [Li(12-c-4)₂][1] and observed free, non-interacting [1]^{•−} radical anions.^[9] Most structural parameters of [1]^{•−} and **1** are very similar, apart from the slightly elongated B–C bonds in the monoanion. Also the propeller conformation of **1** is fully retained in [1]^{•−}, which necessarily limits the degree of π conjugation within the radical (rounded value of the dihedral angles Mes//BC₃: 50°).

An improved π delocalization of the odd electron was achieved by Yamaguchi et al., who formally merged the *ortho*-CH₃ groups of [1]^{•−} to create three methylene bridges between the aryl rings of a planarized radical [2]^{•−} (Scheme 2).^[10] X-ray crystallography on the salt [K([2.2.2]cryptand)][2] revealed that the anion [2]^{•−} in fact adopts a shallow bowl conformation, which is unique to the constrained triphenylborane framework. A structural optimization of [2]^{•−} by DFT predicted this curved local minimum geometry to be comparable in energy to the fully planar conformation. Even though the boron atom of [2]^{•−} is much more exposed to its environment than the boron atom of [1]^{•−}, Yamaguchi's radical does not decompose up to 200 °C

under inert conditions ("stabilization by structural constraint").^[11]

In the absence of structural constraint, a successively lowered steric load in triarylboranes leads to less and less well-protected boron centers and, at some point, promotes ion-pair association to such an extent that the magnetic and spectral properties of the respective radical salt are changed. This effect is nicely demonstrated with the homologous model series BMe_{3–n}Ph_n (*n* = 0–3): While all members bearing at least one Mes substituent form stable radical anions,^[12] [BPh₃]^{•−} is more labile and tends to decompose^[13] with formation of [BPh₄]^{•−} and "[BPh₂]^{•−}".^[12,14] The intermediate formation of the latter species could only be postulated when the corresponding studies were published; we will show below how closely the current state of research has approached such boryl anions (cf. [F]•−). Contrary to Na[1], Na[BPh₃] is diamagnetic in THF solution. It has been suggested that the reason lies in spin pairing through enhanced ion clustering, e.g., to form ion quadruplets (Figure 1).^[14–16] A second way to account for the observed diamagnetism is the formation of a covalent B–C bond between the boron atom of one [BPh₃]^{•−} ion and a *para*-carbon atom of a second such radical.^[16–18] The resulting quinoid molecule (Figure 1) is not only analogous to the famous "Gomberg dimer" of two [CPh₃]^{•−} radicals, but also constitutes a reasonable intermediate along the above-mentioned way from [BPh₃]^{•−} to its decomposition product [BPh₄]^{•−}. As a third viable option, a B–B rather than B–C-bond could be formed between two molecules of [BPh₃]^{•−}.^[14,19] An obvious obstacle would be the severe steric



Scheme 2. Kinetic and/or thermodynamic stabilization of the radical anion $[BPh_3]^{•-}$ through the introduction of bulky mesityl substituents (**[1]^{•-}**), the application of a structural constraint (**[2]^{•-}**), or the delocalization of the odd electron into the vacant $B(p_z)$ orbital of an adjacent neutral borane moiety, which furnishes compounds containing rare B-B 1e2c bonds (**[3]^{•-}**, **[4]^{•-}**).

and electrostatic strain experienced by the resulting diborane(6) dianion (Figure 1), however, these adverse factors could likely be overcompensated by intramolecular cation-anion attractions within its respective sodium salt. Likewise, the structural motif of the elusive hexaphenylethane, Ph_3C-CPh_3 ,^[20] has been realized by exploiting the London dispersion interactions of twelve attached *tert*-butyl substituents.^[21] Not less importantly, electrochemical studies on the reduction of BPh_3 indicated that $[BPh_3]^{•-}$ can interact not only with another such radical but also with the neutral borane to generate an adduct $[Ph_3B-BPh_3]^{•-}$ featuring a 1e2c bond (cf. **[A]^{•-}** → **[B]^{•-}**).^[14,22] The overarching lesson to be drawn from the behavior of BPh_3 after electron uptake is that the reduction chemistry of sterically undemanding triarylboranes has the potential to create fascinating new species, provided that more sophisticated molecular architectures can be designed to channel their inherent reactivity.

One viable strategy to access diboron compounds of type **[B]^{•-}** and **[C]²⁻** is to reinforce their B-B and B-B bonds by a supporting organic bridge. The formal edge fusion of two juxtaposed phenyl rings in $[Ph_3B-BPh_3]^{•-}$ leads to the 1,8-naphthalenediyl-bridged derivative **[3]^{•-}** (Scheme 2).^[23] Gabbai et al. prepared THF solutions of $K[3]$ from metallic K/18-c-6 and **3**, which remained stable at low temperatures of $-25\text{ }^\circ\text{C}$ for several weeks but decomposed when kept at room temperature. Evidence for

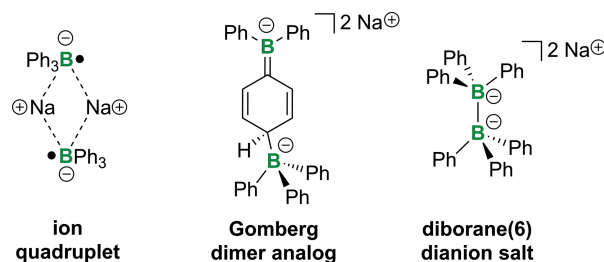
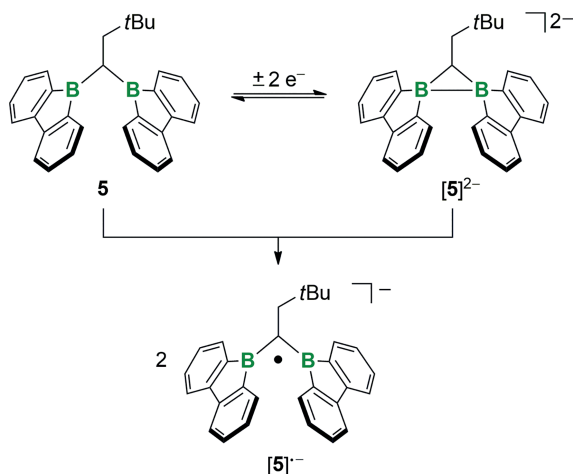


Figure 1. Conceivable dimerization modes of $Na[BPh_3]$ that have been discussed in the literature to explain the observed diamagnetism of this radical anion salt.

the radical nature of **[3]^{•-}** came from EPR spectroscopy. A characteristic seven-line signal was attributed to the hyperfine coupling of the electron spin with the nuclear spins of two magnetically equivalent ^{11}B centers ($I = 3/2$; natural abundance: 80 %). In an attempt to design an even better preorganized electron trap (**4**),^[24] our group replaced the 1,8-naphthalenediyl by a less rigid 2,2'-biphenyldiyl backbone and the two twisted diphenylboranyl fragments by strongly Lewis acidic, planar 9-borofluorenyl (BFlu) moieties.^[25,26] This way, the B...B distance of **4** is adjustable to the requirements of the aimed-for B-B bond with little energy penalty by mere rotations about B-C and C-C axes. Moreover, a closer approach of the two boron atoms now imposes less of a steric burden. Compound **4** prefers a conformation with strongly overlapping boron p_z orbitals, both in solution and in the solid state. According to X-ray crystallography, the B...B distance (2.920(6) Å)^[26] is smaller by 0.082 Å than that in the 1,8-naphthalenediyl-bridged congener **3** (3.002(2) Å). Marked differences are also apparent for the redox potentials of **3** vs. **4**: While **4** accepts an electron already at $E_{1/2} = -1.49\text{ V}$, a significantly more cathodic value of $E_{1/2} = -2.21\text{ V}$ ^[27] is required for the one-electron reduction of **3** (THF; vs. FcH/FcH^+). The injection of a single electron into **4** leads to the radical **[4]^{•-}** (Scheme 2), which has been investigated by UV/Vis and EPR spectroscopy as well as X-ray crystallography and is therefore the first example of a fully characterized compound with B-B one-electron-two-center bond ($[Li(thf)_4][4]$: $d_{BB} = 2.265(4)\text{ \AA}$; see below for a discussion of the electronic structure of **[4]^{•-}**).^[24] So far it was not possible to reduce **[4]^{•-}** further and generate the closed-shell dianion **[4]²⁻** possessing an electron-precise B-B 2e2c bond. Thus, our group developed an alternative system **5**/**[5]^{•-}**/**[5]²⁻**,^[28,29] which is capable of adopting also this third bonding state (Scheme 3). At first glance, the diborylmethane **5** may appear less suitable for B-B- or B-B-bond formation than **4** due to the inherently high strain of the resulting three-membered B_2C heterocycle. Yet, **5** is straightforwardly converted to its dianion **[5]²⁻** upon treatment with excess Li metal in toluene (cf. **[C]²⁻**). The intermediate redox state, **[5]^{•-}**, forms selectively upon comproportionation of **5** and **[5]²⁻** in THF (**5**/**[5]^{•-}**/**[5]²⁻**: $d_{BB} = 2.534(2)/2.166(4)/1.906(3)\text{ \AA}$, B-C-B bond angles = $105.5(2)/86.9(2)/73.2(1)^\circ$).^[29]

Diborane(6) dianions, such as **[5]²⁻**, are rare. Given the synthesis of this compound through simple addition of two electrons to the ditopic borane **5**, it is immediately apparent that the B-B bond should be easily oxidized and sensitive toward electrophiles. Indeed, the addition of triflic acid results in proto-



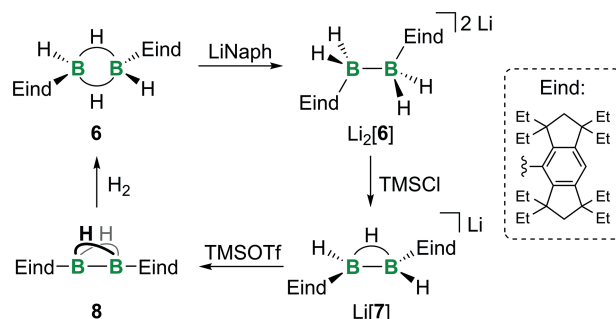
Scheme 3. The two-electron reduction of the diborylmethane **5** generates the diborane(6) dianion [5]²⁻; the comproportionation of **5** and [5]²⁻ affords the B-B-bonded radical anion [5]^{•-}.

nation and generates a new B–H–B core with 2e3c bond.^[29] Even though the apparent nucleophilicity of the B–B bond in [5]²⁻ was soon recognized as a topic of general relevance to the chemistry of diborane(6) dianions, further progress in the field had to await the availability of less sterically encumbered derivatives.

It turned out that a promising access route to such molecules is offered by the two-electron reduction of dimeric organyl(hydro)boranes (A)₂ (cf. (A)₂ → [C]²⁻): At the beginning, the two boron atoms are held together by the bridging hydrogen atoms, which can, however, move into terminal positions as the reaction progresses and thereby vacate orbitals for the incoming electrons. The basic idea dates back to the early days of Stock, who attempted to prepare the ethane isoster [H₃B–BH₃]²⁻ from B₂H₆ and Na/Hg.^[30] Today it is confirmed that the reaction actually produces Na[B₃H₈] and Na[BH₄], but scattered evidence in the literature nevertheless suggests that [H₃B–BH₃]²⁻ appears as an intermediate.^[31]

It finally took until the year 2011 for the synthesis and isolation of the diaryl derivative [6]²⁻ to be reported: Matsuo, Tamao et al. successfully undertook the double reduction of the diborane(6) **6** and decisively benefited from the huge bulk of the organic substituents (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindan-4-yl); Scheme 4).^[32] As a disadvantage, access to the core of [6]²⁻ (*d*_{BB} = 1.924(3) Å) is still severely limited and no reactions of its B–B bond with external substrate molecules have been reported so far. One can nonetheless conduct a stepwise hydride abstraction from [6]²⁻ by using Me₃SiCl or Me₃SiOTf and obtain the corresponding diborane(5) monoanion [7]⁻ or neutral diborane(4) **8**, respectively (Scheme 4; cf. [C]²⁻ → [D]⁻). In these products, a still intact B–B core is reinforced by one or two additional B–H–B 2e3c bond(s) ([7]⁻: *d*_{BB} = 1.655(2) Å; **8**: *d*_{BB} = 1.488(1) Å).^[32,33] The butterfly shape of the central B(μ-H)₂B moiety in **8** was corroborated by single-crystal neutron diffraction on a ²H and ¹¹B isotope-labeled derivative.^[32]

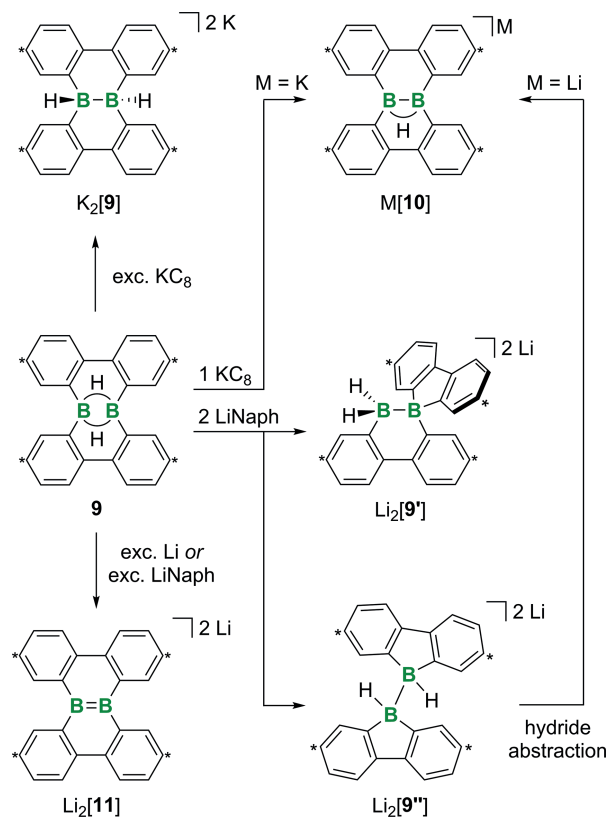
A shortcoming of 1,2-diaryl diboranes Ar(H)B(μ-H)₂B(H)Ar, which limits their utility as starting materials for diborane(6)-dianion syntheses, lies in their tendency to form 1,1,2,2-tetraaryl



Scheme 4. The bulky diborane(6) derivative **6** undergoes two-electron reduction to form the diborane(6) dianion [6]²⁻; stepwise hydride abstraction from [6]²⁻ leads to the hydrogen-bridged diborane(5) monoanion [7]⁻ and neutral diborane(4) **8**. Compound **8** can activate H₂ and thereby close the cycle. LiNaph = Li[C₁₀H₈]; TMS = SiMe₃; OTf = OSO₂CF₃.

diboranes Ar₂B(μ-H)₂BAR₂ or even triarylboranes BAR₃ under substituent scrambling, as soon as the Ar substituents become smaller.^[34]

Our group thus took advantage of the structurally constrained, doubly 2,2'-biphenyldiyl-bridged diborane(6) **9**^[26,28,35] to prepare the sterically little encumbered diborane(6) dianion [9]²⁻ (Scheme 5). The compound K₂[9], featuring a *trans*-HB–BH core, was obtained upon reduction of **9** with 20 equiv. of KC₈



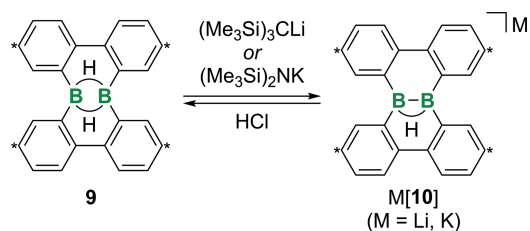
Scheme 5. The reduction of the doubly 2,2'-biphenyldiyl-bridged diborane(6) **9** provides access to diborane(6) dianions ([9]²⁻, [9']²⁻, [9'']²⁻), a diborane(5) monoanion ([10]⁻), and a diborane(4) dianion ([11]²⁻). The reaction outcome depends on the nature of the alkali metal employed and the number of reduction equivalents used. B–B-bond formation can be accompanied by hydride-abstraction and Wagner-Meerwein-type phenyl-shift reactions (* = *tert*-butyl).

in THF (83 % yield; cf. **(A)**₂ → **[C]**²⁻).^[36] An X-ray crystal structure analysis of the thf solvate [K₂(thf)₄]**[9]** revealed a twisted dianion and a B–B-bond length of 1.755(4) Å. Further studies on the reduction behavior of **9** have provided detailed insight into a surprisingly rich and delicate chemistry that is strongly influenced by (i) the number of reduction equivalents and (ii) the nature of the alkali metal employed.

Variation of the parameter (i): The use of only 1 equiv. of KC₈ afforded the diborane(5) monoanion salt K**[10]** as the main product (58 %; Scheme 5). The current view of the reaction mechanism underlying the formation of **[10]**⁻ assumes an initial twofold reduction of **9** and a subsequent hydride transfer from the resulting dianion **[9]**²⁻ to residual Lewis acidic starting material **9** (which can ultimately accept up to two hydride ions).^[36] If the reducing agent is added in a large excess of 20 equiv. KC₈, the starting material **9** is quenched rapidly so that no hydride transfer takes place and K₂**[9]** can be isolated in high yields.

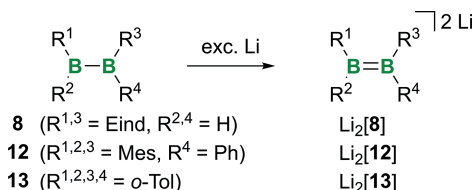
Variation of the parameter (ii): Treatment of **9** with excess Li metal or the homogeneous reducing reagent lithium naphthalene (LiNaph) in THF does not lead to the formation of the diborane(6) dianion salt Li₂**[9]**, as it would be analogous to the case of the reaction with excess KC₈. Rather, the diborane(4) dianion **[11]**²⁻ is generated and was isolated as its thf solvate [Li(thf)₃]₂**[11]** (Scheme 5; cf. **(A)**₂ → **[E]**²⁻).^[36] Due to the higher hydride-ion affinity of Li⁺ compared to K⁺, Li₂**[9]** should eliminate LiH more readily than K₂**[9]** eliminates KH, provided that electrons are present in sufficient supply to replenish electron octets on both boron atoms via B=B-double bond formation. This conclusion was further validated by the controlled two-electron reduction of **9** using only 2 equiv. of LiNaph. Under these conditions, the reaction stops at the stage of two isomeric diborane(6) dianion salts, Li₂**[9'**'] and Li₂**[9''**']', both of which still contain two hydride ligands (Scheme 5).^[36] Along the reaction sequence from **9** via Li₂**[9'**'] to Li₂**[9''**']', the original dibenzo[*g,p*]chrysene-like scaffold is transformed into two mutually connected borafluorene moieties through a stepwise two-fold Wagner-Meerwein-type rearrangement at the B₂ core.

Importantly, the removal of one hydride ion from **[9'**']²⁻ restores a dibenzo[*g,p*]chrysene framework as it forms the H-bridged diborane(5) monoanion **[10]**⁻ (cf. **[C]**²⁻ → **[D']**⁻).^[37] In this way **[10]**⁻ is obtained in only moderate yields due to its pronounced sensitivity toward the Lewis acids used to abstract the hydride substituent from **[9'**']²⁻ (see below). A targeted synthesis of **[10]**⁻ was accomplished through the notable deprotonation of its precursor borane **9** (Scheme 6; cf. **(A)**₂ → **[D']**⁻).^[38] The key to the quantitative conversion to **[10]**⁻ was the prevention of an undesired cleavage of the diborane(6) framework by using bulky, non-nucleophilic Brønsted bases such as (Me₃Si)₃ClLi or (Me₃Si)₂NK. X-ray crystal structure determinations of [Li(OEt)₂]**[10]** and [K(thf)₂]**[10]** revealed differently twisted anions; in both compounds, the respective counter cation coordinates the B–B bond (av. 1.665 and 1.651(6) Å; see Table 1 below) from the side opposite the residual μ-H atom. A further deprotonation of the already negatively charged **[10]**⁻ is possible in principle. However, the obtained yields of the diborane(4) dianion **[11]**²⁻ are below 5 %.^[38]



Scheme 6. The deprotonation of a seemingly hydridic, B⋯B-bridging hydrogen atom in the diborane(6) **9** establishes a B–B σ bond in the diborane(5) monoanion **[10]**⁻. Protonation of this bond in **[10]**⁻ leads back to **9** (* = *tert*-butyl).

An alternative route to diborane(4) dianions **[R₂B=BR₂]²⁻** is based on the two-electron reduction of neutral diborane(4) precursors R₂B–BR₂ (cf. **E** → **[E]**²⁻).^[39] The earliest example, [Li(OEt)₂]₂[Mes₂B=B(Ph)Mes] (Li₂**[12]**; Scheme 7), was published by Power et al.^[40] The scope of the general approach was later expanded to the synthesis of the monoanion radical [Mes₂B–B(Ph)Mes]⁻ (**[12]**⁻), which features a one-electron π bond.^[41,42] The gradual build-up of π bonding along the **12**/**[12]**⁻/**[12]**²⁻ series is thus conceptually related to the increasing degree of σ bonding in **5**/**[5]**⁻/**[5]**²⁻ (see Scheme 3). Recently, the Yamashita group presented a somewhat less sterically shielded derivative, [Li(thf)₂]₂[(*o*-Tol)₂B=B(*o*-Tol)₂] (*o*-Tol = *ortho*-tolyl; Li₂**[13]**; Scheme 7).^[43,44] The solid-state structures of both **[E]**²⁻-type compounds reveal contact-ion pairs in which the respective B=B double bond is coordinated by two Li⁺ cations from above and below. This geometric arrangement is comparable to the B(μ-H)₂B core in diboranes(6), which can be described as containing a B=B double bond with two embedded protons (see section 3 for more details).^[40] Despite its distinct butterfly-shaped structure, also Tamao's neutral diborane(4) **8** accepts two electrons from Li metal in THF to form the diborane(4) dianion salt Li₂**[8]**. Different from [Li(OEt)₂]₂**[12]** and [Li(thf)₂]₂**[13]**, the salt [Li(thf)₂]₂**[8]** shows as a largely planarized Li₂B₂C₂H₂ core in the solid state, which has been attributed to attractive B–H⋯Li⁺ interactions.^[33,45]



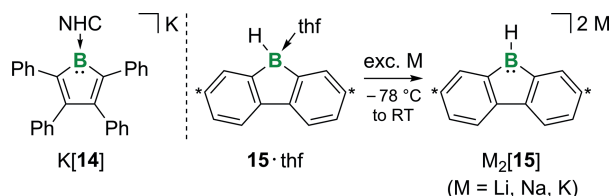
Scheme 7. Synthesis of B=B-bonded diborane(4) dianions **[8]**²⁻, **[12]**²⁻, and **[13]**²⁻ through the two-electron reduction of neutral diborane(4) precursors using excess Li metal. In compound **8**, R^{2,4} are not terminal, but bridging in the form of B–H–B 2e3c-bonds (see Scheme 4).

A challenge that all syntheses based on the reduction of non-heteroatom-substituted diboranes(4) must face is that these precursors are already very reactive. For example, even Yamashita's fairly well protected (*o*-Tol)₂B–B(*o*-Tol)₂ (**13**; Scheme 7) experiences B–B-bond cleavage in the presence of a variety of compounds including H₂, CO, isocyanides, nitriles, and azo compounds.^[46] The four-electron reduction of neutral diboranes(6) Ar₂B(μ-H)₂BAr₂ with in situ elimination of two hydride ions avoids the use of already subvalent starting mate-

rials. This approach, which even provides the so far least sterically loaded B=B-containing dianion (i.e., **[11]**²⁻; see Scheme 5), is therefore a serious competitor in terms of diborane(4)-dianion synthesis.

Following the model of the “Wanzlick equilibrium” between donor-substituted olefins and singlet carbenes,^[47] diborane(4) dianions [Ar₂B=BAR₂]²⁻ can be viewed as formal dimers of still elusive free diarylboryl anions [:BAR₂]⁻ (cf. 2 **[F]**⁻ → **[E]**²⁻).^[37,40,48] Yet, early theoretical calculations on the model system Li₂[H₂B=BH₂] → 2 Li[:BH₂] (¹A₁) indicated prohibitively high dissociation energies.^[49] The fundamental problem concerning singlet-state boryl anions is that they are electron-rich and -poor at the same time, because they have an excess of charge density in one B(sp²) orbital and a shortage of electrons in the B(p_z) orbital.^[50] On the other hand, precisely because of this peculiar electronic structure, type **[F]**⁻ compounds are expected to (i) exhibit boron-centered nucleophilicity or (ii) undergo carbene-like insertion/cycloaddition reactions and thus could serve as valuable building blocks for advanced organoboron compounds.

In 1975, Eisch, Tamao et al. reported that irradiation of Na[BPh₄] (254 nm, THF) led to the reductive elimination of biphenyl and produced “a solution reagent having the properties of sodium diphenylborate(I)” (Na[:BPh₂]).^[51] This report sparked a heated debate about the true nature of the “solution reagent”,^[52] and continues to inspire research today.^[53] Braunschweig’s isolable tetraphenylborolyl–NHC complex **K[14]** (Scheme 8) has been acclaimed as a base-stabilized boryl anion and actually behaves like a π nucleophile toward MeI, affording an NHC-coordinated 1-methyl-2,3,4,5-tetraphenylborole.^[54,55] With the 9*H*-9-borafluorene dianion **[15]**²⁻, our group developed a related borole-anion system, which contains a “hydride ligand” in place of the NHC ligand (Scheme 8; cf. **[A]**²⁻).^[37,56] It was envisaged that **[15]**²⁻ would have the following advantages over **[14]**⁻: (i) a significantly lower steric shielding of the boron center due to the absence of four dangling Ph substituents and the bulky 1,3-dimesitylimidazolidin-2-ylidene base, (ii) a higher accumulation of negative charge onto the boron atom, because the H substituent, unlike the NHC, does not act as a π acceptor in the delocalization of electrons away from the boron center, and (iii) an easier removal of the hydride compared to the NHC ligand from the products of the aimed-for nucleophilic substitution reactions (see section 2). The dianion salts M₂**[15]** (M = Li–K) have been prepared in essentially quantitative yields through the double reduction of the monomeric adduct **15**·thf^[57] with

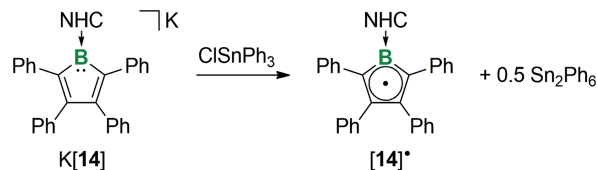


Scheme 8. The borolyl anion **[14]**⁻ has been stabilized through coordination of an N-heterocyclic carbene (NHC = 1,3-dimesitylimidazolidin-2-ylidene). The borane dianion **[15]**²⁻ has been synthesized by two-electron reduction of the 9*H*-9-borafluorene adduct **15**·thf and contains a hydride ligand at boron (* = *tert*-butyl).

excess alkali metal M in THF. The key to success was the strict adherence to a carefully elaborated temperature regime during the synthesis process.^[37]

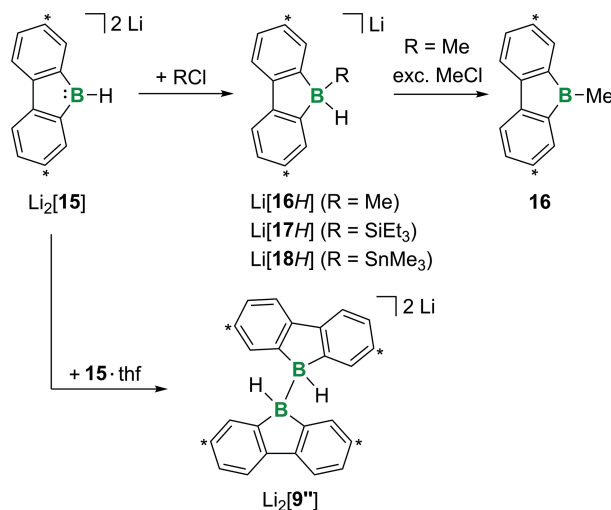
2. Fundamental Reactivity Patterns

The chemistry of boron-centered radicals, such as **[A]**[·],^[58] has been covered by two recent review articles.^[6a,6b] Suffice it to say here that Braunschweig’s NHC-supported boryl anion **[14]**⁻ undergoes single-electron-transfer (SET) reactions when treated with chlorotriorganylstannanes ClSnR₃ (Scheme 9).^[59] In the case of R = Ph, the resulting neutral borolyl radical **[14]**[·] could be isolated and structurally characterized (with Sn₂Ph₆ formed as a by-product), whereas **[14]**[·] in the case of R = Me was only an intermediate that reacted further to form a B–SnMe₃ bond. The occurrence of this product of a formal nucleophilic substitution reaction led the authors to conclude “that the apparent nucleophilicity of the borolyl anion [...] is in fact a consequence of radical reactivity”.^[59]



Scheme 9. The borolyl anion **[14]**⁻ can be transformed into the isolable radical **[14]**[·] through one-electron oxidation with ClSnPh₃.

Our 9*H*-9-borafluorene dianion salt Li₂**[15]** (cf. **[A]**²⁻) reacts with the electrophiles MeCl, Et₃SiCl, Me₃SnCl as a formal boron nucleophile (Li**[16H]**–Li**[18H]**; Scheme 10).^[37] When working with excess MeCl, the reaction does not stop at the stage of the methyl(hydrido)borate Li**[16H]**, but a second equivalent of

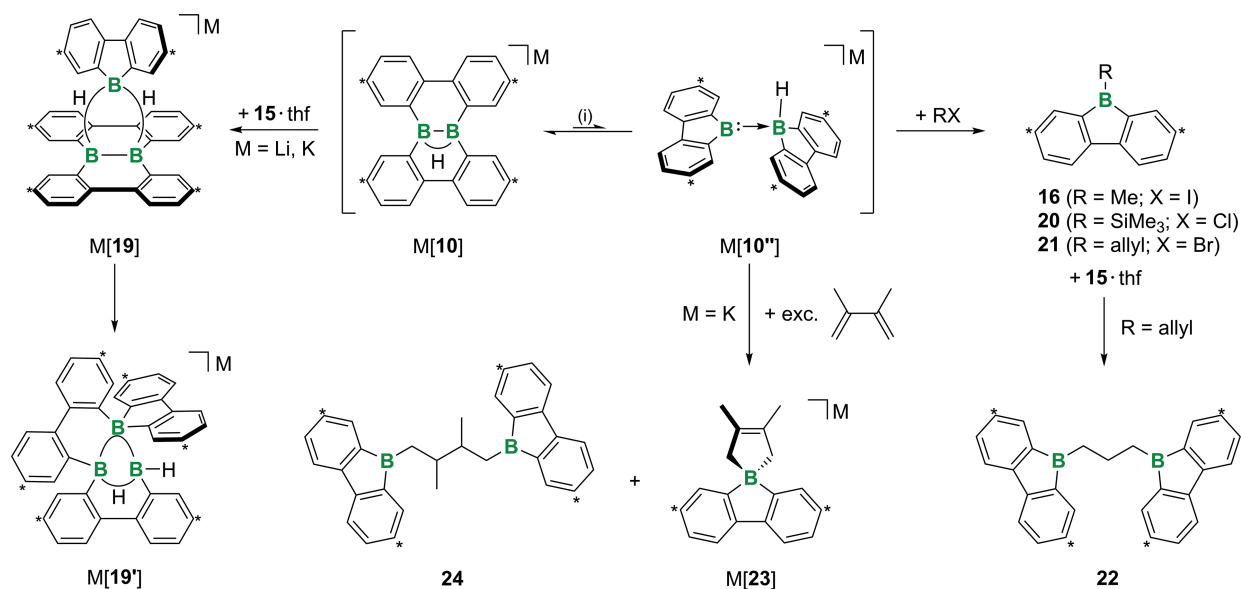


Scheme 10. The 9*H*-9-borafluorene dianion **[15]**²⁻ behaves as a B-centered nucleophile toward B-, C-, Si-, or Sn-centered electrophiles; both open- and closed-shell pathways can contribute to product formation. In a proof-of-principle experiment, the methylborane **16** has been prepared through hydride abstraction from the intermediate **[16H]**⁻, which proves that **[15]**²⁻ can act as a synthetic equivalent of the corresponding boryl anion (* = *tert*-butyl).

MeCl acts as an in situ hydride-abstrating reagent to yield the neutral methylborane **16**. It is thus safe to state that $[\mathbf{15}]^{2-}$ can indeed behave as a hydride adduct of the still unknown free boryl anion $[\text{:BFlu}]^-$ and be used as its synthesis equivalent. Evidence was found for a substrate dependence of closed-shell (presumably preferred for MeCl and Et_3SiCl) vs. open-shell pathways (which contribute in the cases of MeI, Me_3SnCl , and the fast radical clock (bromomethyl)cyclopropane). A particularly noteworthy reaction that takes place between $\text{Li}_2[\mathbf{15}]$ and **15**·thf establishes a B–B bond and thus enables the targeted synthesis of the diborane(6) dianion salt $\text{Li}_2[\mathbf{9}']$ (Scheme 10).^[37] Power et al. serendipitously obtained a dianion with the same core structure as $[\mathbf{9}']^{2-}$ when they reduced 2,6-Trip₂C₆H₃BBr₂ with KC_8 in Et_2O (Trip = 2,4,6-*i*Pr₃C₆H₂). Regarding the reaction mechanism, they postulated an association of two borate radical anion fragments with 9-borafluorenyl structures.^[60] A second related example stems from Finze's group, who achieved the synthesis of the remarkably inert $[(\text{NC})_3\text{B}-\text{B}(\text{CN})_3]^{2-}$ from $[\text{:B}(\text{CN})_3]^{2-}$ and $[\text{FB}(\text{CN})_3]^-$. Here, an $\text{S}_{\text{N}}2$ mechanism involving a triply negatively charged transition state seems to be effective.^[61] Given this background, the reaction underlying the synthesis of $\text{Li}_2[\mathbf{9}']$ from $\text{Li}_2[\mathbf{15}]$ and **15**·thf may as well be an example of either a comproportionation reaction with subsequent radical-radical coupling in the solvent cage (i.e., $[\mathbf{A}]^{2-} + \mathbf{A} \rightarrow 2 [\mathbf{A}]^- \rightarrow [\mathbf{C}]^{2-}$)^[62] or of direct Lewis acid-base pairing (i.e., $[\mathbf{A}]^{2-} + \mathbf{A} \rightarrow [\mathbf{C}]^{2-}$). The dianion $[\mathbf{9}']^{2-}$ shows the expected sensitivity toward air and moisture. Moreover, it easily loses one hydride substituent when it encounters a Lewis acid (such as **15**·thf), whereupon the H-bridged diborane(5) monoanion $[\mathbf{10}]^-$ is formed (cf. $[\mathbf{C}]^{2-} \rightarrow [\mathbf{D}]^-$).^[37] Efforts to abstract the second hydride ion with the aim of obtaining the corresponding free diborane(4) **11** have so far been unsuccessful. The same is true for attempts to generate **11** by the two-electron oxidation of the B=B-centered compound $[\mathbf{11}]^{2-}$. Notably,

Tamao's system $[\mathbf{6}]^{2-}/[\mathbf{8}]^{2-}$ is capable of performing all three conversions (i.e., $[\mathbf{6}]^{2-} \rightarrow [\mathbf{7}]^- + "1 \text{ H}^-"$, $[\mathbf{6}]^{2-} \rightarrow \mathbf{8} + "2 \text{ H}^-"$, and $[\mathbf{8}]^{2-} \rightarrow \mathbf{8} + "2 \text{ e}^-"$), probably because the two bridging hydrogen atoms in **8** contribute to an alleviation of the electron deficiency at the two neighboring boron atoms in the neutral diborane(4) state.^[32,33,63]

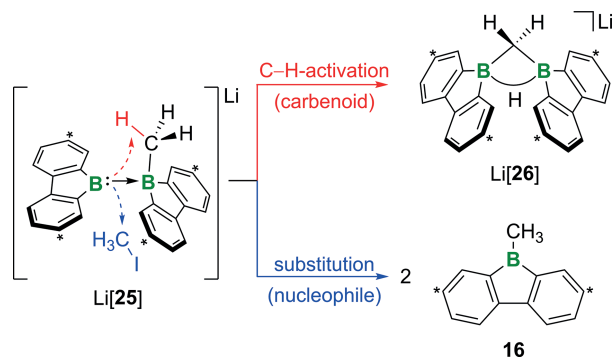
Even though the diborane(5) monoanion $[\mathbf{7}]^-$ is accessible in good yields through hydride abstraction from $[\mathbf{6}]^{2-}$, no boron-centered reactivity has been reported. In stark contrast, the related derivative $[\mathbf{10}]^-$ features an electron-rich B–B σ bond with nucleophilic character. While protonation^[38] leads back to the diborane(6) **9**, the addition of the 9*H*-9-borafluorene adduct **15**·thf provides the B₃ cluster $[\mathbf{19}]^-$, an organyl derivative of the prominent $[\text{B}_3\text{H}_8]^-$ anion (Scheme 11).^[64] The kinetic product $[\mathbf{19}]^-$ has a tendency to isomerize to the thermodynamic product $[\mathbf{19}']^-$ via hydride and phenyl shifts. Such reversible Wagner-Meerwein-type rearrangements are commonly encountered in the chemistry of **9** and its reduction products (compare e.g., $[\mathbf{9}]^{2-}$ vs. $[\mathbf{9}']^{2-}$ vs. $[\mathbf{9}'']^{2-}$; Scheme 5). While these rearrangements were initially perceived as a nuisance, it soon turned out that they rather are the prerequisite for an intriguing follow-up chemistry providing access to synthetically useful "masked 9-borafluorenyl anions", $[\text{:BFlu}]^-$.^[37,48,64] DFT calculations on $[\mathbf{10}]^-$ revealed the existence of four isomeric and energetically comparable minimum structures. Especially the second most favorable one, $[\mathbf{10}']^-$, contributes decisively to the understanding of the reactivity of $[\mathbf{10}]^-$ (Scheme 11).^[64] As a $\text{B}(\text{sp}^2)\text{-B}(\text{sp}^3)$ isomer, $[\mathbf{10}']^-$ can be regarded as an adduct between $[\text{:BFlu}]^-$ (as Lewis base) and HBFu (as Lewis acid; **15**) and is therefore reminiscent of the adducts $[\text{pinB-Bpin}(\text{OR})]^-$ of bis(pinacolato)diboron which are widely used as sources of $[\text{:Bpin}]^-$ nucleophiles.^[65] In agreement with this view, THF solutions of $[\mathbf{10}]^-$ react with MeI or Me_3SiCl to give 9-Me- (**16**) or 9-SiMe₃-9-borafluorene (**20**) and the by-product **15**·thf (Scheme 11).^[64] When the unsatu-



Scheme 11. Evidence for a nucleophilic B–B bond in the diborane(5) monoanion $[\mathbf{10}]^-$ has been gained through adduct formation with **15**·thf, which led to organic derivatives of the triborate anion $[\text{B}_3\text{H}_8]^-$ ($[\mathbf{19}]^-$, $[\mathbf{19}']^-$). The computed structure of the isomer $[\mathbf{10}']^-$, which is energetically comparable to $[\mathbf{10}]^-$ ($\Delta G = 5.1 \text{ kcal mol}^{-1}$), is useful to understand the behavior of $[\mathbf{10}]^-$ as a boryl-anion equivalent in nucleophilic substitutions (cf. the formation of **16**, **20**, or **21**) and electrocyclic reactions (cf. the formation of $[\mathbf{23}]^-$). Compounds **22** and **24** are hydroboration products of the released **15**·thf (* = *tert*-butyl).

rated electrophile allyl bromide is used, the product of the nucleophilic substitution reaction, **21**, traps the in situ generated **15**·thf by a hydroboration reaction at its terminal olefin to generate the 1,3-bis(9-borafluorenyl)propane **22**. The chimeric nature of the $[\text{:BFlu}]^-$ fragment as a nucleophilic or carbenoid species has been proven by treating $[\mathbf{10}]^-$ with the well-established carbene-trapping reagent 2,3-dimethyl-1,3-butadiene (DMB) so that the spiroborate $[\mathbf{23}]^-$ is formed via a [4+1]-electrocyclization; additional DMB is consumed in a double hydroboration reaction with the by-product **15**·thf to give **24** (Scheme 11).^[64]

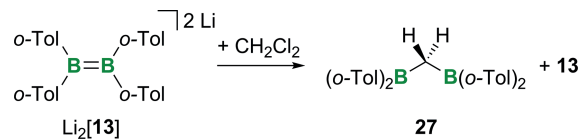
Also the reactivity pattern of the diborane(4) dianion $[\mathbf{11}]^{2-}$ can be explained similarly as in the case of $[\mathbf{10}]^-$. For example, treating $\text{Li}_2[\mathbf{11}]$ with excess MeI yields 2 equiv. of 9-Me-9-borafluorene (**16**), whereas the same reaction with only 1 equiv. of MeI generates a mixture of **16**, the diborylmethane-hydride adduct $\text{Li}[\mathbf{26}]$, and residual $\text{Li}_2[\mathbf{11}]$ (Scheme 12).^[48] It was plausibly assumed that in a first general step the B=B double bond of $[\mathbf{11}]^{2-}$ acts as a π nucleophile toward one molecule of MeI. The methylation of one boron atom, accompanied by two Wagner-Meerwein-type rearrangements, affords the $\text{B}(\text{sp}^2)\text{-B}(\text{sp}^3)$ intermediate $[\mathbf{25}]^-$, formally an adduct between $[\text{:BFlu}]^-$ and MeBFlu (**16**) and a close relative of $[\mathbf{10}']^-$ (see Scheme 11). Accompanied by B–B-bond cleavage, two different scenarios can occur: (i) If MeI is available in sufficient supply to trap $[\text{:BFlu}]^-$ in a nucleophilic substitution reaction, the observed second equivalent of **16** is generated. (ii) As soon as MeI is no longer available, $[\text{:BFlu}]^-$, an isoster of the singlet carbene 9-fluorenylidene,^[66] can insert into a C–H bond of the methyl group already installed in $[\mathbf{25}]^-$ to give $[\mathbf{26}]^-$ (Scheme 12; another example of a C–H-activation reaction through a boryl anion has been postulated in ref.^[41]).



Scheme 12. It has been suggested that the $\text{B}(\text{sp}^2)\text{-B}(\text{sp}^3)$ anion $[\mathbf{25}]^-$ is formed when $[\mathbf{11}]^{2-}$ is treated with 1 equiv. MeI. The occurrence of such an intermediate would explain the behavior of $[\mathbf{11}]^{2-}$ as a masked boryl anion in C–H activations (to give $[\mathbf{26}]^-$) and nucleophilic substitution reactions (to give **16**; * = *tert*-butyl).

We finally emphasize that, analogous to the reactions of $\text{Li}[\mathbf{10}]/\text{Li}_2[\mathbf{11}]$ with MeI and $\text{Li}_2[\mathbf{15}]$ with MeCl, Yamashita's diborane(4) dianion salt $\text{Li}_2[\mathbf{13}]$ reacts with CH_2Cl_2 as a formal B-centered nucleophile to furnish the diborylmethane **27** (65 %; Scheme 13). As an oxidized side product, the neutral diborane(4) **13** was observed in non-negligible amounts (15 %), which points toward twofold single-electron transfer (SET) processes taking place during the reaction.^[43] Similar to the

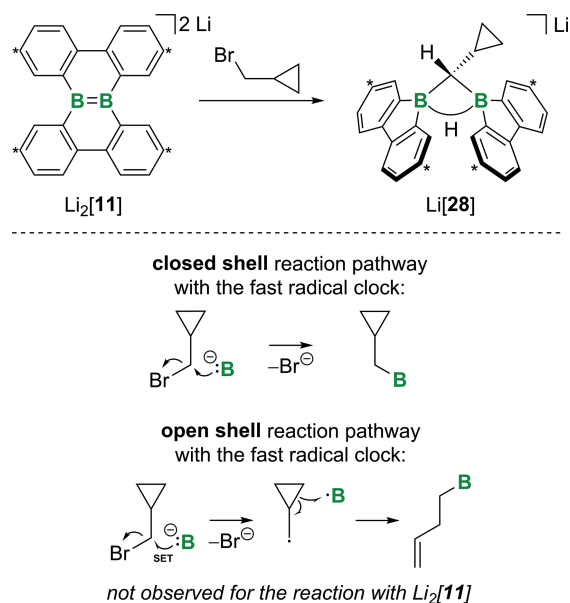
cases of other subvalent boron species mentioned above, SET processes with subsequent radical reactions seem to have a negative impact on the chemoselectivity of this transformation.



Scheme 13. The diborylmethane **27** forms when the diborane(4) dianion $[\mathbf{13}]^{2-}$ reacts with CH_2Cl_2 ; the formation of the neutral diborane(4) **13** indicates the involvement of SET processes.

In stark contrast, the conversion of $\text{Li}_2[\mathbf{11}]$ with 1 equiv. of the radical clock (bromomethyl)cyclopropane occurred under selective formation of $\text{Li}[\mathbf{28}]$ without any indication for a radical-induced opening of the three-membered ring (Scheme 14).^[48]

Taken together, numerous recent publications have shown that reduced aryl(hydro)boranes are capable of performing useful reactions that were largely lacking in the boron chemist's toolbox still 10 years ago. Since the reactivity of a compound is determined by its specific bonding situation, the next section has been devoted to the peculiar electronic structures of subvalent organoboranes.



Scheme 14. Top: The preservation of the cyclopropyl ring in the diborylmethane adduct $[\mathbf{28}]^-$, which is formed by the reaction of the diborane(4) dianion $[\mathbf{11}]^{2-}$ with (bromomethyl)cyclopropane, excludes a radical pathway and indicates a closed-shell scenario with boron-centered nucleophilicity. Bottom: Expected products of closed-shell vs. open-shell reactions between subvalent boron species and the fast radical clock (bromomethyl)cyclopropane (* = *tert*-butyl).

3. Remarks on the Bonding Situations from an Experimentalist's Perspective

One of the structurally simplest organoboranes described herein is BMe_3 (**1**). Despite its propeller shape, the correspond-

ing, largely isostructural radical $[1]^-$ possesses a considerably delocalized odd electron, as has been deduced from experimental observations such as reactivity studies,^[67] EPR spectra,^[68] and electrochemical measurements.^[14] Furthermore, an inspection of the computed LUMO of **1**, which should be qualitatively similar to the SOMO of $[1]^-$, reveals contributions of the aryl π systems in addition to a major contribution of the p_z orbital at the central boron atom.^[69] The transition from propeller-shaped **1** to planarized **2** (see Scheme 2) should be advantageous for electron uptake for both thermodynamic and kinetic reasons: It (i) improves the embedding of the boron p_z orbital in the conjugation path and (ii) results in a rigid molecular architecture so that the structural changes that take place upon reduction to $[2]^-$ remain moderate (high electron-transfer rate due to a small internal reorganization energy).^[70]

One-electron–two-center (1e2c) bonds, as found in the B•B radical anions $[3]^-$, $[4]^-$, and $[5]^-$ (see Scheme 2 and Scheme 3), are not as exotic as they may appear, but rather at the core of quantum chemistry. As early as 1931, Pauling proposed a H•H 1e2c bond in $[H_2]^+$,^[71] and still today this simplest molecule of all serves as a textbook compound in which electron–electron interactions are absent, so that an analytical solution of its electronic Schrödinger equation within the Born–Oppenheimer approximation is possible.^[72] Comparisons of **4** with various reference systems led to the conclusion that its high electron affinity is mainly due to the strong overlap of the two boron-based p_z orbitals and not just attributable to better π delocalization within the BFlu as opposed to the BPh₂ substituents in **3**. One-electron injection into **4** led to a shortening of the B••B distance (2.920(6) Å) by 0.655 Å to a value of 2.265(4) Å in $[Li(thf)_4][4]$, in line with the emergence of a bonding interaction. From the well-resolved seven-line EPR spectrum of $[4]^-$, a hyperfine coupling constant $a(^{11}B) = 4.8 \pm 0.1$ G was obtained and interpreted as pointing toward a dominant $2p_z\sigma(B\cdot B)$ orbital combination. The highly localized nature of the computed SOMO and spin density showed that the added electron is largely restricted to the void space between the two boron centers.^[24] Also along the sequence **5**/ $[5]^-$ / $[5]^{2-}$, the B••B distances (2.534(2)/2.166(4)/1.906(3) Å) decrease continuously, and so do the B–C–B bond angles (105.5(2)/86.9(2)/73.2(1)°), as one would expect when the B••B interaction becomes successively stronger (see Table 1 for the counter cations).^[29] The ready accessibility of $[5]^{2-}$ conveys the important message that the electrostatic repulsion, which builds up between adjacent negative charges, does not automatically prevent the formation of a B–B σ bond – especially when the two charge carriers are added to an adequately pre-organized two-electron trap. Nonetheless, electrostatic interactions certainly contribute to the comparatively long B–B σ bonds in diborane(6) dianions. Additional parameters that affect the bond lengths are reflected in the series $Li_2[6]$, $Na_2[9']$, $Li_2[9'']$, $K_2[9]$, and $[N_2H_6][B_2(CN)_6]$ ($d_{BB} = 1.924(3)$, $1.822(4)$, $1.789(7)$, $1.755(4)$, and $1.784(1)$ Å).^[32,36,37,61b] These factors are (i) steric effects ($[6]^{2-}$ vs. $[9'']^{2-}$), (ii) counter-cation effects ($Na_2[9']$ vs. $Li_2[9'']$), (iii) the consequences of incorporating the HB–BH core into a cyclic framework ($[9'']^{2-}$ vs. $[9]^{2-}$), and (iv) the result of a reduced Coulomb stress due to the presence of small, strongly electron-

withdrawing cyano substituents ($[B_2(CN)_6]^{2-}$). All in all, the implementation of arenyl bridges as in $[9]^{2-}$ appears to be the most efficient way to counter the divergent Coulomb forces. Despite their long B–B bonds not supported by such bridging ligands, both $[6]^{2-}$ and $[9']^{2-}$ are diamagnetic and do not appear to suffer from homolytic bond cleavage under ambient conditions (cf. $2[A]^- \rightleftharpoons [C]^{2-}$).^[32,36,37] The same applies to the B₂C heterocyclic compound $[5]^{2-}$, irrespective of its strained three-membered ring.^[29] It is, though, possible to reductively cleave the B–B bonds of $[5]^{2-}$ and $[9']^{2-}$ by adding alkali metals to their THF solutions and obtain a tetraanionic diborylmethane or 2 equiv. of $[15]^{2-}$, respectively.^[37,73]

Table 1. Crystallographically determined B••B distances in neutral ditopic boranes, one-electron reduced ditopic boranes, and diborane(6) dianions.

Organoboron entity	Complete formula	B••B [Å]	Ref.
4	4	2.920(6)	[26]
$[4]^-$	$[Li(thf)_4][4]$	2.265(4)	[24]
5	5	2.534(2)	[28]
$[5]^-$	$[Li(thf)_4][5]$	2.166(4)	[29]
$[5]^{2-}$	$[Li(OEt_2)_2][Li(OEt_2)][5]$	1.906(3)	[29]
6	6	1.810 ^[a]	[32]
$[6]^{2-}$	$[Li(thf)_2][6]$	1.924(3)	[32]
$[7]^-$	$[Li(dme)_3][7]$	1.655(2)	[32]
8	8	1.488(1)	[33]
$[9]^{2-}$	$[K_2(thf)_4][9]$	1.755(4)	[36]
$[9']^{2-}$	$[Li(thf)_3][Li(thf)_2][9']$	1.810(5)	[36]
$[9'']^{2-}$	$[Li(thf)_3][Li][9'']_2$	1.789(7)	[36]
$[9''']^{2-}$	$[Na(thf)_3]_2[9''']$	1.822(4)	[37]
$[10]^-$	$[Li(OEt_2)_2][10]$	1.665 ^[b]	[38]
$[10]^-$	$[K(thf)_2][10]$	1.651(6)	[36]
$[B_2CN_6]^{2-}$	$[N_2H_6][B_2(CN)_6]$	1.784(1)	[61b]

[a] Computed value; experimental data are not available. [b] Averaged value; the crystal lattice contains two plus two half crystallographically independent molecules in the asymmetric unit with $d_{BB} = 1.664(5)$, $1.662(5)$, $1.678(7)$, and $1.656(6)$ Å.

The previous discussion of bond lengths included only B(sp³)–B(sp³) dianions. We will next keep the coordination numbers constant at a value of four but allow for different charges and boron hybridization states. The B••B distances along the sequence $Li_2[6]$ (1.924(3) Å) > $Li[7]$ (1.655(2) Å) > **8** (1.488(1) Å) and between the two compounds $K_2[9]$ (1.755(4) Å) > $K[10]$ (1.651(6) Å) vary remarkably (Table 1), which is best understood by first examining the pristine diborane(6). B₂H₆ can be described by reference to essentially four canonical forms. Two of them, **GH**₂ (36 % relative contribution) and **G'H**₂ (6 % relative contribution) are shown in Figure 2: **GH**₂ consists of a monoanionic B–B bonded fragment and one proton that interacts with the σ bond; **G'H**₂ can be viewed as a dianionic ethylene analogue $[H_2B=BH_2]^{2-}$ ($[G']^{2-}$) possessing two protons embedded in the π -electron cloud.^[74] Canonical forms similar to **GH**₂ and **G'H**₂ are also useful for modeling the diborane(5) anions $[7]^-$ and $[10]^-$ by a monoprotonated diborane(4) dianion $[G'H]^-$.^[64] Fittingly, the experimentally determined B–B bond lengths in $Li[7]$ and $Li[10]$ (1.655(2) and av. 1.665 Å) are not too much longer than the B=B bonds in $Li_2[11]$ (1.608(4)–1.641(6) Å; Table 1).^[32,36,38,75] To complete the picture, the linear CBBC skeleton of the diborane(4) **8** is closely related to that of a doubly proton-bridged diboryne dianion **HH**₂ (Figure 2).^[33,76] Each of

these two protons interacts with one of two mutually orthogonal π orbitals forming the B≡B triple bond, which accounts for the butterfly shape of **8**.

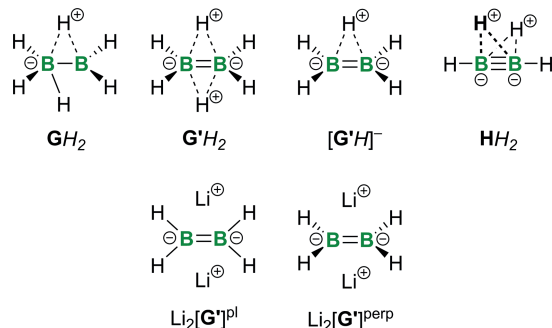


Figure 2. Selected canonical forms describing the diborane(6) B_2H_6 (GH_2 , $G'H_2$), the diborane(5) anion $[B_2H_5]^-$ ($[G'H]^-$), and the diborane(4) B_2H_4 (HH_2); planar vs. perpendicular conformation of the diborane(4) dianion salt $Li_2[B_2H_4]$ ($Li_2[G]^{pl}$ vs. $Li_2[G]^{perp}$).

In addition to B_2H_6 , also the elusive parent diborane(4) dianion salt $Li_2[H_2B=BH_2]$ has been studied computationally.^[49] The all-planar structure $Li_2[G]^{pl}$ represents an energy minimum and is, probably due to agostic $Li^+ \cdots H$ interactions, more stable by $14.9 \text{ kcal mol}^{-1}$ than the inverse sandwich complex $Li_2[G]^{perp}$ (not a minimum, two imaginary frequencies; Figure 2). The B=B-bond length in planar $Li_2[G]^{pl}$ (1.613 Å) has been predicted to be shorter than that in $Li_2[G]^{perp}$ (1.629 Å; Table 2). For a comparison with experimentally determined solid-state structures of lithium diborane(4) dianion salts, we are using the averaged dihedral angles between the respective B_2Li and B_2R_4 planes (the corresponding computed values $B_2Li//B_2R_4$ angles are 0° ($Li_2[G]^{pl}$) and 90° ($Li_2[G]^{perp}$)). Of the five crystallographically characterized diborane(4) dianions, Tamao's $[Li(thf)]_2[8]$ comes closest to the planar $Li_2[G]^{pl}$, because it combines a small $B_2Li//B_2R_4$ angle (18°) and a short B=B bond (1.616(4) Å; Table 2).^[33] In our diborene salt $[Li_2(thf)_3][11]$ (79° ; av. 1.634 Å), the configuration of the perpendicular model system $Li_2[G]^{perp}$ has been experimentally realized, and, as anticipated, the B=B bond is slightly elongated compared to that of $[Li(thf)]_2[8]$ (Table 2).^[36] Two other experimentally determined solid-state structures ($[Li(OEt_2)]_2[12]$ and $[Li(thf)]_2[13]$) have intermediate $B_2Li//B_2R_4$ angles of 40° and 41° and B=B-bond lengths of 1.636(11) Å and 1.633(3) Å (Table 2).^[40,43] A notable outlier is $[Li(thf)_3]_2[11]$, which combines one of the largest dihedral angles with the shortest B=B bond (79° ; 1.608(4) Å).^[75] It is thus reasonable to state that the B=B double-bond length is influenced not only by the position of the cation but also by the solvation shell, which modifies the effective size and the Lewis acidity of the cation (cf. Table 2). Furthermore, the perpendicular $Li_2[G]^{perp}$ can obviously become a minimum structure, as soon as proper substituents are applied. Similar to the cases of diborane(6) dianions such as $[9]^{2-}/[9']^{2-}$, diborane(4) dianions should experience a considerable intramolecular Coulomb repulsion. According to Power et al., this is illustrated by a comparison of the B \cdots B distances upon going from $Mes_2B-B(Ph)Mes$ (1.706(12) Å; **12**)^[77] to $[K(18-c-6)(thf)_2][Mes_2B-B(Ph)Mes]$ (1.649(11) Å; **[12]⁻**),^[41] and $[Li(OEt_2)]_2[Mes_2B-B(Ph)Mes]$ (1.636(11) Å; **[12]²⁻**),^[40] while the injection of the first electron results in a

significant shortening of the B–B bond, very little further contraction occurs after the addition of the second electron even though the π -bond order concomitantly increases from 0 to 0.5 to 1.0. Power et al. have therefore concluded that this increase is compensated in the second step by the electrostatic repulsion between the two negative charges in the dianion.^[41,78] However, in view of the more comprehensive structural information available to-date, a caveat is in order regarding the influence of the nature, positions, and ligand spheres of the complex counter cations $[M(solvent)_n]^+$ on the respective B \cdots B distances.

Table 2. Crystallographically determined B=B-bond lengths in neutral diboranes(4), diborane(4) monoanions, and diborane(4) dianions.

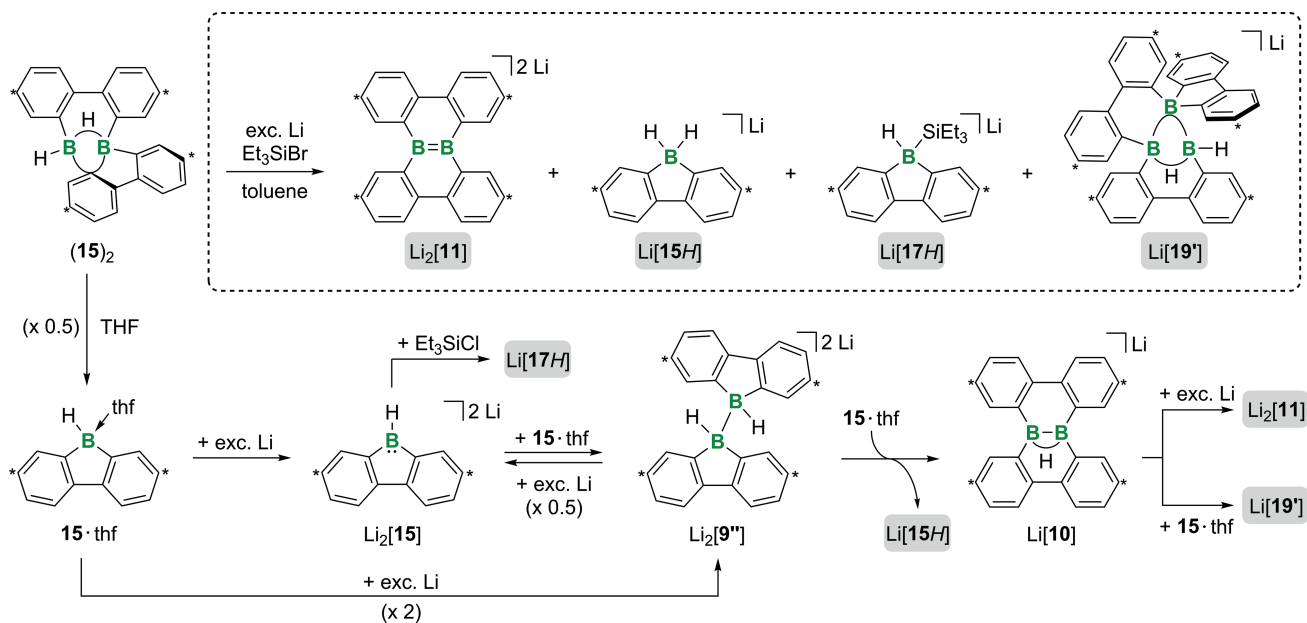
Organoboron entity	Complete formula	B \cdots B [Å]	$B_2Li//B_2R_4$ [$^\circ$] ^[a]	Ref.
[G⁺]²⁻	$Li_2[G]^{pl}$	1.613 ^[b]	0	[49]
[G⁻]²⁻	$Li_2[G]^{perp}$	1.629 ^[b]	90	[49]
[8]²⁻	$[Li(thf)]_2[8]$	1.616(4)	18	[33]
[11]²⁻	$[Li_2(thf)_3][11]$	1.634 ^[c]	79 ^[c]	[36]
[11]²⁻	$[Li(thf)_3]_2[11]$	1.608(4)	79	[75]
12	12	1.706(12)	–	[77]
[12]⁻	$[K(18-c-6)(thf)_2][12]$	1.649(11)	–	[41]
[12]²⁻	$[Li(OEt_2)]_2[12]$	1.636(11)	40	[40]
[13]²⁻	$[Li(thf)]_2[13]$	1.633(3)	41	[43]

[a] Averaged values of the two dihedral angles within each molecule.

[b] Computed value; experimental data are not available. [c] Further averaged value; the crystal lattice contains two crystallographically independent molecules in the asymmetric unit with $d_{BB} = 1.627(6)$ and 1.641(6) Å and $B_2Li//B_2R_4 = 81$ and 76° .

DFT calculations on $Li_2[(o-Tol)_2B=B(o-Tol)_2]$ ($Li_2[13]$),^[43] predict an energetically high-lying HOMO mainly composed of the B=B π orbital, pointing toward a rather localized B=B double bond (cf. the above-mentioned experimentally validated π nucleophilicity of $Li_2[11]$ and $Li_2[13]$).^[43,48] This localization is not surprising given that the sterically enforced torsion of the *o*-Tol substituents out of the central B_2C_4 plane should hamper an efficient π conjugation within the molecule.^[43] One might claim that this argument is no longer valid for the planarized diborane(4) dianion **[11]²⁻**, however, its short B=B bond of 1.608(4)–1.641(6) Å (Table 2) indicates a comparably high bond order.^[36,75] One reason probably lies in the specific annulation pattern of **[11]²⁻**, which, as an isoster of dibenzo[*g,p*]chrysene, can be written with four Clar's sextets and one localized central double bond.^[79]

The observed reactivities of **[11]²⁻** and **[13]²⁻** as synthetic equivalents of two diarylboryl anions $[:BAR_2]^-$ could, in principle, be explained by a simple "Wanzlick equilibrium".^[47] However, the huge dissociation energy of $117.9 \text{ kcal mol}^{-1}$ computed for the model reaction $Li_2[H_2B=BH_2] \rightarrow 2 Li[:BH_2]$ (1A_1) makes such a scenario implausible.^[49,80] Rather, more complex reaction mechanisms, such as those previously outlined, must be taken into account (see Scheme 12).^[40,43,48] The only known monomeric synthetic equivalent of a $[:BAR_2]^-$ species is the 9*H*-9-borafluorene dianion **[15]²⁻**. The dominant contribution to the LUMO of **15**, which corresponds to the HOMO of **[15]²⁻**, comes from the p_z orbital at the boron center, but the orbital coefficients at the carbon atoms are also significant.^[37] This points to a considerable delocalization of the two added electrons in



Scheme 15. Top: Complex product mixture obtained by reduction of the 9H-9-borafluorene dimer ($\mathbf{15}$)₂ with exc. Li metal in toluene. Bottom: Clarification of the underlying processes as achieved until to-date (* = *tert*-butyl).

$[\mathbf{15}]^{2-}$, as has been confirmed by significant high-field shifts of almost all ¹³C NMR resonances. The heavy-atom skeleton undergoes characteristic changes in its B–C- and C–C-bond lengths upon the two-electron reduction of $\mathbf{15}$, and these changes fit perfectly with the nodal structure of the neutral borane's LUMO. Somewhat surprisingly, the bond length alternation in the central C₄B ring of $[\mathbf{15}]^{2-}$ does not indicate a cyclic delocalized Clar's sextet within this substructure, but rather an allylic [CBC][−] fragment in combination with a juxtaposed C–C bond of increased double-bond character.

Conclusion

In 2014, our group published a first report on the reduction chemistry of the 9H-9-borafluorene dimer ($\mathbf{15}$)₂. The addition of metallic lithium to a toluene solution of ($\mathbf{15}$)₂ in the presence of Et₃SiBr as a potential hydride scavenger gave a complex mixture containing the four species Li₂[$\mathbf{11}$], Li[$\mathbf{15H}$], Li[$\mathbf{17H}$], and Li[$\mathbf{19}$] as major components (Scheme 15).^[75] The initial target product, however, the 9-borafluorenyl anion [BFlu][−], could not be found. A breakthrough toward the better comprehension of this reaction was the simple change of solvent from toluene to THF, which led to the less complex monomeric starting material $\mathbf{15}\cdot\text{thf}$.^[36]

Six years later we have elaborated a level of understanding that enables us to postulate a coherent reaction path leading from $\mathbf{15}\cdot\text{thf}$ to all previously observed products (Scheme 15). Each individual step in this scenario has been experimentally confirmed and high-yield syntheses for all seven encountered arylborane anions have been developed.^[36–38,48,64] Depending on the number of reduction equivalents supplied, the adduct $\mathbf{15}\cdot\text{thf}$ is transformed into the mutually interconvertible anions $[\mathbf{9}'']^{2-}$ (the formal dimer of $[\mathbf{15}]^{-}$) or $[\mathbf{15}]^{2-}$. As a boron-centered nucleophile, $[\mathbf{15}]^{2-}$ can attack halosilanes Et₃SiX under B–Si-

bond formation to give $[\mathbf{17H}]^{-}$ (X = Cl, Br). Hydride transfer from $[\mathbf{9}'']^{2-}$ to $\mathbf{15}\cdot\text{thf}$ produces equimolar amounts of $[\mathbf{15H}]^{-}$ and $[\mathbf{10}]^{-}$. This μ -H-bridged diborane(5) monoanion possesses a Lewis amphoteric nature, as it can either accept more electrons from elemental lithium to ultimately form $[\mathbf{11}]^{2-}$ or donate electron density to residual starting material, whereupon the B₃-cluster $[\mathbf{19}]^{-}$ is generated. A detailed understanding of key reaction mechanisms has been achieved and novel reactivity patterns, for example, nucleophilic substitutions, C–H activations, and cycloadditions involving a masked borafluorenyl anion ([BFlu][−]), have been discovered. These and other researchers' contributions to the field have brought essential synthetic building blocks, like Grignard-type boron nucleophiles and boron carbenoids, within closer reach. Contrary to the well-established bis(pinacolato)diboron adducts [pinB–Bpin(OR)][−], which are widely utilized as sources of the [Bpin][−] anion, the subvalent species highlighted in this review exclusively feature non-heteroatom-substituted boryl groups. As a benefit, the boron atoms can unfold their full capacity as electronically perturbing elements in the reactive intermediates and the final products. This is desirable not only with regard to fundamental research, but also when it comes to applications of the latter as small-molecule activators in main-group catalysis^[81] or electron acceptors/light emitters in organic electronics.^[82]

Acknowledgments

T. T. thanks the Fonds der Chemischen Industrie for a Kekulé Ph.D. grant. Open access funding enabled and organized by Projekt DEAL.

Keywords: Anionic boranes · Dynamic covalent chemistry · Organoboranes · Subvalent compounds · Umpolung

- [1] a) J. Arnold, *Dalton Trans.* **2008**, 4334–4335; b) C. Jones, G. A. Koutsantonis, *Aust. J. Chem.* **2013**, *66*, 1115–1117.
- [2] a) H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, London, **1972**; b) D. S. Matteson, *Stereodirected Synthesis with Organoboranes*, Springer-Verlag, Berlin, Heidelberg, **1995**; c) I. A. I. Mkhaliq, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; d) A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737; *Angew. Chem.* **2011**, *123*, 6854–6869; e) D. S. Matteson, *J. Org. Chem.* **2013**, *78*, 10009–10023; f) D. Leonori, V. K. Aggarwal, *Acc. Chem. Res.* **2014**, *47*, 3174–3178.
- [3] a) A. Escande, M. J. Ingleson, *Chem. Commun.* **2015**, *51*, 6257–6274; b) A. Wakamiya, S. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1357–1377; c) L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.* **2017**, *8*, 846–863; d) E. von Grotthuss, A. John, T. Kaese, M. Wagner, *Asian J. Org. Chem.* **2018**, *7*, 37–53; e) M. Hirai, N. Tanaka, M. Sakai, S. Yamaguchi, *Chem. Rev.* **2019**, *119*, 8291–8331; f) S. K. Møllerup, S. Wang, *Chem. Soc. Rev.* **2019**, *48*, 3537–3549; g) S. K. Møllerup, S. Wang, *Trends Chem.* **2019**, *1*, 77–89.
- [4] a) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032; b) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316; c) A. R. Jupp, D. W. Stephan, *Trends Chem.* **2019**, *1*, 35–48.
- [5] T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608–3680.
- [6] For review articles on [A][−]-type compounds, see a) P. Renaud, A. Beauseigneur, A. Brecht-Forster, B. Becattini, V. Darmency, S. Kandhasamy, F. Montermini, C. Ollivier, P. Panchaud, D. Pozzi, E. M. Scanlan, A.-P. Schaffner, V. Weber, *Pure Appl. Chem.* **2007**, *79*, 223–233; b) Y. Su, R. Kinjo, *Coord. Chem. Rev.* **2017**, *352*, 346–378; for selected original papers on [A]^{2−}-type compounds, see; c) J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc.* **1986**, *108*, 379–385; d) G. E. Herberich, M. Hostalek, R. Laven, R. Boese, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 317–318; *Angew. Chem.* **1990**, *102*, 330–331; e) C.-W. So, D. Watanabe, A. Wakamiya, S. Yamaguchi, *Organometallics* **2008**, *27*, 3496–3501; for selected original papers on [C]^{2−}-type compounds, see; f) O. Ciobanu, E. Kaifer, M. Enders, H.-J. Himmel, *Angew. Chem. Int. Ed.* **2009**, *48*, 5538–5541; *Angew. Chem.* **2009**, *121*, 5646–5649; g) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420–1422; h) L. Kong, W. Lu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2016**, *138*, 8623–8629; i) M. Flinker, H. Yin, R. W. Juhl, E. Z. Eikeland, J. Overgaard, D. U. Nielsen, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2017**, *56*, 15910–15915; *Angew. Chem.* **2017**, *129*, 16126–16131; j) L. L. Cao, D. W. Stephan, *Organometallics* **2017**, *36*, 3163–3170; k) J. Horn, A. Widera, S. Litters, E. Kaifer, H.-J. Himmel, *Dalton Trans.* **2018**, *47*, 2009–2017; for selected original papers on [D][−]/[D]^{2−}-type compounds, see; l) P. Bissinger, H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kupfer, K. Radacki, K. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 19044–19047; m) S. R. Wang, D. Prieschl, J. D. Mattock, M. Arrowsmith, C. Pranckevicius, T. E. Stennett, R. D. Dewhurst, A. Vargas, H. Braunschweig, *Angew. Chem. Int. Ed.* **2018**, *57*, 6347–6351; *Angew. Chem.* **2018**, *130*, 6456–6460; for selected original papers on [E]^{2−}-type compounds, see; n) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. von Ragué Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413; o) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337; for selected original papers on [F][−]-type compounds, see; p) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115; q) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079; r) R. Kinjo, B. Donnadiu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610–613; s) D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 7590–7592; *Angew. Chem.* **2013**, *125*, 7739–7742; t) D. A. Ruiz, M. Melaimi, G. Bertrand, *Chem. Commun.* **2014**, *50*, 7837–7839.
- [7] a) M. Yamashita, K. Nozaki, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1377–1392; b) H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* **2013**, *52*, 3574–3583; *Angew. Chem.* **2013**, *125*, 3658–3667; c) H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271–6277; d) M. Arrowsmith, H. Braunschweig, T. E. Stennett, *Angew. Chem. Int. Ed.* **2017**, *56*, 96–115; *Angew. Chem.* **2017**, *129*, 100–120; e) H.-J. Himmel, *Eur. J. Inorg. Chem.* **2018**, *2018*, 2139–2154; f) Q. Zhao, R. D. Dewhurst, H. Braunschweig, X. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 3268–3278; *Angew. Chem.* **2019**, *131*, 3302–3313; g) Y. Su, R. Kinjo, *Chem. Soc. Rev.* **2019**, *48*, 3613–3659.
- [8] T. L. Chu, T. J. Weismann, *J. Am. Chem. Soc.* **1956**, *78*, 23–26.
- [9] M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1986**, *108*, 4235–4236.
- [10] T. Kushida, S. Yamaguchi, *Organometallics* **2013**, *32*, 6654–6657.
- [11] a) Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529–4532; b) ref.^[3e].
- [12] A. Schulz, W. Kaim, *Chem. Ber.* **1989**, *122*, 1863–1868.
- [13] This is true mainly for THF solutions; in DME, the radical is “stable for weeks”: J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan, D. S. Miller, *J. Am. Chem. Soc.* **1970**, *92*, 6825–6830.
- [14] T. J. DuPont, J. L. Mills, *J. Am. Chem. Soc.* **1975**, *97*, 6375–6382.
- [15] T. L. Chu, T. J. Weismann, *J. Am. Chem. Soc.* **1956**, *78*, 3610–3612.
- [16] Both the aggregation state and the reactivity of salts M[BPh₃] (M = Li–K) are governed by the solvent employed; see a) ref.^[14i]; b) ref.^[15i]; c) ref.^[18].
- [17] *Houben-Weyl Methoden der organischen Chemie*, Thieme Verlag, Stuttgart, Vol. XIII, 13b, **1983**, p. 811.
- [18] J. J. Eisch, T. Druzynski, M. Behrooz, *Heteroat. Chem.* **1993**, *4*, 235–241.
- [19] G. E. Coates, K. Wade, *Organometallic Compounds*, Methuen, London, Vol. 1, **1967**, p. 213.
- [20] C. R. Arkin, B. Cowans, B. Kahr, *Chem. Mater.* **1996**, *8*, 1500–1503.
- [21] S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405–410.
- [22] An EPR spectrum of [B₂H₆][−], generated in situ at 4 K through photoexcitation of an Ar matrix containing Na atoms and B₂H₆, has also been reported: P. H. Kasai, D. McLeod Jr., *J. Chem. Phys.* **1969**, *51*, 1250–1251.
- [23] J. D. Hoefelmeyer, F. P. Gabbai, *J. Am. Chem. Soc.* **2000**, *122*, 9054–9055.
- [24] A. Hübner, A. M. Diehl, M. Diefenbach, B. Endeward, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2014**, *53*, 4832–4835; *Angew. Chem.* **2014**, *126*, 4932–4935.
- [25] L. Kaufmann, H. Vitze, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2008**, *27*, 6215–6221.
- [26] A. Hübner, A. M. Diehl, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2013**, *32*, 6827–6833.
- [27] The original paper (ref.^[23]) reports a value of E_{1/2} = −1.81 V for the 3/[3][−] couple (vs. SHE; THF). We used a factor of E_{1/2}(FcH/FcH⁺) = 0.40 V (vs. SHE) to scale this value to the ferrocene standard: C. E. Housecroft, A. G. Sharpe, *Inorganic Chemistry (2nd ed.)*, Pearson Education Limited, Harlow, **2005**, p. 731.
- [28] 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.
- [29] 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.
- [30] a) A. Stock, W. Sütterlin, F. Kurzen, *Z. Anorg. Allg. Chem.* **1935**, *225*, 225–242; b) A. Stock, H. Laudenklos, *Z. Anorg. Allg. Chem.* **1936**, *228*, 178–192.
- [31] a) W. V. Hough, L. J. Edwards, A. D. McElroy, *J. Am. Chem. Soc.* **1956**, *78*, 689; b) R. A. Godfroid, T. G. Hill, T. P. Onak, S. G. Shore, *J. Am. Chem. Soc.* **1994**, *116*, 12107–12108; c) [H₃B–BH₃]^{2−} has been stabilized in the coordination spheres of dinuclear tantalum complexes: C. Ting, L. Messerle, *J. Am. Chem. Soc.* **1989**, *111*, 3449–3450.
- [32] Y. Shoji, T. Matsuo, D. Hashizume, J. Gutmann, H. Fueno, K. Tanaka, K. Tamao, *J. Am. Chem. Soc.* **2011**, *133*, 11058–11061.
- [33] Y. Shoji, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *J. Am. Chem. Soc.* **2010**, *132*, 8258–8260.
- [34] a) H. C. Brown, *Hydroboration*, W. A. Benjamin Inc., New York, **1962**; b) M. Scheibitz, J. W. Bats, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2004**, *23*, 940–942; c) J. B. Heilmann, M. Scheibitz, Y. Qin, A. Sundaraman, F. Jäkle, T. Kretz, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2006**, *45*, 920–925; *Angew. Chem.* **2006**, *118*, 934–939; d) M. Scheibitz, H. Li, J. Schnorr, A. S. Perucha, M. Bolte, H.-W. Lerner, F. Jäkle, M. Wagner, *J. Am. Chem. Soc.* **2009**, *131*, 16319–16329; e) U. D. Eckensberger, M. Weber, J. Wildt, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2010**, *29*, 5301–5309; f) A. Schnurr, K. Samigullin, J. M. Breunig, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2011**, *30*, 2838–2843; g) Ö. Seven, Z.-W. Qu, H. Zhu, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Chem. Eur. J.* **2012**, *18*, 11284–11295; h) K. Samigullin, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2014**, *33*, 3564–3569.
- [35] 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.
- [36] T. Kaese, A. Hübner, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2016**, *138*, 6224–6233.

- [37] J. Gilmer, H. Budy, T. Kaese, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2020**, *59*, 5621–5625; *Angew. Chem.* **2020**, *132*, 5670–5674.
- [38] 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.
- [39] Diborirane, trisboracyclopropenyl, and 1,2-diboratabenzene dianions, in which partial B=B double bonds are embedded in the delocalized π -electron systems of three- and six-membered rings, respectively, have been prepared in other ways: a) R. Wehrmann, H. Meyer, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 788–790; *Angew. Chem.* **1985**, *97*, 779–781; b) H. Meyer, G. Schmidt-Lukasch, G. Baum, W. Massa, A. Berndt, *Z. Naturforsch. B* **1988**, *43*, 801–806; c) T. Kupfer, H. Braunschweig, K. Radacki, *Angew. Chem. Int. Ed.* **2015**, *54*, 15084–15088; *Angew. Chem.* **2015**, *127*, 15299–15303; d) G. E. Herberich, B. Hessner, M. Hostalek, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 642–643; *Angew. Chem.* **1986**, *98*, 637–638.
- [40] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715–2717.
- [41] W. J. Grigsby, P. Power, *Chem. Eur. J.* **1997**, *3*, 368–375.
- [42] For examples of corresponding alkyl- or alkoxy-substituted species, $[(t\text{BuCH}_2)_2\text{B}-\text{B}(\text{CH}_2t\text{Bu})_2]^-$ or $[\text{Li}(\text{OEt}_2)_2][\text{MeO}(\text{Mes})\text{B}-\text{B}(\text{Mes})\text{OMe}]$, see a) H. Klusik, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 870–871; *Angew. Chem.* **1981**, *93*, 903–904; b) ref.^[78].
- [43] S. Akiyama, K. Yamada, M. Yamashita, *Angew. Chem. Int. Ed.* **2019**, *58*, 11806–11810; *Angew. Chem.* **2019**, *131*, 11932–11936.
- [44] Amino-substituted diborane(6) dianions are known as well: $[\text{Li}(\text{OEt}_2)_2][\text{Me}_2\text{N}(\text{Ph})\text{B}=\text{B}(\text{Ph})\text{NMe}_2]$ and $[\text{Li}(\text{OEt}_2)_2][\text{Me}_2\text{N}(\text{R}_2\text{N})\text{B}=\text{B}(\text{NR}_2)\text{NMe}_2]$ ($\text{NR}_2 = \text{pyrrolyl, indolyl, carbazolyl}$): a) A. Moezzi, R. A. Bartlett, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1082–1083; *Angew. Chem.* **1992**, *104*, 1075–1076; b) H. Nöth, J. Knizek, W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, *11*, 1931–1937.
- [45] $[\text{Li}(\text{thf})_2][\mathbf{8}]$ is also accessible by reductive dehalogenation of EindBF_2 with lithium powder in THF (23% yield). The two boron-bonded hydrogen atoms were eliminated from the Eind substituents in the course of the reaction; see ref.^[33].
- [46] a) N. Tsukahara, H. Asakawa, K.-H. Lee, Z. Lin, M. Yamashita, *J. Am. Chem. Soc.* **2017**, *139*, 2593–2596; b) Y. Katsuma, N. Tsukahara, L. Wu, Z. Lin, M. Yamashita, *Angew. Chem. Int. Ed.* **2018**, *57*, 6109–6114; *Angew. Chem.* **2018**, *130*, 6217–6222; c) Y. Katsuma, L. Wu, Z. Lin, S. Akiyama, M. Yamashita, *Angew. Chem. Int. Ed.* **2019**, *58*, 317–321; *Angew. Chem.* **2019**, *131*, 323–327.
- [47] W. Kirmse, *Angew. Chem. Int. Ed.* **2010**, *49*, 8798–8801; *Angew. Chem.* **2010**, *122*, 8980–8983.
- [48] T. Kaese, T. Trageser, H. Budy, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Sci.* **2018**, *9*, 3881–3891.
- [49] E. Kaufmann, P. von Ragué Schleyer, *Inorg. Chem.* **1988**, *27*, 3987–3992.
- [50] M. Wagner, N. J. R. van Eikema Hommes, H. Nöth, P. von Ragué Schleyer, *Inorg. Chem.* **1995**, *34*, 607–614.
- [51] J. J. Eisch, K. Tamao, R. J. Wilcsek, *J. Am. Chem. Soc.* **1975**, *97*, 895–897.
- [52] a) J. D. Wilkey, G. B. Schuster, *J. Org. Chem.* **1987**, *52*, 2117–2122; b) J. J. Eisch, M. P. Boleslawski, K. Tamao, *J. Org. Chem.* **1989**, *54*, 1627–1634.
- [53] J. Radtke, S. K. Mellerup, M. Bolte, H.-W. Lerner, S. Wang, M. Wagner, *Org. Lett.* **2018**, *20*, 3966–3970.
- [54] H. Braunschweig, C.-W. Chiu, K. Radacki, T. Kupfer, *Angew. Chem. Int. Ed.* **2010**, *49*, 2041–2044; *Angew. Chem.* **2010**, *122*, 2085–2088.
- [55] Already previously, closely related pentaarylborel dianions have been reported: a) G. E. Herberich, B. Buller, B. Hessner, W. Oschmann, *J. Organomet. Chem.* **1980**, *195*, 253–259; b) ref.^[6e].
- [56] Investigations into the reduction chemistry of 9-organyl-9-borafluorenes have previously been described a) ref.^[60]; b) R. J. Wehmschulte, M. A. Khan, B. Twamley, B. Schiemenz, *Organometallics* **2001**, *20*, 844–849; c) P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo, M. Parvez, *Organometallics* **2003**, *22*, 1266–1274; d) A. Iida, S. Yamaguchi, *J. Am. Chem. Soc.* **2011**, *133*, 6952–6955.
- [57] For details about the structurally characterized SMe_2 adduct of 9H-9-borafluorene, see: A. Das, A. Hübner, M. Weber, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* **2011**, *47*, 11339–11341.
- [58] a) A. Rajca, S. Rajca, S. R. Desai, *J. Chem. Soc., Chem. Commun.* **1995**, *53*, 1957–1958; b) L. Wang, Y. Fang, H. Mao, Y. Qu, J. Zuo, Z. Zhang, G. Tan, X. Wang, *Chem. Eur. J.* **2017**, *23*, 6930–6936; c) N. Yuan, W. Wang, Y. Fang, J. Zuo, Y. Zhao, G. Tan, X. Wang, *Organometallics* **2017**, *36*, 2498–2501.
- [59] 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.
- [60] W. J. Grigsby, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 7981–7988.
- [61] a) E. Bernhardt, V. Bernhardt-Pitchougina, H. Willner, N. Ignatiev, *Angew. Chem. Int. Ed.* **2011**, *50*, 12085–12088; *Angew. Chem.* **2011**, *123*, 12291–12294; b) 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; c) 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.
- [62] Persistent neutral, NHC- or CAAC-stabilized 9-borafluorene radicals have recently been reported: W. Yang, K. E. Krantz, L. A. Freeman, D. A. Dickie, A. Molino, G. Frenking, S. Pan, D. J. D. Wilson, R. J. Gilliard Jr., *Angew. Chem. Int. Ed.* **2020**, *59*, 3850–3854; *Angew. Chem.* **2020**, *132*, 3878–3882.
- [63] Compound **8** is still reactive enough to activate H_2 at ambient pressure and to regenerate the diborane(6) starting material **6**. Moreover, a further increase in the steric demands of the aryl substituents by the change from Eind to MPind (1,1,7,7-tetramethyl-3,3,5,5-tetrapropyl-*s*-hydryndacen-4-yl) is necessary to force the butterfly-shaped core of **8** into a diborane(4) with two terminal hydrogen substituents and mutually orthogonal MPind(H)B halves. The structural differences between the Eind and MPind derivatives are not restricted to the solid state but also prevail in C_6D_6 solution (^1H , ^{11}B , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy): Y. Shoji, S. Kaneda, H. Fueno, K. Tanaka, K. Tamao, D. Hashizume, T. Matsuo, *Chem. Lett.* **2014**, *43*, 1587–1589.
- [64] T. Trageser, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2020**, *59*, 7726–7731; *Angew. Chem.* **2020**, *132*, 7800–7805.
- [65] a) R. D. Dewhurst, E. C. Neeve, H. Braunschweig, T. B. Marder, *Chem. Commun.* **2015**, *51*, 9594–9607; b) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091–9161; c) A. B. Cuenca, R. Shishido, H. Ito, E. Fernández, *Chem. Soc. Rev.* **2017**, *46*, 415–430.
- [66] P. B. Grasse, B. E. Brauer, J. J. Zupancic, K. J. Kaufmann, G. B. Schuster, *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.
- [67] H. C. Brown, V. H. Dodson, *J. Am. Chem. Soc.* **1957**, *79*, 2302–2306.
- [68] a) S. I. Weissman, H. v. Willigen, *J. Am. Chem. Soc.* **1965**, *87*, 2285–2286; b) ref.^[13]; c) R. G. Griffin, H. v. Willigen, *J. Chem. Phys.* **1972**, *57*, 86–90.
- [69] See the Supporting Information of: H. Asakawa, K.-H. Lee, K. Furukawa, Z. Lin, M. Yamashita, *Chem. Eur. J.* **2015**, *21*, 4267–4271. The SOMO of the triphenylmethyl radical is shown in: *Organic Chemistry: Theory, Reactivity and Mechanisms in Modern Synthesis* (Eds.: P. Vogel, K. N. Houk), Wiley-VCH, Weinheim, **2019**, p. 27.
- [70] a) R. A. Marcus, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111–1121; *Angew. Chem.* **1993**, *105*, 1161–1172; b) Y.-C. Chang, I. Chao, *J. Phys. Chem. Lett.* **2010**, *1*, 116–121.
- [71] L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225–3237.
- [72] W. Kutzelnigg, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 546–562; *Angew. Chem.* **1973**, *85*, 551–568.
- [73] T. Kaese, Ph.D. thesis, Goethe-Universität Frankfurt (Germany), **2018**.
- [74] a) K. S. Pitzer, *J. Am. Chem. Soc.* **1945**, *67*, 1126–1132; b) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218; c) ref.^[40]; d) D. J. Goebbert, H. Hernandez, J. S. Francisco, P. G. Wenthold, *J. Am. Chem. Soc.* **2005**, *127*, 11684–11689.
- [75] A. Hübner, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2014**, *53*, 10408–10411; *Angew. Chem.* **2014**, *126*, 10576–10579.
- [76] K. Lammertsma, T. Ohwada, *J. Am. Chem. Soc.* **1996**, *118*, 7247–7254.
- [77] A. Moezzi, M. M. Olmstead, R. A. Bartlett, P. P. Power, *Organometallics* **1992**, *11*, 2383–2388.
- [78] W. J. Grigsby, P. P. Power, *Chem. Commun.* **1996**, *19*, 2235–2236.
- [79] M. Solà, *Front. Chem.* **2013**, *1*, 22.
- [80] The issue of singlet vs. triplet ground states in LiBH_2 and the free anion $[\text{BH}_2]^-$ has been addressed. We note a discrepancy between the footnote (45) in ref.^[49] and a) J. A. Pople, P. von Ragué Schleyer, J. Kaneti, G. W. Spitznagel, *Chem. Phys. Lett.* **1988**, *145*, 359–364; b) ref.^[50].
- [81] a) A. Lorbach, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2010**, *29*, 5762–5765; b) E. von Grotthuss, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2016**, *55*, 14067–14071; *Angew. Chem.* **2016**, *128*, 14273–14277; c) E. von Grotthuss, S. E.

- Prey, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2018**, *57*, 16491–16495; *Angew. Chem.* **2018**, *130*, 16729–16733; d) E. von Grotthuss, F. Nawa, M. Bolte, H.-W. Lerner, M. Wagner, *Tetrahedron* **2019**, *75*, 26–30; e) E. von Grotthuss, S. E. Prey, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2019**, *141*, 6082–6091; f) ref.^[79].
- [82] a) E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* **2011**, *17*, 12696–12705; b) E. Januszewski, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2012**, *31*, 8420–8425; c) A. Lorbach, A. Hübner, M. Wagner, *Dalton Trans.* **2012**, *41*, 6048–6063; d) C. Reus, S. Weidlich, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2013**, *135*, 12892–12907; e) C. Hoffend, M. Diefenbach, E. Januszewski, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Dalton Trans.* **2013**, *42*, 13826–13837; f) R. R. Cloke, T. Marangoni, G. D. Nguyen, T. Joshi, D. J. Rizzo, C. Bronner, T. Cao, S. G. Louie, M. F. Crommie, F. R. Fischer, *J. Am. Chem. Soc.* **2015**, *137*, 8872–8875; g) V. M. Hertz, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2015**, *54*, 8800–8804; *Angew. Chem.* **2015**, *127*, 8924–8928; h) K. Schickedanz, T. Trageser, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* **2015**, *51*, 15808–15810; i) V. M. Hertz, H.-W. Lerner, M. Wagner, *Org. Lett.* **2015**, *17*, 5240–5243; j) F. Miyamoto, S. Nakatsuka, K. Yamada, K. Nakayama, T. Hatakeyama, *Org. Lett.* **2015**, *17*, 6158–6161; k) V. M. Hertz, J. G. Massoth, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* **2016**, *22*, 13181–13188; l) K. Schickedanz, J. Radtke, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2017**, *139*, 2842–2851; m) J. M. Farrell, D. Schmidt, V. Grande, F. Würthner, *Angew. Chem. Int. Ed.* **2017**, *56*, 11846–11850; *Angew. Chem.* **2017**, *129*, 12008–12012; n) R. J. Kahan, D. L. Crossley, J. Cid, J. E. Radcliffe, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2018**, *57*, 8084–8088; *Angew. Chem.* **2018**, *130*, 8216–8220; o) S. Brend'amour, J. Gilmer, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* **2018**, *24*, 16910–16918; p) J. M. Farrell, C. Mützel, D. Bialas, M. Rudolf, K. Menekse, A.-M. Krause, M. Stolte, F. Würthner, *J. Am. Chem. Soc.* **2019**, *141*, 9096–9104; q) J. Radtke, K. Schickedanz, M. Bamberg, L. Menduti, D. Schollmeyer, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Sci.* **2019**, *10*, 9017–9027; r) K. Yuan, R. J. Kahan, C. Si, A. Williams, S. Kirschner, M. Uzelac, E. Zysman-Colman, M. J. Ingleson, *Chem. Sci.* **2020**, *11*, 3258–3267.

Received: August 17, 2020