

A Simple and Efficient Preparation of High-Purity and High-Yield Unsolvated Lithium Dodecaborate

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Abstract

We present a new and simple approach for the synthesis of lithium dodecaborate ($\text{Li}_2\text{B}_{12}\text{H}_{12}$) in high purity and high yield, based on the reaction between borane dimethyl sulfide complex ($\text{DMS}\cdot\text{BH}_3$) and lithium borohydride (LiBH_4) in glymes (monoglyme or diglyme). The reaction can conveniently be performed either in a Schlenk flask with or without reflux, or in an autoclave. This strategy exhibits various advantages over existing methods, including high product purity, high reaction yields (up to 96%), and operational simplicity. The enclosed system provided by an autoclave is shown to be more favorable for the synthesis of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion and enables obtaining the highest yields. The reaction mechanism has been investigated by ^{11}B NMR spectroscopy, revealing a stepwise formation of B_2H_7^- , B_3H_8^- , $\text{B}_9\text{H}_{14}^-$, $\text{B}_{11}\text{H}_{14}^-$ and $\text{B}_{11}\text{H}_{13}^{2-}$ intermediates. This synthesis method is extended to the $\text{M}_2\text{B}_{12}\text{H}_{12}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) series, yielding metal dodecaboranes coordinated with glymes, characterized by single crystal X-ray diffraction. We show that glymes can be removed through simple exchange with weaker coordinating solvents like DMSO or H_2O , followed by heating under vacuum.

Keywords: Dodecaborate; Undecaborate; $\text{B}_{12}\text{H}_{12}^{2-}$; $\text{B}_{11}\text{H}_{13}^{2-}$; $\text{B}_{11}\text{H}_{14}^-$

1. Introduction

Efficient synthesis of boron-hydrogen based compounds has garnered considerable interest in recent years, especially in the context of energy-related applications.^{1–10} Notably, the dodecahydro-closo-dodecaborate anion, $B_{12}H_{12}^{2-}$, possesses unique bonding configurations typified by electron delocalization, remarkable chemical and thermal stabilities and salt-like behavior.^{9,11} Those properties have contributed to its increasing importance in areas such as polymer chemistry,¹² cancer treatment,¹³ nuclear waste extraction¹⁴ and solid state electrolytes.^{15–18}

$B_{12}H_{12}^{2-}$ features a high-symmetry structure of closed icosahedral boron cluster with terminal hydrogen atoms and was initially predicted by Longuet-Higgins and Roberts in 1955 based on calculations.¹⁹ Its isolation by Hawthorn in 1960 initiated extensive research efforts towards its large-scale synthesis over the next decades.²⁰ However, up to now, the high commercial cost of metal-salt derivatives of $B_{12}H_{12}^{2-}$ remains an important constraint for its broader application.

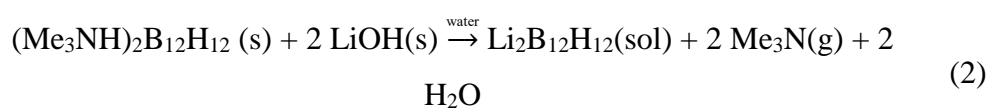
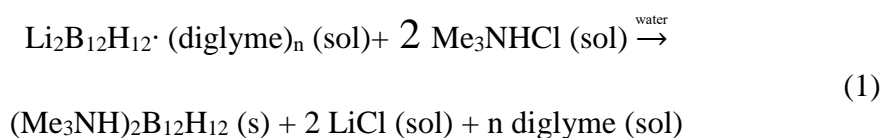
The current synthesis pathways towards $B_{12}H_{12}^{2-}$ rely on solution-based and solvent-free techniques. The former involves the use of borane precursors, such as B_2H_6 , B_5H_9 or $B_{10}H_{14}$, that are reacted with a borane triethylamine complex, leading to $[Et_3NH]_2B_{12}H_{12}$. Ion-exchange of this compound with metal hydroxides subsequently enables to obtain $Na_2B_{12}H_{12}$.²¹ While this method yields high-purity metal dodecaboranes in a solvated form and has been the preferred choice in earlier studies, its main drawbacks are the complexity of operation and high cost.^{9,22–24} More recent solvent-free approaches, based on ball-milling or annealing, have gained popularity in recent years due to their ability to produce anhydrous $B_{12}H_{12}^{2-}$ salts in a single step.^{4,5,25} However, these approaches lead to formation of the $B_{12}H_{12}^{2-}$ with other boron-rich compounds. Furthermore, both approaches present concerns about the yield and purity of the product, as well as regarding toxicity and reactivity of specific borane precursors, which continue to pose significant challenges.

Incremental improvements of synthetic approaches towards $B_{12}H_{12}^{2-}$ have been mainly focusing on the replacement of diborane by reducing agents presenting less handling issues.^{3,26,27} With this in mind, we recently succeeded the synthesis of unsolvated sodium and potassium dodecaborates ($Na_2B_{12}H_{12}$ and $K_2B_{12}H_{12}$) by reacting borane dimethyl sulfide complex ($DMS \cdot BH_3$) with the corresponding borohydride ($NaBH_4$ or KBH_4) in diglyme by heating in an autoclave. The use of diglyme was found to facilitate the removal of all intermediate products formed during the reaction, leading to high-purity $M_2B_{12}H_{12}$ ($M = Na$ or K).²⁶

The formation mechanism of $B_{12}H_{12}^{2-}$ from BH_4^- has long been discussed without a definitive conclusion to date, which is not helping in the development of more efficient synthetic strategies. Since the observation of its formation as a “boron sink” during the dehydrogenation of BH_4^- , extensive experimental and computational work has been carried out to demystify the conversion process into $B_{12}H_{12}^{2-}$.^{25,28–30} These works demonstrate that BH_4^- features a wealth of pathways to higher monovalent anions such as $B_3H_8^-$, $B_9H_{14}^-$ and $B_{11}H_{14}^-$. The stepwise formation of larger polyhedral boranes from smaller boron clusters can be described as a series of reactions involving the incorporation of neutral boron hydrides, such as B_2H_6 , into the BH_4^- anion. Indeed, the small charged boron species, such as BH_4^- and $B_3H_8^-$ tend to react with strongly electrophilic neutral boron hydrides like $L \cdot BH_3$ ($L =$ Lewis base), B_2H_6 , B_4H_{10} , $B_{10}H_{14}$ due to their nucleophilicity.^{28,31,32} However, the formation mechanism of the final dianion ($B_{12}H_{12}^{2-}$) from monovalent anions and neutral boron hydrides has not yet been experimentally understood.

In contrast to sodium and potassium dodecaborates, limited research has been conducted concerning direct synthetic approaches in solution to obtain $Li_2B_{12}H_{12}$. The latter is recently seen as a very important precursor for producing Li-ion solid-state electrolytes.⁷ Due to the tendency of Li^+ towards strong coordination with ethereal solvents used for the synthesis, the production of unsolvated $Li_2B_{12}H_{12}$ is very challenging.^{4,25,27,33} One alternative consists in exchanging Li^+ by large monovalent cations, such as trimethylammonium, to yield water-insoluble products, enabling the

removal of diglyme (eq. 1). Anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ can then be obtained through a second cation substitution in the resulting $(\text{Me}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$ using LiOH in water, which can be readily removed through heat treatment (eq. 2).³⁴ However, this approach proceeds in several steps and, if the amount of LiOH is not carefully controlled, may bring in impurities.



In this contribution, we present a novel and convenient two-step synthetic approach towards anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The first step is based on reacting LiBH_4 with $\text{DMS} \cdot \text{BH}_3$ under heating in a solvent using either conventional Schlenk techniques (Figure S1-3) or in an autoclave. In the second step, a solvent exchange strategy coupled with a thermal treatment is used to desolvate the product. Finally, the formation mechanism of $\text{B}_{12}\text{H}_{12}^{2-}$ is experimentally investigated by solution-state ^{11}B nuclear magnetic resonance spectroscopy (^{11}B NMR).

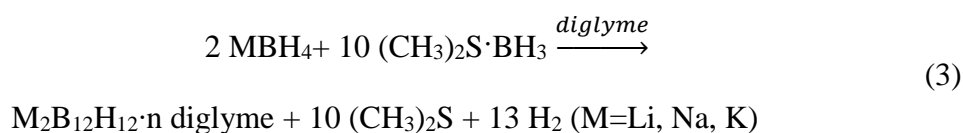
2. Experimental Section

Experimental details can be seen in Supporting information.

3. Results and Discussion

3.1 Synthesis of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ from LiBH_4 and $\text{DMS}\cdot\text{BH}_3$ in a Schlenk flask and its optimization

In the first step of our new synthetic method, LiBH_4 is reacted with $\text{DMS}\cdot\text{BH}_3$ in diglyme to produce $\text{Li}_2\text{B}_{12}\text{H}_{12}$, following eq. 3 This reaction was firstly investigated using a classical Schlenk setup at a reaction temperature of 120°C with a molar ratio of 1: 5.5 (10% excess of $\text{DMS}\cdot\text{BH}_3$) (Figure S4).



In 24 hours the yield of $\text{B}_{12}\text{H}_{12}^{2-}$ found in the solid product reaches 45 %, as shown by the sole presence of a doublet around -15.2 ppm on the proton-coupled ^{11}B solution-state NMR spectrum of the solid product dissolved in DMSO-d_6 (Figure 1a).^{22,35,36} NMR analysis of the filtrate (Figure 1b) reveals the presence of residual intermediates such as B_3H_8^- and higher nuclearity boron clusters including $\text{B}_9\text{H}_{14}^-$, $\text{B}_{10}\text{H}_{13}^-$ and $\text{B}_{11}\text{H}_{14}^-$, all of which are soluble in diglyme.^{1,3,37,38}

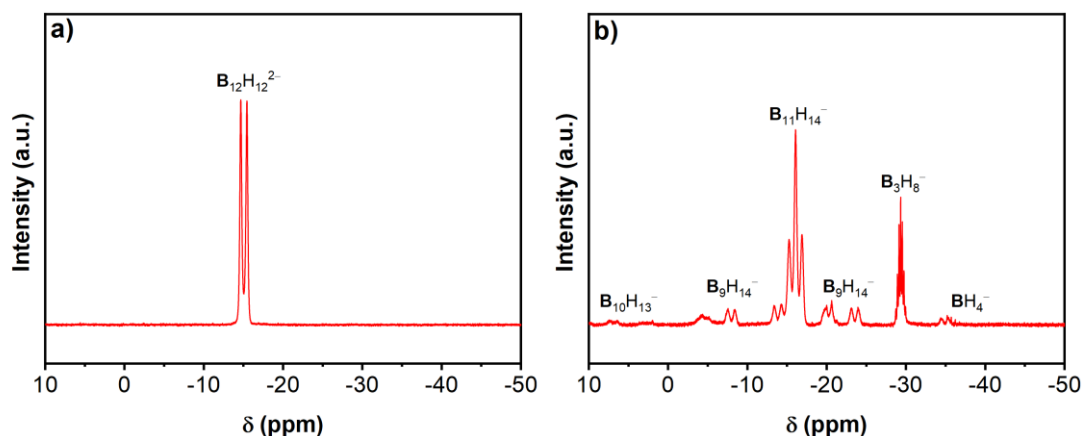


Figure 1. Proton-coupled ^{11}B NMR spectra of a) solid precipitate and b) filtrate after reaction at 120°C for 24h in a Schlenk setup (5 mmol LiBH_4 + 27.5 mmol $\text{DMS}\cdot\text{BH}_3$ in 20 ml diglyme)

To optimize the reaction conditions, the $\text{DMS}\cdot\text{BH}_3$ ratio was varied while maintaining all other reaction parameters constant (5 mmol LiBH_4 , 20 mL of diglyme

and 24h of heating at 120°C). Experiments were carried out with LiBH₄/DMS·BH₃ molar ratios of 1:2 and 1:10. A 1:2 ratio stoichiometry for the synthesis of B₃H₈⁻ provided yields of Li₂B₁₂H₁₂ around 11 %, based on the used amount of LiBH₄, with B₃H₈⁻ remaining as the main boron species in the filtrate (Figure S4-5 and Table S2-3). In contrast, a 1:10 ratio resulted in a 30 % yield and produced B₁₁H₁₄⁻ as main boron species in the filtrate. Excessive concentrations of DMS·BH₃ thus lead to low yields, likely due to the formation of higher nuclearity boron clusters (B₉H₁₄⁻, B₁₁H₁₄⁻), which likely prevent the two reactants from interacting efficiently.³

Temperature has always been regarded as being a crucial factor for the synthesis of polyhedral borates,⁹ and has thus been investigated for our new approach as well. In our synthetic procedure, when a lower temperature (85 °C) was used, an incomplete conversion of BH₄⁻ and DMS·BH₃ into B₃H₈⁻, B₉H₁₄⁻, B₁₀H₁₃⁻ and B₁₁H₁₄⁻ occurred after 24 hours, as shown by ¹¹B NMR (Figure S6), leading to a yellow reaction solution without a precipitate. By prolonging the reaction to 48 hours, a very small amount of precipitate appeared, and the ¹¹B NMR spectrum of the reaction mixture (Figure S6) indicates weak signals of B₁₂H₁₂²⁻ and nearly complete depletion of LiBH₄. Applying a higher reaction temperature (160 °C), without condenser, led directly to the formation of a complicated borate anion (Figure S7). We speculate that the formation of a complicated borate anion might be due to the reaction between B₁₁H₁₄⁻ and the dehydrogenated B₁₂H_{12-x}²⁻ anion. The dehydrogenation occurring in the icosahedral B₁₂H₁₂²⁻ results in a change in charge, no longer identical, and symmetry of the twelve BH vertices. This leads to the formation of a disubstituted anion when reacted with electrophilic compounds.³⁹

Performing the same experiment at 160 °C but using a setup equipped with a condenser resulted in the formation of B₁₂H₁₂²⁻, along with some B₁₀H₁₀²⁻ and partially dehydrogenated B₁₂H_{12-x}²⁻ anion (Figure S8).⁴⁰ The use of a condenser also increases the yield when performing the reaction at 120°C, as indicated in Table S3. Additionally, the presence of B₁₁H₁₄⁻ as the main boron species in the filtrate (Figure S9) indicates that refluxing promotes the conversion of lower boranes to B₁₂H₁₂²⁻.

Similar reactions at 160 °C in Schlenk flasks (Figure S10 and Table S4) equipped with a condenser, where LiBH_4 was substituted by NaBH_4 and KBH_4 , produced $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$ in isolated yields of 92% and 88%, respectively. In this case, higher temperature favors the formation of $\text{B}_{12}\text{H}_{12}^{2-}$, which is in line with previous research showing that the thermal decomposition of BH_4^- and B_3H_8^- salts can lead to the formation of closo-boranes such as $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$.^{33,41–44} Furthermore, on the contrary to diglyme solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, the solvates of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$ are much more stable at this temperature.²⁶ The small amounts of $\text{B}_{10}\text{H}_{10}^{2-}$ impurities in $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$ obtained by this procedure can be completely removed by washing with diglyme. These results indicate that using a Schlenk setup equipped with a condenser is the proper choice for the synthesis of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$ but is not ideal for obtaining $\text{Li}_2\text{B}_{12}\text{H}_{12}$ in high yield.

3.2 Synthesis of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ from LiBH_4 and $\text{DMS}\cdot\text{BH}_3$ in an autoclave

Further optimization of the synthesis conditions was performed by varying reactants concentrations and reaction times. Additionally, the reactions were performed either in a Schlenk setup without condenser or in an autoclave, as the use of the latter enables keeping all generated gaseous species, such as B_2H_6 and DMS , confined in the volume. Indeed, we speculate that B_2H_6 could highly accelerate the hydroboration reaction from BH_4^- to $\text{B}_{11}\text{H}_{14}^-$, thus improving the yield of $\text{B}_{12}\text{H}_{12}^{2-}$.^{22,37} Detailed reaction conditions are summarized in Tables S3-7 and Figures S11-14. To prevent the loss of the volatile species during the argon flush of the autoclave system, an excess amount of 10 % $\text{DMS}\cdot\text{BH}_3$ was used. As a general trend, the yields of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ obtained in the autoclave were much higher than in the Schlenk setup. In addition, longer reaction times allowed complete conversion of the reactants, resulting in higher yields. Remarkably, an isolated 96% yield of pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was achieved in the autoclave, representing the highest yield achieved thus far in the preparation of metal dodecaborates (Table S8), to the best of our knowledge. When the concentration of reactants in the autoclave was increased, a drop in yield was observed. This contrasts with the reactions in the Schlenk setup, for which increasing reactant concentrations or

reaction times did not have significant impact on the final yield of $B_{12}H_{12}^{2-}$.

Signals of $B_{10}H_{13}^-$ were not observed in the ^{11}B NMR spectra (Figure S15) of filtrates resulting from autoclave experiments. The autoclave keeps all gaseous species confined under high pressure inside the reactor system, and the B_2H_6 dimer can thus be retained in the reaction mixture. We speculate that the pyrolysis of B_2H_6 directly leads to the formation of higher boranes, such as B_4H_{10} or B_6H_{10} , resulting in an increased content of $B_{11}H_{14}^-$ in the solution and a slow reaction between $B_3H_8^-$ and $B_{11}H_{14}^-$.^{45,46} Remaining $DMS \cdot BH_3$ can be observed in NMR spectra of products obtained in the autoclave system but not on those resulting from reactions performed in a Schlenk flask.

The synthesis of $Li_2B_{12}H_{12}$ in an autoclave can also be carried out using a lighter ether, such as monoglyme (b. p. of 85 °C), as solvent. Figure 2 shows the ^{11}B NMR spectrum of the solid precipitate and the filtrate obtained upon reaction of 10 mmol $LiBH_4$ with 55 mmol $DMS \cdot BH_3$ in 20 ml monoglyme. The ^{11}B NMR spectra (Figure 2a and Figure S16) demonstrate that under those conditions pure monoglyme solvated $Li_2B_{12}H_{12}$ is obtained, with an isolated yield of 42%. However, a considerable amount of $Li_2B_{12}H_{12}$ remains as small particles in the filtrate (Figure 2b), which makes full recovery of the formed product difficult. Cooling the reaction solution in the fridge at 10 °C overnight before filtration allows addressing this issue, by increasing the crystallite size. By doing so and washing the product with cold monoglyme (10 °C), a monoglyme-rich solvated $Li_2B_{12}H_{12}$ was obtained with an isolated yield of 89 %.

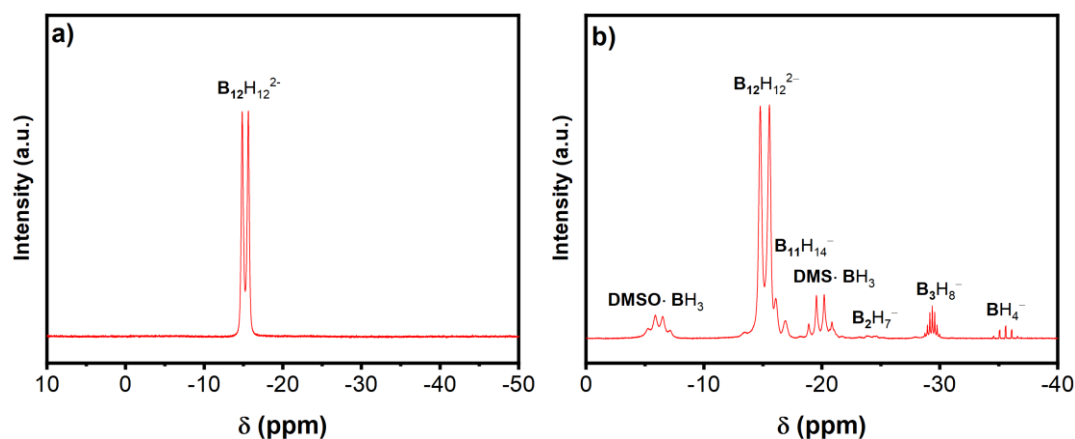


Figure 2. Proton-coupled ^{11}B NMR spectra of a) solid precipitate and b) filtrate (10 mmol LiBH_4 , autoclave, 24 h). The particles of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ that remained suspended in the filtrate were fully dissolved by addition of $\text{DMSO-}d_6$ prior to analysis.

3.3 Thermal behavior and desolvation of as synthesized $\text{M}_2\text{B}_{12}\text{H}_{12}$

After initial drying, the crude products contained a variable amount of diglyme molecules per formula unit, as evidenced by NMR spectroscopy (see above). Attempts to remove the coordinated solvent from $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ diglyme by thermal treatment were unsuccessful. Thermogravimetric analysis (TGA) was performed to investigate the thermal stability and composition of $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ diglyme (Figure S17). Thermal decomposition occurs in three steps: removal of free diglyme starts at 25 °C (-9.5 wt.%), followed by a larger mass loss of 15.5 wt.% starting around 150 °C and a third mass loss of 5 wt.% between 200 °C and 300 °C, the two latter steps corresponding to removal of coordinated diglyme.

An in situ synchrotron radiation powder X-ray diffraction (SR-PXD) experiment was performed to further investigate the behavior of $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ diglyme during thermal treatment (Figure S18). The only crystalline phase observed on the diffraction patterns corresponds to $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 2$ diglyme, which is thermally stable until 179 °C and then decomposes into an amorphous phase. The structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 2$ diglyme was resolved by single crystal X-ray diffraction (SC-XRD, see Figure 3a and SI). In this solvate, two Li ions are threefold coordinated with three O atoms from two diglyme molecules, evidencing strong interaction with the solvent molecules. It is noteworthy

that when reaching the decomposition temperature, the solid sample starts melting and bubbling. The loss of hydrogen from the boron cages was evidenced by ^1H NMR and ^{11}B NMR (Figures S19-21), as the characteristic asymmetric multiplet of $\text{B}_{12}\text{H}_{12}^{2-}$ (1.6–0 ppm) disappears after thermal treatment at 170 °C under vacuum for 12 h, indicating competition between desolvation and dehydrogenation.⁴⁷ This suggests that direct removal of diglyme by thermal treatment is not possible.

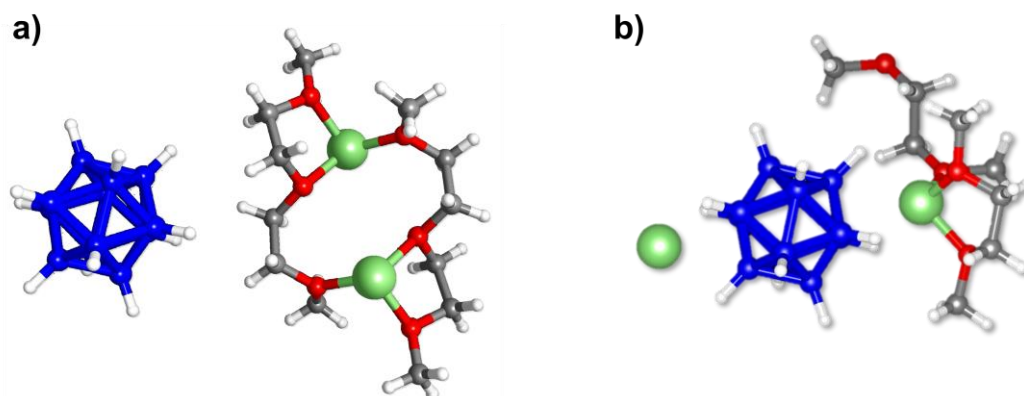


Figure 3. Fragments of the crystal structures of a) $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 2$ diglyme and b) $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 1.5$ monoglyme, illustrating the coordination modes of the glymes to Li^+ . Color code: **Li**, green; **B**, dark blue; **H**, light grey; **O**, red; **C**: dark grey.

Single crystals of diglyme solvated $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$ were isolated from the reaction mixtures upon synthesis as well, and their structures determined by SC-XRD as being $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 4$ diglyme and $\text{K}_2\text{B}_{12}\text{H}_{12}\cdot 4$ diglyme (Figure 4). Unlike Li^+ , Na^+ and K^+ possess a lower charge density and larger cation size, resulting in a higher cation-to-anion size ratio.⁴⁸ This leads to a different coordination environment for Na^+ and K^+ , with $\text{M}^+\cdots\text{O}$ bonds ($\text{Na}^+\cdots\text{O} = 2.378\text{--}2.446$ Å, $\text{K}^+\cdots\text{O} = 2.728\text{--}2.844$ Å) longer than $\text{Li}^+\cdots\text{O} = 1.958\text{--}2.039$ Å, meaning that less energy will be needed to break these coordination bonds. This explains why direct heat treatment of diglyme solvated $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (150 °C) and $\text{K}_2\text{B}_{12}\text{H}_{12}$ (200 °C) under vacuum was effective for direct removal of diglyme in our previous work, while it is ineffective for the Li^+ derivative.²⁶

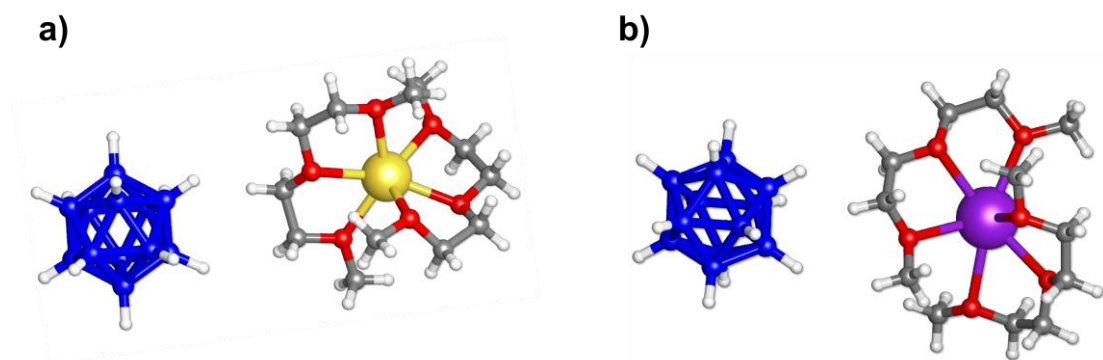


Figure 4. Fragments of the single crystal structures of a) $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 4$ diglyme (RT) and b) $\text{K}_2\text{B}_{12}\text{H}_{12} \cdot 4$ diglyme, illustrating the coordination modes of the glymes to the alkali metal cations. Color code: **Na**, Yellow; **K**, purple; **B**, dark blue; **H**, light grey; **O**, red; **C**: dark grey.

Interestingly, by drying crystals of the diglyme solvated $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at 80°C for 2 hours, a single crystal to single crystal transformation occurred, leading to a high temperature (HT) diglyme solvated form of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (Figure 5). The decomposition of the HT form of $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2$ diglyme leads directly to the disordered HT phase of $\text{Na}_2\text{B}_{12}\text{H}_{12}$, as indicated in our previous work (Figures S22-28).

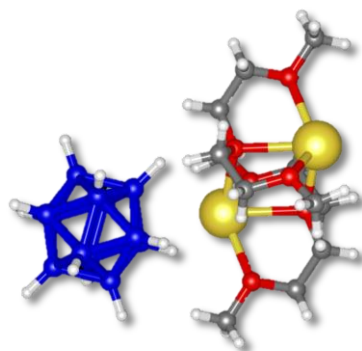


Figure 5. Fragment of the single crystal structure of the HT form of $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2$ diglyme, illustrating the coordination mode of diglyme to Na^+ . Color code: **Na**, Yellow; **B**, dark blue; **H**, light grey; **O**, red; **C**: dark grey.

We investigated a new method to obtain anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ from the glymes solvates, eliminating the need for the inconvenient previously utilized ion exchange strategy, by using dimethyl sulfoxide (DMSO) or *N,N*-Diethylformamide (DEF) as solvent exchange agents. This approach is aimed to overcome the strong chelation of

diglyme with dodecaborate salts containing small cations such as Li^+ and Na^+ . The methodology consisted of adding 10 ml of DMSO or DEF to 1 g of the diglyme solvated product and drying the solution under vacuum at 100 °C for 12 hours. Upon this treatment, the formation of completely exchanged DMSO or DEF solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is achieved, as demonstrated by PXRD and FTIR analyses (Figures S29-30). The ^1H NMR (Figure 6) analysis of $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ DMSO before and after desolvation indicates that DMSO completely substitutes diglyme. Additionally, DMSO can be removed from the solvate by thermal treatment without decomposition of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion. This evidences that DMSO can be used as an effective solvent for the removal of diglyme in $\text{Li}_2\text{B}_{12}\text{H}_{12}$. Subsequently, drying the solvent-exchanged products at 200 °C under vacuum resulted in the formation of unsolvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, as shown by (in situ) PXRD and NMR (Figures S31-35). The choice of DMSO and DEF for the solvent exchange is justified by their higher boiling points and weaker coordinating strength compared to diglyme.⁴⁹ Although both solvents can effectively substitute diglyme, DMSO is the more economically viable option given the much higher price of DEF.

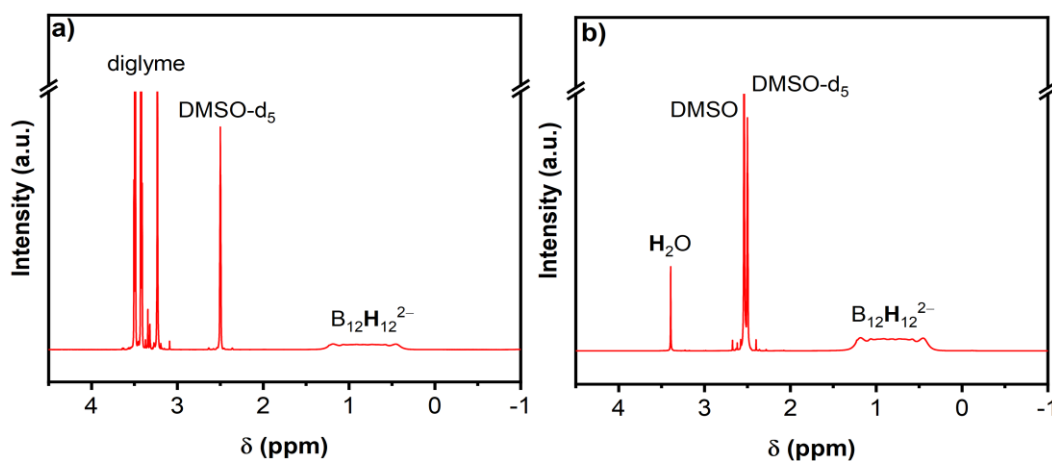


Figure 6. ^1H NMR spectra of a) $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ diglyme and b) $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n$ DMSO.

When monoglyme is used for the synthesis, the crystalline phase of the obtained solvate corresponds to $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 1.5$ monoglyme, as evidenced by its structure determined by SC-XRD (see Figure 3b and SI). In this structure, monoglyme shows a similar coordinating ability to Li^+ as diglyme in solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, and thus poses similar challenges for desolvation.

However, compared to diglyme solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, in situ PXRD data (Figure S36) reveals that monoglyme solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ exhibits different phase changes during thermal desolvation before leading to $\text{Li}_2\text{B}_{12}\text{H}_{12}$. Diffraction peaks of monoglyme solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ disappear at around 150 °C, while $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is formed at this temperature. At 310 °C, the phase transition from the α - $\text{Li}_2\text{B}_{12}\text{H}_{12}$ to the β - $\text{Li}_2\text{B}_{12}\text{H}_{12}$ polymorph is observed, and decomposition to a hydrogen-poor γ - $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$ phase occurs at higher temperatures.^{50,51} This last phase transition occurs about 50 °C below the previously reported temperature, likely due to the experiment being performed under vacuum. An attempt to directly remove monoglyme from solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ by heating at 180 °C under vacuum for 12 hours resulted in a small amount of $\text{Li}_2\text{B}_{12}\text{H}_{12-x}\cdot n$ monoglyme, as observed in the ^{11}B NMR spectrum (Figure S37).

Although complete removal of monoglyme from $\text{Li}_2\text{B}_{12}\text{H}_{12}$ through direct heating is difficult, our above proposed solvent exchange strategy can in this case be carried out with even lighter, more abundant and greener solvents, such as H_2O , as compared to DMSO and DEF for the diglyme solvated dodecaborate. Indeed, upon exchange with water and applying vacuum at 40°C, monoglyme can be completely removed, as shown by ^1H NMR, PXRD and FTIR analyses (Figures S38-42), and pure hydrated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ can be obtained. Water can then be easily removed from the hydrated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ without damaging the $\text{B}_{12}\text{H}_{12}^{2-}$ clusters. It is worth noting that $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is commercially available in its hydrated form, which can be simply obtained by our solvent exchange strategy, without the last heating step.

3.4 Synthesis in Toluene

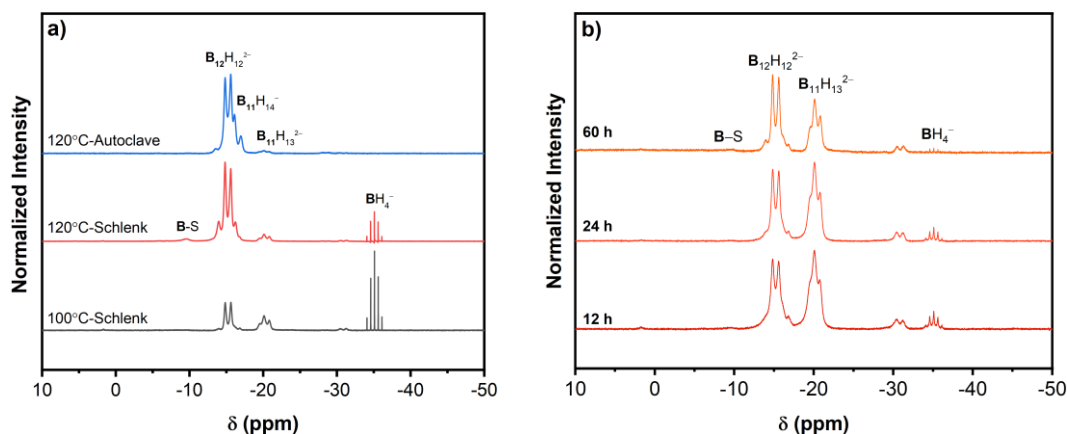


Figure 7. Proton coupled ^{11}B NMR spectra of (a) solid compounds obtained from 5 mmol LiBH_4 + 27.5 mmol $\text{DMS}\cdot\text{BH}_3$ in 20 ml toluene at 100°C and 120°C for 24 hours, in a Schlenk flask or autoclave and (b) of 5 mmol ball-milled LiBH_4 with 27.5 mmol of $\text{DMS}\cdot\text{BH}_3$ after various reaction times at 120°C in a Schlenk flask.

The reactions were also attempted in toluene, a non-coordinating solvent, with the aim of obtaining directly unsolvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$.^{4,5,25} The NMR spectra (Figure 7 and Figures S43-44) of the solid sample obtained from reaction in a Schlenk setup shows the presence of the desired $\text{B}_{12}\text{H}_{12}^{2-}$ along with BH_4^{-} , $\text{B}_{11}\text{H}_{14}^{-}$, and $\text{B}_{11}\text{H}_{13}^{2-}$ and in the final solid. The formation of $\text{B}_{12}\text{H}_{11}\text{S}(\text{CH}_3)^{2-}$ can be attributed to the self-condensation of $\text{DMS}\cdot\text{BH}_3$.⁵² The diffraction patterns (Figures S45-47) of the sample obtained by running the reaction at 100 °C however indicates $\text{Li}_2\text{B}_{12}\text{H}_{12}$ as the only crystalline phase. A higher temperature of 120 °C leads to a solid showing diffraction peaks of impurity phases along the desired phase. In contrast, experiments performed in an autoclave enabled the complete conversion of BH_4^{-} into $\text{B}_{11}\text{H}_{14}^{-}$, $\text{B}_{11}\text{H}_{13}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$.

We also ball milled LiBH_4 prior to the synthesis in toluene in the Schlenk setup to further improve the synthesis, as this reactant exhibits insolubility in this solvent. ^{11}B NMR spectra (Figure 8b and Figures S48-50) shows that this led to the presence of only BH_4^{-} and $\text{B}_{11}\text{H}_{13}^{2-}$ along with $\text{B}_{12}\text{H}_{12}^{2-}$ in the final solid. A considerable amount of $\text{B}_{11}\text{H}_{13}^{2-}$ is obtained after 24 hours and a longer reaction time is required for its conversion into $\text{B}_{12}\text{H}_{12}^{2-}$. As we observed that $\text{B}_{11}\text{H}_{13}^{2-}$ is insoluble in THF-d_8 (Figure

S52), its isolation was attempted by washing the synthesized sample with excess THF (Figure S53). However, we did not succeed in purifying the desired product, as $B_{12}H_{12}^{2-}$ and BH_4^- were still present after this washing procedure, completely isolating unsolvated $B_{11}H_{13}^{2-}$ without other boron-hydrogen compounds is challenging. It is noteworthy that similar reactions performed with ball milled $NaBH_4$ instead of $LiBH_4$ resulted in the formation of $NaB_{12}H_{11}S(CH_3)_2$ as the main product (Figures S54-55).

3.5 Elucidation of the formation mechanism of $B_{12}H_{12}^{2-}$

To gain insight into the formation mechanism of $B_{12}H_{12}^{2-}$, ^{11}B NMR was employed to monitor the composition of the reaction mixture over the course of the synthesis. Figure 8 shows the ^{11}B NMR spectra of aliquots of a mixture of $LiBH_4$ and $DMS \cdot BH_3$ in diglyme collected before heating (0 h) and at different reaction times during solvothermal reaction at 120 °C.

In the initial mixture at room temperature, a signal at -24 ppm can be observed together with those of the reactants, which is ascribed to $B_2H_7^-$.³⁷ This intermediate is then quickly converted into $B_3H_8^-$, in accordance with previous observations, together with $B_9H_{14}^-$, during the first half hour of the solvothermal reaction. Notably, the intensities of the BH_4^- and $DMS \cdot BH_3$ signals drop rapidly after initiating heating, coupled to an increase in the concentration of $B_9H_{14}^-$ and $B_{11}H_{14}^-$ during the first hour of the reaction, consistent with earlier reports on the dehydrocondensation of $B_3H_8^-$ with B_2H_6 .⁵³ Notably, the appearance of the characteristic doublet of $B_{12}H_{12}^{2-}$ can be observed already after 2 h of reaction, and its intensity then constantly increases while the reaction progresses. In contrast, the intensities of the $B_9H_{14}^-$ and $B_{11}H_{14}^-$ signals remain almost constant over the whole duration of the reaction, while slow consumption of $B_3H_8^-$ is observed. The constant concentration of $B_9H_{14}^-$ and $B_{11}H_{14}^-$ over nearly the whole reaction time indicates that those species act as intermediates in a chemical equilibrium, being consumed rapidly after their formation to yield the final product. The reaction pathway for $B_{12}H_{12}^{2-}$ from BH_4^- is represented in Figure 9.

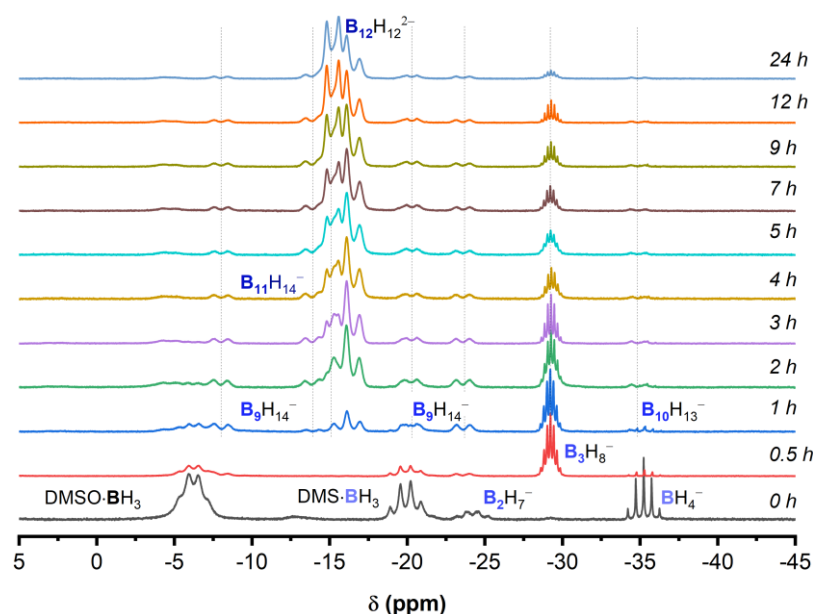


Figure 8. ^1H -coupled ^{11}B NMR spectra of aliquots taken from a reaction mixture containing LiBH_4 and $\text{DMS}\cdot\text{BH}_3$ in diglyme at $120\text{ }^\circ\text{C}$ at different time intervals ($t = 0\text{ h}$ was sampled before heating the mixture and intensities were normalized to the most intense signal).

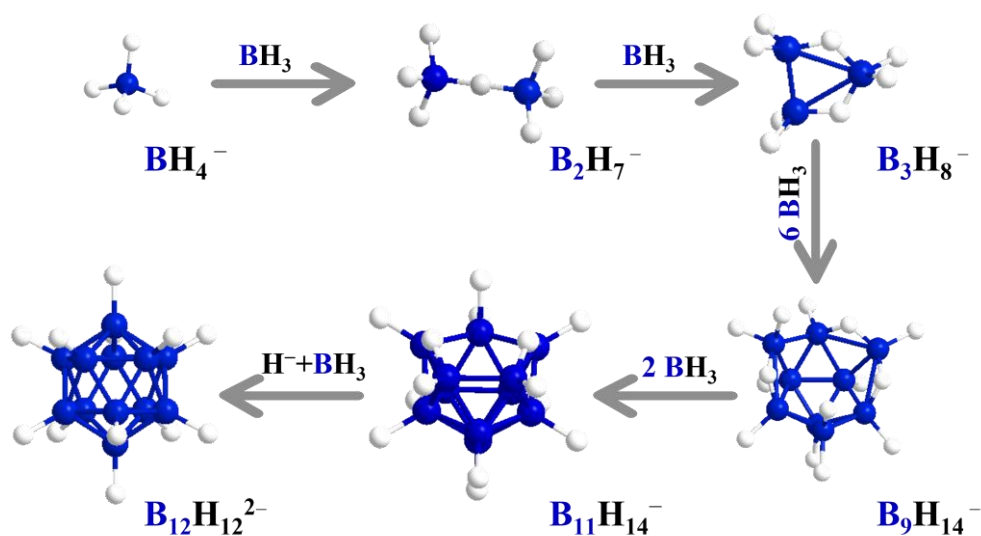


Figure 9. Proposed mechanism for the stepwise buildup of $\text{B}_{12}\text{H}_{12}^{2-}$ from BH_4^- .

The above experiment demonstrates that B_3H_8^- , $\text{B}_9\text{H}_{14}^-$ and $\text{B}_{11}\text{H}_{14}^-$ are stable intermediates in the sequential buildup of $\text{B}_{12}\text{H}_{12}^{2-}$ from BH_4^- and BH_3 . To understand the final step of the formation mechanism of lithium dodecaborate, the isolation of the intermediate, $\text{B}_{11}\text{H}_{14}^-$, is critical. After various trials (see SI, Figures S56-59), we achieved this by subjecting the reaction filtrate obtained from the initial synthetic step to thermal treatment at $160\text{ }^\circ\text{C}$ (Figures S60-61). In order to understand what species

adds to $B_{11}H_{14}^-$ to form dodecaborate, a solution of the isolated $LiB_{11}H_{14}$ in diglyme was reacted with various lower boranes, including $DMS \cdot BH_3$ and BH_4^- , at 120 °C in a Schlenk flask for 3 hours. As shown in Figure 10, direct reaction of $LiB_{11}H_{14}$ with BH_4^- did not yield $B_{12}H_{12}^{2-}$, but instead led to $B_{11}H_{13}^{2-}$ through the deprotonation of $B_{11}H_{14}^-$ by BH_4^- . On the other hand, the reaction of $B_{11}H_{14}^-$ with $DMS \cdot BH_3$ resulted in the successful formation of $B_{12}H_{12}^{2-}$. Previous reports have demonstrated the isolation of the $B_{12}H_{12}^{2-}$ anion through similar reactions, such as the one between $B_{11}H_{14}^-$ and triethylamine borane at 150 °C. $Na_2B_{12}H_{12}$ could however be obtained through reaction of $NaB_{11}H_{14}$ with $NaBH_4$ in boiling diglyme (b.p. = 162 °C).^{3,24,27,54,55} Our results indicate that at a lower reaction temperature of 120 °C, deprotonation is likely favored over direct hydroboration.

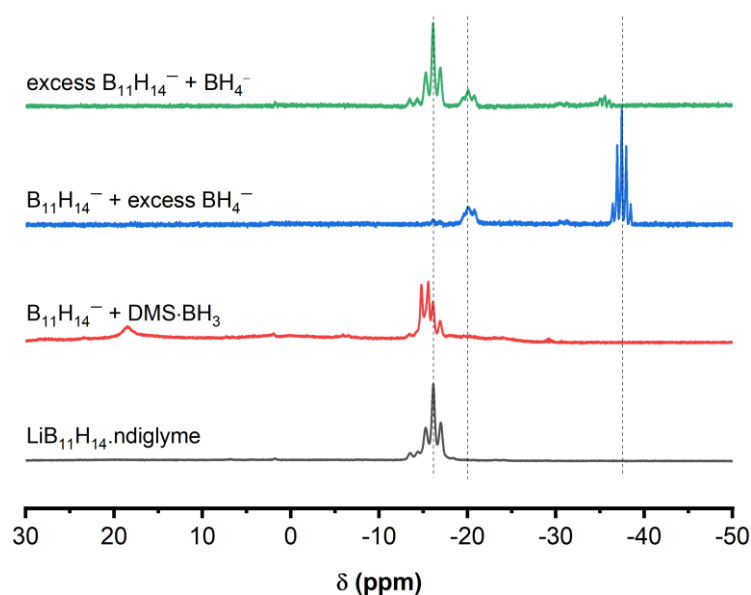


Figure 10. Proton coupled ^{11}B NMR spectra of reaction mixtures containing $LiB_{11}H_{14}$ and $DMS \cdot BH_3$ or $LiBH_4$ in diglyme.

4 Conclusions

We developed a simple solvothermal synthesis method enabling the synthesis of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and, by extension, its Na^+ and K^+ counterparts, in high purity and yield. Our innovative approach involves the reaction between the respective alkali borohydride and $\text{DMS}\cdot\text{BH}_3$ in glymes, either in an autoclave or in a Schlenk flask.

The yield of $\text{B}_{12}\text{H}_{12}^{2-}$ increases with temperature and reaction time, with optimal conditions for obtaining $\text{Li}_2\text{B}_{12}\text{H}_{12}$ being 120 °C in an autoclave for 48 hours, resulting in a 96 % yield. Lower reaction temperatures resulted in incomplete conversion of BH_4^- to $\text{B}_{12}\text{H}_{12}^{2-}$, due to the slow reaction kinetics between B_3H_8^- on the one hand, and $\text{B}_9\text{H}_{14}^-$ and $\text{B}_{11}\text{H}_{14}^-$ on the other hand. Higher temperatures led to the direct formation of partially dehydrogenated $\text{Li}_2\text{B}_{12}\text{H}_{12-x}\cdot n$ diglyme. The closed system of an autoclave, enabling a higher (autogenous) pressure of DMS, prevented decomposition of BH_3 into higher boranes and facilitated the reaction between B_3H_8^- and $\text{B}_{11}\text{H}_{14}^-$. In turn, the conditions in the Schlenk flask favored the formation of $\text{B}_{11}\text{H}_{14}^-$. For the syntheses of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{12}\text{H}_{12}$, refluxing diglyme in a Schlenk flask at 160 °C led to 92% and 88% yields, respectively.

The use of glymes as solvents resulted in the formation of glyme-solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, with strong coordination with Li^+ , evidenced by single crystal X-ray diffraction. Thermal treatment was ineffective to diglyme from the solvate. In that case, a methodology consisting in exchange of diglyme by higher boiling point polar solvents such as DMSO or *N,N*-diethylformamide followed by heating under vacuum was demonstrated as being successful for obtaining unsolvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$. In addition, substitution of diglyme by monoglyme as reaction solvent in an autoclave led to pure DME-solvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$, which, in contrast to the diglyme solvate could be converted into unsolvated $\text{Li}_2\text{B}_{12}\text{H}_{12}$ by a simple heat treatment. Additionally, substitution of DME by H_2O allows for the preparation of chemically pure $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot n \text{H}_2\text{O}$. Performing the reaction in toluene can yield crystalline pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$, similar to the solvent-free synthetic method, but further purification or extraction steps are required.

Finally, the formation mechanism of $B_{12}H_{12}^{2-}$ under the developed reaction conditions was elucidated through ex situ follow up of reaction intermediates using ^{11}B NMR. This evidenced a stepwise buildup mechanism of $B_{12}H_{12}^{2-}$ from BH_4^- through $B_2H_7^-$, $B_3H_8^-$, $B_9H_{14}^-$, $B_{11}H_{14}^-$ intermediates. Furthermore, $B_{11}H_{13}^{2-}$ was proposed as the final intermediate based on experiments starting from isolated $B_{11}H_{14}^-$.

The developed synthetic method represents a significant improvement compared to previous strategies in terms of yield, purity, and cost-effectiveness for lithium and other alkali metal dodecaborates under their solvated and desolvated forms.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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