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

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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 producing $L_2B_3H_6^+$. 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 $L_2B_2H_5^+ HB(C_6F_5)_3^-$.

Keywords

boranes; borylation; borenium; homogeneous catalysis; C–H activation

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 (i.e. B–N dehydrocoupling), it appears that other dehydrogenative events can also occur in activated Lewis base borane complexes. This communication highlights 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 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 neutral covalent adducts **2** and boronium ions **3** are preferentially formed under more basic conditions, 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:**1**, borenium **5** can also

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form a 3-center-2-electron (3c2e) bonded adduct with **1**, giving rise to the H-bridged $L_2B_2H_5^+$ complex **4**,^[1a,4a,9] which is the cationic analog of the well-known $B_2H_7^-$ anion.

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 equiv of $Ph_3C^+B(C_6F_5)_4^-$ in either PhBr or PhF, hydride abstraction from *N,N*-dimethylnorbornylamine borane (**6**) leads to formation of 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, resulting in a facile dehydrogenative borenium C–H insertion, 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 the neutral cyclic product **10** and H_2 . The initial mechanistic rationale assumed that the process involves intramolecular C–H insertion in borenium **8**, which is generated by the thermal dissociative loss of **6** from the 3c2e-bonded cation **7**. However, multiple discrepancies between this simple mechanism and experimental observations were soon identified and explicitly summarized in a previous communication,^[2c] 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 borenium **8** into the B–H bond of amine borane **6**, in a fashion similar to the C–H insertion in the stoichiometric borylation process. Indeed, a sufficiently low-lying transition state (TS) **13** ($G^\ddagger = 27.8$ kcal/

mol) was identified for the process 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 cation **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 cation **8**. Because of this stabilizing interaction, cation **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 (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, 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 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 locating the appropriate TS **15** ($G^\ddagger = 29.4$ kcal/mol), 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**, completing the catalytic cycle.^[12] The new mechanism is in good agreement with the requirements defined by the previous experimental work (*vide supra*), 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 anionic and neutral, but not cationic setting.^[13] It should also be noted that this 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 the H-bridged cation **7** to the starting amine borane **6** and borenium **8** is endergonic by 16.4 kcal/mol, and the C–H insertion transition state **11** is located even higher on the free energy profile ($G^\ddagger = 35.9$ kcal/mol).^[14] The chain of events leading from transition state **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, controlled thermal decomposition of $L_2B_2H_5^+$ salts was performed.^[15] Hydride abstraction from Me_3P-BH_3 by 0.5 equiv 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, $J_{P-B} = 90$ Hz) (Figure 2). Heating to 90 °C led to disappearance of **18a**, and formation of H_2 was detected by 1H NMR (δ^{1H} 4.51 ppm). Three new signals ($\delta^{11}B$ –9.8, –33.4 and –38.9 ppm in ca. 1:1:2 ratio) attributable to cationic boron species were observed by ^{11}B NMR at this point, while stability of the counterion and Ph_3CH byproduct under the reaction conditions was

confirmed by ^{19}F and ^1H NMR spectroscopy, respectively. The multiplet at $\delta^{11}\text{B}$ –33.4 ppm upon proton decoupling transformed into a triplet with $J_{\text{P-B}} = 90$ Hz, and was thus identified as originating from the unremarkable boronium cation **19a**. The H-coupled broad signal at $\delta^{11}\text{B}$ –9.8 ppm did not show any detectable coupling to ^{31}P , while the complex multiplet at $\delta^{11}\text{B}$ –38.9 ppm was transformed into a doublet with $J_{\text{P-B}} = 110$ 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] although formation of $\text{L}_2\text{B}_3\text{H}_6^+$ cations from $\text{L}_2\text{B}_2\text{H}_5^+$ has not been reported previously. Cation **20a** can be viewed as an adduct of $\text{L}_2\text{B}_2\text{H}_3^+$ (fragment highlighted in Figure 2) and “ BH_3 ”, thus explaining formation of boronium salt **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 boronium **19a** and triboron cation **20a**, respectively, the intense m/z 177 signal is due to $\text{L}_2\text{B}_2\text{H}_3^+$ cation, apparently arising from fragmentation of **20a**, emphasizing close relationship of the two species.

Similar observations were made when the activated trimethylamine borane derivative **18b** ($\text{L} = \text{Me}_3\text{N}$, $\text{X} = \text{B}(\text{C}_6\text{F}_5)_4^-$) was heated at 90 °C in d_5 -PhBr. In this case disappearance of the $\text{L}_2\text{B}_2\text{H}_5^+$ signal at $\delta^{11}\text{B}$ –0.3 ppm was accompanied by appearance of new H-coupled peaks at $\delta^{11}\text{B}$ –10.2 ppm and –15.8 ppm, although the latter partially overlapped with the $\text{B}(\text{C}_6\text{F}_5)_4^-$ peak at –16.1 ppm. The signals were identified as the BH_2 (–10.2 ppm) and LBH (–15.8 ppm) subunits of **20b**,^[18a] and formation of L_2BH_2^+ boronium cation **19b** ($\delta^{11}\text{B}$ 3.6 ppm) was also observed. In this case ESI MS+ pattern (m/z 131 (**19b**), 143 ($\text{L}_2\text{B}_2\text{H}_3^+$), 157 (**20b**)) paralleled that observed in Me_3P derivatives, supporting the general similarity of events in activated amine and phosphine boranes.^[21]

Conversion of $\text{L}_2\text{B}_2\text{H}_5^+$ (**18**) to $\text{L}_2\text{B}_3\text{H}_6^+$ (**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 H-bridged cations **7** and **18** is thus expected to generate cationic analogs 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 $\text{L}_2\text{B}_3\text{H}_6^+$ 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 $\text{L}_2\text{B}_2\text{H}_4$ complex prevented independent generation of **14** by hydride abstraction,^[26] it should be noted that the ability of $\text{L}_2\text{B}_2\text{H}_3^+$ 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 that are less stable to electrophilic attack, and the reactivity of amine and phosphine boranes with $\text{B}(\text{C}_6\text{F}_5)_3$ was thus explored. Addition of $\text{Et}_3\text{N–BH}_3$ to 0.5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$

in CD₂Cl₂ at rt resulted in a rapid hydride abstraction and formation of the H-bridged cation **21** (B–H–B, ¹H δ –2.0—3.3 ppm; ¹¹B 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(C₆F₅)₃[–] counterion (δ ¹¹B –25.4 ppm, d, J_{B–H} = 80 Hz), and the difference in the counterion structure and stability was found to have a prominent effect on the subsequent events. Thus, even at rt degradation of the H-bridged cation **21** was evident, and heating the solution to 40 °C resulted in formation of B₂H₆, and another compound identified as **22** (δ ¹¹B –14.2 ppm) upon isolation. Formation of **22** is the result of disproportionation involving some HB(C₆F₅)₃[–] derivative, and despite the 1:1.5 “R₃N–BH₃”：“C₆F₅” reaction stoichiometry, only C₆F₅BH₂ complexes were formed.^[28]

The reaction was further developed to a preparative protocol, optimized with respect to decreasing the amount of B(C₆F₅)₃ used (0.36 equiv vs. 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 C₆F₅BH₂ complexes of simple tertiary amines and phosphines.^[29]

To summarize, involvement of highly electrophilic L₂B₂H₃⁺ 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 sp²–sp³ diborane(4) cations are formally isoelectronic to B₂H₅[–], and appear to arise from the thermally induced dehydrogenative borenium B–H insertion within the isolable H-bridged cations L₂B₂H₅⁺. High reactivity of the cation L₂B₂H₃⁺ manifests itself either in high-yielding intramolecular C–H insertions proceeding with the cleavage of the B–B bond, or in BH₃ incorporation resulting in formation of the more stabilized L₂B₃H₆⁺ 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 sp²–sp³ type.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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25. For a recent review of approaches to building electron-precise B–B bonds, see: Braunschweig H, Dewhurst RD, Mozo S. *ChemCatChem.* 2015; 7:1630–1638.
26. Attempts were made to prepare L₂B₂H₄ complexes by reacting THF·B₃H₇ with *t*-BuCH₂NMe₂, BnNMe₂, *t*-BuCH₂PPh₂, (*o*-Tol)₃P, *n*-Bu₃P, 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 LB₃H₇ and L₂B₂H₄ producing LBH₃ and higher boranes (M. Ishii, G. Kodama, *Inorg. Chem.* 1990, 29, 817–820) 2) Inherent instability of L₂B₂H₄ complexes: (Me₃P)₂B₂H₄ decomposes at rt under N₂ (Hertz RK, Denniston ML, Shore SG. *Inorg Chem.* 1978; 17:2673–2674. Even (Ph₃P)₂B₂H₄, which is the most robust L₂B₂H₄ complex due to 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 = Me₃N and Ph₃P were prepared successfully, and therefore the process appears to be highly dependent on the nature of L. Reacting (Ph₃P)₂B₂H₄ with N-heterocyclic carbene BnMeImd produced complex mixtures containing some of the desired L₂B₂H₄ (δ ¹¹B –34 ppm, br t) which could not be isolated due to sensitivity, 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 L₃B₃H₄⁺ cations in the electrophilic activation of L₂B₂H₄ (Ref. 9a) can now be interpreted as L₂B₂H₃⁺ insertion into B–B bond.
28. No H₂ was produced, ruling out the dehydrogenative pathway proposed above for salts with more stable anions. Involvement of L–BH₂–H–B(C₆F₅)₃ appears plausible based on a limited NMR evidence.
29. Disproportionation between Me₂S–BH₃ and B(C₆F₅)₃: Fuller AM, Hughes DL, Lancaster SJ, White CM. *Organometallics.* 2010; 29:2194–2197. C₆F₅-transfer in activated Me₃N–BH₃: Ménard G, Stephan DW. *Dalton Trans.* 2013; 42:5447–5453. [PubMed: 23423186]

Figure 1.

The major features of the reaction profile calculated at M06-2X/6-311++G(3df,2p)//MP2/cc-pVDZ level of theory in PhMe solvent (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.

Figure 2.

Formation of triboron cations **20** ($\text{L}_2\text{B}_2\text{H}_3^+$ fragment highlighted) in the thermal decomposition of the H-bridged complexes **18**. Below: ^{11}B NMR spectra ($L = \text{Me}_3\text{P}$, $X = \text{B}(\text{C}_6\text{F}_5)_4^-$) (i) immediately following generation of **18a** in $d_5\text{-PhBr}$, and (ii) after 18 h at 90°C . Other signals: $\text{B}(\text{C}_6\text{F}_5)_4^-$, -16.2 ppm; $\text{Me}_3\text{P-BH}_3$, -36.4 ppm.

Scheme 1.

Lewis base borane complex activation by electrophiles, a few selected alternatives (L = tertiary amine or phosphine, E = “hydridophile”, X = counterion, Solv = Lewis basic solvent).

Scheme 2.

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

Scheme 3.

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

Table 1Synthesis of C₆F₅BH₂ complexes^[a]

Entry	Substrate	Solvent	Product	Yield
1 ^[b]	Et ₃ N–BH ₃	PhF	Et ₃ N–BH ₂ C ₆ F ₅ (22)	>99%
2	Me ₃ N–BH ₃	CH ₂ Cl ₂	Me ₃ N–BH ₂ C ₆ F ₅ (23)	97%
3	BnMe ₂ N–BH ₃	PhF	BnMe ₂ N–BH ₂ C ₆ F ₅ (24)	>99%
4 ^[c]	Ph ₃ P–BH ₃	CH ₂ Cl ₂	Ph ₃ P–BH ₂ C ₆ F ₅ (25)	71%

^[a] 0.36:1 B(C₆F₅)₃:L–BH₃; 50 °C; 1 h; the reaction performed in sealed vials.^[b] 3 h.^[c] 40 °C.