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Selective synthesis of the $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$ borane derivatives and the general mechanisms of the B–H bond condensation

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Polyhedral boranes are a class of well-known boron molecular clusters with unique physical and chemical properties, and great efforts have been made in the past decades to find more effective synthetic methods. However, the established synthetic methods suffer from low efficiency and low selectivity because the mechanism of the B–H bond condensation reaction, critical for the synthesis of the polyhedral boranes, is not well understood. Here we report highly selective and efficient synthetic methods of the salts of the tetradecahydridoundecaborate (1–) ($B_{11}H_{14}^{-}$) and dodecahydrido-dodecaborates (2–) ($B_{12}H_{12}^{2-}$) anions by employing commercially available and inexpensive starting materials. Both theoretical and experimental investigations are carried out to elucidate the reaction mechanisms. We have found that the nature of the B–H bond condensation is the dihydrogen bonding interaction in which the positively charged hydrogens (bridged hydrogens) play a crucial role. The current study has not only led to more effective and selective synthetic methods for $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$ but also unveiled the nature of the B–H bond condensation and the general formation mechanisms of polyhedral boranes. This finding will facilitate the development of more effective synthetic methods for polyhedral boranes and spur their wide application.

Boranes, polyhedral boranes, dihydrogen bond, nucleophilicity

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1 Introduction

Polyhedral boranes are a class of well-known boron molecular clusters widely used in energy, chemistry, medicine, and material science because of their unique structure and physical and chemical properties [1]. Therefore, the synthesis of polyhedral boranes has attracted great attention. The established synthetic methods for over almost a century [2] are mainly based on reactions of borohydrides with diborane (6) (B_2H_6) (in pressure equipment) [2c,2d,2h], pentaborane (9) (B_5H_9) [2e], and decaborane (14) ($B_{10}H_{14}$) [2b,2f,2m] for the synthesis of various polyhedral borane anions, including $B_3H_8^{-}$, $B_{11}H_{14}^{-}$, and $B_{12}H_{12}^{2-}$. In these reactions, an essential point is how to form the B–B bonds through the B–H bond condensation reaction [2g]. However, the condensation reactions of the small borane complexes are carried out under elevated temperatures in different solvents, resulting in problems of products hardly predictable and controllable. The reaction mechanisms proposed in previous reports are not fully understood [2h,3]. As a result, mixtures of several polyhedral boranes are frequently obtained in such reactions [4]. Therefore, understanding the factors underlying these reactions and exploring the mechanism of the B–H bond

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condensation reaction are crucial for finding highly selective and efficient syntheses of polyhedral boranes and have been a long-sought goal in boron chemistry.

Recently, during our systematical investigation of the synthetic methods of amine boranes and the $B_3H_8^-$ anion, we found that the B–H bonding pair electrons, similar to the lone pair electrons of the traditional nucleophiles, can be used in the nucleophilic substitution reaction to substitute the leaving group to form B–H–B 3c–2e bond (Figure 1) [5]. The energy profiles of these reactions depend on the nucliophilicity of the B–H bonding pair electrons, the leaving groups, the stability of the products, and solvents, as shown in Table S2 (Supporting Information online). Further experimental and computational studies on the formation mechanisms of the $B_3H_8^-$ anion through the reactions of the alkali metal salt of borohydride (MBH_4) and Lewis base borane adducts ($L•BH_3$) revealed that the B_2H_6 species formed *in situ* is a crucial intermediate [5a,5e]. The acidic character of the bridging hydrogens of B_2H_6 plays an essential role that can readily interact with the negatively charged terminal hydrogen of boranes to form an H_2-boron complex [5a,5e]. With H_2 release and isomerization, a new B–B or B–H–B bond is formed. The formation of the $B_3H_8^-$ anion is the first stage for the formation of polyhedral boranes because the [B3] delta-unit is the basic structural moiety of polyhedral boranes [5a,5e]. More recently, Filinchuk *et al*. [6] has reported the synthesis of $M_2B_{12}H_{12}$ (M = Na, K), along with the formation of intermediates of $B_3H_8^-$, $B_9H_{14}^-$, and $B_{11}H_{14}^-$, by increasing the reaction temperature and pressure using borohydride and borane Lewis base adducts.

Inspired by the successful synthesis of the $B_3H_8^-$ anion [5a], we have endeavored to investigate synthetic methods of large polyhedral boranes based on the nucleophilicity of the B–H bonding pair electrons and explore their general mechanisms and the nature of the B–H bond condensation reaction.

Among all polyhedral borane anions, the icosahedral $B_{12}H_{12}^{2-}$ anion is the most stable and it can be readily synthesized. However, the selective preparation of the $B_9H_{14}^-$ and $B_{11}H_{14}^-$ anions, as the intermediates of the synthesis of the $B_{12}H_{12}^{2-}$ anion, is more difficult, because the lower polyhedral anions are more likely converted to the thermodynamically favored $B_{12}H_{12}^{2-}$ anion at elevated reaction temperatures [2d,2o,6]. On the other hand, the $B_{11}H_{14}^-$ anion is a useful starting material for conversion to other 11-vertex borane compounds [7,8] and preparation of decaborane [9]. In addition, the *nido*-$B_{11}H_{14}^-$ anion is a structurally favored precursor for the synthesis of hetero-polyhedral *colso*-boranes, such as carboranes and metallaboranes, by reacting with p-block and transition metal compounds [7,10]. However, the lack of efficient synthetic methods hinders its wide application.

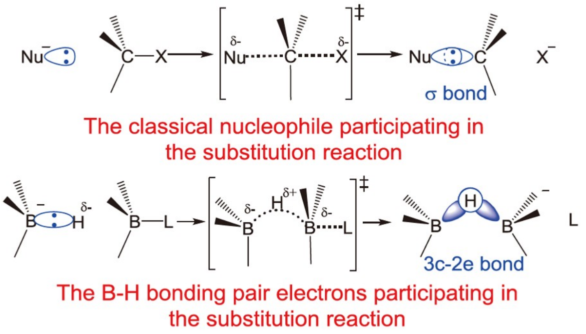


Figure 1 The nucleophilic substitution reactions with a typical nucleophile (top) or with borohydride acting as a nucleophile (bottom) (color online).

In this article, we report highly selective and efficient synthetic methods of the alkali metal salts of the $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$ anions by employing commercially available and inexpensive borohydrides and Lewis base borane adducts as starting materials, instead of the more reactive and hazardous B_2H_6, B_5H_9, and $B_{10}H_{14}$. The reaction mechanisms have been elucidated using both theoretical and experimental investigations. More importantly, a general reaction mechanism for the B–H bond condensation has been advanced for the efficient synthesis of polyhedral boranes under relatively mild conditions.

2 Results and discussion

2.1 Synthesis of $MB_{11}H_{14}$ (M = Li, Na, K)

The B–H bond condensation reaction is the main synthetic method of polyhedral boranes, but it is hardly controllable, so a mixture of polyhedral boranes is usually obtained [4]. When we systematically studied the reactions of potassium borohydride (KBH_4) and dimethyl sulfide borane ($(CH_3)_2S·BH_3$), we found that the final products are dependent on the reactant ratio, reaction time and temperature. When the reaction was conducted with a molar ratio of KBH_4 to $(CH_3)_2S·BH_3$ in a 1:10 in 1,4-dioxane at 90 °C for 5 d, the main product is the $B_{11}H_{14}^-$ anion and the unsolvated potassium salt ($KB_{11}H_{14}$) was isolated with 86% yield (Figure S5). This result is different from that of the previous report, where the reaction of KBH_4 and $(CH_3)_2S·BH_3$ in a 1:2 molar ratio for 48 h afforded the $B_3H_8^-$ anion as the main product, which was isolated with 89% yield [5e]. The $KB_{11}H_{14}$ product is characterized by ^{11}B, $^{11}B\{^1H\}$, ^1H, and $^1H\{^{11}B\}$ nuclear magnetic resonance (NMR) and infrared radiation (IR) spectroscopy (Figures S6–S8, Supporting Information online). Using $LiBH_4$ or $NaBH_4$ instead of KBH_4 in a similar procedure, the solvated lithium salt ($Li(O_2C_4H_8)_2B_{11}H_{14}$) and solvent-free sodium salt ($NaB_{11}H_{14}$) were also obtained with 75% and 65% yields, respectively (Figures S9–S12 and S13–S16). It is worth noting that alkali metal salts of $MB_{11}H_{14}$ (M = Li, Na, and K) were synthesized [2b,2e,2h,11a], but the highly reactive and hazardous B_2H_6, B_5H_9, and $B_{10}H_{14}$ were used. In addition, $Me_3NHB_{11}H_{14}$ can be prepared by a one-pot reaction of $NaBH_4$ and $C_2H_5O{\bullet}BF_3$ [11b]. In this work, a more stable and inexpensive Lewis base borane adduct of $(CH_3)_2S{\cdot}BH_3$ was used from which B_2H_6 is believed to be formed *in situ* and then reacting with alkali metal salts of borohydride to afford alkali metal salts of $MB_{11}H_{14}$ (M = Li, Na, and K).

Additionally, we investigated the effects of solvent and temperature on this reaction. When 1,2-dimethoxyethane (DME) was selected as the solvent under reflux conditions, although the reaction goes similar to that in 1,4-dioxane (Figure S17), the $MB_{11}H_{14}$ product could not be isolated and separated from the sticky crude mixture by recrystallization due to the strong coordination of alkali metal cations and the solvents (DME and THF). Notably, temperature is another important factor in this reaction. With the reaction temperature decreased from 90 to 80 °C, the reaction was completed at the NaB_3H_8 stage rather than $NaB_{11}H_{14}$ (Figure S18a, Table S1, Entry 1). However, increasing temperature causes more by-products, making separation difficult and decreasing the yield (Figure S18c). The reaction of KBH_4 and $(CH_3)_2S{\cdot}BH_3$ can produce $KB_{11}H_{14}$ at 80 °C, but the yield was significantly decreased than that at 90 °C (Figure S19, Table S1, Entry 3). We determined that MBH_4 and $(CH_3)_2S{\cdot}BH_3$ in dioxane at 90 °C is the optimized condition to obtain the desired product $MB_{11}H_{14}$.

2.2 Synthesis of $M_2B_{12}H_{12}$ (M = Na, K)

Although the $B_{12}H_{12}^{2-}$ anion was observed when we monitored the reaction of KBH_4 and $(CH_3)_2S{\cdot}BH_3$ (Figure S20), it could not be obtained as a major product by simply adjusting the reaction conditions such as temperature, reactant ratio, and reaction time. We also attempted to use the formed potassium $B_{11}H_{14}^-$ salt to react with $THF{\cdot}BH_3$, $(CH_3)_2S{\cdot}BH_3$, or KBH_4, respectively, and no derivatives of the $B_{12}H_{12}^{2-}$ anion were observed, which are different from the reactions of $NaB_{11}H_{14}$ and $Me_3NHB_{11}H_{14}$ [2h]. However, when $KB_{11}H_{14}$ reacted with KB_3H_8 at a 1:1 molar ratio in diglyme at 120 °C for 36 h, $K_2B_{12}H_{12}$ was obtained with 82% yield (Figures S24–S26). Using a similar reaction of $NaB_{11}H_{14}$ reacting with NaB_3H_8 at a 1:1 molar ratio in diglyme at 140 °C for 40 h, we obtained $Na_2B_{12}H_{12}$ in 80% yield (Figures S27–S29).

2.3 Reaction mechanisms

The solution and the formed precipitate during the reaction were monitored at different intervals by ^{11}B NMR spectroscopy to gain insight into the reaction mechanisms. As the reaction proceeded, a white precipitate formed. The ^{11}B NMR spectra of the reaction solution demonstrated the formation of the $B_3H_8^-$, $B_9H_{14}^-$, and $B_{11}H_{14}^-$ intermediates (Figures S5, S9, S13, and S17). $B_3H_8^-$ was observed to be formed first, and then $B_9H_{14}^-$ and $B_{11}H_{14}^-$ were sequentially formed. This observation provides important information for understanding the formation mechanisms.

On the basis of these observations and the theoretical results using the Gaussian 09 program [12], we proposed a mechanism for the formation of the $B_{11}H_{14}^-$ anion through the direct reaction of $(CH_3)_2S{\cdot}BH_3$ and BH_4^-. The proposed mechanism indicated that B_2H_6 was first formed *in situ* by dimerization of $(CH_3)_2S{\cdot}BH_3$, and then polyhedral boranes were formed step-by-step by reacting with the nascent B_2H_6 intermediate. In the first step, the $B_3H_8^-$ anion is formed through the reaction of the BH_4^- anion and B_2H_6. The reaction mechanism for this step was discussed in our previous work [5a,5e].

In the following stage, one of the terminal B–H bonds in the formed $B_3H_8^-$ anion attacks the B atom in B_2H_6 to form the $B_3H_7(\mu\text{-}H)BH_2(\mu\text{-}H)BH_3^-$ intermediate. Then an H_2-boron complex, $B_3H_7(\eta\text{-}H_2)BH(\mu\text{-}H)BH_3$, is formed through a dihydrogen bonding interaction. With the liberation of the H_2 molecule, the $B_5H_{12}^-$ anion is formed. Repeating the formation process of the H_2-boron complex and the release of H_2, the $B_5H_{10}^-$ anion is formed (Figure 2). Similarly, the $B_7H_{12}^-$, $B_9H_{14}^-$, and $B_{11}H_{14}^-$ anions are progressively formed stepwise *via* reactions of one B_2H_6 molecule with the formed intermediates in the previous step, following H_2 release and isomerization (Figures S1–S3). The highest energy barrier in the whole process is 33.2 kcal/mol for the $B_7H_{12}^-$(I) formation (Figure S1), which can be overcome readily at 90 °C. Figure 2 shows the optimized structures of the intermediates and products from $B_3H_8^-$ to $B_5H_{10}^-$. The details of the theoretical calculations are given in the Supporting Information online.

The proposed mechanism is supported by experimental evidence. The intermediates of $B_3H_8^-$ and $B_9H_{14}^-$ were isolated or characterized spectroscopically, and the released

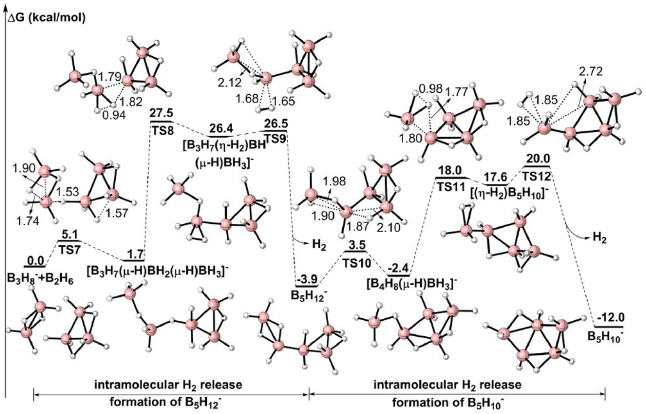


Figure 2 The reactions associated with the structural transformation from $B_3H_8^-$ and B_2H_6 to $B_5H_{10}^-$ (distance in Å) (color online).

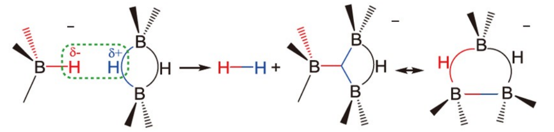
hydrogen gas was captured by the C_6D_6 solution (Figure S34). We also conducted the reaction of KB_3H_8 with $(CH_3)_2S\cdot BH_3$ at a 1:8 molar ratio, and the potassium salt of the $B_{11}H_{14}^-$ anion was obtained with a 75% yield (Figures S21–S23). The previously reported conversion of $B_3H_8^-$ or $B_9H_{14}^-$ into $B_{11}H_{14}^-$ by reacting with B_2H_6 [2e,4e] also supports the proposed mechanism. Furthermore, we proved no reaction between KB_9H_{14} and KB_3H_8 in 1,4-dioxane at 90 °C (Figure S30). However, when the reaction was carried out in diglyme at 120 °C for 3.5 d, $K_2B_{12}H_{12}$ was exclusively afforded in a 92% isolated yield (Figures S31–S33). Based on these results, we conclude that the formed $B_9H_{14}^-$ anion rapidly reacts with B_2H_6 to form $B_{11}H_{14}^-$ under a relatively mild condition, but in the absence of B_2H_6, it directly reacts with $B_3H_8^-$ to give $B_{12}H_{12}^{2-}$ at the elevated temperature.

2.4 The nature of the B–H bond condensation reaction and its general mechanism

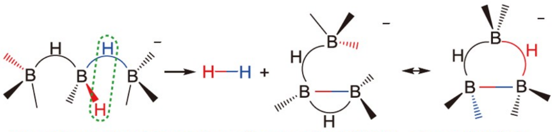
After analyzing the reported methods for the synthesis of polyhedral boranes through the B–H bond condensation reaction [2–11], we found that the nature of the B–H bond condensation reaction can be generally described as a dihydrogen bonding interaction between a positively charged hydrogen and a negatively charged hydrogen leading to the formation of a dihydrogen molecule boron complex. The B–B bond is formed upon the H_2 release. As shown in Figure 3, the reaction of BH_4^- and B_2H_6 or dehydrogenation of $B_3H_{10}^-$ to form $B_3H_8^-$ and H_2 are illustrated as simple examples through the inter- or intra-dihydrogen bonding interaction, resulting in the breaking of the B–H σ bonds and the formation of H–H and B–B σ bonds under mild conditions. In addition, the σ aromaticity of the [B3] delta-unit increases its stability [13]. This mechanism also applies to the reactions of borohydrides with the other neutral boranes, such as B_5H_9 and $B_{10}H_{14}$ [2], in which the bridging hydrogens also display positively charged characteristics (Figure S4).

Based on the understanding of the nature of the B–H bond condensation reaction and the formation mechanism of the $B_3H_8^-$ anion [5a,5e], a general mechanism of the B–H bond condensation reaction of the borohydrides and the borane Lewis base adducts to form the polyhedral boranes is summarized as three important steps: (1) Conversion of terminal hydrogen (B–H) into bridging hydrogen (B–H–B). The driving force of the condensation reaction is the dihydrogen bond interaction between a positively charged hydrogen and a negatively charged hydrogen. However, all of the terminal hydrogen atoms, either in borohydride (BH_4^-) or in borane Lewis base adduct ($L\cdot BH_3$), appear negatively charged ($H^{\delta-}$) because the electronegativity of hydrogen (2.1) is higher than that of the B atom (2.0). Thus, it is necessary to reverse the hydrogen atom from negatively charged $H^{\delta-}$ (red color) to positively charged $H^{\delta+}$ (blue color) because the bridging hydrogen in a neutral borane is partially positively charged (Figure S4). Usually two $L\cdot BH_3$ molecules are dimerized into B_2H_6 (Figure 4A) which then reacts with borohydrides ($B_nH_{(n+5)}^-$, n = 3, 5, 7, 9) (Figure 4B). (2) Formation of a H_2-boron complex $(\eta^2\text{-}H_2)BR_3$. Intra-molecular dihydrogen interactions between the bridging hydrogen and the terminal hydrogen ($B\text{–}H^{\delta+}\bullet\bullet\bullet H^{\delta-}\text{–}B$) afford an H_2-boron complex, $(\eta^2\text{-}H_2)BR_3$ (Figure 4C). (3) Formation of the [B3] delta unit. The H_2-boron complex is unstable, resulting in the rapid release of the H_2 molecule when the nucleophilic B–H or B–B bonding pair electrons attack the H_2-boron complex [5a,5c,5e]. Then a similar process is repeated to release the second H_2 molecule, resulting in the formation of new B–H–B or B–B–B bonds and completing the [B3] delta unit upon isomerization (Figure 4D).

Based on the understanding of the nature of the B–H bond condensation reaction and the general formation mechanism of polyhedral boranes, we can further explain why the alkali metal salts of borohydride can stably exist alone even at high

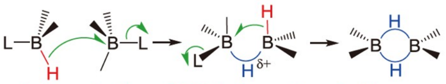


The inter-molecular condensation reaction between BH_4^- and B_2H_6 formed $B_3H_8^-$

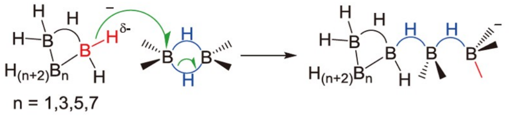


The intra-molecular condensation reaction of $B_3H_{10}^-$ formed $B_3H_8^-$

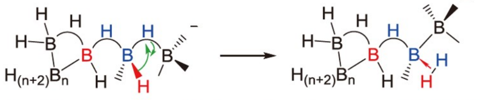
Figure 3 The inter- or intra-molecular B–H bond condensation reaction resulting in the formation of delta B3 unit (color online).



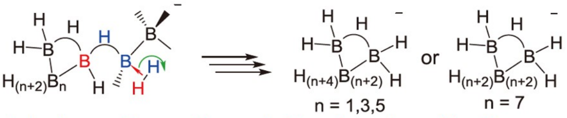
A. dimerization of LBH_3, foramtion of diborane



B. nucleophilic substitution, foramtion of the 3c-2e bond



C. intra-dihydrogen bond interaction, formation of $(\eta^2\text{-}H_2)BR_3$



D. dehydrogenation and isomerization, formation of the $B_{(n+2)}$ cage

Figure 4 The general formation mechanism of polyhedral boranes from small boranes through the B–H bond condensation reaction (color online).

temperatures but can react with neutral borane under relatively mild conditions to form polyhedral boranes because of the protonic character of their bridging hydrogen of these neutral boranes. On the other hand, the H_2 release reaction is irreversible, differentiating from those organic condensation reactions in which an equilibrium may occur because the impetus of those reactions is the formation of water or alcohol [14]. Thus, selecting and controlling the initial reaction conditions are critical for developing the highly selective synthesis of the polyhedral boranes, because once the byproduct is formed it will go to the final product, leading to a mixture of products.

It is worth noting that in the whole procedure of the reactions, the $B_{10}H_{10}^{2-}$ anion was not detected in our synthetic methods. However, it was often reported in the literature that the $B_{10}H_{10}^{2-}$ anion was a co-product formed with $B_9H_{14}^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ [2k,4a,4h]. This observation indicated that the formation conditions and mechanisms of $B_{10}H_{10}^{2-}$ are different from those of $B_{12}H_{12}^{2-}$ and the current conditions are not suitable for the $B_{10}H_{10}^{2-}$ anion. Thus, the conditions for the formation of the $B_{10}H_{10}^{2-}$ anion appear to be very delicate and it would be interesting to conduct further research for the selective synthesis of $B_{10}H_{10}^{2-}$.

3 Conclusions

In conclusion, based on our previous study on the synthesis and mechanism of the $B_3H_8^-$ anion, we developed highly selective and efficient synthetic methods for the $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$ polyhedral boranes using safer and commercially available borohydride and Lewis base borane adducts. The formation mechanism of the $B_{11}H_{14}^-$ anion was elucidated experimentally and computationally. Furthermore, we found that the nature of the B–H bond condensation reaction is a dihydrogen bonding interaction leading to the formation of the B–B bond with the release of an H_2 molecule. The conversion of the negatively charged terminal hydrogen to the positively charged bridging hydrogen is crucial for developing efficient synthetic methods of polyhedral boranes under mild conditions. The current findings pave the way for the development of controllable synthetic methods for polyhedral boranes and for their broader applications.

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Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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