Elucidation of the Formation Mechanisms of the Octahydrotriborate Anion $(B_3H_8^-)$ through the Nucleophilicity of the B–H Bond

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Supporting Information

ABSTRACT: Boron compounds are well-known electrophiles. Much less known are their nucleophilic properties. By recognition of the nucleophilicity of the B-H bond, the formation mechanism of octahydrotriborate $(B_3H_8^{-})$ was elucidated on the bases of both experimental and computational investigations. Two possible routes from the reaction of BH_4^- and $THF \cdot BH_3$ to $B_3H_8^-$ were proposed, both involving the B_2H_6 and BH_4^- intermediates. The two pathways consist of a set of complicated intermediates, which can convert to each other reversibly at room temperature and can be represented by a reaction circle. Only under reflux can the B2H6 and BH4 intermediates be converted to $B_2H_5^-$ and $BH_3(H_2)$ via a high energy barrier, from which H_2 elimination occurs to yield the $B_3H_8^-$ final product. The formation of B_2H_6 from THF·BH₃ by nucleophilic substitution of the B-H bond was captured and identified, and the reaction of B2H6 with BH4 to produce B3H8 was confirmed experimentally. On the bases of the formation mechanisms of B3H8, we have



developed a facile synthetic method for MB₃H₈ (M = Li and Na) in high yields by directly reacting the corresponding MBH₄ salts with THF·BH₃. In the new synthetic method for MB₃H₈, no electron carriers are needed, allowing convenient preparation of MB₃H₈ in large scales and paving the way for their wide applications.

INTRODUCTION

The octahydrotriborate anion, as a basic hydroborate unit following BH_4^- and $B_2H_7^-$, plays important roles in boron chemistry.^{1,2} The preparation of the alkali salts of octahydrotriborate dated back to Stock's work in the 1920s.^{2a} By shaking potassium or sodium amalgam in the presence of diborane gas, a new compound with an empirical formula of $K(B_2H_6)$ or $Na(B_2H_6)$ was obtained.^{2a-c} In 1949, Newkirk found that the compound with the empirical composition of $Na(B_2H_6)$ had an identical X-ray powder diffraction pattern to sodium borohydride $(NaBH_4)$ ³ the structure of which was first characterized by X-ray powder diffraction in 1947.⁴ The products of the reaction between sodium amalgam and diborane were finally determined to be a mixture of NaB3H8 and NaBH4 in 1:1 ratio based on the results of X-ray, infrared, and elemental chemical analyses in the late 1950s.⁵ Since then, the preparation methods for octahydrotriborate salts have been continually improved,^{2a-j} but its formation mechanisms have not been fully understood.^{1a,2k-o} Recently, the bonding in the $B_3H_8^-$ anion has also been analyzed, highlighting its high stability.⁶

The incremental improvement of the synthetic methods for octahydrotriborate^{2a-j} has been mainly focused on using other boranes to replace the flammable and toxic diborane^{2d-i} or dispersing sodium on other media (eq 1), instead of using sodium amalgam, which causes health and safety concerns.^{2e}

$$2M/(media) + 4THF \cdot BH_3 = MB_3H_8 + MBH_4 + 4THF$$

$$M = alkili metals$$
(1)

Potassium, rubidium, and cesium salts of B₃H₈⁻ were also prepared by the reactions of THF·BH₃ with the corresponding alkali metal amalgams.^{2d} Very recently, K/Na alloy was successfully used to prepare the potassium salt of $B_3H_8^{-2}$. Here we report an investigation on the formation mechanisms of $B_{2}H_{8}^{-}$ upon recognition of the importance of the B–H bond nucleophilic properties, leading to a more convenient preparative method for LiB₃H₈ and NaB₃H₈ by simply using the more convinient MBH_4 compounds (eq 2):

$$MBH_4 + 2THF \cdot BH_3 = MB_3H_8 + H_2 + 2THF$$
$$M = Li \text{ and } Na$$
(2)

Boron and boron-containing compounds are characterized by their electron deficiency so that BH₃ or BR₃ groups usually act as Lewis acids in reactions with Lewis bases to form Lewis acid-base adducts.⁷ Hydroborations are well-known for borane complexes.⁸ In this class of reactions, it is generally understood that the electron-deficient boron uses its empty 2p orbital to

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interact with the electron-rich C=C, C=O, C=N double bonds or C=C triple bond of substrates, leading to an addition reaction of the B–H bond (Scheme 1A).⁹ On the other hand,

Scheme 1. Hydroboration Reactions of Borane Complexes (A) and Nucleophilic Substitution Reactions of Borane Complexes (B)



the slightly lower electronegativity of boron (2.0 in the Pauling scale) compared to that of hydrogen (2.1) makes the hydrogen atoms on boron slightly negative in boron hydrides ($B^{\delta^+}-H^{\delta^-}$). Thus, the partially negatively charged hydrogen atoms in boron hydrides possess Lewis base properties. This Lewis base property of the B–H bond enables R"BH₃ (R" = H⁻, NH₂⁻, THF, and NH₃) to be a nucleophilic reagent in nucleophilic substitution reactions as shown in Scheme 1B. Even though the Lewis acid property of boron complexes has been well recognized, ^{7f,10} relatively little is known about the Lewis base property of the B–H bond.

In a few known examples of nucleophilic substitution reactions involving the B-H bond as a nucleophilic reagent (red in Scheme 1B), the hydride on the B-H bond usually attacks another boron atom (blue) to form an unsupported B-H–B 3c–2e bond. In fact, the dimerization of two BH₃ groups to form diborane belongs to this type of reactions (Scheme S1a). With this important property of the B-H bond, new boron chemistry has been developed recently.^{11a-d} For example, the hydride of the B-H bond in ammonia borane (NH₃BH₃, AB) has been used to substitute THF in THF·BH₃ to form ammonia diborane (NH₃BH₂(μ -H)BH₃, AaDB), which is unstable but can be observed in ¹¹B NMR.^{11a} The observation of this intermediate involving the unsupported B-H-B bond is critical for understanding the formation mechanism of the diammoniate of diborane $([H_2B(NH_3)_2])$ -[BH₄], DADB), which has puzzled chemists for many years.^{11a,d-i} Furthermore, by use of the same nucleophilic substitution of NH₃BH₃ and THF·BH₃, a facile preparative method for aminodiborane $(NH_2B_2H_5, ADB)$ has been developed.^{11b,c} From this point of view, the borohydrate (BH_4^{-}) and its organic borohydrate derivatives $(BH_2R_2^{-})$ can also be considered as a nucleophilic reagent and their reactions with transition metal or lanthanide cations to form single, double, or triple M-H-B bonds should belong to the nucleophilic substitution reactions.¹²

RESULTS AND DISCUSSION

Nucleophilic Behaviors of the B–H Bond. According to the Lewis base property of the B–H bond, four-coordinated $R''BH_3$ complexes ($R'' = H^-$, NH_2^- , THF, and NH_3) can act as a nucleophile using its B–H bond to substitute a weaker base from a Lewis acid–base adduct. The role of the bonding pair

electrons in the B–H bond in this reaction is similar to that of the lone pair electrons in classical nucleophiles. For example, both the lone pair electrons and the B–H bond in the $\rm NH_2BH_3^-$ anion can act as a nucleophile leading to nucleophilic substitution reactions, but the products are different. When NaNH₂BH₃ reacted with AB, the lone pair electrons on N attacked the B atom in AB to form Na[NH₂(BH₃)₂] with one NH₃ leaving (Figure S1 and Scheme 2A).¹³ In contrast, when NaNH₂BH₃ reacted with THF·BH₃,

Scheme 2. Reactions of $NaNH_2BH_3$ with AB (A) or THF-BH₃ (B)



the final products are $(NH_2BH_2)_n$ polymer and BH_4^{-14} It is believed that in this reaction the B–H bond in the $NH_2BH_3^{-14}$ anion acts as a nucleophile to attack the B atom in THF·BH₃ to form $NH_2BH_2(\mu$ -H)BH₃⁻ first and then convert to $(NH_2BH_2)_n$ polymer and BH_4^{-14} with the bridge hydrogen moving to the BH₃ moiety in the unsupported B–H–B bond (Scheme 2B).

Stability of the Unsupported B–H–B Bond. The newly formed unsupported B–H–B bond by the B–H bond nucleophilic substitution is unstable and can easily cleave. The unsupported B–H–B bond only occurs in weak or noncoordinating solvents or when it is stabilized by additional chemical bonding via a subsequent reaction. The B–H–B bond has three possibilities in subsequent reaction steps.

(1) The unsupported B–H–B bond is cleaved by a subsequent reaction. As described above, when $NH_2BH_3^-$ reacted with THF·BH₃ to form $NH_2BH_2(\mu-H)BH_3^-$, the unsupported B–H–B bond broke, resulting in the formation of the final products of the $(NH_2BH_2)_n$ polymer and BH_4^- anions.¹⁴ In this reaction, the formation of the $(NH_2BH_2)_n$ precipitate and the stable BH_4^- anion provides the reaction driving force. Another example is the $B_2H_7^-$ anion formed by the reaction of BH_4^- with THF·BH₃: it can reversibly convert to THF·BH₃ and BH_4^- by cleaving the unsupported B–H–B bond (Figure S2). It is beleived that, compared with a bridge hydride, the coordinating solvents are better eletron donors and the solvent molecules can readily break the weak B–H–B bond to replace the bridge hydride from the B atom in the B–H–B bond.

(2) The unsupported B–H–B bond survives in noncoordinating solvents. The stability of the B–H–B bond depends on the countercation and the coordination ability of the solvents. Although LiB₂H₇ cannot be isolated from the reaction of LiBH₄ and THF·BH₃ in THF solution (Figure S2), the reaction of NR₄BH₄ (R = C₂H₅, C₄H₉) with B₂H₆ in CH₂Cl₂ solution afforded NR₄B₂H₇ which was isolated (eq 3):¹⁵

$$NR_4BH_4 + \frac{1}{2}B_2H_6 \rightarrow NR_4B_2H_7$$
 (R = C₂H₅, C₄H₉)
(3)

This result indicates that $B_2H_7^-$ is only stable in noncoordinating solvents with an organic counter cations.

(3) The unsupported B–H–B bond survives in the final products with the cooperation of other chemical bonds. In the reaction of AB with THF·BH₃ in THF solution, the hydride in AB attacked the B in THF·BH₃ to substitute THF forming the AaDB intermediate, which is unstable and can only be observed in its ¹¹B NMR in the reaction solution.^{11a} However, the subsequent molecular hydrogen elimination resulted in the formation of a stable four-membered ring compound (ADB), in which the formation of the B–NH₂–B bond stabilizes the B–H–B bond,^{11b,c} as depicted in Scheme 3 and Scheme S1b.

Scheme 3. Formation of ADB by Reaction of NH_3BH_3 and $THF \cdot BH_3$ in Which the Formation of the $B-NH_2-B$ Bond Stabilizes the Formed B-H-B Bond



Another example is the dimerization of two BH_3 groups to form diborane in which one unsupported B-H-B bond formed first and the second B-H-B bond formed subsequently, resulting in a relatively stable B_2H_6 (Scheme S1a).

These reactions demonstrate that the nucleophilic substitution of the B–H bond can lead to a new B–H–B bond. However, whether the resulting B–H–B bond can survive in the final product depends on the reaction conditions¹⁵ or if a subsequent reaction can take place to form a stable final product.^{11b,c} This is probably why the nucleophilic substitution of the B–H bond has not attracted much attention, even though it has been known to occur for a long time.

Formation Mechanisms of Octahydrotriborate Anion. The formation mechanism of octahydrotriborate has been discussed previously, but it has not been fully under-stood. $^{1a,2k-o}$ On the basis of the nucleophilic properties of the B-H bond discussed above, we have elucidated the formation mechanisms of octahydrotriborate. Due to the better solubility of lithium borohydride in THF, we have chosen the reaction of LiBH₄ with THF·BH₃ for the mechanistic study. In this reaction, the BH_4^{-} anion acts as a nucleophilic reagent, using the B-H bond to attack the B in THF BH3 and substitute THF to give B₂H₇⁻ by forming an unsupported B-H-B bond (Scheme 1B). The $B_2H_7^-$ product was clearly observed in solution on the basis of ¹¹B NMR, even though the product could not be isolated because of a reversible reaction (Figure S2). Envisioning that the resulting $B_2H_7^-$ anion may undergo a similar substitution reaction with a second THF·BH₃ to form a $H_3B(\mu-H)BH_2(\mu-H)BH_3$ anion $(B_3H_{10}^{-})$, we reacted LiBH₄ with 2 equiv of THF·BH₃. However, only the starting materials and the $B_2H_7^-$ signals were observed in the ¹¹B NMR at room temperature (Figure S3) or even at 50 °C (Figure 1a). But when the reaction mixture was refluxed, the $B_3H_8^-$ signal appeared (Figure 1b) and THF·BH₃ could be completely consumed after reflux for about 36 h (Figure 1e).

In order to gain more insights into the formation mechanism of $B_3H_8^-$, density functional theory (DFT) calculations were performed using the Gaussian 09 program.¹⁶ The theoretical results are consistent with the experimental observations: BH_4^- reacts with the first THF·BH₃ to form $B_2H_7^-$ by attacking the B of THF·BH₃ with the B–H bond. The free energy barrier of



Figure 1. ¹¹B NMR spectra of LiBH₄ and THF \cdot BH₃ in THF (a) at 50 °C for 12 h and under reflux condition for (b) 6 h, (c) 15 h, (d) 24 h, and (e) 36 h.

the transition state TS1 is computed to be 15.8 kcal/mol in THF solvent (Table 1). Then, a terminal hydride of $B_2H_7^-$

Table 1. Calculated Electronic Energy (at 0 K), Enthalpy (at 298 K), and Free Energy (at 298 K) in kcal/mol

	$\Delta E (0 \text{ K})$	ΔH (298 K)	$\Delta G/\Delta G_{\rm corr}^{a}$ (298 K)
$\text{THF} \cdot \text{BH}_3 + \text{BH}_4^-$	0	0	0
TS1	20.6	18.9	18.6/15.8
THF + $B_2H_7^-$	2.5	2.4	0.7
$\text{THF} \cdot \text{BH}_3 + \text{B}_2 \text{H}_7^-$	0	0	0
TS2	15.4	14.3	13.1/10.3
THF + $B_{3}H_{10}^{-}$	9.9	9.0	7.9
$B_{3}H_{10}^{-}$	0	0	0
TS3	5.9	4.8	6.0
$B_2H_6 + BH_4^-$	1.3	1.2	0.9
TS4	34.3	31.4	32.0
$B_2H_5 + BH_3(H_2)$	33.5	31.8	31.4
TS5	42.4	38.1	36.6
$B_{3}H_{8}^{-} + H_{2}$	-4.9	-6.1	-11.2
$2THF \cdot BH_3$	0	0	0
TS1-1	13.9	14.7	15.5/12.7
$THF \cdot B_2H_6 + THF$	5.0	8.9	10.1
$THF \cdot B_2 H_6$	0	0	0
TS2-1	3.1	4.8	5.1
$B_2H_6 + THF$	-6.7	-0.1	-2.0
AC AC 28 halfmal based on free release theory for			

 ${}^{a}\Delta G_{\rm corr} = \Delta G - 2.8$ kcal/mol, based on free volume theory for bimolecular reactions in solution.

further attacks the B in the second THF·BH₃ to replace THF to form $B_3H_{10}^-$ (Figure 2). This reaction requires a free energy of 10.3 kcal/mol, but the reverse energy barrier is much lower (2.4 kcal/mol, Figure 2).

The DFT calculation further provides significant insight about how $B_3H_{10}^-$ converts to $B_3H_8^-$ by eliminating molecular hydrogen, which is important because no intermediates could be captured experimentally. First, we calculated the NPA charges and found that the charges of all the hydrogen atoms are negative (Figure 3a), implying that direct hydrogen release from $B_3H_{10}^-$ would be difficult. Interestingly, a transition state TS3 for the formation of B_2H_6 and BH_4^- was located with an energy barrier of only 6.0 kcal/mol (Figure 4). The natural population analysis (NPA) charges of the $B_2H_6\cdots BH_4^-$ complex showed that the bridge hydrogens are positively charged (0.11 and 0.19) and the hydrogens of BH_4^- are negatively charged (Figure 3b), suggesting the possibility of hydrogen elimination by the $H^{\delta_1}\cdots H^{\delta_-}$ interaction, a dihydrogen bond.^{11d}



Figure 2. Energy profiles for the reactions from BH_4^- and $THF \cdot BH_3$ to $B_3H_{10}^-$.



Figure 3. NPA charges of (a) $B_3H_{10}^-$ and (b) $B_2H_6\cdots BH_4^-$.



Figure 4. Energy profiles for the reaction from $B_3H_{10}^-$ to $B_3H_8^-$.

The $B_2H_5^-$ and $BH_3(H_2)$ intermediates were formed through TS4 with a calculated energy barrier of 31.1 kcal/mol in THF solvent. Then molecular hydrogen elimination (TS5) resulted in the formation of $B_3H_8^-$, which is exothermic by 11.2 kcal/mol (Figure 4).

According to the energy profiles of Figures 2 and 4, the B_2H_6 intermediate has two possible reactions: reacting with BH_4^- to reversibly re-form $B_3H_{10}^-$ and further to $B_2H_7^-$ (reaction 1) or reacting with BH_4^- to convert to $B_3H_8^-$ by releasing one H_2 (reaction 2). Furthermore, B_2H_6 could also react with the THF solvent to form THF·BH₃ as the reverse reactions shown in Figure 5 (reaction 3). Though the possible reactions 1 and 3 have relatively low energy barriers of 5.1 and 2.4 kcal/mol (TS3 and TS2, reverse reactions) and 7.1 and 2.6 kcal/mol (TS2-1 and TS1-1, reverse reactions) (Figure 5), respectively, a higher temperature would be required to form $B_3H_8^-$ via reaction 2.



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Figure 5. Formation mechanism of B_2H_6 from two THF·BH₃.

Once formed, the final product $B_3H_8^-$ is stable and cannot be reversibly converted to B_2H_6 and BH_4^- due to the high reversereaction energy barrier (47.8 kcal/mol). The escape of the resulting H_2 gas from the system would also make the reverse reaction impossible.

The experimental and computational results are fundamentally consistent with the proposed formation mechanism of B3H8-. The low energy barriers of the two nucleophilic substitution reactions of BH_4^- and $B_2H_7^-$ with $THF{\cdot}BH_3$ molecules to yield $B_3H_{10}^-$ (15.8 and 10.3 kcal/mol, respectively, in Table 1 and Figure 2) suggested that both reactions could occur at room temperature (Figure S2). Only the signal of $B_2H_7^-$ could be observed in the ¹¹B NMR due to the fact that the resulting $B_3H_{10}^-$ would be rapidly converted back to $B_2H_7^-$ with an energy barrier of only 2.4 kcal/mol (TS2, reverse reaction) or further converted to B_2H_6 and $BH_4^$ via TS3 with an energy barrier of only 6.0 kcal/mol. The calculated energy barrier of 31.1 kcal/mol (TS4) for the reaction of B_2H_6 and BH_4^- to produce $B_3H_8^-$ in THF supports the experimental observation that this reaction only occurred under reflux condition. Furthermore, the transformation from B_3H_{10} to B_3H_8 is exothermic by 11.2 kcal/mol, so B_3H_8 is expected to be very stable once formed.

Observation of the B₂**H**₆ **Intermediate and Its Roles in the Reactions To form B**₃**H**₈⁻. The B₂H₆ formed via TS3 seems to be a key intermediate in the proposed mechanism. Hence, it would be important to find out how B₂H₆ is formed and the roles it plays in the reactions. However, it is difficult to detect the formed B₂H₆ in THF solution because B₂H₆ would rapidly react with THF to produce the starting material THF·BH₃ (reaction 3). On the other hand, it is known that the BH₃ group exists as a B₂H₆ dimer rather than L·BH₃ in diethyl ether (Et₂O).¹⁷ We also did experiment and found that the BH₃ group exists as the B₂H₆ dimer in dimethoxyethane (DME), albeit with a limited solubility (Figure S4).^{11j} So we chose Et₂O to trap the resulting gases in the reaction of LiBH₄ with THF·BH₃. We indeed captured B₂H₆ and identified it by ¹¹B NMR (Figure S5).

In order to determine the roles of the B_2H_6 intermediate in the reactions, we used Et_2O and DME as solvents to investigate the reaction of B_2H_6 with LiBH₄ to gain further insight into the proposed mechanisms. In both Et_2O and DME solvents, we expect that the hydride of BH_4^- attacks the B in B_2H_6 , breaking one of its H-bridge bond to form $B_3H_{10}^-$ by one step (Scheme 4). Even though the nascent $B_3H_{10}^-$ cannot be observed experimentally, its lower-barrier reverse reactions via TS2 (Figure 2) should be able to be observed.

Indeed, when an excess amount of B_2H_6 was bubbled into a DME solution of LiBH₄ at low temperature (-78 °C), the signals corresponding to the BH₄⁻ starting material and the

Scheme 4. Proposed Mechanisms of the Reaction between B_2H_6 with $LiBH_4$ in DME To Produce LiB_2H_7 and $LiBH_4$ or Produce LiB_3H_8 under Reflux



expected $B_2H_7^-$ product were clearly observed in ^{11}B NMR (Figure S6a). This observation confirmed that B_2H_6 reacted with BH_4^- at low temperature to form $B_3H_{10}^-$ via TS3 (the energy barrier of 5.1 kcal/mol, reverse reaction), which then form $B_2H_7^-$ facilely via TS2 (barrier of only 2.4 kcal/mol). The observation of the BH4- signal implies that the reaction could not be completed at low temperature. No B₂H₆ signal was observed, probably due to the limited solubility of B2H6 in DME at the low temperature. When the experiment was carried out at room temperature, only B2H7 signal was observed (Figure S6b), suggesting that BH_4^- can completely react with excessive B₂H₆ in DME at room temperature. Furthermore, when the B₂H₆ bubbling experiment was carried out under reflux condition, the $B_3H_8^-$ signal appeared (Figure S6c) and simultaneously a large amount of BH₄⁻ formed. This observation indicated that the reflux temperature of DME provides enough reaction driving force for the formation of $B_3H_8^-$ by crossing the high energy barrier of TS4 (31.1 kcal/ mol). The large amount of BH₄⁻ is expected, due to the low energy barrier for the formation of BH₄⁻ via TS1 (reverse reaction).

Similar B_2H_6 bubbling experiment was also carried out in Et₂O with similar observations. Both $B_2H_7^-$ and BH_4^- signals were observed at low and room temperatures (Figures S7, S8a). However, when the B_2H_6 bubbling experiment was carried out under reflux, only a BH_4^- signal was observed in ¹¹B NMR without the $B_3H_8^-$ signal (Figure S8b). We think the low boiling point of Et₂O cannot drive the reaction to cross the high energy barrier of TS4 (31.1 kcal/mol). On the other hand, the formed $B_2H_7^-$ anion could convert to BH_4^- after cleaving BH₃ under reflux by crossing TS1 (reverse reaction, Figure 2). The cleaved BH₃ dimerized to B_2H_6 , which escaped from the reaction mixture. Thus, only BH_4^- signal was observed under reflux (Scheme S2). These results confirmed the two possible reactions 1 and 2 of B_2H_6 and BH_4^- in the proposed mechanism.

Trapping B₂**H**₆ **Formed from THF·BH**₃. After finding the crucial roles of the B₂H₆ intermediate in the reactions to form B₃H₈⁻, we further explored whether B₂H₆ could be formed by other pathways, other than from B₃H₁₀⁻. The BH₃ group was known to exist as a B₂H₆ dimer in Et₂O, so it was used to trap the resulting gases when a THF·BH₃ solution (1 M) was refluxed without addition of LiBH₄ for 36 h. Indeed, we found that B₂H₆ and other unidentified boranes were formed (Figure S9). We were surprised that B₂H₆ could also be trapped in Et₂O when N₂ was simply bubbled through a THF·BH₃ solution (1

M) at room temperature (Figure S10).¹⁸ Thus, the formed B_2H_6 in the proposed mechanism might be from the THF·BH₃ solution. With this consideration, the second possible pathway was proposed (Scheme 4) and the calculation results support the new proposed pathway for the formation of B_2H_6 (Figure 4).

In THF·BH₃ solution, the B–H bond in one THF·BH₃ molecule acts as a nucleophile to attack the B in another THF·BH₃ molecule to form THF·B₂H₆ (TS1-1, 12.7 kcal/mol) (Figure 5). Then, the terminal hydride of the BH₃ moiety in THFBH₂(μ -H)BH₃ attacked another B in the same intermediate to form B₂H₆ with THF leaving and ring closing (TS2-1, 5.1 kcal/mol) (Figure 5, Scheme S1). The resulting B₂H₆ can react with BH₄⁻ through reaction 1 or 2 as described above.

Isotopic experiment indicated that the deuteride/hydride exchange between THF·BD₃ and LiBH₄ occurred rapidly; thus the rate of the formation of $B_2H_7^-$ did not change obviously (Figure S11, Scheme S3). However, the rate of the formation of LiB₃H₈ is much slower, which revealed that the cleavage of the B–H bond to form H₂ is the rate-limiting step (Figure S12). This result is consistent with the proposed mechanisms.

The combination of experimental and computational studies indicated that B_2H_6 can be formed via both proposed pathways. The formation of B_2H_6 by the second pathway needed to cross the highest energy of 12.7 kcal/mol (TS1-1), but in the first one it is 15.8 kcal/mol (TS1). On considering the fact that B_2H_7 can be formed at both room and low (-78 °C) temperatures (Figure S13), the second proposed pathway seems to be more favorable. A previous report of the reaction between B₂H₆ and alkali metal borohydrides in ethers at 100 °C readily produced octahydrotriborate salts.^{2k} Recent studies indicated that B_2H_6 produced in situ reacted with sodium borohydride to produce NaB_3H_8 .^{21-o} A gas-solid reaction of B_2H_6 with MgNiH₄ was found to produce Mg(B_3H_8)₂. It is believed that the $Mg(BH_4)_2$ intermediate continually reacted with B₂H₆ to produce the final product.^{1a} All of these experimental results seem to support the second pathway, but the first one cannot be ruled out.

The experimental and computational results discussed above suggested that the two proposed pathways from the starting reagents of THF·BH₃ and BH₄⁻ to the B₂H₆ + BH₄⁻ intermediates consist of a complicated set of reactions and reverse reactions that can be represented by a reaction circle at room temperature (Scheme S4). All the species in the circle, THF·BH₃ + BH₄⁻, B₂H₇⁻, B₃H₁₀⁻, B₂H₆ + BH₄⁻, and THF·BH₂(μ -H)BH₃, could be reversibly converted to its neighboring species at room temperature. The elimination of H₂ could not happen directly from B₃H₁₀⁻ to produce B₃H₈⁻. Only at reflux condition could the reaction of B₂H₆ with BH₄⁻ afford the B₂H₅⁻ and BH₃(H₂) intermediates, from which a H₂ elimination led to the formation of B₃H₈⁻ (Scheme S4). This level of complexity underlies the reason why it has been difficult to understand the formation mechanisms of B₃H₈⁻.

New Methods for the Syntheses of Lithium and Sodium Octahydrotriborate. The previously reported syntheses of the octahydrotriborate anion were all carried out by reacting boranes (diborane or THF·BH₃) with alkali metal amalgam or alkali metal dispersing in other media such as silica gel or inert salt or in the presence of other electron carriers (naphthalenide and tetraphenylborate).^{2a-j} Moreover, in these reactions the final products are $B_3H_8^-$ and BH_4^- salts in 1:1 ratio (eq 1); i.e., at least a quarter of boranes did not convert to the expected product. There has been no report for preparation

of octahydrotriborates by straightforwardly reacting borohydride with THF·BH₃. On the basis of the understanding of the nucleophilicity of the B–H bond and the formation mechanism of $B_3H_8^-$, we have developed a new and facile synthetic method for lithium and sodium salts of octahydrotriborate (eq 2). A mixture of LiBH₄ and THF·BH₃ in 1:2 ratio in THF solution was refluxed for 36 h. We observed that most of the starting materials were converted to $B_3H_8^-$, according to eq 2.

Only a small amount of $LiBH_4$ was left in the solution on the basis of the ¹¹B NMR (Figure 6a). After a small amount of



Figure 6. ¹¹B NMR spectra of the reaction solution of $LiBH_4$ and THF·BH₃ in THF refluxed for 36 h (a) and after addition of water (0.5 mL) into the reaction solution (b).

water was added to consume the unreacted LiBH₄ (Figure 6b), the reaction mixture was filtered and the filtrate was then pumped under kinetic vacuum to produce an oily solid product, which was confirmed by ¹¹B and ¹H NMR (Figures S14 and S15) to be the desired Li(THF)_{1.5}B₃H₈ product with a purity of 95% in 41% isolated yield.

A small amount of the LiBH₄ reactant was always observed in the reaction solution, even if an excess amount of THF·BH₃ was used. This observation was mainly due to the fact that part of THF·BH₃ reactant was converted to B₂H₆ and other borane complexes (unidentified currently) when the THF·BH₃ solution was refluxed. The formed B₂H₆ was evaporated from the reacting system, as mentioned above (Figure S9), resulting in a net loss of the THF·BH₃ reactant. We found that the loss of THF·BH₃ via the release of B₂H₆ depended on the THF· BH₃ concentration. When a 1 M THF·BH₃ solution was refluxed for 36 h, about 32% of BH₃ was lost on the basis of the integrated values in ¹¹B NMR using NMe₃BH₃ as an internal standard (Figure S16). When a 0.5 M THF·BH₃ solution was refluxed for 40 h, about 25% of BH₃ was lost (Figure S17). When a 0.25 M THF·BH₃ solution was refluxed for 40 h, about 14% of BH₃ was lost (Figure S18). The inevitable loss of THF \cdot BH₃ via B₂H₆ release under reflux was the reason why a small amount of unreacted LiBH4 was always observed, even when an excess amount of THF·BH₃ was used.

The reactions of LiBH₄ with different concentrations of THF·BH₃ were carried out in order to examine the influence of the THF·BH₃ concentration on the yields and to optimize the reaction condition. As expected, a higher yield was obtained with a lower concentration of THF·BH₃. When a 0.5 and 0.25 M THF·BH₃ solution reacted with LiBH₄, the yields were 65% and 73%, respectively, based on the integrated values in ¹¹B NMR (NMR yield,¹⁹ Figures S19 and S20), and the isolated yields were 54% and 66%, respectively. These are much higher than 55% (NMR yield) and 41% (isolated yield) of the reaction using 1 M THF·BH₃ solution (Figure S21). Furthermore, when a 20% excess amount of 0.5 or 0.25 M THF·BH₃ solution was

used in the reaction, the yield was further increased to 79% and 81% (NMR yield) (Figures S22 and S23), and 69% and 73% (isolated yield) were calculated on the basis of LiBH₄.

In order to prevent the resulting B_2H_6 from escaping from the reaction system, we further carried out the reaction in an autoclave. When a 1 M THF·BH₃ solution reacted with LiBH₄ in the autoclave at 65 °C for 15 h, a NMR yield of 78.5% (Figure S24) and an isolated yield of 68% were achieved. Hence, we conclude that the reaction in autoclave is an efficient way for the preparation of lithium octahydrotriborate.

Slight decomposition of LiB_3H_8 to $LiBH_4$ was also observed in refluxing THF after 36 h (Figure S25). The unreacted or decomposed $LiBH_4$ could be easily removed by the addition of a small amount of water.

Sodium octahydrotriborate can be similarly prepared by using NaBH₄ and THF·BH₃, according to eq 2. A longer reaction time (66 h) was required because of poor solubility of NaBH₄ in THF. The purification procedure is similar to that of LiB₃H₈ (Figure S26). It is worthy to note that in this newly developed procedure, unsolvated NaB₃H₈ can be obtained simply by addition of only CH₂Cl₂ without further additoin of Et₂O as described in the literature.^{2g} The purity of the final product is more than 95% on the basis of ¹¹B and ¹H NMR (Figures S27, S28) with a 43% isolated yield.

The isolated yield of NaB_3H_8 was incressed to 51% by using an autoclave at 65 °C for 24 h via the reaction of $NaBH_4$ with 1 M THF·BH₃, which is not a huge increase in comparison with the 43% yield for the reaction under reflux. The increase of the isolated yield is not as much as that in the LiBH₄ reaction. This could be attributed to the longer reaction time because of the limited solubility of NaBH₄ in THF, leading to more THF·BH₃ decomposition.

We should point out that the similar procedure cannot be used to prepare potassium octahydrotriborate probably due to the very low solubility of KBH₄ in THF (Figure S29).

CONCLUSIONS

In summary, the formation mechanisms of $B_3H_8^-$ from the direct reaction of BH₄⁻ and THF·BH₃ have been elucidated by the combination of experimental and computational studies based on the understanding of the nucleophilicity of the B-H bond. An intuitive mechanism for the formation of LiB₃H₈ was proposed. The nucleophilic substitution of the B-H bond in BH_4^- to THF in THF·BH₃ produced $B_2H_7^-$. The terminal B-H bond in $B_2H_7^{\,-}$ further substitutes THF in a second THF- BH_3 to produce $B_3H_{10}^{-}$. Theoretical calculations indicated that a H_2 molecule cannot be directly eliminated from $B_3H_{10}^{-}$ to form $B_3H_8^-$, but $B_3H_{10}^-$ could convert to B_2H_6 and BH_4^- and then to $B_2H_5^-$ and $BH_3(H_2)$ intermediates, from which the elimination of H_2 resulted in the final $B_3H_8^-$ product. The high calculated energy barrier of the $B_2H_6 + BH_4^- \rightarrow B_2H_5^- +$ $BH_3(H_2)$ step (TS4 in Figure 4) is consistent with the experimental observation that this step can only take place under reflux. The $B_2H_7^-$ intermediate was observed in ${}^{11}B$ NMR, and the resulting B_2H_6 intermediate was captured. In another proposed mechanism, an initial reaction of two THF· BH₃ molecules produced B₂H₆, which further reacted with BH_4^- to form $B_2H_5^- + BH_3(H_2)$ and then to $B_3H_8^-$. The conversion from B_2H_6 to $B_3H_8^-$ was confirmed experimentally. The fact that $B_2H_7^-$ can be formed not only at room temperature but also at low temperature (-78 °C) suggests that the second proposed pathway seems to be more favorable for the formation of $B_3H_8^-$, but the first one cannot be ruled out. The two proposed pathways consist of a reaction circle in which all species of THF·BH₃ + BH₄⁻, B₂H₇⁻, B₃H₁₀⁻, B₂H₆ + BH₄⁻, and THF·BH₂(μ -H)BH₃ could be reversibly converted to its neighboring species at room temperature. Only under reflux can the B₃H₁₀⁻ intermediate be converted to the B₃H₈⁻ via H₂ elimination. On the basis of the understanding of the formation mechanisms of B₃H₈⁻, a facile method for the synthesis of MB₃H₈ (M = Li and Na) with high yields has been developed by the reactions of MBH₄ and THF·BH₃ under reflux. The synthetic method significantly simplifies the reaction procedures without using the highly toxic and reactive diborane, electron carriers, or other reaction media and allows convenient preparation of MB₃H₈ in large scales.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out on a Schlenk line or in a glovebox filled with high-purity nitrogen. The ¹¹B NMR spectra were obtained at 128 or 193 MHz and externally referenced to BF₃·OEt₂ in C_6D_6 ($\delta = 0.00$ ppm). The ¹H NMR and ¹H{¹¹B} spectra were obtained at 400 MHz.

Chemicals of LiBH₄, NaBH₄, KBH₄, NaH, NaBD₄, and I₂ were purchased from Sigma-Aldrich, and the NaH was washed with tetrahydrofuran (THF) and *n*-hexane. THF·BH₃, Me₃NBH₃, and NH₃BH₃ were purchased from United Boron (Zhengzhou) Energy Materials S&T LLC and used as received. NaNH₂BH₃ was prepared according to the literature.²⁰ B₂H₆ was prepared by the reaction of NaBH₄ with I₂ in DME (see Supporting Information).²¹ THF, dimethoxyethane (DME), diethyl ether (Et₂O), *n*-hexane, and toluene were dried over sodium/benzophenone and freshly distilled prior to use. Dichloromethane was dried over calcium hydride.

Computational Details. All DFT calculations were performed using the Gaussian 09 program.¹⁶ The geometries were optimized at M062X/6-311++G(d,p) level of theory, and single-point energy calculations in the THF solvent with the SMD approach²² were carried out using the fully optimized geometries in vacuum. M062X functional was proved to be very accurate for reproducing thermodynamic data, barrier heights, and isomerization energies.² Vibrational frequencies were calculated at the same level to determine whether a species was an equilibrium structure or a transition state (TS). Occurence of imaginary vibrational frequencies would suggest the related species to be a TS. Natural population analysis (NPA) was used to evaluate atomic charges. Gibbs free energy (ΔG , kcal/mol at 298 K) barriers were computed to understand the reactions. For bimolecular reactions, it was difficult to accurately estimate activation entropies for the solution-based reactions. We corrected the activation Gibbs free energy ΔG (in kcal/mol) at 298 K using the free volume theory.²⁴ This provided a rate for a solution-based bimolecular reaction that was about 80 times faster than the corresponding reaction in the gas phase. This result suggested that the activation free energy for a solution reaction should be about 2.8 kcal/mol smaller than the value calculated in the gas phase. The Cartesian coordinates and vibrational frequencies of the studied model species are listed in the Supporting Information.

Reaction of LiBH₄ with THF·BH₃ at Room Temperature. In a drybox, LiBH₄ (0.11 g, 5 mmol) was put into a 50 mL flask which was connected to a Schlenk line and then 20 mL of THF·BH₃ (20 mmol) was condensed in to the flask at -78 °C. The reaction mixture was stirred for 20 h at room temperature. After the LiBH₄ reagent was completely consumed (Figure S2a), THF and excess THF·BH₃ were removed from the reaction solution under dynamic vacuum. The final residue sticky solid was identified as LiBH₄ by ¹¹B NMR (Figure S2b).

Reaction of LiBH₄ with THF·BH₃ at Low Temperature. In a drybox, LiBH₄ (0.11 g, 5 mmol) was put into a 25 mL flask which was connected to a Schlenk line and then 10 mL of THF·BH₃ (10 mL, 10 mmol) was condensed into the flask at -78 °C. The reaction mixture was stirred for 2 h at -78 °C, and then the mixture solution was transferred into a NMR tube which was kept in a -78 °C bath. The mixture was monitored by ¹¹B NMR at -88 °C (Figure S13).

Reaction of NaNH₂BH₃ with NH₃BH₃. NaNH₂BH₃ (0.53 g, 10 mmol) and NH₃BH₃ (0.31 g, 10 mmol) were placed in a 100 mL flask. About 30 mL of THF was condensed into the flask, and the reaction mixture was refluxed for 9 h. Then 30 mL of *n*-hexane was added into the solution and a white precipitate was formed. After filtration, THF and *n*-hexane were removed from the filtrate under dynamic vacuum to leave a white powder product Na[BH₃NH₂BH₃] (0.25 g, 38%, Figure S1). ¹¹B NMR (128 MH_Z, THF-*d*₈): δ –19.9 (d, *J* = 90 Hz) ppm.

Reaction of B₂H₆ with LiBH₄ in DME. Lithium borohydride (0.11 g, 5 mmol) was added to a 25 mL flask and then 10 mL of DME was condensed into the flask at -78 °C. The prepared B₂H₆ by the reaction of NaBH₄ and I₂ (excess, about 10–15 mmol) with N₂ was bubbled into the reaction solution under stirring, and then the solution was monitored by ¹¹B NMR (Figure S6a). Similar precedures were carried out at both room temperature and under reflux. The resulting solutions were monitored by ¹¹B NMR (Figures S6b and S6c).

The reaction of B_2H_6 with LiBH₄ in Et₂O was similar to the reaction in DME. Detailed procedures are described in Supporting Information.

Stability of THF·BH₃. A sample of Me₃NBH₃⁻ (0.73 g, 10 mmol) was added to a 50 mL flask, and then about 20 mL of 1 M THF·BH₃ was condensed into the flask. Then the solution was refluxed for 36 h and the evaporated gases were trapped by Et₂O (Figure S9) through the ice—water condenser. The mixture solution of Me₃NBH₃ and THF·BH₃ was determined by ¹¹B NMR before and after reflux (Figure S16). Similar procedures to examine the stability of 0.5 and 0.25 M THF·BH₃ under reflux are described in Supporting Information.

A sample of 1 M THF·BH₃ (20 mL, 20 mmol) solution was condensed into a 50 mL flask. At room temperature, N_2 was bubbled through the reaction solution at a flow rate of 5 mL min⁻¹ for 6 h under constant stirring. And then the gases were trapped by Et₂O through ice–water condenser. The trapped Et₂O solution was examined by ¹¹B NMR (Figure S10).

Synthesis of Li(THF)_{1.5}B₃H₈. Lithium borohydride (0.44 g, 20 mmol) was added to a 100 mL flask, and then 1 M THF·BH₃ (40 mL, 40 mmol) was condensed into the flask. The reaction mixture was refluxed under stirring for 36 h. The formed gases were passed through tol- d_{8} , in which the formed H₂ was identifed (Figure S30). After reaction, a small amount of water (0.5 mL) was injected into the solution to destroy the residue LiBH₄. After filtration, THF was removed from the filtrate under dynamic vacuum to leave Li(THF)_{1.5}B₃H₈ as a clear oily product (NMR yield of about 55%, isolated yield of 1.27 g, 41% (Figures S14 and S15). $^{11}\mathrm{B}$ NMR (128 MH_z, D₂O): δ -31.2 (nonet, J = 33 Hz) ppm. ¹¹B NMR (128 MH_z, CD_3CN : δ -30.8 (nonet, J = 33 Hz) ppm. ¹H NMR (400 MH_z) D_2O): δ 3.77 (m, 4 α -H of THF), 1.91 (m, 4 β -H of THF), 0.30 (decet, J = 33 Hz, 8H of B₃H₈) ppm. ¹H{¹¹B} (400 MH₇, D₂O): δ 3.78 (m, 4α -H of THF), 1.92 (m, 4β -H of THF), 0.3 (s, 8H of B₃H₈) ppm. ¹H NMR (400 MH_Z, CD₃CN): δ 3.65 (m, 4 α -H of THF), 1.80 (m, 4 β -H of THF), 0.13 (decet, I = 33 Hz, 8H of B_3H_8) ppm. ¹H{¹¹B} (400 MH_Z, CD₃CN): δ 3.65 (m, 4 α -H of THF), 1.81 (m, 4 β -H of THF), 0.13 (s, 8H of B_3H_8) ppm.

Similar procedures for synthesis of $\text{Li}(\text{THF})_{1,5}\text{B}_3\text{H}_8$ by LiBH_4 with different concentrations of $\text{THF}\cdot\text{BH}_3$ solutions are described in Supporting Information.

Synthesis of Li(THF)_{1.5}**B**₃**H**₈ **in Autoclave.** Lithium borohydride (0.22 g, 10 mmol) was added to a 50 mL autoclave, and then 1 M THF·BH₃ (20 mL, 20 mmol) was condensed into the autoclave. The reaction mixture was stirred for 15 h at 65 °C. Then THF and residue THF·BH₃ were removed from the reaction solution to leave a oily product. 20 mL of THF and water (0.1 mL) were injected into the oily product to remove the residue LiBH₄. After the formed precipitate was filtered, THF was removed from the filtrate under dynamic vacuum to leave Li(THF)_{1.5}B₃H₈ as a clear oily product (NMR yield of about 78.5%, isolated yield of 1.06 g, 68%, Figure S24).

Synthesis of Unsolvated NaB₃H₈. Sodium borohydride (0.76 g, 20 mmol) was added to a 100 mL flask, and then THF·BH₃ (40 mL, 40 mmol) was condensed into the flask. The reaction mixture was refluxed for 66 h under stirring. After filtration, water (0.05 mL) was injected into the solution to consume the soluble residue NaBH₄ in

solution. The formed precipitate was filtered, and then THF was removed from the filtrate under dynamic vacuum to leave an oily product. The oily product was dissolved in CH_2Cl_2 and converted into suspension under stirring. After filtration, unsolvated NaB_3H_8 was obtained and dried under dynamic vacuum. Approximately 0.55 g of NaB_3H_8 was obtained with the 43% isolated yield (Figures S27 and S28; no NMR yield is available because $NaBH_4$ cannot be completely disolved in THF). ¹¹B NMR (128 MH₂, CD₃CN): δ –30.0 (nonet, *J* = 33 Hz) ppm. ¹H NMR (400 MH₂, CD₃CN): δ 0.14 (decet, *J* = 33 Hz) ppm.

Synthesis of Unsolvated NaB₃**H**₈ in Autoclave. Sodium borohydride (0.38 g, 10 mmol) was added to a 50 mL autoclave, and then 1 M THF·BH₃ (20 mL, 20 mmol) was injected into the autoclave. The reaction mixture was stirred for 24 h at 65 °C. After the insoluble NaBH₄ was filtered away, the THF and residue THF·BH₃ were removed from the reaction solution to leave a oily product. 20 mL of THF and water (0.05 mL) were injected into the oily product to destroy the soluble residue NaBH₄. After filtration, THF was removed from the filtrate under dynamic vacuum to leave a clear oily product. The oily product was dissolved in CH₂Cl₂ and converted into suspension under stirring. After filtration, unsolvated NaB₃H₈ was obtained and dried under dynamic vacuum (0.32 g, 51%).

Reaction of KBH₄ with **THF·BH**₃. Potassium borohydride (0.54 g, 10 mmol) was added to a flask, and then THF·BH₃ (20 mL, 20 mmol) was condensed into the flask. The reaction mixture was refluxed for 80 h under stirring, and a very small amount of $B_3H_8^-$ product was observed (Figure S29).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03785.

Details for experiments, characterizations, and computations (PDF)

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Notes

The authors declare no competing financial interest.

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