



Article **A Simple and Efficient Way to Directly Synthesize Unsolvated Alkali Metal (M = Na, K) Salts of [CB_{11}H_{12}]^{-}**

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Abstract: Alkali metal (M = Na, K) salts of the $[CB_{11}H_{12}]^-$ anion have attracted increasing attention in many fields such as catalysis and all-solid-state batteries. However, tedious and low-yielding synthetic methods have seriously limited their application in these fields. We developed a facile method for the direct synthesis of the unsolvated potassium and sodium salts of the $[CB_{11}H_{12}]^$ anion in 66% and 68% yields, respectively, by reactions of Na[B₁₁H₁₄] with NaH/NaHMDS (sodium bis(trimethylsilyl)amide), CF₃SiMe₃ in THF and K[B₁₁H₁₄] with KH, CF₃SiMe₃ in DME. This method avoids the exchange of cation and significantly simplifies the reaction setup, thus enabling convenient large-scale synthesis. It is believed that this method will support further application of Na[CB₁₁H₁₂] and K[CB₁₁H₁₂] as solid electrolytes for an all-solid-state battery.

Keywords: Na[CB₁₁H₁₂]; K[CB₁₁H₁₂]; Na[B₁₁H₁₄]; K[B₁₁H₁₄]; one-pot synthesis



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1. Introduction

The monocarborane $[CB_{11}H_{12}]^-$ anion and dicarbaborane $C_2B_{10}H_{12}$ are two important icosahedral derivatives of $[B_{12}H_{12}]^{2-}$ in which one or two BH vertices are replaced by CH [1]. The $[CB_{11}H_{12}]^-$ anion was synthesized for the first time by Knoth in 1967 [2]. Recently, the study on complexes containing the $[CB_{11}H_{12}]^-$ anion has been of interest because they are well known as weakly coordinating anions [3]. Monocarborane anions with halogen substituents, such as $[CB_{11}Me_6X_6]^-$, $[CB_{11}H_6X_6]^-$ (X = Cl, Br, I) and [CHB₁₁Cl₁₁] are amongst the least coordinating, least basic and most chemically inert anions presently known, and have been used to stabilize many new extremely reactive cations [4,5]. $H(CHB_{11}Cl_{11})$ is the strongest isolable Brønsted acid [6]. Additionally, they can also be applied in the fields of coordination [7], supramolecular chemistry [8] and medicine [9], as well as fluorescence [10] and materials [11]. More importantly, it has been found that $M[CB_{11}H_{12}]$ (M = K, Na) have great application prospects as solid electrolytes [12,13]. However, compared to the large study on the application and functionalization of dicarbaborane $C_2B_{10}H_{12}$ [14–16], the research on the monocarborane [$CB_{11}H_{12}$]⁻ anion has been much more scarce [17–19]. This should be attributed to its complicated synthetic method and the fact that it is hard to commercialize. So the development of an efficient method to directly synthesize the $[CB_{11}H_{12}]^-$ anion is highly desired.

The counter cation is $[Me_3NH]^+$ in most synthetic methods reported for the synthesis of the $[CB_{11}H_{12}]^-$ anion when considering the solubility of the salts of $[CB_{11}H_{12}]^-$ in organic solvents. These methods have been improved since 1967 (Scheme 1). In early reported methods, decaborane $(B_{10}H_{14})$ was mainly used as a starting material, which is toxic and flammable. The first preparation of $[CB_{11}H_{12}]^-$ was achieved by Knoth through the reaction of decaborane with sodium cyanide (Scheme 1A) [2]. A safer and more convenient modification of the synthesis was developed by the group of Hughes using alkyl isocyanides replacing toxic cyanide to form the initial C-B bond (Scheme 1B) [20]. Later, the group of Kennedy used formaldehyde and decaborane to form the B-C bond,

which could simplify the synthetic route and save the trouble of a C-N bond fracture (Scheme 1C) [21]. However, the conditions for closing the cage by adding $Me_2S \cdot BH_3$ require harsh reaction conditions such as 3 days of heating.



Scheme 1. Synthesis of [Me₃NH][CB₁₁H₁₂] from B₁₀H₁₄ (A-C) and [Me₃NH][B₁₁H₁₄] (D-F).

To avoid the use of toxic decaborane, the $[B_{11}H_{14}]^-$ anion was introduced to the synthesis of $[CB_{11}H_{12}]^-$ [22–25]. In 2001, Michl's group reported a relatively safe way to synthesize $[CB_{11}H_{12}]^-$ by deprotonation of $[B_{11}H_{14}]^-$, followed by the insertion of dichlorocarbene, but the yield was very low due to the low activity of the selected carbene source (Scheme 1D). Agnes Kütt and co-workers found that $[Me_3NH][CB_{11}H_{12}]$ could be obtained by reacting $[B_{11}H_{14}]^-$ with NaH and CF₃SiMe₃ in up to 95% yield (Scheme 1E) [24]. By improving the above method, $[CB_{11}H_{12}]^-$ was synthesized with common laboratory reagents such as NaOH, K₂CO₃ and CHCl₃, despite the yield being relatively low (40%) (Scheme 1F) [25]. Obviously, recent studies mainly focused on the synthesis for the $[Me_3NH]^+$ salt of $[CB_{11}H_{12}]^-$, while methods on the direct synthesis of alkali metal (M = Na, K) salts of the $[CB_{11}H_{12}]^-$ anion are still very limited, which is inconsistent with the great application of alkali metal (M = Na, K) salts of the $[CB_{11}H_{12}]^{-1}$ anion. Recently, we improved the synthetic method of [Et₄N][closo-1-CHB₉H₉] [26], and on the basis of our previous work on the condensation reaction of the B-H bond for the synthesis of polyhedral boranes [27-30] and the application of a dihydrogen bond in amine boranes [31–33], we developed a straightforward method for the synthesis of unsolvated

potassium and sodium salts of the $[CB_{11}H_{12}]^-$ anion. This method avoids the exchange of cation, significantly simplifies the reaction procedure and can be easily scaled-up.

2. Materials and Methods

2.1. Starting Materials

All manipulations were carried out on a Schlenk line or in a glovebox filled with highpurity nitrogen. Dry THF and DME were obtained by distillation from Na/benzophenone. K[B₁₁H₁₄] and Na[B₁₁H₁₄] were purchased from ZhengzhouYuanli technology. Potassium hydride, (trifluoromethyl)trimethylsilane, sodium hydride, sodium bis(trimethylsilyl)amide, tetrahydrofuran, 1,2-dimethoxyethane, DMSO-*d*₆ (D, 98%) were purchased from Energy Chemicals, Aladdin, Heowns or Royaltech. The ¹H and ¹H{¹¹B} NMR spectra were obtained using a Bruker Advance NEO 400 MHz instrument from Germany. The ¹³C NMR spectra were recorded at 101 Hz. The ¹¹B, ¹¹B{¹H} and ¹¹B-¹¹B cosy NMR spectra were recorded at 128 MHz. All ¹¹B chemical shifts were referenced to BF₃·OEt₂ in C₆D₆ (0.0 ppm), with a negative sign indicating an upfield shift. All ¹H chemical shifts were measured relative to internal residual hydrogens from the lock solvents (98% DMSO-*d*₆).

2.2. Synthesis of $Na[CB_{11}H_{12}]$

Na[B₁₁H₁₄] (1.58 g, 10 mmol), NaH (0.72 g, 30 mmol) and NaHMDS (1.84 g, 10 mmol) were added to a 100 mL Schlenk flask, which was equipped with a reflux condenser. The flask was connected with a Schlenk line and 40 mL 1,2-dimethoxyethane was injected. The reaction mixture was stirred under 0 $^{\circ}$ C for 15 min and (trifluoromethyl)trimethylsilane (4 mL, 30 mmol) was added. Then, the mixture was stirred at 60 $^{\circ}$ C for 3 days and a large amount of yellow precipitate was generated. After cooling down to room temperature and quenched with water (1 mL). The residue was subjected to extractive workup with ether $(4 \times 60 \text{ mL})$ and H₂O $(4 \times 60 \text{ mL})$. The organic phases were combined, and the solvent was evaporated to give a yellow oily product. Then, 1,4-dioxane was added into the oil residue until a large amount of white solid precipitate. The precipitate was filtered and then dried under dynamic vacuum to produce a 1,4-dioxane solvated Na[CB₁₁H₁₂] white powder. Solvent free Na[$CB_{11}H_{12}$] (1.14 g, 68% yield) was obtained by dissolving in 20 mL water and drying it first in a rotary evaporator and then under dynamic vacuum at 100 °C for 2 h. ¹¹B NMR (128 MHz, DMSO- d_6) δ –6.95 (d, J = 140.0 Hz, 1B), –13.27 (d, J = 136.3 Hz, 5B), -16.15 (d, J = 150.6 Hz, 5B). ¹¹B{¹H} NMR (128 MHz, DMSO- d_6) δ -7.01 (1B), -13.27 (5B), -16.16 (5B). ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.36 (s, 1H), 2.24–0.70 (m, 11H). ¹H{¹¹B} NMR (400 MHz, DMSO- d_6) δ 2.36 (s, 1H), 1.55 (s, 6H), 1.40 (s, 5H). ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 50.65 (s).

2.3. Synthesis of $K[CB_{11}H_{12}]$

 $K[B_{11}H_{14}]$ (1.74 g, 10 mmol) and KH (1.20 g, 30 mmol) were added to a 100 mL Schlenk flask. The flask was connected with a Schlenk line and 40 mL of tetrahydrofuran was injected. The reaction mixture was stirred under 0 °C for 15 min and then (trifluoromethyl)trimethylsilane (4 mL, 30 mmol) was added. The Schlenk flask was equipped with a reflux condenser. The mixture was stirred at 60 $^{\circ}$ C for 3 days and a large amount of yellow precipitate was generated. After cooling down to room temperature and quenched with water (1 mL), the residue was subjected to extractive workup with ether (4 \times 60 mL) and H_2O (4 \times 60 mL). The organic phases were combined, and the solvent was removed under reduced pressure to give a yellow oily product. Then, 1,4-dioxane was added into the filtrate until a large amount of white solid precipitate. The precipitate was filtered and then dried under dynamic vacuum to produce 1,4-dioxane solvated $K[CB_{11}H_{12}]$ white powder. The precipitate was washed with dichloromethane (3 \times 30 mL) and hexane (3 \times 30 mL), and then dried under dynamic vacuum to produce an unsolvated $K[CB_{11}H_{12}]$, white powder (1.21 g, 66% yield). ¹¹B NMR (128 MHz, DMSO-*d*₆) δ –6.95 (d, *J* = 140.0 Hz, 1B), –13.27 (d, J = 136.3 Hz, 5B), -16.15 (d, J = 150.6 Hz, 5B). ¹¹B{¹H} NMR (128 MHz, DMSO- d_6) δ -7.01 (s), -13.27 (s), -16.16 (s). ¹H NMR (400 MHz, DMSO- d_6) δ 2.36 (s, 1H), 2.24–0.70 (m,

11H). ¹H{¹¹B} NMR (400 MHz, DMSO-*d*₆) δ 2.36 (s, 1H), 1.55 (s, 6H), 1.40 (s, 5H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 50.69 (s) (in Supplementary Materials).

3. Results and Discussion

The $[CB_{11}H_{12}]^-$ anion was discovered by Knoth using toxic decaborane $B_{10}H_{14}$ as starting material in 1967 [2]. Since $B_{10}H_{14}$ was synthesized from NaBH₄ via the $[B_{11}H_{14}]^{-1}$ ion, to obviate the toxicity and tedious synthetic steps, the group of Michl [19] developed an alternative approach, using $[B_{11}H_{14}]^-$ as a starting material and dichlorocarbene as the carbon source, but in a poor yield. On the basis of this innovative method, Kütt's group reported an improved method to obtain $[Me_3NH][CB_{11}H_{12}]$ from boron cluster $[B_{11}H_{14}]^-$ in up to 95% yield using difluorocarbene as the carbon source [21]. In 2021, the research group of Mark Paskevicius reported a cost-effective method to synthesize the $[CB_{11}H_{12}]^-$ anion in 40% yield from $[B_{11}H_{14}]^-$ using common laboratory reagents [22]. Generally speaking, the synthetic procedure of $[CB_{11}H_{12}]^-$ from $[B_{11}H_{14}]^-$ includes four steps represented by Equations (1)–(4), as reported in the literature, in which the cation exchange reactions are carried out (Equations (1) and (4)) considering the solubility of different salts. It is known that $Na_2[B_{11}H_{13}]$ can be formed by the deprotonation of $[Me_3NH][B_{11}H_{14}]$ with NaOH or NaH. The formed Me₃N must be removed because the presence of NMe₃ has previously been found to cause the formation of an excessive amount of $2-Me_3NCB_{11}H_{11}$ byproduct (Equation (2)) [19]. The Na₂[$B_{11}H_{13}$] can then be used to synthesize the [CB₁₁H₁₂]⁻ anion, by insertion of $:CCl_2$ or $:CF_2$ sourced from $CHCl_3$ or CF_3SiMe_3 (Equation (3)). However, because of the limitation in the availability of suitable purification, the ion exchange through the metathesis reaction of Na[CB₁₁H₁₂] with Me₃N·HCl is carried out at room temperature in the aqueous medium (Equation (4)).

$$Na[B_{11}H_{14}] (aq) + Me_3N \cdot HCl (s) \rightarrow [Me_3NH][B_{11}H_{14}] (s) + NaCl (s)$$
(1)

$$[Me_{3}NH][B_{11}H_{14}](s) + NaH(s) \text{ or } NaOH(s) \rightarrow Na_{2}[B_{11}H_{13}](aq) + H_{2} \text{ or } H_{2}O + NMe_{3}$$
(2)

$$Na_{2}[B_{11}H_{13}] (aq) + NaH (s) \text{ or } NaOH (s) + :CX_{2} \rightarrow Na[CB_{11}H_{12}] (aq)$$
(3)

$$Na[CB_{11}H_{12}] (aq) + Me_3N \cdot HCl (s) \rightarrow [Me_3NH][CB_{11}H_{12}] (s) + NaCl (s)$$
(4)

Considering the great importance of the alkali metal salts of the $[CB_{11}H_{12}]^-$ anion in the fields of catalysis and all-solid-state batteries, we developed a simple, quick, and one-step procedure to directly synthesize unsolvated $M[CB_{11}H_{12}]$ using $M[B_{11}H_{14}]$ (M = K, Na) as starting materials. The overall yields of $M[CB_{11}H_{12}]$ were up to 66–68%. $M[B_{11}H_{14}]$ is commercially available and we first screened different bases with $K[B_{11}H_{14}]$ as substrate. The results showed that KH was the best choice. Then, we examined different molar ratios of $K[B_{11}H_{14}]$ to KH (Table 1). It was found that the optimized ratio of $K[B_{11}H_{14}]$ to KH to CF_3SiMe_3 was 1:3:3 in the overall preparation of $K[CB_{11}H_{12}]$.

On the other hand, we attempted to synthesize $Na[CB_{11}H_{12}]$ under similar conditions but failed. By using the same molar ratio of $Na[B_{11}H_{14}]:NaH:CF_3SiMe_3 = 1:3:3$, no reaction was observed and the starting material was monitored by ¹¹B NMR spectroscopy. The reaction could not be observed even if we increased the amount of NaH up to six times. These results indicated that NaH could not abstract hydrogen from $Na[B_{11}H_{14}]$ to form the $Na_2[B_{11}H_{13}]$ intermediate in this reaction. The observation further revealed that the reaction of Na[B₁₁H₁₄] with NaH was different from that of [Me₃NH][B₁₁H₁₄] with NaH in which the deprotonation occurred. Thus, it was concluded that the counter cation influenced the reactions of the salts of the $[B_{11}H_{14}]^-$ anion. Then, we examined the reactivity of NaHMDS in this reaction in consideration with its strong basicity and good solubility in organic solvent. However, when three equivalent NaHMDS were used instead of NaH in the reaction, the decomposition of the boron cage was observed but no product was obtained. If only one equivalent NaHMDS was used in the reaction, Na₂[B₁₁H₁₃] was monitored by ¹¹B NMR. Based on these results, we speculated that NaHMDS could abstract hydrogen from Na $[B_{11}H_{14}]$ to form $Na_2[B_{11}H_{13}]$, but NaHMDS would continually react with the formed $Na_2[B_{11}H_{13}]$, resulting in a decomposition to unidentified small boron cages. In considering that NaH can react with CF₃SiMe₃ to provide carbene: CF₂, thus, we selected the combination of NaHMDS and NaH, and screened the different molar ratios of $Na[B_{11}H_{14}]$ to NaHMDS to NaH (Table 2). After a series of screenings, the 1:1:3:3 molar ratio of $Na[B_{11}H_{14}]$ to NaHMDS to NaH to CF_3SiMe_3 was used in the overall preparation of $Na[CB_{11}H_{12}]$. Furthermore, it is worth noting that when we examined DME as a solvent, the yields were relatively higher than those in THF, probably because the slight polarity

of DME. Therefore, the reactions of sodium salts were carried out in DME, differentiating from the reaction of potassium salts.

2⊖ ⊖ K⊕ Θ 2 K⊕ ĸ⊕ KH CF₃SiMe₃ 0 °C 60 °C Entry K[B₁₁H₁₄]:KH t/d Yield (%) 1 3 1:1 no product 2 3 1:2 58 3 3 1:3 66 4 3 1:4 65 5 3 1:5 64 6 3 1:6 66

Table 1. Screening of the molar ratio of K[B₁₁H₁₄] to KH^{*a*}.

^a reaction conditions: K[B₁₁H₁₄] (1 mmol), KH (1–6 mmol), CF₃SiMe₃ (3 mmol) in THF.

Table 2. Screening of the molar ratio of $Na[B_{11}H_{14}]$	to base ^{<i>a</i>} .
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^a reaction conditions: Na[B₁₁H₁₄] (1 mmol), NaHMDS (1–3 mmol), NaH (0–6 mmol), CF₃SiMe₃ (3 mmol) in DME.
 ^b NaB₁₁H₁₄ degrade. ^c Na₂B₁₁H₁₃ was formed.

In summary, the highly pure potassium and sodium salts of the $[CB_{11}H_{12}]^-$ anion can be directly synthesized with $M[B_{11}H_{14}]$ as starting materials (M = K, Na) (Figure 1) without converting the alkali cation into amine by a cation exchange reaction. The ¹¹B and ¹¹B{¹H} NMR spectra of the reaction mixture indicated that the reaction highly selectively converted to the $[CB_{11}H_{12}]^-$ anion as shown in Figure 1a,b,e,f. These results make the purification of the crude product simple and efficient.



Figure 1. ¹¹B{¹H} and ¹¹B NMR spectra: (a) crude reaction mixture of K[CB₁₁H₁₂] after 3 days of heating at 60 °C (¹¹B{¹H} NMR); (b) crude reaction mixture of K[CB₁₁H₁₂] after 3 days of heating at 60 °C (¹¹B NMR); (c) purified K[CB₁₁H₁₂] in DMSO-*d*₆ (¹¹B{¹H} NMR); (d) purified K[CB₁₁H₁₂] in DMSO-*d*₆ (¹¹B{¹H} NMR); (d) purified K[CB₁₁H₁₂] in DMSO-*d*₆ (¹¹B{¹H} NMR); (f) crude reaction mixture of Na[CB₁₁H₁₂] after 3 days of heating at 60 °C (¹¹B{¹H} NMR); (f) crude reaction mixture of Na[CB₁₁H₁₂] after 3 days of heating at 60 °C (¹¹B{¹H} NMR); (g) purified Na[CB₁₁H₁₂] in DMSO-*d*₆ (¹¹B{¹H} NMR); (h) purified Na[CB₁₁H₁₂] in DMSO-*d*₆ (¹¹B NMR).

4. Conclusions

We developed a simple and effective method to directly synthesize the unsolvated potassium and sodium salts of the $[CB_{11}H_{12}]^-$ anion in one step with 66–68% yields. Differentiating from the previous synthesis of $[CB_{11}H_{12}]^-$ anion, this method avoided the exchange of cation and significantly simplified the reaction procedure, thus enabling a convenient large-scale synthesis. It paves the way for the application of $K[CB_{11}H_{12}]$ and $Na[CB_{11}H_{12}]$ in many fields such as in solid ionic conductors.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12101339/s1, ¹H, ¹H{¹¹B}, ¹¹B, ¹¹B{¹H}, ¹³C{¹H} NMR spectra copy of Na[CB₁₁H₁₂] and K[CB₁₁H₁₂], ¹¹B-¹¹B NMR spectra copy of K[CB₁₁H₁₂].

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