

# Synthesis of *closo*-CB<sub>11</sub>H<sub>12</sub><sup>-</sup> salts using common laboratory reagents

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## ABSTRACT

Lithium and sodium salts of the *closo*-carbadodecaborate anion (CB<sub>11</sub>H<sub>12</sub><sup>-</sup>) have been shown to form stable solid-state electrolytes with excellent ionic conductivity for all solid-state batteries (ASSB). However, potential commercial application is currently hindered by the difficult, low yielding and expensive synthetic pathways. We report a novel and cost effective method to synthesise the CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anion in a 40 % yield, using common laboratory reagents. The method avoids the use of expensive and dangerous reagents such as NaH, decaborane and CF<sub>3</sub>SiMe<sub>3</sub>, and shows excellent reproducibility in product yield and purity.

## INTRODUCTION

All solid-state batteries (ASSB) have the potential to surpass current liquid-electrolyte based batteries in energy density, safety and production costs. Unlike liquid electrolytes, that use air-sensitive solvents such as ethylene carbonate, solid electrolytes offer a solvent-free approach, that also offers increased energy density.<sup>1,2</sup> Lithium and sodium salts,  $\text{LiCB}_{11}\text{H}_{12}$  and  $\text{NaCB}_{11}\text{H}_{12}$ , have previously been shown to have a polymorphic crystalline phase transition to high temperature structures with enhanced ionic conductivity at  $\approx 127\text{ }^\circ\text{C}$  and  $107\text{ }^\circ\text{C}$ , respectively.<sup>3</sup> This phase change occurs at lower temperatures than analogous lithium and sodium borohydride salts,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , at  $> 320\text{ }^\circ\text{C}$  and  $256\text{ }^\circ\text{C}$ , respectively.<sup>3</sup> The *closo*-carbadodecaborate anion,  $\text{CB}_{11}\text{H}_{12}^-$ , is structurally large, allowing for ample interstitial sites in the crystal lattice for cation movement.<sup>4</sup> The anion is also thermally and chemically stable, owing to its delocalised, almost aromatic electronic structure as well as being weakly coordinating, making them ideal counter-anions for Na and Li solid electrolytes.<sup>5,6</sup> These properties have increased interest in the use of  $\text{LiCB}_{11}\text{H}_{12}$  and  $\text{NaCB}_{11}\text{H}_{12}$  as potential electrolytes for ASSB.

The practical use of the  $\text{CB}_{11}\text{H}_{12}^-$  anion for solid-state electrolytes has been limited due to the complicated, lengthy and expensive synthetic processes involved to synthesise the initial  $\text{CB}_{11}\text{H}_{12}^-$  anion in significant quantities. Early reaction pathways relied on the use of the decaborane ( $\text{B}_{10}\text{H}_{14}$ ) molecule as a starting material. Decaborane is a known precursor for dicarboranes via reaction with acetylene gas.<sup>7</sup> However, it is a toxic, flammable and expensive chemical. In early approaches decaborane was reacted with sodium cyanide (Scheme 1a), followed by a lengthy, stepwise synthesis that included deamination using sodium in liquid ammonia, prior to closing the cage via thermolysis, yielding a mix of *closo*- $\text{CB}_{11}\text{H}_{12}^-$  and *closo*- $\text{CB}_9\text{H}_{10}^-$ .<sup>8</sup> Variations to this method, led to closing the cage with  $\text{H}_3\text{B}\cdot\text{NET}_3$ , before deamination to form the final product.<sup>9,10</sup> The safety of

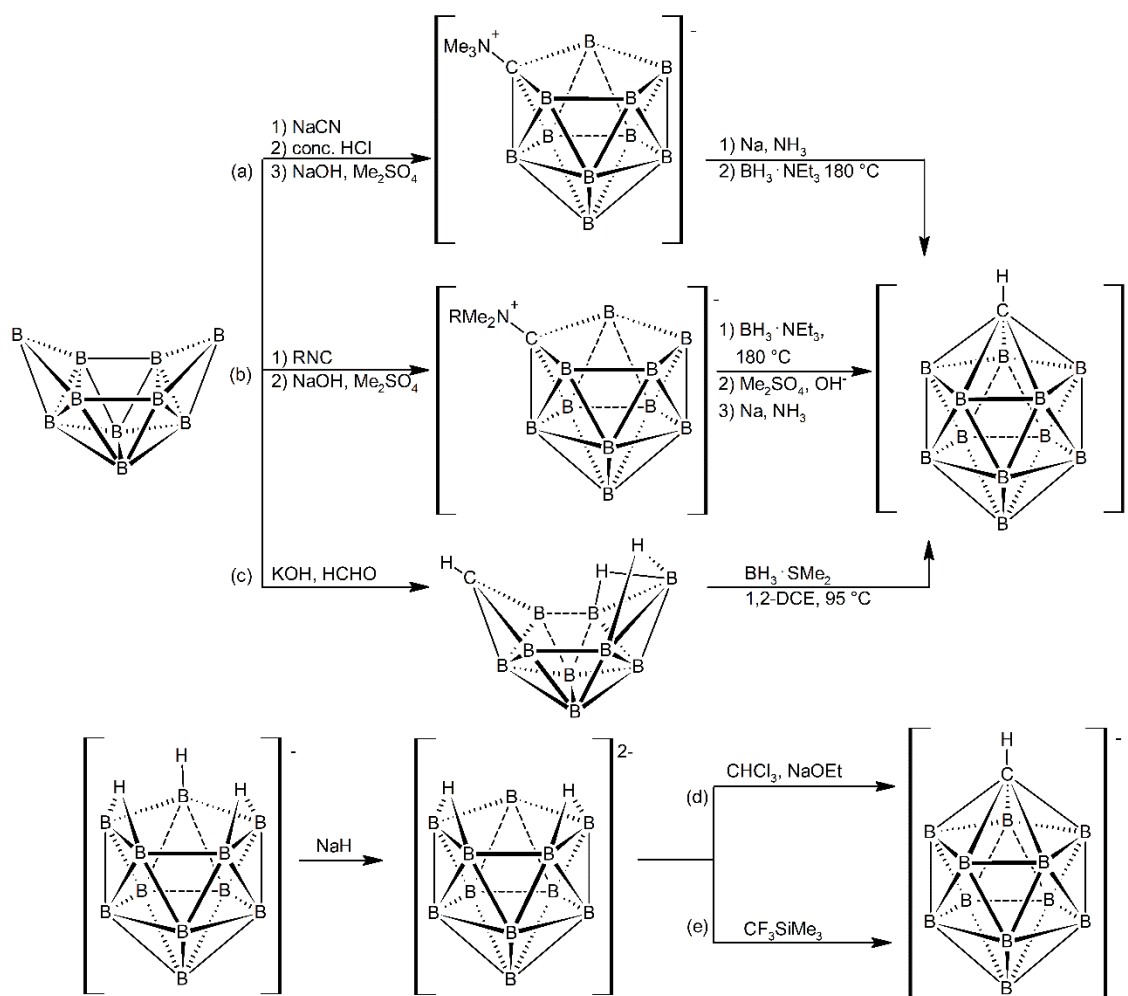
this synthesis route was improved by replacing NaCN, which in the above reaction formed HCN as a by-product, with tertbutyl-isocyanide (tBuNC) or cyclohexyl-isocyanide (CyNC) to form the initial C-B bond (Scheme 1b).<sup>11,12</sup> Alkyl isocyanides improved the overall safety of the synthesis, but the overall cost was higher and deamination with Na/NH<sub>3</sub> was required.<sup>11</sup> Using *para*-formaldehyde to form the initial B-C bond to decaborane proved to simplify the synthetic route, as many of the steps involving cleaving the C-N bond were not needed (Scheme 1c). However, the closing of the cage required excess H<sub>3</sub>B·SMe<sub>2</sub> and three days of heating before the reaction was complete.<sup>13</sup>

Rather than using a decaborane precursor, the synthesis of the CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anion has also been successfully achieved using *nido*-B<sub>11</sub>H<sub>14</sub><sup>-</sup>, which is accessible through the single-step reaction of NaBH<sub>4</sub> with BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> or C<sub>5</sub>H<sub>11</sub>Br in diglyme.<sup>14</sup> Deprotonation of *nido*-B<sub>11</sub>H<sub>14</sub><sup>-</sup> to *nido*-B<sub>11</sub>H<sub>13</sub><sup>2-</sup> with NaH in THF followed by the insertion of dichlorocarbene from chloroform (CHCl<sub>3</sub>) was found to synthesise CB<sub>11</sub>H<sub>12</sub><sup>-</sup> (Scheme 1d).<sup>15</sup> However, this method must be undertaken under inert gas, has a low overall yield (~ 20 – 25 %), is difficult to scale up and produces side products such as the 2-EtO-CB<sub>11</sub>H<sub>12</sub><sup>-</sup> and 2-Cl-CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anions.<sup>15,16</sup> Two similar methods using difluorocarbene (CF<sub>2</sub>) to insert into B<sub>11</sub>H<sub>13</sub><sup>2-</sup> were published in 2019 (Scheme 1e).<sup>16,17</sup> These both use trimethyl(trifluoromethyl)silane (CF<sub>3</sub>SiMe<sub>3</sub>) or Ruppert's reagent as a source of difluorocarbene to be inserted in a one-pot synthesis (Scheme 1e).<sup>16,17</sup> Similar to other syntheses using Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>], NaH is used to deprotonate B<sub>11</sub>H<sub>14</sub><sup>-</sup> to B<sub>11</sub>H<sub>13</sub><sup>2-</sup>, before reacting with CF<sub>3</sub>SiMe<sub>3</sub> in an Ace pressure tube to ensure the volatile reagent's evaporation, at 60 °C for 3 days.

<sup>17</sup> An overall yield of 95 % could be achieved, with the reaction successfully scaled from 1.5 g Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] to 15 g of starting material. The second method used dried LiCl to form CF<sub>2</sub> from CF<sub>3</sub>SiMe<sub>3</sub> under reflux conditions for 16 hours to achieve a 78 % yield of product, therefore,

decreasing the time needed for reaction. While both methods had high yields, they are limited by the fact that  $\text{CF}_3\text{SiMe}_3$  is a specialised and expensive reagent. All of the above methods also use  $\text{NaH}$  as a base, which is highly flammable and expensive.

Because of the need for expensive and dangerous reagents, as well as low yields and long stepwise procedures, it has become imperative that a new cost effective and simple synthesis be developed to allow further investigation of the  $\text{CB}_{11}\text{H}_{12}^-$  anion for solid-state electrolyte research.



**Scheme 1.** Synthesis methods of 1-carbadodecaborate starting with a-c) decaborane ( $\text{B}_{10}\text{H}_{14}$ ) and trimethylammonium nido-undecaborate ( $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$ ). Reactions starting with decaborane

form initial B-C bond with reagents such as, a) sodium cyanide,<sup>8,9</sup> b) alkyl isocyanide (RNC),<sup>11</sup> or, c) formaldehyde.<sup>13</sup> Whereas, after deprotonation of the  $B_{11}H_{14}^-$  to  $B_{11}H_{13}^{2-}$  by NaH, and elimination of the trimethylamine cation, dihalocarbene, ( $CX_2$ ), is formed in situ and inserts into the cage.  $CX_2$  is sourced by the d), treatment of  $CHCl_3$  with a base to form  $CCl_2$  or, e) formation of  $CF_2$  from  $CF_3SiMe_3$  with either a pressure tube<sup>17</sup> or using LiCl/TBAB as an initiator.<sup>16</sup> (RNCs most commonly used are *tert*butyl isocyanide or cyclohexylisocyanide<sup>11</sup>) TBAB = tetrabutylammonium bromide.

## EXPERIMENTAL METHODS

### Synthesis

All solvents were anhydrous and used as purchased from Merck. All metal carbonates and bicarbonates were purchased from Merck (> 99 % purity), with the exception of  $CoCO_3$  which was purchased from Walker Ceramics. Anhydrous potassium carbonate,  $K_2CO_3$  (anhydrous,  $\geq 99$  %), sodium hydroxide (NaOH,  $\geq 98$  %), potassium hydroxide (KOH,  $\geq 85$  %), aluminium oxide nano-particles ( $Al_2O_3$ , 10 nm, 99.8 %) and 4 Å molecular sieves (8 - 12 mesh) were also purchased from Merck. Molecular sieves were activated in a 300 °C furnace for 3 hours before use.  $Me_3NH[B_{11}H_{14}]$  was synthesised in a previously described method from sodium borohydride,  $NaBH_4$ .<sup>14</sup> Briefly, 50 g of  $NaBH_4$  was added to a 1000 mL 3-necked flask under Ar. Diglyme (400 mL) was added to the reaction vessel and the mixture was heated to 105 °C. Once this temperature was reached, 1-bromopentane (150 mL) was added dropwise, ensuring the reaction never exceeded 120 °C. The reaction was further stirred for 6 hours at 105 °C and allowed to cool to room temperature where solid NaBr was removed by filtration. The yellow filtrate was then dried under

vacuum to form an oily yellow residue, which was dissolved in hot deionised water. Addition of  $\text{Me}_3\text{N.HCl}$  (20 g) precipitated  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  that was cooled, filtered and washed with excess cold deionised water to give an off-white product (10 – 12 g, approx., 48 % yield).

**General method for synthesis:  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$**

$\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  (10.0 g, 0.0518 mol) in a 500 mL round bottom flask was dissolved in a 80 mL aqueous solution of NaOH (0.311 mol, 6 equiv.) and stirred for 30 minutes at 80 °C. The solution was then dried to a white powder under reduced pressure at 80 °C. This was then placed under an argon atmosphere and 150 mL of dimethoxyethane (DME) was added. Powdered NaOH (0.156 mol, 3 equiv.) and  $\text{K}_2\text{CO}_3$  (0.208 mol, 4 equiv.) was added and the mixture was cooled to 0 °C in an ice bath, and stirred for 15 minutes.  $\text{CHCl}_3$  (0.155 mol, 3 equiv.) was added to the reaction dropwise and with stirring, the mixture was allowed to warm to room temperature over 2 hours. After 2 hours the reaction was left at 20 - 25 °C to stir for a further 3 hours. The solvent was then removed under reduced pressure and 50 - 70 mL of deionised water was added to dissolve the white powder. The solution was acidified with 3 M HCl and filtered to remove any solid material. Excess  $\text{Me}_3\text{N.HCl}$  (10 g, 0.1 mol) was added and the precipitate was filtered and washed with deionised water. The white powder was left overnight in air to dry before being weighed and characterised with  $^{11}\text{B}$  NMR.  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  final yield of 4.2 g (40 %).  $^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 3.04 (s, 9H,  $\text{HNCH}_3$ ), 2.11 (s, 1H,  $\text{BCH}$ ), 1.98 – 0.73 (bm, 11H,  $\text{BH}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : -6.7 (1B), 13.1 (5B), 16.2 (5B).

Separation of mixed samples of  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  and  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  were done by dissolving the sample in excess NaOH and stirring for 1 hour at 80 °C. When the solution was cooled, the solution was extracted using  $\text{Et}_2\text{O}$ , and the ether layer dried under vacuum. When dry, the residue

was dissolved in deionised water and treated with excess  $\text{Me}_3\text{N}\cdot\text{HCl}$  to precipitate  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$ . The aqueous layer was treated with  $\text{HCl}$  to neutralise any remaining  $\text{NaOH}$  and  $\text{Me}_3\text{N}\cdot\text{HCl}$  was added to precipitate  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$ .

## Characterisation

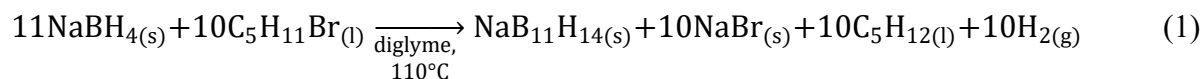
Nuclear Magnetic Resonance (NMR) spectra ( $^1\text{H}$ ,  $^{11}\text{B}$  decoupled and  $^{11}\text{B}$  coupled) were collected on a Bruker Avance III 400 MHz NanoBay spectrometer at room temperature. The  $^{11}\text{B}$  NMR spectra were referenced to a boron trifluoride etherate ( $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ) external standard, and the  $^1\text{H}$  spectra were referenced to a tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$ ) external standard. Powdered samples were dissolved in 600  $\mu\text{L}$  of deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) prior to analysis.

Powder X-ray diffraction (pXRD) patterns were collected using a Bruker D8 Advance using a  $\text{CuK}\alpha$  radiation source. Data was collected between  $5 - 80^\circ 2\theta$  at  $0.02^\circ$  steps over 1 hour.

## RESULTS AND DISCUSSION

The *nido*- $\text{B}_{11}\text{H}_{14}^-$  precursor can be easily synthesised as a  $\text{Me}_3\text{NH}^+$  salt,  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$ , in a 48 % yield from the reaction of sodium borohydride,  $\text{NaBH}_4$ , and 1-bromopentane,  $\text{C}_5\text{H}_{11}\text{Br}$  in diglyme (Equation 1) and precipitation with trimethylamine hydrochloride ( $\text{Me}_3\text{N}\cdot\text{HCl}$ ) (Equation 2). The precursor can then be used to synthesise the  $\text{CB}_{11}\text{H}_{12}^-$  anion, by insertion of  $\text{CCl}_2$  sourced from chloroform, as previously documented by Franken *et al.*<sup>15</sup> This method was believed to be the safer option than the alternatives which use toxic reagents to form the initial carbon insertion into decaborane ( $\text{B}_{10}\text{H}_{14}$ )<sup>8,11,13,18</sup> or use expensive niche compounds such as  $\text{CF}_3\text{SiMe}_3$ .<sup>16,17</sup> Initially, the Franken method<sup>15</sup> (Scheme 1d) was attempted where  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  was deprotonated to  $\text{B}_{11}\text{H}_{13}^{2-}$  by  $\text{NaH}$ , before carbene insertion.  $\text{NaOEt}$  formed *in situ*, by deprotonation

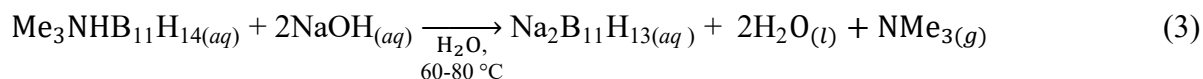
of ethanol by NaH, was then used to deprotonate CHCl<sub>3</sub>, forming CCl<sub>2</sub>. Ethanol was necessary as NaH was too insoluble in THF to effectively deprotonate CHCl<sub>3</sub>. Due to the instability of NaH in air and water, the reaction required the use of a Schlenk line set up to ensure a dry and inert environment. The original procedure reported a 42 % yield,<sup>15</sup> but yields were later reported to be closer to 20-25 %, <sup>16</sup> with other studies indicating yields as low as 9 %.<sup>19</sup> Our own attempts found that the latter reports were correct as the reaction proved to be difficult and poorly scalable with yields of 12 % and 15 % when starting with 1 g and 5 g of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>], respectively. In order to avoid the aforementioned issues, the substitution of NaH and EtONa for a different base would prove to be advantageous.



The insertion of CCl<sub>2</sub> into *nido*-B<sub>11</sub>H<sub>13</sub><sup>2-</sup> has previously been attempted with CHCl<sub>3</sub> using other bases, such as *n*-BuLi, MeONa, EtONa, and <sup>t</sup>BuONa, but were low yielding.<sup>20</sup> NaOH had also been used, however, this yield was also low and produced a mixture of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] and Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>]. The difficulty with using NaOH as a base in this reaction was that as NaOH deprotonates CHCl<sub>3</sub>, H<sub>2</sub>O is formed, which without immediate removal via phase-transfer, would interfere with the reaction between CCl<sub>2</sub> and *nido*-B<sub>11</sub>H<sub>13</sub><sup>2-</sup> that can only occur fully under anhydrous conditions. When only NaOH as a base in dimethoxyethane (DME) was attempted, this hypothesis was proven to be correct, with only a 5 % yield of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] isolated after extraction with Et<sub>2</sub>O (Figure 1, Trial 1) and a significant amount of unreacted starting material (Figure S1). Hence, NaOH did act as a base in the reaction, but presented problems with yield. It is known that Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] can be formed by the deprotonation of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] in aqueous



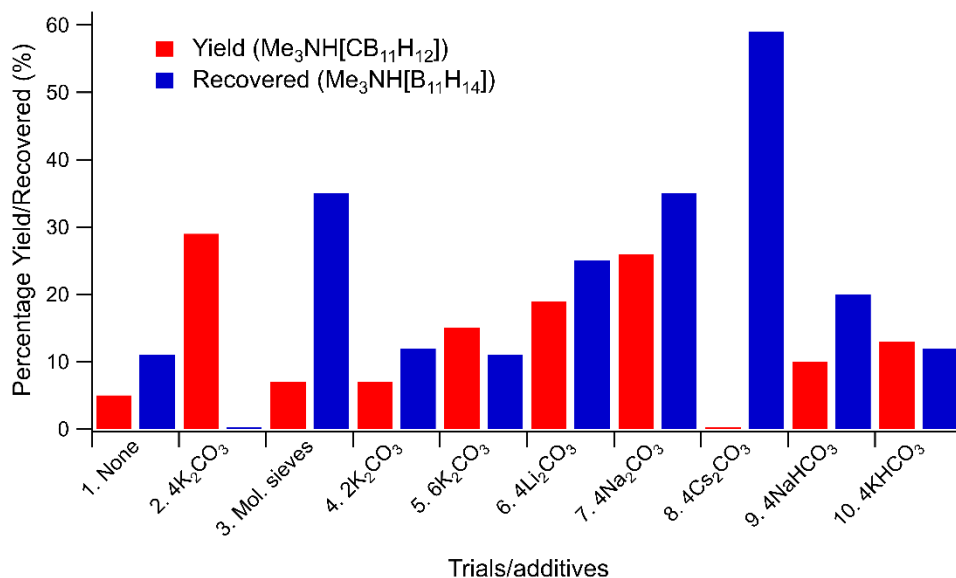
NaOH (Equation 3).<sup>21</sup> Nevertheless, attempts to do this step in polar aprotic solvents, such as DME, found that while Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] did form, however this included many other by-products including BH<sub>4</sub><sup>-</sup>, B<sub>3</sub>H<sub>8</sub><sup>-</sup>, and OB<sub>11</sub>H<sub>12</sub><sup>-</sup> (Figure S2). This did not occur to the same extent when the same reaction was attempted in aqueous NaOH, with only a small amount of BH<sub>4</sub><sup>-</sup> and B(OH)<sub>4</sub><sup>-</sup> detected in <sup>11</sup>B NMR (Figure S2). To avoid NaOH solvation issues, Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] was converted to Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] in excess aqueous NaOH at 80 °C, followed by drying under reduced pressure until no water was present in the reaction vessel. By fully drying the reaction mixture it also ensures that all Me<sub>3</sub>N is removed. This is important as the presence of Me<sub>3</sub>N has previously been found to form the by-product, 2-Me<sub>3</sub>NCB<sub>11</sub>H<sub>12</sub>.<sup>15</sup>



Due to water inhibiting the insertion of CCl<sub>2</sub> into the B<sub>11</sub>H<sub>13</sub><sup>2-</sup> cage, it became necessary to find a drying agent that would be effective in non-aqueous basic media. Many common drying agents, such as magnesium sulfate (MgSO<sub>4</sub>), or calcium chloride (CaCl<sub>2</sub>), are lewis acids and would not be appropriate for this reaction. Potassium carbonate, K<sub>2</sub>CO<sub>3</sub>, is a mildly basic alternative that is moderately dehydrating, and can act as a proton/acid scavenger. As such, the use of K<sub>2</sub>CO<sub>3</sub> in alkylation, arylation and acylation reactions is well known.<sup>22</sup> Mixed NaOH and K<sub>2</sub>CO<sub>3</sub> systems have also been shown to work in other heterogeneous reactions, for example, the N-alkylation of diphenylphosphinic hydrazide.<sup>23</sup> As such, it is postulated that the addition of K<sub>2</sub>CO<sub>3</sub> would limit the amount of free water in the reaction, preventing ‘aggregation’ of NaOH as well as acting as a mild base.<sup>23</sup> In fact, the addition of 9 molar equivalents of NaOH and 4 molar equivalents of K<sub>2</sub>CO<sub>3</sub> result in all B<sub>11</sub>H<sub>13</sub><sup>2-</sup> being reacted after 5 hours by <sup>11</sup>B NMR (Figure S3) resulting in a 29 % yield of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] (Figure 1, Trial 2). Alternatively, 4 Å molecular sieves were used in the place

of  $K_2CO_3$  to determine the effect of a generic drying agent. Interestingly, molecular sieves do not have the same impact as  $K_2CO_3$ , with 35 % of  $Me_3NH[B_{11}H_{14}]$  being recovered at the end of the reaction (Figure 1, Trial 3, Figure S3). This indicates that  $K_2CO_3$  could have had a synergetic effect on the reaction, conceivably as an acid scavenger (Equation 5). Nevertheless,  $K_2CO_3$  enhances the reaction, increasing yield, and ensures no  $B_{11}H_{13}^{2-}$  remains in the reaction. Variation of the molar equivalents of  $K_2CO_3$  from 4 to 2 and 6 molar equivalents did not improve the yield of  $Me_3NH[CB_{11}H_{12}]$ , and in fact, decreased the yield significantly in both reactions (Figure 1, Trial 4 and 5, Figure S3). Decreasing the amount of  $K_2CO_3$  may have decreased its ability to mop up the side products created in the reaction (Equations 4 and 5), thus, it can be concluded that  $K_2CO_3$  is involved in the reaction as a reagent and does not act as a catalyst. However, as an increase in the molar equivalents of  $K_2CO_3$  also showed a decrease in yield, it could be concluded that this excessive amount of solid hindered mixing of the reaction. This outcome supports later results which show decreased yield of  $Me_3NH[CB_{11}H_{12}]$  when the solvent volume is decreased significantly (Figure 4).





**Figure 1.** Effect of metal carbonates and bicarbonates on the synthesis of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>]. Reactions run with 250 mg of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] in 5 mL DME and 9 molar equivalents of NaOH. Yield determined by <sup>11</sup>B NMR.

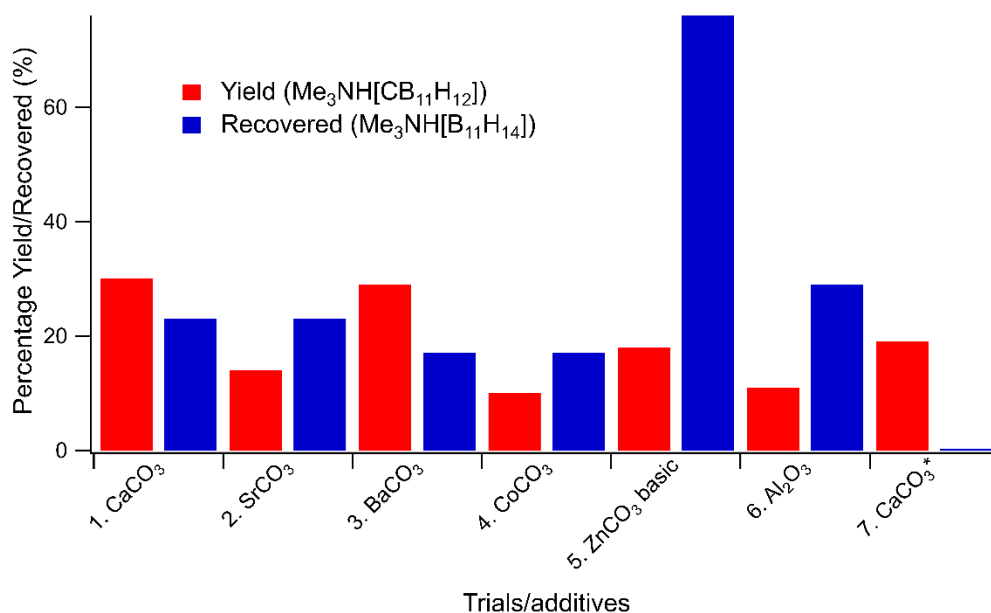
### Impact of different additives

Various metal carbonates, bicarbonates and oxides were analysed to compare their impact on the reaction progress to K<sub>2</sub>CO<sub>3</sub> (Figure 1). Interestingly, many of the metal carbonates achieved reasonable yields of the CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anion, after 5 hours, in DME. Lighter group 1 metal carbonates, Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> had lower yields of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] than for K<sub>2</sub>CO<sub>3</sub>, with yields of 19 % and 26 % each, respectively, compared with 29 %. This indicated a trend within these early group 1 metal carbonates, Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> with an increase in yield as the carbonate cation size increased (Figure 1, Trials 6, 7 and 2, Figure S4). However, the largest of the group 1 metal carbonates tested, Cs<sub>2</sub>CO<sub>3</sub>, resulted in no Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] production with only 59 % of the

starting  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  recovered, indicating some cage decomposition. Analysis of  $^{11}\text{B}$  NMR of the filtrate after acidic work up and precipitation of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  identified the presence of  $\text{B}(\text{OH})_3$  as a significant by-product of the reaction as well as the presence of  $\text{CH}_3\text{B}(\text{OH})_2$  in smaller quantities (Figure S5). A possible explanation is that  $\text{Cs}_2\text{CO}_3$  is reasonably soluble in many organic solvents, including DME whilst the other group 1 metal carbonates are not particularly soluble, thus, it can be concluded that it is important for the additive to remain a solid in the reaction system. This also indicates that the reaction may occur on the surface of the carbonate, and therefore surface area might be important. Group 1 metal bicarbonates,  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  were also tested (Figure 1, Trials 9 and 10, Figure S4), but had significantly lower yields than any of the group 1 metal carbonates, achieving yields of 10 % and 13 %, respectively. This was slightly higher than the reaction without any  $\text{K}_2\text{CO}_3$  (5 %), however, both bicarbonate reactions also had high quantities of  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  recovered. It could be concluded that because bicarbonate is a theoretical by-product of the reaction of  $\text{K}_2\text{CO}_3$  and water/ $\text{H}^+$  formed during the insertion of  $\text{CCl}_2$  into the cage that this limits the amount of product that could be yielded. This theory has proven difficult to demonstrate as pXRD analysis of the solid filtered from the reaction mixture (after 5 hours reaction) revealed that the major solid formed during the reaction was  $\text{KCl}$ , with a small amount of  $\text{Na}_2\text{B}(\text{OH})_4\text{Cl}$  (Figure S6). Thus, the reaction is somewhat driven by this salt formation, potentially due to the better solvation of  $\text{Na}^+$  in DME, due to a more negative binding enthalpy.<sup>24</sup>

Other metal carbonates were also tested included the group 2 metal carbonates,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  and transition metal carbonates,  $\text{CoCO}_3$  and  $\text{ZnCO}_3$  (basic) (Figure 2). Some of these additives had reasonable yields of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  in comparison to the attempts with  $\text{K}_2\text{CO}_3$ . However, in all reactions, significant quantities of  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  were also attained (Figure S7). Rationale for these differences could be due to variations in the reactive surface area between the

metal carbonates analysed. However, the addition of nano-sized  $\text{Al}_2\text{O}_3$  (10 nm) showed little improvement when compared to tests with no  $\text{K}_2\text{CO}_3$  added. Due to the higher yield of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  when  $\text{K}_2\text{CO}_3$  was substituted with  $\text{CaCO}_3$ , further analysis was performed to judge if this would be a suitable additive with a longer reaction time as the reaction showed  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  after 5 hours (Figure 2, Trial 1). However, it was noted, that there was a lower yield of product,  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$  (Figure 2, Trial 7), than in previous tests. There was also no  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  detected in the  $^{11}\text{B}$  NMR (Figure S8) at the end of the reaction. Thus, it can be concluded that excess NaOH causes the decomposition of both unreacted starting material as well as some of the product, forming  $\text{B}(\text{OH})_3$  when left for extended times.

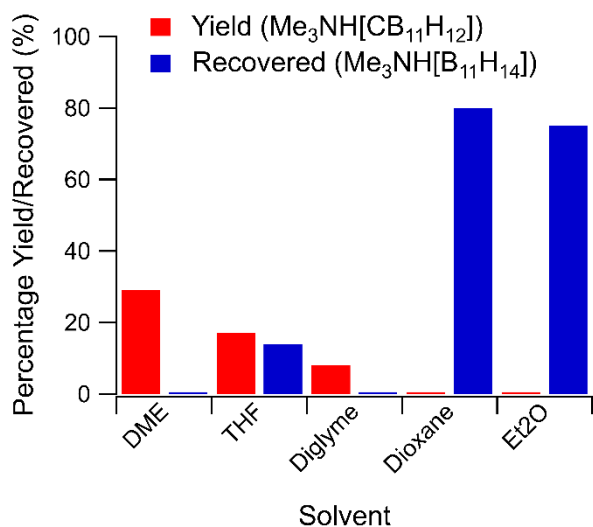


**Figure 2.** Effect of group 2 metal carbonates on the synthesis of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$ . Reactions were run with 250 mg of  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  in 5 mL DME and 9 molar equivalents NaOH. \*Trial 7 was a repeat of trial 1, however, extending reaction time from 5 hours to 16 hours.

## Solvent effects

Initial screening reactions were performed in DME but alternative solvents were also tested for their viability (Figure 3). DME was primarily chosen as it is slightly more polar than THF, and experimental and computational analysis has shown that DME will coordinate to  $\text{Na}^+$ , therefore, potentially enhance the dissolution of NaOH.<sup>24</sup> DME fits into the glyme family of solvents, which are polar aprotic, and chemically stable.<sup>25</sup> As reported above, in DME, the reaction yielded 29 % of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$ , whereas, in THF, the yield was lower at 17 % (Figure 3).  $^{11}\text{B}$  NMR (Figure S9) showed that 14 % of  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  was recovered in the reaction in THF compared to that in DME.

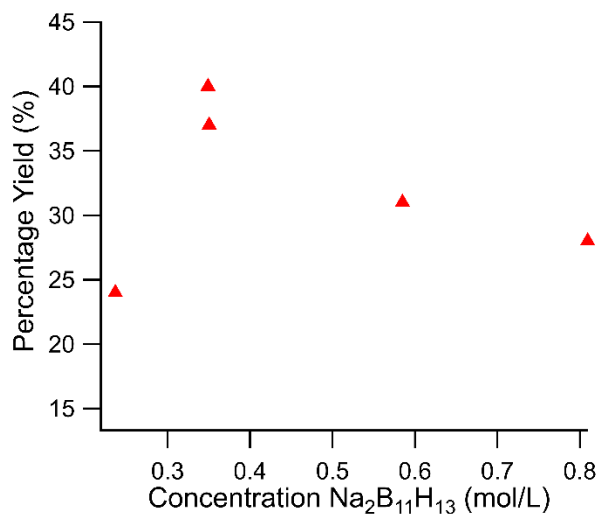
Other solvents were screened to determine their suitability as shown in Figure 3. When the reaction solvent was changed to the less-polar solvents,  $\text{Et}_2\text{O}$  or dioxane, the reaction did not produce  $\text{CB}_{11}\text{H}_{12}^-$ , with only  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  being isolated. Furthermore,  $\text{Na}_2[\text{B}_{11}\text{H}_{13}]$  does not dissolve appreciably in  $\text{Et}_2\text{O}$  or dioxane, therefore it shows that the reactant needs to be relatively soluble in the solvent that is used. Diglyme was also tested and was determined to yield only 8 %  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$ , with no  $\text{B}_{11}\text{H}_{13}^{2-}$  detected at the end of the reaction (Figure S9).



**Figure 3.** Effect of different solvents on the synthesis of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>]. Reactions run with 500 mg of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] in 10 mL solvent and 9 molar equivalents NaOH.

### Optimisation of Reaction

To optimise the 1-carbadodecaborate reaction the concentration of Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] was also analysed (Figure 4). The reaction was found to be highly dependent on the concentration of Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] in DME. However, increasing overall concentration of the reaction mixture to 0.35 mol/L, the yield increased to 37.5 % when starting with 1.35 g Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>]. When the amount of starting material increased to 10 g, the yield peaked at 40 % (Figure 4). The observed trend was also found to occur in THF, as an increase in concentration from 0.26 mol/L to 0.3496 mol/L, increased yield from 31 % to 40 %. Unfortunately, higher concentrations of Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] above 0.35 mol/L resulted in decreased yield.



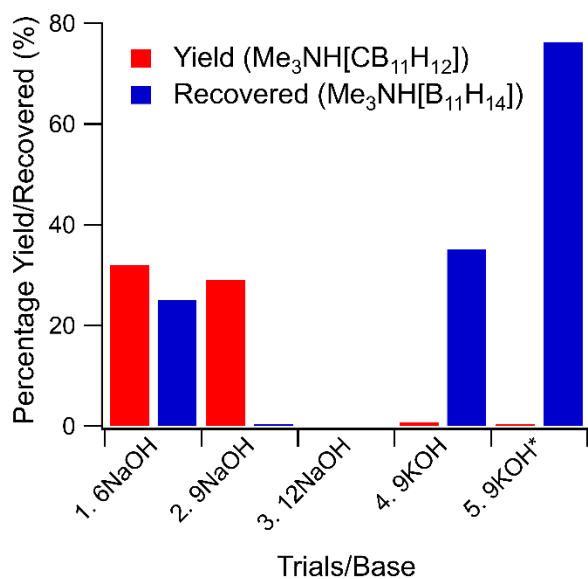
**Figure 4.** Effect of concentration of Na<sub>2</sub>[B<sub>11</sub>H<sub>13</sub>] on yield. Trials used 1.35 g of Me<sub>3</sub>NHB<sub>11</sub>H<sub>12</sub>.

Changing the total amount of NaOH in the synthesis of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] was analysed.

When the amount of NaOH was decreased from a total of 9 molar equivalents to 6, a significant amount of B<sub>11</sub>H<sub>13</sub><sup>2-</sup> was detected by <sup>11</sup>B NMR, even after 48 hours of stirring (Figure S10). With longer reaction times, the presence of the oxa-nido-dodecaborate anion (B<sub>11</sub>H<sub>12</sub>O<sup>-</sup>) and an increase in B(OH)<sub>4</sub><sup>-</sup> was noted in the <sup>11</sup>B NMR (Figure S10). These by-products form due to the reaction of B<sub>11</sub>H<sub>13</sub><sup>2-</sup> with excess OH<sup>-</sup>.<sup>26,27</sup> After 3 days of stirring under argon, a significant amount of Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>] was recovered when the reaction was worked up (Figure 5). When the total amount of NaOH used in the reaction was increased to 12 molar equivalents, all B<sub>11</sub>H<sub>13</sub><sup>2-</sup> was determined to have been fully reacted within 1 hour, however, only a beige residue could be isolated, and the product had impurities, as determined by <sup>11</sup>B NMR (Figure 5, Figure S11). Attempts to change the base from NaOH for KOH were unsuccessful. This was attempted in both DME and THF with 9 molar equivalents of KOH. However, only an insignificant amount of



$\text{CB}_{11}\text{H}_{12}^-$  was detected by  $^{11}\text{B}$  NMR, in DME, with none detected in THF (Figure S12). Thus, NaOH was favoured over KOH as the base in this reaction, due to the higher affinity for  $\text{Na}^+$  over  $\text{K}^+$  for DME. It is also important to note that the amount of NaOH used has to be enough to ensure a full conversion of  $\text{B}_{11}\text{H}_{14}^-$  to  $\text{CB}_{11}\text{H}_{12}^-$ , however, it was noted that excessive base had a detrimental effect on the yield.



**Figure 5.** The effect of base on the synthesis of  $\text{Me}_3\text{NH}[\text{CB}_{11}\text{H}_{12}]$ . Reactions were run with 500 mg of initial  $\text{Me}_3\text{NH}[\text{B}_{11}\text{H}_{14}]$  and 4 molar equivalents of  $\text{K}_2\text{CO}_3$  with NaOH changing from 6 molar equivalents to 12 or 9 molar equivalents of KOH. Trials 1 - 4 were run in DME. Trial 5 was run in THF.

The overall cost of reagents (not including solvents and common laboratory consumables), to synthesise 1 g of  $\text{Me}_3\text{NHCB}_{11}\text{H}_{12}$  from the different published reactions is shown in Table 1. It should be noted that even though these costs do not reflect bulk prices they do act as a good means

of comparison. Many of the reactions are prohibitively expensive, due to the expensive starting reagent, decaborane (Table 1, 1-4).<sup>8,9,11,13</sup> Added to this, most of the reactions that use decaborane, have other expensive reagents such as Me<sub>2</sub>SO<sub>4</sub>, Et<sub>3</sub>N·BH<sub>3</sub> and/or CyNC.<sup>8,9,11</sup> Me<sub>2</sub>SO<sub>4</sub> is toxic and corrosive, however, due to its use as a methylating agent, it is restricted and necessitates a license to purchase in Australia.<sup>28</sup> Reaction of decaborane with formaldehyde (Table 1, 4) is the simplest of the reactions involving decaborane. By avoiding the need for methylating reagents and sodium metal to remove the C-N bond present in 1 – 3,<sup>13</sup> the cost to synthesise 1 g of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] is reduced to the cost of decaborane. For methods starting with Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>], (Table 1, 5 - 7), the cost of reagents to synthesise 1 g of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] is similar, approximately \$100. Expensive reagents such as NaH (95 %) (Table 1, 5) and CF<sub>3</sub>SiMe<sub>3</sub> (Table 1, 6 - 7), significantly raise the cost to produce Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>].<sup>15-17</sup> In this work (Table 1, 8), as most reagents are common laboratory consumables such as NaOH, the cost of reaction is comprised of the expense to synthesise Me<sub>3</sub>NH[B<sub>11</sub>H<sub>14</sub>].

	<b>Reagents<sup>a</sup></b>	<b>Approximate materials cost<sup>b</sup> per gram product</b>	<b>Reference</b>
<b>1</b>	Decaborane(14) (B <sub>10</sub> H <sub>14</sub> ) Sodium Cyanide (NaCN) Dimethylsulfate (Me <sub>2</sub> SO <sub>4</sub> ) Sodium metal (Na) Borane triethylamine (Et <sub>3</sub> N·BH <sub>3</sub> )	\$220.70 (\$162.33 <sup>c</sup> )	<i>J. Am. Chem. Soc.</i> 89, 1274–1275 (1967). <sup>8</sup>
<b>2</b>	Decaborane(14) (B <sub>10</sub> H <sub>14</sub> ) Sodium Cyanide (NaCN) Dimethylsulfate (Me <sub>2</sub> SO <sub>4</sub> ) Sodium metal (Na) Borane triethylamine (Et <sub>3</sub> N·BH <sub>3</sub> )	\$71.65	<i>Collect. Czechoslov. Chem. Commun.</i> 49, 1559–1562 (1984). <sup>9</sup>
<b>3</b>	Decaborane(14) (B <sub>10</sub> H <sub>14</sub> ) Cyclohexyl-isocyanide (CyNC) Dimethylsulfate (Me <sub>2</sub> SO <sub>4</sub> )	\$71.30 <sup>d</sup>	<i>J. Chem. Soc. Dalt. Trans.</i> 2624–2631 (2002). <sup>11</sup>

4	Decaborane(14) (B <sub>10</sub> H <sub>14</sub> ) Formaldehyde (37 %) (HCHO) Borane dimethylsulfide (BH <sub>3</sub> ·SMe <sub>2</sub> )		\$59.06 (\$44.04 <sup>e</sup> )	<i>New J. Chem.</i> 28, 1499–1505 (2004). <sup>13</sup>
5	Trimethylammonium undecaborane(14) (Me <sub>3</sub> NH[B <sub>11</sub> H <sub>14</sub> ]) Sodium Hydride dry (NaH) Chloroform (CHCl <sub>3</sub> )	<i>nido-</i>	\$40.38	<i>Collect. Czechoslov. Chem. Commun.</i> 66, 1238–1249 (2001). <sup>15</sup>
6	Trimethylammonium undecaborane(14) (Me <sub>3</sub> NH[B <sub>11</sub> H <sub>14</sub> ]) Sodium Hydride (60 %) (NaH) Trimethyl(trifluoromethyl)silane (99 %) (Me <sub>3</sub> SiCF <sub>3</sub> )	<i>nido-</i>	\$66.60	<i>Dalt. Trans.</i> 48, 7499– 7502 (2019). <sup>17</sup>
7	Trimethylammonium undecaborane(14) (Me <sub>3</sub> NH[B <sub>11</sub> H <sub>14</sub> ]) Sodium Hydride (60 %) (NaH) Trimethyl(trifluoromethyl)silane (99 %) (Me <sub>3</sub> SiCF <sub>3</sub> ) Anhydrous Lithium chloride (LiCl)	<i>nido-</i>	\$69.56 (\$51.68 <sup>e</sup> )	<i>Molecules</i> 24, 1–13 (2019). <sup>16</sup>
8	Trimethylammonium undecaborane(14) (Me <sub>3</sub> NH[B <sub>11</sub> H <sub>14</sub> ]) Potassium Carbonate (K <sub>2</sub> CO <sub>3</sub> ) Chloroform (CHCl <sub>3</sub> )	<i>nido-</i>	\$13.44	This Work

**Table 1.** Cost to synthesise 1 g of Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>]. Analysis used current prices available from Merck and <sup>a</sup>ignores the costs of common laboratory consumables, such as, NaOH and HCl, and solvents, e.g., THF. <sup>b</sup>All prices in USD. <sup>c</sup>Originally synthesised as CsCB<sub>11</sub>H<sub>12</sub>. <sup>d</sup>Cost to synthesise precursor *nido*-7-CB<sub>10</sub>H<sub>12</sub>. <sup>e</sup>Originally synthesised as NEt<sub>4</sub>CB<sub>11</sub>H<sub>12</sub>.

## CONCLUSION

A new method to synthesise Me<sub>3</sub>NH[CB<sub>11</sub>H<sub>12</sub>] using cheap, easily accessible materials and equipment has been developed. This method is proven to be easily scalable and while not as high yielding as other methods reported, the lower cost of the materials used makes this method a viable option for the general synthetic chemist. Using a mix of NaOH and K<sub>2</sub>CO<sub>3</sub> has proven to be significant to the yield and completion of the reaction. All reactants are easily lab accessible and significantly less dangerous than those used in alternative methods. It also avoids some more

dangerous bases such as NaH. Most importantly, the reported method will support further work in the research, development and potential commercialisation of the  $\text{CB}_{11}\text{H}_{12}^-$  anion salt electrolytes for an all solid-state battery.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## REFERENCES

- (1) Riphaut, N.; Stiaszny, B.; Beyer, H.; Indris, S.; Gasteiger, H. A.; Sedlmaier, S. J. Understanding Chemical Stability Issues between Different Solid Electrolytes in All-Solid-State Batteries. *J. Electrochem. Soc.* **2019**, *166* (6), A975–A983. <https://doi.org/10.1149/2.0351906jes>.
- (2) Sun, C.; Liu, J.; Gong, Y.; Wilkinson, D. P.; Zhang, J. Recent Advances in All-Solid-State Rechargeable Lithium Batteries. *Nano Energy*. Elsevier Ltd March 1, 2017, pp 363–386.

<https://doi.org/10.1016/j.nanoen.2017.01.028>.

- (3) Tang, W. S.; Unemoto, A.; Zhou, W.; Stavila, V.; Matsuo, M.; Wu, H.; Orimo, S.; Udovic, T. J. Unparalleled Lithium and Sodium Superionic Conduction in Solid Electrolytes with Large Monovalent Cage-like Anions. *Energy Environ. Sci.* **2015**, *8* (12), 3637–3645. <https://doi.org/10.1039/C5EE02941D>.
- (4) Skripov, A. V.; Skoryunov, R. V.; Soloninin, A. V.; Babanova, O. A.; Tang, W. S.; Stavila, V.; Udovic, T. J. Anion Reorientations and Cation Diffusion in LiCB<sub>11</sub>H<sub>12</sub> and NaCB<sub>11</sub>H<sub>12</sub>: <sup>1</sup>H, <sup>7</sup>Li, and <sup>23</sup>Na NMR Studies. *J. Phys. Chem. C* **2015**, *119* (48), 26912–26918. <https://doi.org/10.1021/acs.jpcc.5b10055>.
- (5) Padma Kumar, P.; Yashonath, S. Ionic Conduction in the Solid State. *ChemInform* **2006**, *37* (24), 135–154. <https://doi.org/10.1002/chin.200624229>.
- (6) Dimitrievska, M.; Shea, P.; Kweon, K. E.; Berex, M.; Varley, J. B.; Tang, W. S.; Skripov, A. V.; Stavila, V.; Udovic, T. J.; Wood, B. C. Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB<sub>11</sub>H<sub>12</sub> and NaCB<sub>11</sub>H<sub>12</sub>. *Adv. Energy Mater.* **2018**, *8* (15), 1703422. <https://doi.org/10.1002/aenm.201703422>.
- (7) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. A New Series of Organoboranes. I. Carboranes from the Reaction of Decaborane with Acetylenic Compounds. *Inorg. Chem.* **1963**, *2* (6), 1089–1092. <https://doi.org/10.1021/ic50010a002>.
- (8) Knoth, W. H. 1-B<sub>9</sub>H<sub>9</sub>CH<sup>-</sup> and B<sub>11</sub>H<sub>11</sub>CH<sup>-</sup>. *J. Am. Chem. Soc.* **1967**, *89* (5), 1274–1275.
- (9) Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. A Convenient Preparation of 1-CB<sub>11</sub>H<sub>12</sub><sup>-</sup> and Its C-Amino Derivatives. *Collect. Czechoslov. Chem. Commun.* **1984**, *49* (7), 1559–1562. <https://doi.org/10.1135/cccc19841559>.
- (10) Knoth, W. H. B<sub>10</sub>H<sub>12</sub>CNH<sub>3</sub>, B<sub>9</sub>H<sub>9</sub>CH<sup>-</sup>, B<sub>11</sub>H<sub>11</sub>CH<sup>-</sup>, and Metallomonocarboranes. *Inorg. Chem.* **1971**, *10* (3), 598–605.
- (11) Batsanov, A. S.; Fox, M. A.; Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Malget, J. M.

- A Convenient Cyanide-Free “One-Pot” Synthesis of Nido-Me<sub>3</sub>N-7-CB<sub>10</sub>H<sub>12</sub> and Nido-7-CB<sub>10</sub>H<sub>13</sub>-. *J. Chem. Soc. Dalton Trans.* **2002**, No. 13, 2624–2631. <https://doi.org/10.1039/b200930g>.
- (12) Noyes, W. A.; Hyatt, D. E.; Owen, D. A.; Todd, L. J. Preparation of B<sub>10</sub>CH<sub>13</sub>- Derivatives Contribution from the The Preparation of BiOCHi<sub>3</sub>- Derivatives by Carbon Atom Insertion with Alkyl Isocyanides<sup>1</sup>. *Inorg. Chem.* **1966**, 5 (10), 1749–1751.
- (13) Franken, A.; Bullen, N. J.; Jelínek, T.; Thornton-Pett, M.; Teat, S. J.; Clegg, W.; Kennedy, J. D.; Hardie, M. J. Structural Chemistry of Halogenated Monocarbaboranes: The Extended Structures of Cs[1-HCB<sub>9</sub>H<sub>4</sub>Br<sub>5</sub>], Cs[1-HCB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>] and Cs[1-HCB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>]. *New J. Chem.* **2004**, 28 (12), 1499–1505. <https://doi.org/10.1039/b410929e>.
- (14) Dunks, G. B.; Ordonez, K. P. A One-Step Synthesis of B<sub>11</sub>H<sub>14</sub>- Ion from NaBH<sub>4</sub>. *Inorg. Chem.* **1978**, 17 (6), 1514–1516. <https://doi.org/10.1021/ic50184a025>.
- (15) Franken, A.; King, B. T.; Rudolph, J.; Roa, P.; Noll, B. C.; Michl, J. Preparation of [Closoborane]by Dichlorocarbene Insertion into [Nido-B<sub>11</sub>H<sub>14</sub>]-. *Collect. Czechoslov. Chem. Commun.* **2001**, 66 (8), 1238–1249. <https://doi.org/10.1135/cccc20011238>.
- (16) Pecyna, J.; Rončević, I.; Michl, J. Insertion of Carbenes into Deprotonated Nido-Undecaborane, B<sub>11</sub>H<sub>13</sub>(2-). *Molecules* **2019**, 24 (20), 1–13. <https://doi.org/10.3390/molecules24203779>.
- (17) Toom, L.; Kütt, A.; Leito, I. Simple and Scalable Synthesis of the Carborane Anion CB<sub>11</sub>H<sub>12</sub>-. *Dalt. Trans.* **2019**, 48 (22), 7499–7502. <https://doi.org/10.1039/c9dt01062a>.
- (18) Jelínek, T.; Plešek, J.; Mareš, F.; Heřmánek, S.; Štíbr, B. Some Electrophilic Substitution Reactions of Closo-[1-CB<sub>11</sub>H<sub>12</sub>]- and One-Boron Insertion into Nido-7-L-7-CB<sub>10</sub>H<sub>12</sub> (L = H- or Me<sub>3</sub>N) Compounds. Isolation of All Three B-Substituted Closo-Me<sub>3</sub>N-1-CB<sub>11</sub>H<sub>11</sub> Derivatives. *Polyhedron* **1987**, 6 (11), 1981–1986. [https://doi.org/10.1016/S0277-5387\(00\)84535-0](https://doi.org/10.1016/S0277-5387(00)84535-0).
- (19) Hepp, A.; Labbow, R.; Reiß, F.; Schulz, A.; Villinger, A. Carba-Closo-Dodecaborates – Synthesis, Structure, and Energetics. *Eur. J. Inorg. Chem.* **2018**, 2018 (25), 2905–2914.

<https://doi.org/10.1002/ejic.201800219>.

- (20) Franken, A.; King, B. T.; Michl, J. Method for Preparation of Carborane Anions, January 9, 2007.
- (21) Aftandilian, V. D.; Miller, H. C.; Parshall, G. W.; Muetterties, E. L.; V. D. AFTANDILIAN, H. C. MILLER, G. W. PARSHALL, A. E. L. M. Chemistry of Boranes. V. First Example of a B<sub>11</sub> Hydride, the B<sub>11</sub>H<sub>14</sub><sup>-</sup> Anion. *Inorg. Chem.* **1962**, *1* (4), 734–737. <https://doi.org/10.1021/ic50004a003>.
- (22) Mondal, R.; Mallik, A. K. Recent Applications of Potassium Carbonate in Organic Synthesis. *Org. Prep. Proced. Int.* **2014**, *46* (5), 391–434. <https://doi.org/10.1080/00304948.2014.944402>.
- (23) Młotkowska, B.; Zwierzak, A. Solid NaOH/K<sub>2</sub>CO<sub>3</sub> - A New Highly Effective Base for Phase-Transfer Catalysed N-Alkylation of Diphenylphosphinic Hydrazide. *Tetrahedron Lett.* **1978**, *19* (47), 4731–4734. [https://doi.org/10.1016/S0040-4039\(01\)85717-8](https://doi.org/10.1016/S0040-4039(01)85717-8).
- (24) Hill, S. E.; Feller, D.; Glendening, E. D. Theoretical Study of Cation/Ether Complexes: Alkali Metal Cations with 1,2-Dimethoxyethane and 12-Crown-4. *J. Phys. Chem. A* **1998**, *102* (21), 3813–3819. <https://doi.org/10.1021/jp980522p>.
- (25) Tang, S.; Zhao, H. Glymes as Versatile Solvents for Chemical Reactions and Processes: From the Laboratory to Industry. *RSC Adv.* **2014**, *4* (22), 11251. <https://doi.org/10.1039/c3ra47191h>.
- (26) Yang, X.; Jiao, H.; von Ragué Schleyer, P. *Ab Initio Geometries and Chemical Shift Calculations for Neutral Boranes and Borane Anions. In Electron Deficient Boron and Carbon Clusters*; Wiley, 1995; Vol. 19.
- (27) Yang, X.; Jiao, H.; Schleyer, P. von R. Structures of the 12-Vertex Oxa- and Thia- Nido - Dodecaborates and B<sub>13</sub>H<sub>13</sub>2<sup>-</sup> - : A Theoretical DFT/GIAO/NMR Investigation . *Inorg. Chem.* **1997**, *36* (21), 4897–4899. <https://doi.org/10.1021/ic970498e>.
- (28) Australian Government - Attorney-General's Department. National Code of Practice for

Chemicals of Security Concern. **2016**, 24.