C–H Activation

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Thermal Dehydrogenation of Base-Stabilized $B_2H_5^+$ Complexes and Its Role in C–H Borylation

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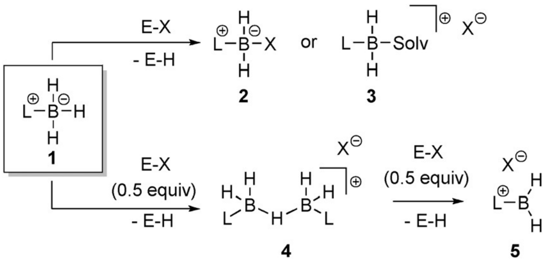
Dedicated to Professor Edwin Vedejs

Abstract: *Thermally induced dehydrogenation of the H-bridged cation $L_2B_2H_5^+$ (L = Lewis base) is proposed to be the key step in the intramolecular C–H borylation of tertiary amine boranes activated with catalytic amounts of strong "hydridophiles". Loss of H_2 from $L_2B_2H_5^+$ generates the highly reactive cation $L_2B_2H_3^+$, which in its sp^2-sp^3 diborane(4) form then undergoes either an intramolecular C–H insertion with B–B bond cleavage, or captures BH_3 to produce $L_2B_3H_6^+$. The effect of the counterion stability on the outcome of the reaction is illustrated by formation of $LBH_2C_6F_5$ complexes through disproportionation of $L_2B_2H_5^+$ $HB(C_6F_5)_3^-$.*

Electrophilic activation of B–H bonds is the essential step in metal-free dehydrogenation of amine borane complexes,[1] as well as in some electrophilic C–H borylations.[2,3] While the majority of studies to date have focused on dehydrogenation of amine borane complexes possessing at least one hydrogen atom at the amine nitrogen atom (i.e. B–N dehydrocoupling), it appears that other dehydrogenative events can also occur in activated Lewis base borane complexes. Highlighted herein is the ability of activated amine and phosphine boranes to undergo thermal B–B dehydrocoupling,[4] and the significance of this event in certain electrophilic C–H borylations.

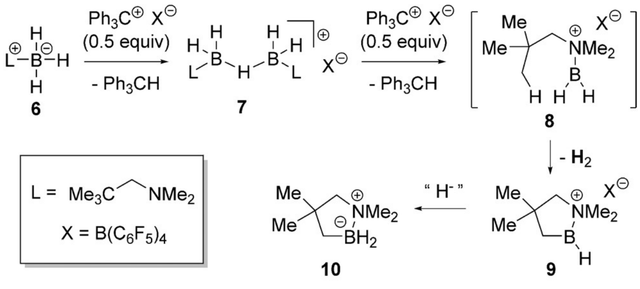
The partial hydridic character of B–H bonds in a tetracoordinate boron environment dictates their high reactivity towards electrophilic agents, and is central to the reducing properties of borane complexes.[5] The outcome of the electrophilic activation of tertiary amine and phosphine borane complexes (**1**) depends on availability of Lewis bases in the reaction medium (Scheme 1).[6] Thus, while the neutral covalent adducts **2** and boronium ions **3** are preferentially formed under more basic conditions, the tricoordinate borenium ions **5**[2,7] (or even their respective dicationic dimers)[8] are accessible when the coordinating ability of the reaction medium is limited. Depending on the ratio of electrophile to **1**, **5** can also form a three-center-two-electron (3c2e) bonded adduct with **1**, thus giving rise to the H-bridged $L_2B_2H_5^+$ complex **4**,[1a,4a,9] which is the cationic analogue of the well-known $B_2H_7^-$ anion.



Scheme 1. Lewis base borane complex activation by electrophiles. L = tertiary amine or phosphine, E = "hydridophile", X = counterion, Solv = Lewis-basic solvent.

Tertiary amine boranes possessing suitably placed C–H bonds have been shown previously to undergo intramolecular borylation upon stoichiometric activation with strong electrophiles (Scheme 2).[2a–c] In the reaction sequence involving 1 equivalent of Ph_3C^+ $B(C_6F_5)_4^-$ in either PhBr or PhF, hydride abstraction from *N*,*N*-dimethylneopentylamine borane (**6**) leads to formation of the unstabilized borenium **8** through the 3c2e bonded $L_2B_2H_5^+$ intermediate **7**. Availability of both an empty orbital and a partially hydridic H at the borenium center of **8** determines its high reactivity towards adjacent σ-bonds, thus resulting in a facile dehydrogenative borenium C–H insertion and leading to the cyclic cation **9**. Quenching **9** with a suitable hydride source afforded the isolable cyclic amine borane **10**.

It is also possible to perform intramolecular borylations by using only a catalytic amount of a strong electrophile.[2b,c] In this case only a small amount of **7** was produced by activation of the starting amine borane, and heating above 120 °C (typically in PhMe) was required to drive the process towards formation of **10** and H_2. The initial mechanistic rationale assumed that the process involves intramolecular



Scheme 2. The mechanism of dehydrogenative C–H borylation of *N*,*N*-dimethylneopentylamine borane (**6**) using stoichiometric Ph_3C^+ activation.[2a–c]

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C–H insertion of **8**, which is generated by the thermal dissociative loss of **6** from **7**. However, multiple discrepancies between this simple mechanism and experimental observations were soon identified and explicitly summarized in a previous communication,[2c] thus outlining a clear need for a new mechanistic picture.

In proposing an alternative mechanism for the catalytic borylation, the following experimental observations must be accounted for:[2c] 1) The role of H-bridged cations such as **7** is clearly significant, since the catalytic reaction was only shown to proceed efficiently with those electrophiles that led to generation of the $L_2B_2H_5^+$ species. 2) The catalytic and stoichiometric processes display different regiochemical trends. 3) The rate-limiting step of the catalytic process appears to be a C–H insertion, and is primarily dominated by steric factors.

For C–H borylation to occur in a concerted insertion step, the key intermediate must be a coordinatively unsaturated boron species possessing both a sufficiently empty p orbital, and a perpendicular filled orbital, such as an unshared electron pair in borylenes,[10] or a hydridic B–H in boranes or borenium ions. The search for an alternative mechanism for the catalytic borylation began by noting that the $L_2B_2H_5^+$ species are unstable with respect to loss of H_2 at 90 °C in [D$_5$]PhBr solutions, even when no intramolecular borylation is possible. This observation suggested that the key borylating intermediate may be generated by the thermally induced loss of H_2 from $L_2B_2H_5^+$, and computational studies (M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ, SMD solvation) were performed to outline a plausible mechanism for the cyclization of **6** in PhMe (Figure 1). Since **7** can be viewed as the σ complex of **8** and **6**, it follows that the 3c2e-bonded cation **7** preorganizes the components for a dehydrogenative insertion of **8** into the B–H bond of **6**, in a fashion similar to C–H insertion in the stoichiometric borylation process. Indeed, a sufficiently low-lying transition state (TS **13**; $G^{\neq} = 27.8$ kcal mol^{-1}) was identified for the process, thus leading from **7** to the B–B bonded $L_2B_2H_3^+$ cation **14** and H_2 (Figure 1, Path A). In the most stable conformation of **14**, the tricoordinate boron atom enjoys some stabilization from a C–H bond in the proximal neopentyl group, much like the borenium center in the lowest energy conformation of **8**. Because of this stabilizing interaction, **14** preferentially exists in the open borenium form, although the isomeric C_2-symmetric H-bridged form is higher in energy by only 1.4 kcal mol^{-1} (gas phase; see the Supporting Information).

Natural bond orbital (NBO) analysis of the lowest-energy structure of **14** reveals that natural charges of the two interconnected boron atoms are distinctly different, +0.80 and −0.42 for the tri- and tetracoordinate B centers, respectively. Additionally, the LUMO of **14** has a substantial contribution from the unoccupied p orbital of the tricoordinate B center, while the B–B σ-bonding orbital is contributing to the HOMO of the cation.[11] Therefore, since the tricoordinate B atom of **14** possesses an empty p orbital (acid) orthogonal to the strongly polarized B–B σ bond (base), it satisfies the requirements for a species capable of inserting into adjacent C–H σ bonds. Indeed, the ability of diborane(4) **14** to react with proximal C–H bonds was confirmed by identifying the appropriate TS **15** ($G^{\neq} = 29.4$ kcal mol^{-1}), thus leading directly to a new H-bridged product (**16**) containing the cyclized amine borane subunit. Hydride exchange between **16** and **6** delivers the final product **10**, and regenerates the crucial intermediate **7**, thus completing the catalytic cycle.[12] The new mechanism is in good agreement with the requirements defined by the previous experimental work (see below), as H_2 loss from **7** indeed precedes the C–B bond formation, and the steric demands in **15** are more prominent than in **11**, which is consistent with the higher selectivity of the catalytic process for less hindered borylation products.[2c] The open form of **14** can also be viewed as a sp^2–sp^3 diborane(4), and the synthetic potential of this structural motif has recently been recognized in an anionic and neutral, but not cationic, setting.[13] It should also be noted that this

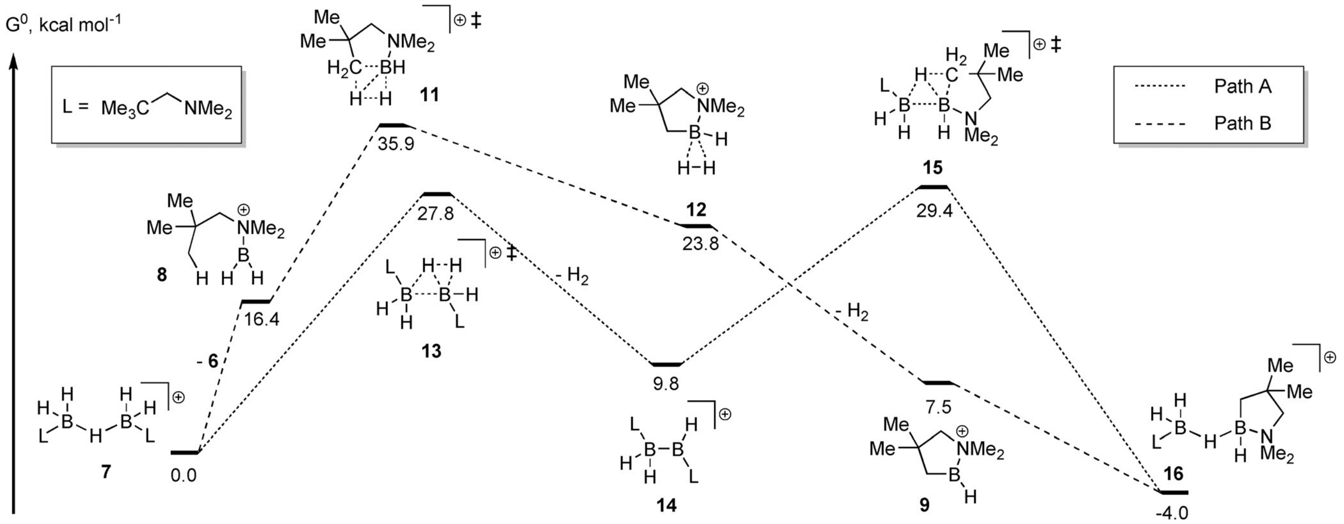


Figure 1. The major features of the reaction profile calculated at the M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ level of theory in PhMe (SMD solvation). Path A represents the B–B dehydrocoupling mechanism proposed in this article, while Path B shows the previously considered mechanism inspired by the stoichiometric reaction. See the Supporting Information for details.

appears to be the first example of a cationic sp^2–sp^3 diborane(4) being formed in situ from L-BH$_3$ complexes, and functioning as the key species in the catalytic cycle.

In contrast, the borylation pathway proceeding via the same primary borenium **8**, as in the stoichiometric transformation, is characterized by a higher activation barrier (Figure 1, Path B). Dissociation of **7** to the starting amine borane **6** and **8** is endergonic by 16.4 kcal mol^{-1}, and the C–H insertion transition state **11** is located even higher on the free-energy profile ($G^{\neq} = 35.9$ kcal mol^{-1}).[14] The chain of events leading from **11** to the cyclized product via the thermodynamically unstable borenium H$_2$ complex **12** follows that of the stoichiometric borylation.[2a]

Seeking experimental support for the reaction mechanism outlined in the computational studies, a controlled thermal decomposition of $L_2B_2H_5^+$ salts was performed.[15] Hydride abstraction from Me$_3$P–BH$_3$ by 0.5 equivalents of Ph_3C^+ $B(C_6F_5)_4^-$ in [D$_5$]-PhBr resulted in formation of the H-bridged cation **18a** ($\delta = {}^{11}$B −25.6 ppm, $J_{P\text{-}B} = 90$ Hz; Figure 2). Heating to 90 °C led to the disappearance of **18a**, and formation of H$_2$ was detected by ^{1}H NMR spectroscopy ($\delta = {}^1$H 4.51 ppm). Three new signals ($\delta = {}^{11}$B −9.8, −33.4, and −38.9 ppm in about a 1:1:2 ratio), attributable to cationic boron species, were observed by ^{11}B NMR spectroscopy at this point, while stability of the counterion and Ph$_3$CH byproduct under the reaction conditions was confirmed by ^{19}F and ^{1}H NMR spectroscopy, respectively. The multiplet at $\delta = {}^{11}$B −33.4 ppm upon proton decoupling transformed into a triplet with $J_{P\text{-}B} = 90$ Hz, and was thus identified as originating from the unremarkable boronium cation **19a**. The H-coupled broad signal at $\delta = {}^{11}$B −9.8 ppm did not show any detectable coupling to ^{31}P, while the complex multiplet at $\delta = {}^{11}$B −38.9 ppm was transformed into a doublet with $J_{P\text{-}B} = 110$ Hz upon proton decoupling. Both signals were shown to originate from non-equivalent B atoms in the same boron cation, which was ultimately identified as the base-stabilized $B_3H_6^+$ species **20a**.[16] Several triboron cations of this type have been prepared previously by either basic cleavage of tetraborane(10),[17] or by reacting diborane(4) derivatives with boron Lewis acids,[18,19] but formation of $L_2B_3H_6^+$ cations from $L_2B_2H_5^+$ has not been reported previously. The cation **20a** can be viewed as an adduct of $L_2B_2H_3^+$ (fragment highlighted in Figure 2) and "BH$_3$", thus explaining formation of **19a**.[20] Electrospray ionization mass spectra (ESI MS+) of the reaction mixture showed signals with *m*/*z* 165, 177 and 191, and the isotope peaks of the latter two signals were consistent with the presence of two and three B atoms, respectively. While the signals with *m*/*z* 165 and 191 are due to **19a** and **20a**, respectively, the intense *m*/*z* 177 signal is due to the $L_2B_2H_3^+$ cation, apparently arising from fragmentation of **20a** and thus emphasizing the close relationship of the two species.

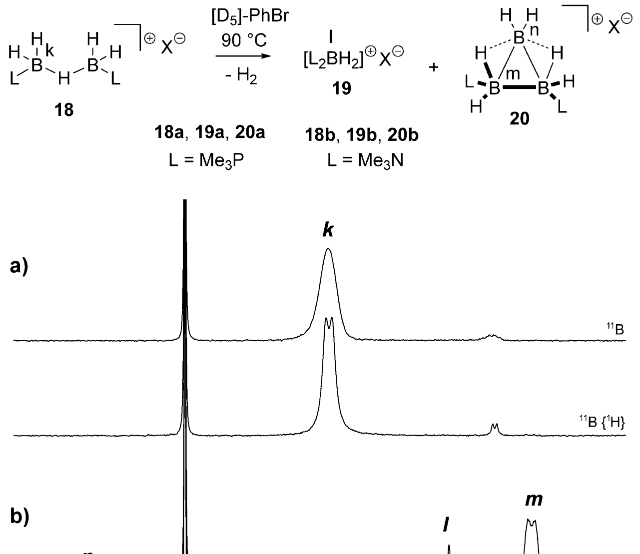
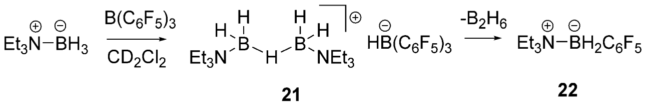


Figure 2. Formation of the triboron cations **20** ($L_2B_2H_3^+$ fragment highlighted) in the thermal decomposition of the H-bridged complexes **18**. The ^{11}B NMR spectra [L = Me$_3$P, X = B(C$_6$F$_5$)$_4$] are shown: a) immediately following generation of **18a** in [D$_5$]-PhBr, and b) after 18 h at 90 °C. Other signals: $B(C_6F_5)_4^-$: $\delta = -16.2$ ppm; Me$_3$P–BH$_3$: $\delta = -36.4$ ppm.

Similar observations were made when the activated trimethylamine borane derivative **18b** [L = Me$_3$N, X = $B(C_6F_5)_4^-$] was heated at 90 °C in [D$_5$]-PhBr. In this case disappearance of the $L_2B_2H_5^+$ signal at $\delta = {}^{11}$B −0.3 ppm was accompanied by appearance of new H-coupled peaks at $\delta = {}^{11}$B −10.2 and −15.8 ppm, although the latter partially overlapped with the $B(C_6F_5)_4^-$ peak at $\delta = -16.1$ ppm. The signals were identified as the BH$_2$ ($\delta = -10.2$ ppm) and LBH ($\delta = -15.8$ ppm) subunits of **20b**,[18a] and formation of **19b** ($\delta = {}^{11}$B 3.6 ppm) was also observed. In this case the ESI MS+ pattern [*m*/*z* 131 (**19b**), 143 ($L_2B_2H_3^+$), 157 (**20b**)] paralleled that observed for Me$_3$P derivatives, thus supporting the general similarity of events for activated amine and phosphine boranes.[21]

Conversion of $L_2B_2H_5^+$ (**18**) into $L_2B_3H_6^+$ (**20**) is reminiscent of the processes observed in isostructural boron anions, such as formation of the stable σ-aromatic $B_3H_8^-$ anion by thermolysis of $B_2H_7^-$,[22] which is believed to proceed via the poorly known $B_2H_5^-$.[23,24] Thermal dehydrogenation of **7** and **18** is thus expected to generate cationic analogues of $B_2H_5^-$ (i.e., **14**), which subsequently stabilize either by intramolecular C–H insertion (formation of **16**) or BH$_3$ incorporation leading to $L_2B_3H_6^+$ cations such as **20**. Since **20** was shown previously to produce diborane(4) derivatives upon treatment with Lewis bases,[17,18] thermolysis of **18**, followed by basic cleavage of the resulting triboron cation **20** can be viewed as a method for building electron-precise B–B bonds from mononuclear L–BH$_3$ complexes.[4c,25] While instability of the corresponding neutral L$_2$B$_2$H$_4$ complex prevented independent generation of **14** by hydride abstraction,[26] it should be noted that the ability of $L_2B_2H_3^+$ to insert into σ bonds is not without precedent.[27]

It was also of interest to explore the thermal behavior of H-bridged cations paired with anions which are less stable to electrophilic attack, and the reactivity of amine and phos-



Scheme 3. Formation of **22** by disproportionation of **21**.

phine boranes with $B(C_6F_5)_3$ was thus explored. Addition of Et_3N-BH_3 to 0.5 equivalents of $B(C_6F_5)_3$ in CD_2Cl_2 at room temperature resulted in a rapid hydride abstraction and formation of the H-bridged cation **21** (B-H-B, ^1H δ −2.0–3.3 ppm; ^{11}B δ −3.0 ppm, unres. t.; Scheme 3). Unlike in the trityl activation experiments described above, the other product of the hydride abstraction was the $HB(C_6F_5)_3^-$ counterion ($\delta = {}^{11}B$ −25.4 ppm, d, $J_{B\text{-}H} = 80$ Hz), and the difference in the anion structure and stability was found to have a prominent effect on the subsequent events. Thus, even at room temperature degradation of **21** was evident, and heating the solution to 40 °C resulted in formation of B_2H_6, and another compound, identified as **22** ($\delta = {}^{11}B$ −14.2 ppm), upon isolation. Formation of **22** is the result of disproportionation involving some $HB(C_6F_5)_3^-$ derivative, and despite the 1:1.5 R_3N-BH_3/C_6F_5 reaction stoichiometry, only $C_6F_5BH_2$ complexes were formed.[28]

The reaction was further developed into a preparative protocol, optimized with respect to decreasing the amount of $B(C_6F_5)_3$ used (0.36 equiv versus theoretical 0.33 equiv), and simplified product isolation, which in most cases was accomplished by filtering the reaction mixture through a plug of silica gel, followed by removal of the solvent. The results listed in Table 1 suggest that this method can be conveniently used to access $C_6F_5BH_2$ complexes of simple tertiary amines and phosphines.[29]

To summarize, involvement of highly electrophilic $L_2B_2H_3^+$ complexes in the high-temperature intramolecular C−H borylation of amine boranes activated with catalytic amounts of strong "hydridophiles" is postulated based on experimental and theoretical studies. Such sp^2–sp^3 diborane(4) cations are formally isoelectronic to $B_2H_5^-$, and appear to arise from the thermally induced dehydrogenative borenium B−H insertion within the isolable H-bridged cations $L_2B_2H_5^+$. High reactivity of the cation $L_2B_2H_3^+$ manifests itself either in high-yielding intramolecular C−H insertions proceeding with the cleavage of the B−B bond, or in BH_3 incorporation resulting in formation of the more stabilized $L_2B_3H_6^+$ cation. In view of these findings, it appears plausible that new borylating reagents can be identified among electrophilically activated diborane(4) derivatives, particularly those of the sp^2–sp^3 type.

Table 1: Synthesis of $C_6F_5BH_2$ complexes.[a]

Entry	Substrate	Solvent	Product	Yield [%]
1[b]	Et_3N-BH_3	PhF	$Et_3N-BH_2C_6F_5$ (**22**)	> 99
2	Me_3N-BH_3	CH_2Cl_2	$Me_3N-BH_2C_6F_5$ (**23**)	97
3	$BnMe_2N-BH_3$	PhF	$BnMe_2N-BH_2C_6F_5$ (**24**)	> 99
4[c]	Ph_3P-BH_3	CH_2Cl_2	$Ph_3P-BH_2C_6F_5$ (**25**)	71

[a] 0.36:1 $B(C_6F_5)_3/L-BH_3$, 50 °C, 1 h, the reaction performed in sealed vials. [b] 3 h. [c] 40 °C.

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[15] Several Me_3P-based complex boron cations were reported previously (Refs. [9a, 17, 18]), thus justifying the choice of L for the initial studies.

[16] According to computational modeling, the cation **20a** is structurally similar to other species related to $B_3H_8^-$. See the Supporting Information for details. The calculated ^{11}B NMR chemical shifts of **20a** in PhBr (GIAO, SMD solvation) of $\delta = -9.3$ and -40.9 ppm are within 2 ppm of the experimental values.

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[21] $L_2B_2H_5^+$ ($\delta = {}^{11}B$ −20.9 ppm) prepared from 1,3,4,5-tetramethylimidazolidene borane and 0.5 equiv Ph_3C^+ $B(C_6F_5)_4^-$ in [D_5]-PhBr upon heating to 90 °C yielded qualitatively similar results ($\delta = {}^{11}B$ −7.2 (H-coupled, broad), −32.3 (t, $J_{B\text{-}H} = 80$ Hz), −34.2 ppm (H-coupled, broad)).

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[25] For a recent review of approaches to building electron-precise B−B bonds, see: H. Braunschweig, R. D. Dewhurst, S. Mozo, *ChemCatChem* **2015**, *7*, 1630 – 1638.

[26] Attempts were made to prepare $L_2B_2H_4$ complexes by reacting THF·B_3H_7 with *t*BuCH_2NMe_2, BnNMe_2, *t*BuCH_2PPh_2, (o-Tol)$_3$P, *n*Bu_3P, BnMeImd, and in all cases the desired neutral complex either did not form at all, or persisted in the reaction mixture only for a short time, before it could be isolated. This appears to be due to 1) Fast reaction between LB_3H_7 and $L_2B_2H_4$ to produce LBH_3 and higher boranes (M. Ishii, G. Kodama, *Inorg. Chem.* **1990**, *29*, 817 – 820) 2) Inherent instability of $L_2B_2H_4$ complexes: $(Me_3P)_2B_2H_4$ decomposes at room temperature under N_2 (R. K. Hertz, M. L. Denniston, S. G. Shore, *Inorg. Chem.* **1978**, *17*, 2673 – 2674). Even $(Ph_3P)_2B_2H_4$, which is the most robust $L_2B_2H_4$ complex because of its high crystallinity, decomposes at only 90 °C (M. D. Levicheva, L. V. Titov, L. V. Zhemchugova, *Izv. Akad. Nauk SSSR* **1987**, 2120 – 2122). In full agreement with literature reports, complexes with L = Me_3N and Ph_3P were prepared successfully, and therefore the process appears to be highly dependent on the nature of L. Reacting $(Ph_3P)_2B_2H_4$ with the N-heterocyclic carbene BnMeImd produced complex mixtures containing some of the desired $L_2B_2H_4$ ($\delta = {}^{11}B$ −34 ppm, br t) which could not be isolated, in agreement with the previous report by Curran et al. (Ref. [10b]).

[27] In view of the mechanism outlined in Figure 1, previously reported formation of $L_3B_3H_4^+$ cations in the electrophilic activation of $L_2B_2H_4$ (Ref. [9a]) can now be interpreted as $L_2B_2H_3^+$ insertion into B−B bond.

[28] No H_2 was produced, thus ruling out the dehydrogenative pathway proposed above for salts with more stable anions. Involvement of L-BH_2-H-$B(C_6F_5)_3$ appears plausible based on limited NMR evidence.

[29] a) Disproportionation between Me_2S−BH_3 and $B(C_6F_5)_3$: A.-M. Fuller, D. L. Hughes, S. J. Lancaster, C. M. White, *Organometallics* **2010**, *29*, 2194 – 2197; b) C_6F_5-transfer in activated Me_3N−BH_3: G. Ménard, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 5447 – 5453.

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