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Facile synthesis of the dodecahydridododecaborate ($B_{12}H_{12}^{2-}$) from borane Lewis base adducts

Yi Jing[1], Xin-Ran Liu[2], Xinghua Wang[1], Hui Han[1], Sha-Sha Liang[1], Xi-Meng Chen[2], Donghui Wei[1*], Lai-Sheng Wang[3*] & Xuenian Chen[1,2*]

[1]*College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*
[2]*School of Chemistry and Chemical Engineering, Henan Key Laboratory of Boron Chemistry and Advanced Materials, Henan Normal University, Xinxiang 453007, China*
[3]*Department of Chemistry, Brown University, Providence, RI 02912, USA*

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Polyhedral boranes are a class of well-known boron molecular clusters widely used in energy, chemistry, medicine, and materials science because of their unique physical and chemical properties. Great efforts have been made in the past decades to find more effective synthetic methods for this important class of boron compounds. However, existing synthetic methods suffer from low efficiency and low selectivity. Herein, we report a facile one-pot synthesis of $[(CH_3)_3S]_2B_{12}H_{12}$ with moderate yields at mild conditions. The mechanisms for the multi-step chemoselective synthesis of $B_{12}H_{12}^{2-}$ without other by-products are elucidated based on theoretical results and our previous work. The Lewis base used in B–H bond condensation reaction, which acts as a hydrogen or to balance the newly generated polyhedral borane charges, is proposed and studied in detail. The current study has led to a more effective and selective synthetic method for $B_{12}H_{12}^{2-}$ and has also implicated the syntheses of other new polyhedral boranes.

dodecahydridododecaborates, boranes, polyhedral boranes, borane Lewis base adducts, B–H bond condensation reactions

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1 Introduction

Polyhedral boranes are a homologous series of inorganic compounds consisting of boron and hydrogen [1]. Among the thousands of known boranes and their derivatives, the dodecahydridododecaborate anion ($B_{12}H_{12}^{2-}$) is the most important boron species due to its unique properties and high energy density [2]. Its derivatives have been widely investigated and utilized in many fields, including energy [3–6], medicine [7–9], chemistry [10,11], materials science [12–14], and especially as boron carriers in boron neutron capture therapy (BNCT) for cancer treatment [15,16]. The icosahedral structure of $[B_{12}H_{12}]$ was first proposed by Lipscomb and co-workers in 1954 [17]. One year later, Longuet-Higgins and Roberts predicted that the icosahedral $[B_{12}H_{12}]$ borane would be stable only in its dianion form ($B_{12}H_{12}^{2-}$) by theoretical calculations [18]. In 1960, Hawthorne and Pitochelli first synthesized $B_{12}H_{12}^{2-}$ from the reaction of 2-iododecaborane and triethylamine in refluxing benzene with low yield [19]. Since then, many methods for the synthesis of $B_{12}H_{12}^{2-}$ have been developed based on various boron-containing starting materials [20–34].

Our group has been dedicated to the synthesis of new

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*Corresponding authors (email: donghuiwei@zzu.edu.cn; Lai-Sheng_Wang@brown.edu; xuenian_chen@zzu.edu.cn)

boron compounds and exploring their applications [34–43]. By comprehensively analyzing the different synthetic methods established for $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$ derivatives, we have elucidated the nature of B–H bond condensation reactions [34,43]. This type of reaction occurs through a stepwise condensation process dominated by dihydrogen bonding interactions (DHB) between the positively charged bridged hydrogen ($H^{\delta+}$) and the negatively charged terminal hydrogen ($H^{\delta-}$) of boranes. Then DHB interactions lead to the formation of the B–B bond, with the release of one H_2 molecule. This elucidation explained why most synthetic methods based on the direct reactions between neutral boranes, such as B_2H_6, B_5H_9, and $B_{10}H_{14}$, and borohydride anions, such as BH_4^{-} and $B_3H_8^{-}$, could be performed under relatively mild conditions [27–32,43]. In addition to the direct reaction of borohydrides and neutral boranes, some other reactions of borohydrides alone could also form $B_{12}H_{12}^{2-}$. This occurs because the neutral boranes are formed *in situ* and then react with borohydrides, as shown in the mechanistic studies [23,29]. For example, the pyrolysis of Et_4NBH_4 forms the $B_{12}H_{12}^{2-}$ anion in good or moderate yields, with Et_4NBH_4 converting into $Et_3N{\cdot}BH_3$ and EtH, as shown in Eq. (1) [23]. The reactions of $NaBH_4$ with I_2 and $BF_3{\cdot}Et_2O$ could produce the $B_{12}H_{12}^{2-}$ anion [24,30] because B_2H_6 was first formed in the reactions, as shown in Eqs. (2) and (3) [44,45]. Some reactions of borohydrides and polyhedral borates were also used to synthesize $B_{12}H_{12}^{2-}$ because there are bridged hydrogens in these polyborohydrides, such as $B_3H_8^{-}$, $B_9H_{14}^{-}$, and $B_{11}H_{14}^{-}$, as shown in Eqs. (4) and (5) [34]. Therefore, all these reactions for the formation of the $B_{12}H_{12}^{2-}$ anion are based on the DHB interactions, as discussed above.

$$Et_4NBH_4 \rightarrow Et_3N{\cdot}BH_3 + EtH \tag{1}$$

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2 \tag{2}$$

$$3NaBH_4 + 4BF_3{\cdot}Et_2O \rightarrow 2B_2H_6 + 3NaBF_4 + 4Et_2O \tag{3}$$

$$NaB_3H_8 + NaB_9H_{14} \rightarrow Na_2B_{12}H_{12} + 5H_2 \tag{4}$$

$$NaB_3H_8 + NaB_{11}H_{14} \rightarrow Na_2B_{12}H_{12} + B_2H_6 + 2H_2 \tag{5}$$

$$2Et_3N + 6B_2H_6 \rightarrow (Et_3NH)_2B_{12}H_{12} + 11H_2 \tag{6}$$

$$12Et_4NBH_4 \rightarrow (Et_3NH)_2B_{12}H_{12} + 10Et_3N + 12EtH + 11H_2 \tag{7}$$

$$9KB_3H_8 \rightarrow K_2B_{10}H_{10} + K_2B_{12}H_{12} + 5KBH_4 + 15H_2 \tag{8}$$

On the other hand, the charge changes are worthy of note during the formation of polyhedral boranes via the abstraction of hydrogen (a protic $H^{\delta+}$ or a hydridic $H^{\delta-}$). The abstraction of one $H^{\delta-}$ will quench one negative charge, and the abstraction of one $H^{\delta+}$ will add one negative charge in the formed polyhedral borane. Thus, organic groups can play important roles in the synthesis of the polyhedral borane anions to adjust the charges of the final products (Figure 1). For example, the reaction of Et_3N and B_2H_6 affords $(Et_3NH)_2B_{12}H_{12}$ (Eq. (6)), in which two negative charges are generated on $B_{12}H_{12}^{2-}$ [$6B_2H_6$ (neutral) $\rightarrow$ $B_{12}H_{12}^{2-}$ (dianion)] through abstraction of H^{+} by Et_3N to form Et_3NH^{+} [29]. In contrast, the conversion of Et_4NBH_4 to $(Et_4N)_2B_{12}H_{12}$ requires the dissipation of extra negative charges to form the borane dianion ($12BH_4^{-} \rightarrow B_{12}H_{12}^{2-}$) through the conversion of the Et_4N^{+} cation to neutral Et_3N and EtH by abstraction of a H^{-} anion (Eq. (7) and Figure 1) [22,23]. Metal salts of boranes can also alter the charges of the products through disproportionation reactions, which generally take place at high temperatures, such as the conversion of KB_3H_8 into $K_2B_{10}H_{10}$, $K_2B_{12}H_{12}$, and KBH_4 at 185 °C, as shown in Eq. (8) [22]. Thus, hydrogen abstraction by an alkyl group or organic base enhances the B–H bond condensation reaction so that the temperatures of the thermolytic condensation of organic borate salts are lower than those of metal salts [22,23,30].

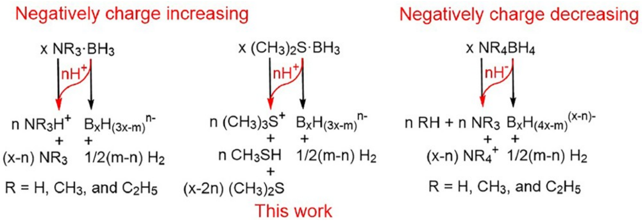

Figure 1 (Color online) The abstraction of hydrogen (H^{+} or H^{-}) by organic groups to alter the charges of polyhedral boranes.

Consequently, we wondered whether a class of borane Lewis base adducts can form polyhedral boranes at relatively low temperatures. Herein, we presented a highly selective and efficient synthetic method of $B_{12}H_{12}^{2-}$ as a trimethylsulfonium salt ($[(CH_3)_3S]_2B_{12}H_{12}$) with moderate yield under mild conditions from the starting material, dimethyl sulfide borane ($(CH_3)_2S{\cdot}BH_3$), a commercially available chemical.

2 Results and discussion

2.1 The selection of appropriate borane Lewis base adduct for synthesizing the $B_{12}H_{12}^{2-}$ anion

Based on the formation mechanism of polyhedral boranes, the appropriate borane Lewis base adduct for developing the strategy for the synthesis of the $B_{12}H_{12}^{2-}$ anion should satisfy two criteria: (1) the coordinating atom of the Lewis base should have a moderate ability to interact with the B atom and should be capable of readily dissociating the BH_3 moiety to participate in the B–H bond condensation reaction under mild conditions; (2) the Lewis base can extract a protic hydrogen to form a counter cation to balance the charges.

To find borane Lewis base adducts suitable for synthesizing the $B_{12}H_{12}^{2-}$ salts under mild conditions, we have tested different types of borane Lewis base adducts. A 1 M solution of $THF{\cdot}BH_3$ was refluxed in THF (tetrahydrofuran), yielding only B_2H_6 without any $B_{12}H_{12}^{2-}$ (Figures S1 and S5b, Supporting Information online) [35]. We speculated that this is due to the difficulty for THF to abstract hydrogen from boranes to form oxonium ions at the refluxing THF temperature. To verify this hypothesis, we examined the reaction of KB_3H_8 and $THF·BH_3$ under the reflux temperature and observed $B_9H_{14}^-$ and $B_{11}H_{14}^-$ (Figures S2 and S5c). We believe that B_2H_6 was first formed from $THF·BH_3$, and it reacted with $B_3H_8^-$ to form the $B_9H_{14}^-$ and $B_{11}H_{14}^-$ products, which follows a similar process of $B_3H_8^-$ reacting with $(CH_3)_2S·BH_3$ to produce $B_{11}H_{14}^-$ [34,35]. And polyhedral borane anions are produced because the K^+ is a counter-balance cation in the reaction. In addition, no $B_{12}H_{12}^{2-}$ was detected, because the temperature of the refluxing THF was not high enough.

Another readily available borane is amine borane, whose N atoms can extract protons from the reaction to form quaternary ammonium ions [29]. By refluxing $Et_3N·BH_3$ in 1,2-dimethoxyethane (DME), no $B_{12}H_{12}^{2-}$ was found, and only the starting material $Et_3N·BH_3$ was detected (Figures S3 and S5d) because the strong dative bond between Et_3N and BH_3 in the $Et_3N·BH_3$ adduct does not allow the dissociation of the BH_3 group at the refluxing temperature of DME. However, refluxing $Et_3N·BH_3$ in diglyme at a higher temperature led to the formation of $B_{12}H_{12}^{2-}$ along with $B_{10}H_{10}^{2-}$, as shown by ^{11}B nuclear magnetic resonance (^{11}B NMR) (Figures S4 and S5e), which is consistent with the literature work [29]. Recently, our group [43] reported an improved strategy for the synthesis of $M_2B_{12}H_{12}$ (M = Na, K) by reacting MBH_4 with *N*,*N*-dipropylaniline borane. To weaken the coordination between the N and B atoms to facilitate the dissociation of BH_3 at relatively lower temperatures, the aniline compounds $C_6H_5N(CH_3)_2·BH_3$ and $C_6H_5N(n\text{-}C_3H_7)_2·BH_3$ were studied under DME reflux conditions, respectively. It was found that no $B_{12}H_{12}^{2-}$ was monitored in the reaction of $C_6H_5N(CH_3)_2·BH_3$, but $C_6H_5N(n\text{-}C_3H_7)_2·BH_3$ can be converted into $B_{12}H_{12}^{2-}$ (Figures S6 and S7). We inferred that this may be due to the larger steric hindrance of the propyl group compared to the methyl group, making it easier to dissociate BH_3 and generate B_2H_6 to participate in the B–H bond condensation reaction. However, the reaction temperature is still not high enough, resulting in a significant amount of starting material remaining.

The dative bond strength of the borane Lewis base adducts is related to the electron-donating ability of the coordination atom. The theoretical studies suggested that a strong Lewis base makes the $L·BH_3$ adduct more stable, i.e., more difficult to dissociate the BH_3 group (Figure 2a) or to form B_2H_6 by displacing L through the B–H nucleophilic attack (Figure 2b). Thus, thioether borane adducts likely convert to polyhedral boranes more easily than amine borane adducts under mild conditions. To our delight, we have found that dimethyl sulfide borane, $(CH_3)_2S·BH_3$, a readily available material, is the ideal starting reagent for the synthesis of the derivatives of $B_{12}H_{12}^{2-}$ and $(CH_3)_3S^+$ is the counter-cation (Figure S5a).

2.2 The facile synthesis of $B_{12}H_{12}^{2-}$ via thioether borane adducts

After optimizing the reaction conditions (Table S1, Supporting Information online), we were able to obtain $[(CH_3)_3S]_2B_{12}H_{12}$ with a 60% yield by refluxing a 6.7 M DME solution of $(CH_3)_2S·BH_3$ at 84 °C (Eq. (9), Figures S8, S9 and Table S1). This method is the simplest one-pot reaction reported, which proceeds under 100 °C conditions from commercially available reagent through the thermolytic method. The $[(CH_3)_3S]_2B_{12}H_{12}$ salt can be easily converted to $Na_2B_{12}H_{12}$ by cation exchange (Figures S10 and S11). By a similar procedure, the ^{10}B-enriched $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ can be prepared with 60% yields (Figures S12 and S13). Although the tetrahydrothiophene borane ($THT·BH_3$) can be used as a starting material to produce $B_{12}H_{12}^{2-}$ under standard reaction conditions (Figure S14), unfortunately, the cation cannot be identified. Furthermore, we have also selected an odorless sulfide alternative, $n\text{-}C_{12}H_{25}S(CH_3)$, as a starting material $[n\text{-}C_{12}H_{25}S(CH_3)_2]_2B_{12}H_{12}$ could be obtained under reflux in DME with a 30% yield (Figures S15–S17).

$$12(CH_3)_2S·BH_3$$
$$\rightarrow [(CH_3)_3S]_2B_{12}H_{12} + 8(CH_3)_2S + 2CH_3SH + 11H_2 \qquad (9)$$

The single crystals of $[(CH_3)_3S]_2B_{12}H_{12}$ and $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ were obtained by recrystallization from aqueous solution, and their structures have been determined by single-crystal X-ray diffraction. The crystal system of both of $[(CH_3)_3S]_2B_{12}H_{12}$ and $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ is trigonal and belongs to the *R*-3*m* space group (Figure 3). Comparing the crystal parameters of $[(CH_3)_3S]_2B_{12}H_{12}$ and $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$, the different isotopes have no significant effect on the crystal structures (Tables S2–S4). Important bond lengths are mentioned in Table S4. The S–C bond lengths in the cation of $[(CH_3)_3S]_2B_{12}H_{12}$ (1.788 Å) are very similar to that of $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ (1.785 Å). The B–B bond lengths in $[(CH_3)_3S]_2B_{12}H_{12}$ fall in a small range from 1.781 to 1.785 Å, which is the same with $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$. And B–H bond lengths in $[(CH_3)_3S]_2B_{12}H_{12}$ range between 1.08 to 1.18 Å, whereas those of $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ fall in the range from 1.09 to 1.16 Å.

2.3 The formation of $(CH_3)_3S^+$ cation

The formation of the $(CH_3)_3S^+$ cation rather than the desirable $(CH_3)_2SH^+$ cation is to our surprise. Based on our previous work and theoretical calculations, we speculated that the cation formation underwent the following process. Under the refluxing condition in DME, a nucleophilic attack by the B–H bond from one $(CH_3)_2S·BH_3$ molecule can readily displace the weak Lewis base $(CH_3)_2S$ of another $(CH_3)_2S·BH_3$ molecule to form B–H–B and subsequently form B_2H_6 (Figure 4) [34,36]. The Lewis base $(CH_3)_2S$ can abstract a

(a) $THF{\cdot}BH_3 \longrightarrow THF + BH_3$ ΔG = 14.6 kcal/mol
$(CH_3)_2S{\cdot}BH_3 \longrightarrow (CH_3)_2S + BH_3$ ΔG = 15.3 kcal/mol
$Et_3N{\cdot}BH_3 \longrightarrow Et_3N + BH_3$ ΔG = 26.4 kcal/mol

(b) $2\ THF{\cdot}BH_3 \longrightarrow 2\ THF + B_2H_6$ ΔG = 0.7 kcal/mol
$2\ (CH_3)_2S{\cdot}BH_3 \longrightarrow 2\ (CH_3)_2S + B_2H_6$ ΔG = 2.0 kcal/mol
$2\ Et_3N{\cdot}BH_3 \longrightarrow 2\ Et_3N + B_2H_6$ ΔG = 24.3 kcal/mol

Figure 2 (a) The dissociation energies of $L{\cdot}BH_3$; (b) the conversion energies of $L{\cdot}BH_3$ into B_2H_6.

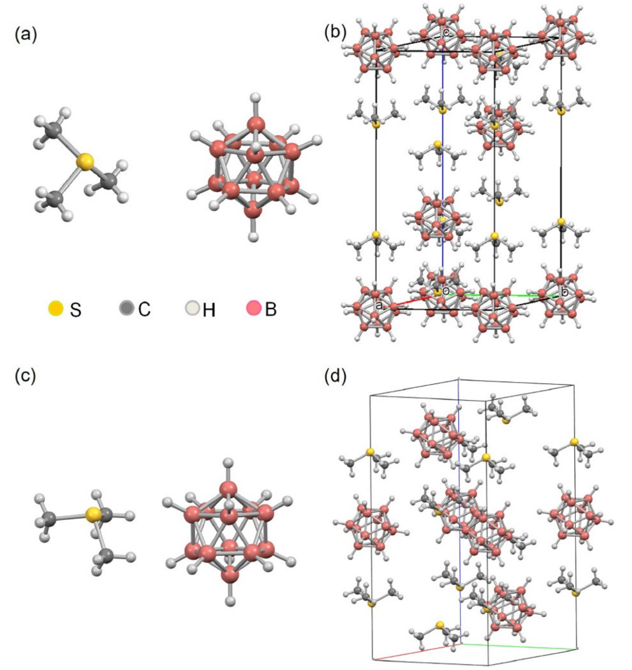

Figure 3 (Color online) Single-crystal structure of the (a) $[(CH_3)_3S]_2B_{12}H_{12}$ (b) and crystal cell. The single-crystal structure of (c) $[(CH_3)_3S]_2{}^{10}B_{12}H_{12}$ and (d) crystal cell.

bridged hydrogen (H^+) to form the metastable $(CH_3)_2SH^+$ cation, which then converts to $(CH_3)_3S^+$ and CH_3SH by reacting with another $(CH_3)_2S$ molecule (Figure 5). It is noteworthy that Shore *et al.* [46] reported in 1996 the self-condensation reaction of $(CH_3)_2S{\cdot}BH_3$ in the absence of a solvent at 150 °C to form 1,7-$(S(CH_3)_2)_2B_{12}H_{10}$ and 1,12-$(S(CH_3)_2)_2B_{12}H_{10}$, and at 60 °C $[(CH_3)_3S][B_{12}H_{11}(S(CH_3)_2)]$ was formed but $[(CH_3)_3S]_2B_{12}H_{12}$ was not observed.

2.4 The formation mechanisms of $B_{12}H_{12}{}^{2-}$

To investigate the detailed reaction mechanisms, we monitored both the solution and the gas products during the reaction. The released gases were captured by diethyl ether and characterized by ^{11}B NMR spectroscopy. As shown in Figure S18, the released gases included B_2H_6. As the reaction proceeded, the reaction solution gradually turned yellow, and a precipitate formed. The ^{11}B NMR spectra of the reaction solution revealed the formation of $B_3H_8{}^-$, $B_9H_{14}{}^-$, and $B_{11}H_{14}{}^-$ intermediates (Figure S19), which are similar to the reaction intermediates of $MB_{11}H_{14}$ through MBH_4 and $(CH_3)_2S{\cdot}BH_3$ [34]. And $B_3H_8{}^-$ was observed to be formed first, and then $B_9H_{14}{}^-$ and $B_{11}H_{14}{}^-$ were formed sequentially.

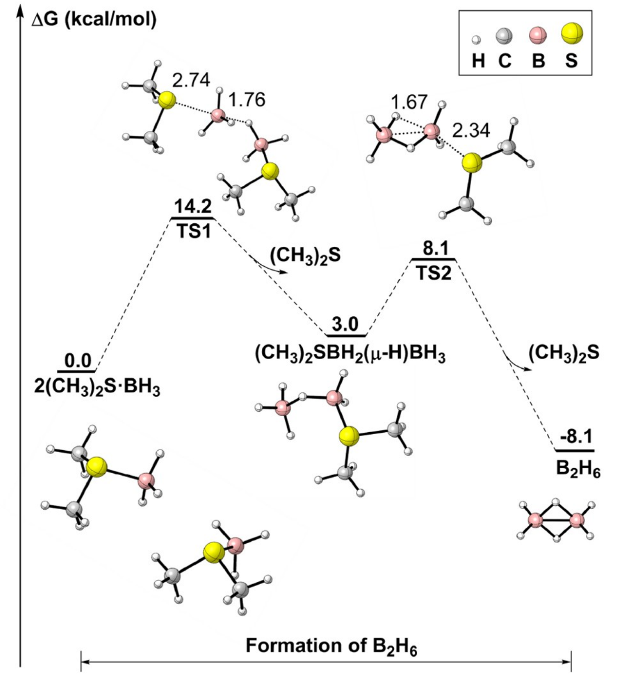

Figure 4 (Color online) The formation pathways for B_2H_6 (distance in Å).

Based on these experimental observations and theoretical calculations, we have proposed a mechanism for the formation of $[(CH_3)_3S]_2B_{12}H_{12}$ through direct reactions of $(CH_3)_2S{\cdot}BH_3$ in DME at the reflux temperature. The proposed mechanism includes six stages (Figure 6). In the first stage, two $(CH_3)_2S{\cdot}BH_3$ molecules react with each other through nucleophilic substitution to form B_2H_6 (Figure 4) that further reacts with another $(CH_3)_2S{\cdot}BH_3$ to form $B_3H_8{}^-$ and $(CH_3)_2SH^+$. The $(CH_3)_2SH^+$ cation reacts with another $(CH_3)_2S$ molecule to form a stable $(CH_3)_3S^+$ cation as a counterion (Figure 5), leading to the final $[(CH_3)_3S]_2B_{12}H_{12}$ product (Figure 6). The formation mechanism of $B_3H_8{}^-$ via a similar reaction between $BH_4{}^-$ and B_2H_6 has been reported previously [36]. The energy barrier of the formation of $B_3H_8{}^-$ here by the reaction of $(CH_3)_2S{\cdot}BH_3$ is 31.9 kcal/mol, which is lower than the reported possible pathway [36].

The process from the second to the fifth stages has been reported in our previous work [34,36]. Under the similar heating condition of the reaction of MBH_4 and $(CH_3)_2S{\cdot}BH_3$, $B_7H_{12}{}^-$, $B_9H_{14}{}^-$, and $B_{11}H_{14}{}^-$ were progressively formed stepwise via reactions one B_2H_6 molecule with the intermediate in the previous stage. This sequential reaction with B_2H_6 is accompanied by H_2 release and isomerization of the intermediates. It is worth noting that the B_2H_6 molecule plays a crucial role in the first five stages, facilitating the con-

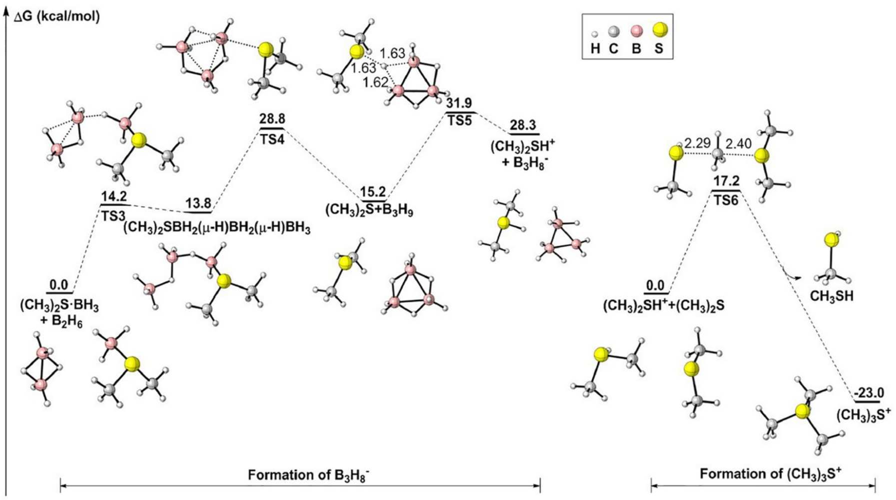

Figure 5 (Color online) The reaction stage 1 associated with the formation of $B_3H_8^-$ and $S(CH_3)_3^+$ (distance in Å).

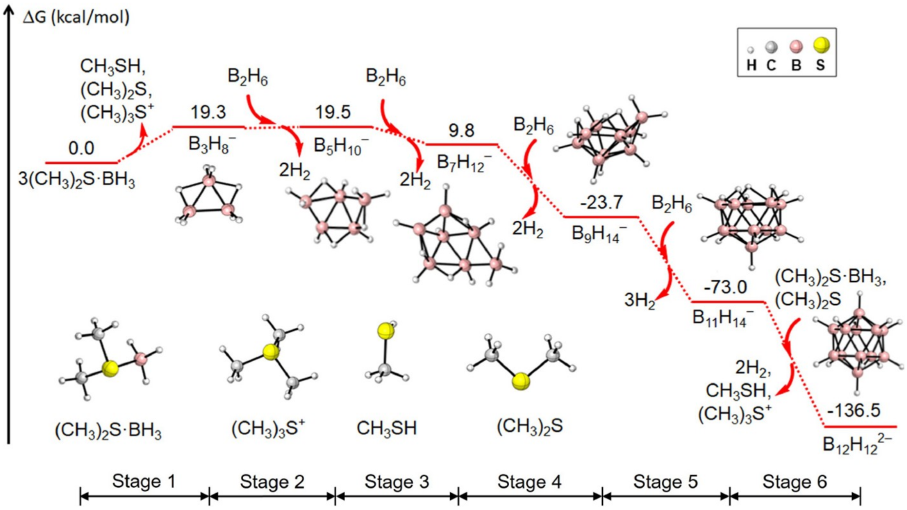

Figure 6 (Color online) The formation process of $[(CH_3)_3S]_2B_{12}H_{12}$ from $(CH_3)_2S·BH_3$.

densation reaction from one boron to eleven boron atoms.

In the last stage, the $B_{11}H_{14}^-$ intermediate reacts with $(CH_3)_2S·BH_3$ to form $B_{12}H_{17}^-$ and $(CH_3)_2S$. Subsequently, two H_2 molecules are released along with the formation of $B_{12}H_{13}^-$, which is further deprotonated by $(CH_3)_2S$ and transformed into the $B_{12}H_{12}^{2-}$ final product (Figure 7). The newly formed $(CH_3)_2SH^+$ cation can react with another $(CH_3)_2S$ molecule to give $(CH_3)_3S^+$ and CH_3SH (Figure 5). The formation of $B_{12}H_{12}^{2-}$, $(CH_3)_3S^+$, and CH_3SH is highly exothermic (Figures 6 and 7), so the $B_{12}H_{12}^{2-}$ product is extremely stable once formed.

2.5 Experimental verification of the mechanisms

The above mechanisms for the synthesis of $B_{12}H_{12}^{2-}$ have been verified experimentally. We used KB_3H_8 as a starting material to react with $(CH_3)_2S·BH_3$ in refluxing DME, and ^{11}B NMR showed the formation of $B_9H_{14}^-$, $B_{11}H_{14}^-$ and the final $B_{12}H_{12}^{2-}$ product (Figures S20 and S21). At the last stage of the reaction, each molecule of $B_{11}H_{14}^-$ reacts with one molecule of $(CH_3)_2S·BH_3$ to form $B_{12}H_{12}^{2-}$, as reported previously [29]. We performed a reaction of $Et_4NB_{11}H_{14}$ and $(CH_3)_2S·BH_3$ in equivalence in refluxing DME and found the final product was $B_{12}H_{12}^{2-}$ (Figure S22). We should point out that the intermediates $B_5H_{10}^-$ and $B_7H_{12}^-$ were not detected by ^{11}B NMR, probably because their lifetimes were too short on the NMR time scale, considering the small Gibbs free energy barriers and activation energy barriers (Figure 6) [34].

Two $(CH_3)_3S^+$ cations were formed in the first and last stages, respectively, as described in the proposed mechan-

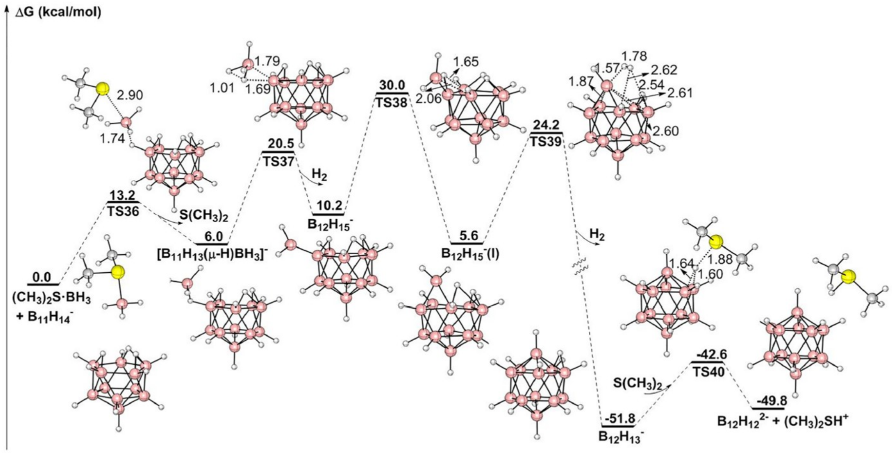

Figure 7 (Color online) The reaction stage 6 associated with the structural transformation from $B_{11}H_{14}^{-}$ and $(CH_3)_2S·BH_3$ to $B_{12}H_{12}^{2-}$ (distance in Å).

isms (Figures 5 and 7). To confirm this result, we refluxed a $(CH_3)_2S·BH_3$ in DME solution for 1 h and monitored the reaction by NMR. The ^{11}B NMR spectrum showed that $B_3H_8^{-}$ and a trace amount of $B_9H_{14}^{-}$ were present (Figure S19B), and the ^{1}H NMR spectrum indicated the formation of $(CH_3)_3S^{+}$ (Figure S23). This result indicated that one $(CH_3)_3S^{+}$ cation was formed in the first stage. Furthermore, the conversion from $B_{11}H_{14}^{-}$ to $B_{12}H_{12}^{2-}$ through the reaction with $(CH_3)_2S·BH_3$ needs one more cation; thus, it is believed that the second $(CH_3)_3S^{+}$ cation is formed in the last stage [29]. These observations confirm the theoretical results (Figure 7).

3 Conclusions

In summary, we report an efficient and straightforward method for the synthesis of the archetypical $B_{12}H_{12}^{2-}$ polyhedral borane by the thermolysis of the commercially available thioether borane adducts under related mild conditions with moderate yields to generate pure $B_{12}H_{12}^{2-}$ product without the accompanying $B_{10}H_{10}^{2-}$ by-product, frequently observed in the previously reported methods. This synthetic strategy also facilitates the production of ^{10}B-enriched $[(CH_3)_3S]_2B_{12}H_{12}$ for BNCT drug development. The reaction mechanism has been proposed based on both theoretical and experimental investigations, which indicates the weak ability of the Lewis base to coordinate with the BH_3 group and its strong ability to abstract the proton play crucial roles in this process. The thioether borane adducts produce a counterbalance cation in the reaction and dissociate BH_3 under mild conditions so that the B–H bond condensation reaction can proceed smoothly. The current findings may be further developed for the generally controllable synthetic methods for polyhedral boranes from $[B_3]$ to $[B_{12}]$ or even higher boranes.

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Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://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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