

# Facile Synthesis of Unsolvated Alkali Metal Octahydrotriborate Salts $\text{MB}_3\text{H}_8$ ( $\text{M} = \text{K}, \text{Rb}, \text{and Cs}$ ), Mechanisms of Formation, and the Crystal Structure of $\text{KB}_3\text{H}_8$

Xi-Meng Chen<sup>+</sup>, Nana Ma<sup>+</sup>, Xin-Ran Liu, Changgeng Wei, Chong-Chao Cui, Bu-La Cao, Yanhui Guo,<sup>\*</sup> Lai-Sheng Wang,<sup>\*</sup> Qinfen Gu, and Xuenian Chen<sup>\*</sup>

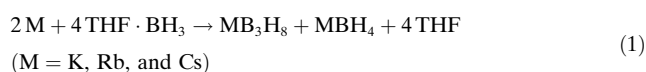
**Abstract:** A facile synthesis of heavy alkali metal octahydrotriborates ( $\text{MB}_3\text{H}_8$ ;  $\text{M} = \text{K}, \text{Rb}, \text{and Cs}$ ) has been developed. It is simply based on reactions of the pure alkali metals with  $\text{THF} \cdot \text{BH}_3$ , does not require the use of electron carriers or the addition of other reaction media such as mercury, silica gel, or inert salts as for previous procedures, and delivers the desired products at room temperature in very high yields. However, no reactions were observed when pure  $\text{Li}$  or  $\text{Na}$  was used. The reaction mechanisms for the heavy alkali metals were investigated both experimentally and computationally. The low sublimation energies of  $\text{K}, \text{Rb}, \text{and Cs}$  were found to be key for initiation of the reactions. The syntheses can be carried out at room temperature because all of the elementary reaction steps have low energy barriers, whereas reactions of  $\text{LiBH}_4/\text{NaBH}_4$  with  $\text{THF} \cdot \text{BH}_3$  have to be carried out under reflux. The high stability and solubility of  $\text{KB}_3\text{H}_8$  were examined, and a crystal structure thereof was obtained for the first time.

The octahydrotriborate anion,  $\text{B}_3\text{H}_8^-$ , has attracted widespread attention because its derivatives can be used as chemical hydrogen storage materials ( $\text{NH}_3\text{B}_3\text{H}_7$  and  $\text{NH}_4\text{B}_3\text{H}_8$ ),<sup>[1–4]</sup> chemical vapor deposition (CVD) precursors

$[\text{Mg}(\text{B}_3\text{H}_8)_2 \text{ and } \text{Cr}(\text{B}_3\text{H}_8)_2]$ ,<sup>[5,6]</sup> and reducing agents for a series of organic reactions.<sup>[7,8]</sup> However, although its synthesis and reactivity have been continually improved and explored, its mechanism of formation has not been fully understood.<sup>[8–18]</sup> Very recently, our group reported that  $\text{MB}_3\text{H}_8$  ( $\text{M} = \text{Li}$  and  $\text{Na}$ ) could be synthesized by reacting the corresponding borohydrides with  $\text{THF} \cdot \text{BH}_3$  in  $\text{THF}$  under reflux.<sup>[19a]</sup> The reaction mechanism of the formation of  $\text{B}_3\text{H}_8^-$  was elucidated, and found to involve a key  $\text{B}_3\text{H}_{10}^-$  intermediate, which undergoes  $\text{H}_2$  elimination via a high barrier.<sup>[19a]</sup> We also found that the nucleophilicity of the  $\text{B}–\text{H}$  bond in  $\text{BH}_4^-$  and  $\text{B}_2\text{H}_7^-$  played an important role. Surprisingly, this convenient synthetic method did not work for the preparation of  $\text{KB}_3\text{H}_8$ , probably because of the poor solubility of  $\text{KBH}_4$  in  $\text{THF}$  solution.<sup>[19]</sup>

Herein, we report a facile method for the synthesis of the heavier alkali metal salts of  $\text{B}_3\text{H}_8^-$ ,  $\text{MB}_3\text{H}_8$  ( $\text{M} = \text{K}, \text{Rb}, \text{and Cs}$ ), which is based on directly reacting the respective alkali metals with  $\text{THF} \cdot \text{BH}_3$  in  $\text{THF}$  at room temperature. In the current method, no electron carriers, such as naphthalene or triphenylboron, or other reaction media, such as mercury, silica gel, or inert salts, were used, as done in previous works.<sup>[8,12–16,20–22]</sup> The simplified synthetic method enables the convenient preparation of the heavier  $\text{MB}_3\text{H}_8$  alkali salts on large scale in very high yields. We also report a detailed study of the mechanism of  $\text{KB}_3\text{H}_8$  formation and its crystal structure for the first time.

In our new synthetic method, pure alkali metals ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) are reacted directly with  $\text{THF} \cdot \text{BH}_3$  to produce  $\text{MB}_3\text{H}_8$  and  $\text{MBH}_4$  at room temperature according to Equation (1).



The reaction rate depended mainly on the particle size of the metals. To prepare  $\text{KB}_3\text{H}_8$ , we cut 5.85 g (150 mmol) of potassium into pieces of approximately  $3 \times 3 \times 3 \text{ mm}^3$  in size, and reacted it with 1M  $\text{THF} \cdot \text{BH}_3$  solution (300 mL, 300 mmol). The reaction was complete in 12 h, and the reactants were converted quantitatively into  $\text{KB}_3\text{H}_8$  and  $\text{KBH}_4$  according to  $^{11}\text{B}$  NMR analysis (see the Supporting Information, Figure S1). Upon completion of the reaction, the  $\text{KBH}_4$  precipitate was removed by filtration, and the  $\text{THF}$  in the filtrate was removed under dynamic vacuum to produce a  $\text{THF}$ -solvated  $\text{KB}_3\text{H}_8$  product. Addition of toluene to the  $\text{THF}$ -solvated product led to the precipitation of unsolvated  $\text{KB}_3\text{H}_8$ , which was isolated in 90% yield upon filtration

[\*] X.-M. Chen,<sup>[†]</sup> Dr. N. Ma,<sup>[†]</sup> R.-X. Liu, C. Wei, C.-C. Cui, B.-L. Cao, Prof. Dr. X. Chen

School of Chemistry and Chemical Engineering  
Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, Henan Normal University  
Xinxiang, Henan 453007 (China)  
E-mail: xnchen@htu.edu.cn

Prof. Dr. X. Chen  
College of Chemistry and Molecular Engineering  
Zhengzhou University  
Zhengzhou, Henan 450001 (China)

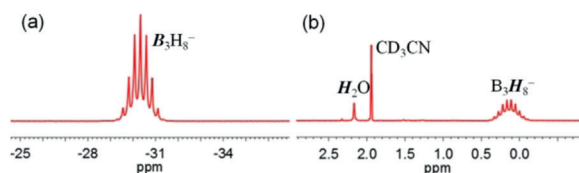
Prof. Dr. Y. Guo  
Department of Materials Science, Fudan University  
Shanghai, 200433 (China)  
E-mail: gyh@fudan.edu.cn

Prof. Dr. L. S. Wang  
Department of Chemistry, Brown University  
Providence, RI 02912 (USA)  
E-mail: Lai-Sheng\_Wang@brown.edu

Dr. Q. Gu  
Australian Synchrotron (ANSTO)  
800 Blackburn Rd, Clayton, 3168 VIC (Australia)

[†] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/anie.201812795>.

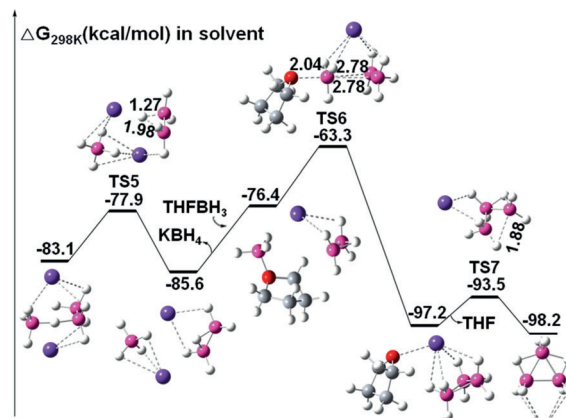


**Figure 1.** a)  $^{11}\text{B}$  NMR and b)  $^1\text{H}$  NMR spectra of the unsolvated  $\text{KB}_3\text{H}_8$  in  $\text{CD}_3\text{CN}$ .

(Figures 1 and S2); this represents the highest yield achieved thus far for the preparation of octahydrotriborate alkali metal salts (Table S1).

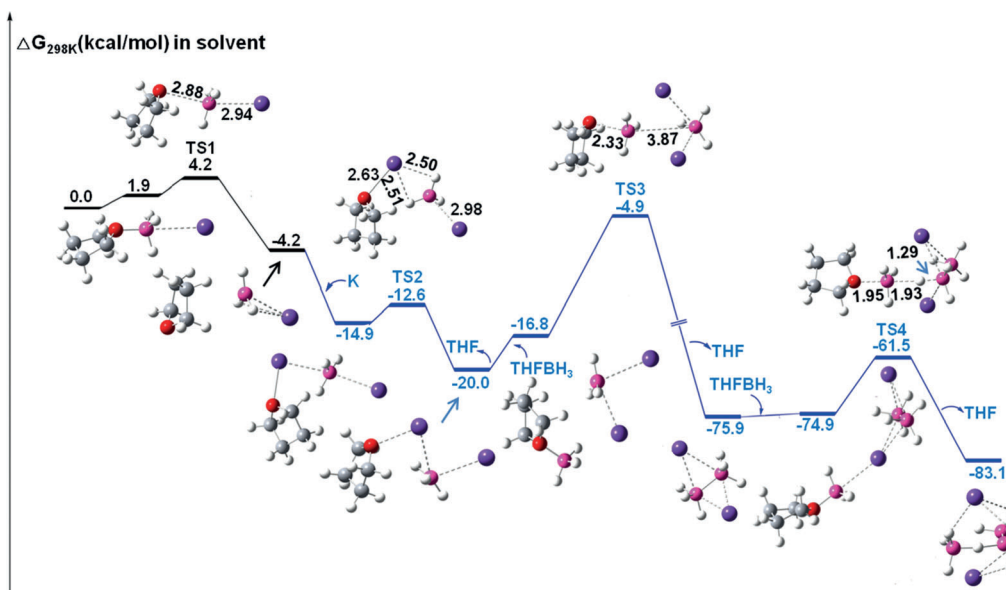
Similar reactions at room temperature for Rb and Cs produced unsolvated  $\text{RbB}_3\text{H}_8$  and  $\text{CsB}_3\text{H}_8$ , which were isolated in yields of 70 % and 73 %, respectively (Figures S3–S10). The reaction times were 5 h for Rb and 2 h for Cs, and thus much shorter than for K. However, similar procedures using Na or Li could not produce  $\text{NaB}_3\text{H}_8$  or  $\text{LiB}_3\text{H}_8$  even at elevated temperatures (Figures S11 and S12).

We further investigated the mechanisms of formation of the octahydrotriborate salts from the direct reactions of K, Rb, and Cs with  $\text{THF}\cdot\text{BH}_3$  both experimentally and theoretically. Theoretical calculations were performed by density functional theory (DFT) in the Gaussian09 program.<sup>[23]</sup> The proposed mechanism includes seven steps (Figure 2 and Figure 3). In the first step, bulk K is solvated by  $\text{THF}\cdot\text{BH}_3$  and THF, which is followed by a single-electron donation from the K atom to the  $\text{BH}_3$  group in the  $\text{THF}\cdot\text{BH}_3$  complex to form  $\text{BH}_3^-$ . Then, the second K atom donates its valence electron to  $\text{BH}_3^-$  to form  $\text{BH}_3^{2-}$ . The free energy barriers of the two transition states (TS) are 4.2 (TS1) and 2.3  $\text{kcal mol}^{-1}$  (TS2) for the reactions of K (on the basis of the K gas state) with  $\text{THF}\cdot\text{BH}_3$  in THF solvent (Table 1). In the next step, the  $\text{BH}_3^{2-}$  species undergoes a nucleophilic substitution reaction using its lone pair electrons to replace THF from a second  $\text{THF}\cdot\text{BH}_3$  to form  $\text{B}_2\text{H}_6^{2-}$  with an energy barrier of 15.1  $\text{kcal}$



**Figure 3.** Energy profile for the reaction of  $(2\text{K}^+)\text{B}_3\text{H}_9^{2-} \rightarrow \text{KB}_3\text{H}_8$  calculated at the SMD(THF)/M062X/6-311++G(d,p) level of theory.

$\text{mol}^{-1}$  (TS3). This step is exothermic by  $71.0 \text{ kcal mol}^{-1}$  (Figure 2). Then,  $\text{B}_2\text{H}_6^{2-}$  attacks the B center in a third  $\text{THF}\cdot\text{BH}_3$  unit to replace THF using one of its B–H bonds to form  $\text{B}_3\text{H}_9^{2-}$  ( $[\text{BH}_3\text{BH}_2(\mu\text{-H})\text{BH}_3]^{2-}$ ). The free energy barrier of TS4 was calculated to be  $14.4 \text{ kcal mol}^{-1}$  in THF solvent (Table 1), which implies that the nucleophilicity of the B–H bond in  $\text{B}_2\text{H}_6^{2-}$  is similar to that of the B–H bond in  $\text{BH}_4^-$  and  $\text{B}_2\text{H}_7^-$ , which reacted with  $\text{THF}\cdot\text{BH}_3$  to form  $\text{B}_2\text{H}_7^-$  and  $\text{B}_3\text{H}_{10}^-$  with free energy barriers of 15.8 and  $10.3 \text{ kcal mol}^{-1}$ , respectively.<sup>[19]</sup> The nascent  $\text{B}_3\text{H}_9^{2-}$  ion in this reaction is then cleaved to give  $\text{B}_2\text{H}_5^-$  and  $\text{BH}_4^-$  (TS5) with a free energy of  $5.2 \text{ kcal mol}^{-1}$  (Figure 3). Finally, the  $\text{B}_2\text{H}_5^-$  intermediate reacts with  $\text{BH}_3$  in the fourth  $\text{THF}\cdot\text{BH}_3$  adduct to form  $\text{B}_3\text{H}_8^-$  (TS6,  $22.3 \text{ kcal mol}^{-1}$ ), which is converted into the  $\text{B}_3\text{H}_8^-$  final product via TS7 with a free energy barrier of  $3.7 \text{ kcal mol}^{-1}$ . In another possible pathway, if  $\text{BH}_3^-$  reacted with two  $\text{THF}\cdot\text{BH}_3$  molecules, a  $\text{B}_3\text{H}_9^-$  ( $[\text{BH}_3\text{BH}_2(\mu\text{-H})\text{BH}_3]^-$ ) ion and not  $\text{B}_3\text{H}_9^{2-}$  would be formed (red part in Scheme S1). This reaction will proceed via two transition



**Figure 2.** Energy profile for the reaction of  $\text{K} + \text{THF}\cdot\text{BH}_3 \rightarrow (2\text{K}^+)\text{B}_3\text{H}_9^{2-}$  calculated at the SMD(THF)/M062X/6-311++G(d,p) level of theory.

**Table 1:** Calculated electronic energies, enthalpies, and free energies.

	$\Delta E$ (0 K) [kcal mol <sup>-1</sup> ]	$\Delta H$ (298 K) [kcal mol <sup>-1</sup> ]	$\Delta G$ (298 K) [kcal mol <sup>-1</sup> ]
(THF·BH <sub>3</sub> )(K)	0.0	0.0	0.0
THF·BH <sub>3</sub> + K	-4.8	-4.0	1.9
TS1	11.7	0.2	4.2
K <sup>+</sup> BH <sub>3</sub> <sup>-</sup> -THF	9.7	-5.4	-4.2
(K <sup>+</sup> BH <sub>3</sub> <sup>-</sup> -THF) + K	-13.9	-27.0	-14.9
TS2	-12.2	-25.7	-12.6
2 K <sup>+</sup> BH <sub>3</sub> <sup>2-</sup> -THF	-19.0	-31.7	-20.0
2 K <sup>+</sup> BH <sub>3</sub> <sup>2-</sup> + THF·BH <sub>3</sub>	-34.4	-39.8	-16.8
TS3	-13.1	-25.6	-4.9
2 K <sup>+</sup> B <sub>2</sub> H <sub>6</sub> <sup>2-</sup> -THF	-79.4	-99.0	-74.1
2 K <sup>+</sup> B <sub>2</sub> H <sub>6</sub> <sup>2-</sup>	-65.2	-90.6	-75.9
2 K <sup>+</sup> B <sub>2</sub> H <sub>6</sub> <sup>2-</sup> + THF·BH <sub>3</sub>	-74.5	-97.0	-74.9
TS4	-65.7	-87.2	-61.5
2 K <sup>+</sup> B <sub>3</sub> H <sub>9</sub> <sup>2-</sup> -THF	-95.0	-105.5	-81.4
2 K <sup>+</sup> B <sub>3</sub> H <sub>9</sub> <sup>2-</sup>	-82.6	-97.3	-83.1
TS5	-76.7	-91.0	-77.9
KBH <sub>4</sub> + KBH <sub>3</sub>	-85.4	-98.3	-85.6
KB <sub>2</sub> H <sub>5</sub> + THF·BH <sub>3</sub>	-69.3	-89.6	-76.4
TS6	-52.2	-76.8	-63.3
KB <sub>2</sub> H <sub>5</sub> -BH <sub>3</sub> -THF	-90.6	-110.2	-97.2
TS7	-68.7	-96.9	-93.5
KB <sub>3</sub> H <sub>8</sub>	-91.0	-110.9	-98.2
TS2-1	32.1	9.2	9.3
K <sup>+</sup> B <sub>2</sub> H <sub>6</sub> <sup>-</sup> -THF	8.1	-6.0	-6.0
TS3-1	23.5	10.8	13.5
K <sup>+</sup> B <sub>3</sub> H <sub>9</sub> <sup>-</sup> -THF	8.5	-0.2	1.2

states TS2-1 and TS3-1 with relative free energies of 13.5 and 19.5 kcal mol<sup>-1</sup>, which are much higher than TS2 and TS3 (Table 1). Hence, the reaction via the BH<sub>3</sub><sup>2-</sup> intermediate is more favorable than the direct conversion of BH<sub>3</sub><sup>-</sup> into B<sub>3</sub>H<sub>9</sub><sup>-</sup>.

The proposed mechanism is supported by experimental observations. The reactions of K, Rb, and Cs with THF·BH<sub>3</sub> can be carried out at room temperature while the reactions of Li and Na borohydrides with THF·BH<sub>3</sub> have to be run at reflux in THF solution.<sup>[19]</sup> The different temperature dependence of the two types of reactions is consistent with the different reaction mechanisms. In the reaction of K with THF·BH<sub>3</sub>, the B<sub>3</sub>H<sub>9</sub><sup>2-</sup> intermediate (after TS4 in Figure 3) can be directly cleaved to B<sub>2</sub>H<sub>5</sub><sup>-</sup> and BH<sub>4</sub><sup>-</sup>. The B<sub>2</sub>H<sub>5</sub><sup>-</sup> intermediate then reacts directly with THF·BH<sub>3</sub> to form the final B<sub>3</sub>H<sub>8</sub><sup>-</sup> product. Over all steps, the highest energy barrier is 22.3 kcal mol<sup>-1</sup> (TS6). Thus the reaction can be carried out at room temperature, but not at low temperatures (Figure S13). The total reaction is exothermic by 98.2 kcal mol<sup>-1</sup>, and is thus irreversible. On the other hand, in the reaction of LiBH<sub>4</sub> with THF·BH<sub>3</sub> as reported recently,<sup>[19]</sup> a B<sub>3</sub>H<sub>10</sub><sup>-</sup> intermediate was suggested to be cleaved to B<sub>2</sub>H<sub>6</sub> and BH<sub>4</sub><sup>-</sup> first; then, dihydrogen interactions between a partially negatively charged H<sup>δ-</sup> in the BH<sub>4</sub><sup>-</sup> group and the partially positively charged bridging H<sup>δ+</sup> in the B<sub>2</sub>H<sub>6</sub> molecule lead to the formation of B<sub>2</sub>H<sub>5</sub><sup>-</sup> and (H<sub>2</sub>)BH<sub>3</sub>. Subsequently, one H<sub>2</sub> molecule is eliminated from (H<sub>2</sub>)BH<sub>3</sub>, and the resulting BH<sub>3</sub> group is combined with B<sub>2</sub>H<sub>5</sub><sup>-</sup> to form the final B<sub>3</sub>H<sub>8</sub><sup>-</sup> product. A high energy barrier (31.0 kcal mol<sup>-1</sup>)<sup>[19]</sup> was found in the dihydrogen interaction, so that this reaction can only take place under reflux with the release of H<sub>2</sub>.

The formation of the BH<sub>3</sub><sup>2-</sup> and B<sub>2</sub>H<sub>6</sub><sup>2-</sup> intermediates was previously monitored by <sup>11</sup>B NMR spectroscopy in the reaction of potassium naphthalide and B<sub>2</sub>H<sub>6</sub> in THF solution.<sup>[24]</sup> However, when we monitored the reaction of K with THF·BH<sub>3</sub> by <sup>11</sup>B NMR spectroscopy in the current study, we only observed the starting material THF·BH<sub>3</sub> and the product KB<sub>3</sub>H<sub>8</sub> (Figure S14). The other KBH<sub>4</sub> product is completely insoluble in THF, so that its NMR resonance was not detected but its formation was confirmed by X-ray diffraction (XDR; Figure S15). No intermediate signals were detected in the whole reaction. These observations suggested that the transformation from K(s) to solvated [K(THF)<sub>6</sub>]<sup>+</sup>, and at the same time, from THF·BH<sub>3</sub> to BH<sub>3</sub><sup>-</sup> and BH<sub>3</sub><sup>2-</sup>, is the rate-determining step, which is consistent with the theoretical results. Under the current conditions, THF·BH<sub>3</sub> is always present in excess, so that once BH<sub>3</sub><sup>-</sup> and BH<sub>3</sub><sup>2-</sup> have been formed they will be rapidly transformed into the next intermediate all the way to the final product because the energy barriers of all steps are low.

In the current mechanism, the influence of the different alkali metals on the reaction should mainly concern the first two steps, in which the alkali metals donate their valence electron to the BH<sub>3</sub> group to form BH<sub>3</sub><sup>2-</sup> (black part in Figure 2 and Scheme S1) while the energy profiles in the subsequent steps should be similar for the different alkali metals (blue part and black part in Figure 2, Figure 3, and Scheme S1). Thus we expected the different chemical activities of the alkali metals to be crucial to explain why pure Li and Na could not initiate the reaction. However, the computational results indicated that the free energy barriers of TS1 and TS2 for Li, Na, and K are similar (Table S2). It should be pointed out that the DFT calculations started from the gaseous alkali metal atoms, that is, an M(g) atom reacting with THF·BH<sub>3</sub> to form BH<sub>3</sub><sup>-</sup>, whereas in the experiment, the reaction started from solid metal. Thus, the sublimation energy of the alkali metals must be the key factor that determines whether the reaction proceeds or not. The high sublimation energies of Li (38.0 kcal mol<sup>-1</sup>) and Na (25.6 kcal mol<sup>-1</sup>; Table S3)<sup>[25]</sup> prevent the Li or Na atoms from escaping from the metal lattice to take part in the reaction. This conclusion is supported by the fact that Li/Hg and Na/Hg alloys can react with THF·BH<sub>3</sub> to form B<sub>3</sub>H<sub>8</sub><sup>-</sup>.<sup>[12,22]</sup>

Further evidence is provided by the fact that the reaction rate of K with THF·BH<sub>3</sub> is influenced by the size of the metal species. When potassium metal was cut to 5 × 5 × 5 mm<sup>3</sup>, the reaction time increased to 20 h, which is significantly longer than 12 h for a smaller piece of potassium (3 × 3 × 3 mm<sup>3</sup>), at room temperature. For a smaller particle with a larger surface area, the interaction of K with THF·BH<sub>3</sub> is enhanced, leading to the faster reaction. Both Rb and Cs have lower melting points than K. Under vigorous stirring, the metal pieces easily deform and seem to display fluid-like behavior. Thus the reactions of Rb and Cs with THF·BH<sub>3</sub> are much more vigorous, and the reaction times are much shorter.

In the literature, pure alkali metals have been reported to react with THF·BH<sub>3</sub> to afford MB<sub>3</sub>H<sub>8</sub> and MBH<sub>4</sub> (M = Na, K) in moderate yields only when they were adsorbed on silica gel at 160 °C, finely dispersed in inert salts by ball milling,<sup>[13,14]</sup> or present in the form of a liquid K/Na alloy.<sup>[15]</sup> Compared with

these previous methods, the current synthetic strategy using pure potassium metal with THF·BH<sub>3</sub> has several advantages. First, the reaction is carried out without using mercury or any other electron carriers, greatly simplifying the subsequent workup. Furthermore, the quantitative conversion and short reaction time make the reaction much more efficient. Finally, the solubility difference between KB<sub>3</sub>H<sub>8</sub> and KBH<sub>4</sub> allows these two compounds to be readily separated: KB<sub>3</sub>H<sub>8</sub> is soluble in THF while KBH<sub>4</sub> is almost insoluble in THF.

Unsolvated KB<sub>3</sub>H<sub>8</sub> is more stable than unsolvated NaB<sub>3</sub>H<sub>8</sub> in the solid state and in aqueous or THF solution (Figure S16).<sup>[26]</sup> Although NaB<sub>3</sub>H<sub>8</sub> is soluble in ethers,<sup>[12–14]</sup> strong solvation makes it difficult to be accurately weighed for further use.<sup>[2,27]</sup> Unsolvated NaB<sub>3</sub>H<sub>8</sub> can be obtained by dissolving the oily THF-solvated product in diethyl ether and dichloromethane, which will help to break the coordination between THF and the Na<sup>+</sup> cations to completely remove THF.<sup>[12–14]</sup> For KB<sub>3</sub>H<sub>8</sub>, the coordination bond between the THF molecule and the potassium cation is so weak that unsolvated KB<sub>3</sub>H<sub>8</sub> can be conveniently prepared. After the reaction of potassium and THF·BH<sub>3</sub> [Eq. (1)], the KBH<sub>4</sub> precipitate was removed by filtration, and the THF in the filtrate was removed under dynamic vacuum to produce THF-solvated KB<sub>3</sub>H<sub>8</sub> product. The addition of toluene to the THF-solvated product led to the precipitation of unsolvated KB<sub>3</sub>H<sub>8</sub>. With pure unsolvated KB<sub>3</sub>H<sub>8</sub> in hand, its structure was characterized by synchrotron X-ray powder diffraction (XRPD; see Figure S17 for the refinement profile). Most of the diffraction peaks can be indexed into a monoclinic unit cell in space group *P*2<sub>1</sub> (No. 4), with lattice parameters of *a* = 5.4804 Å, *b* = 8.2153 Å, *c* = 5.4926 Å, and β = 95.271°. Details of the structure solution can be found in the Supporting Information (Tables S4 and S5). Figure 4 shows bridging K–H bonds in the range of 2.849 to 3.112 Å. Each K cation coordinates to six B<sub>3</sub>H<sub>8</sub> anions with an overall K/B<sub>3</sub>H<sub>8</sub> ratio of 1:1. There are two types of asymmetric K–H bridges linked through each pair of K cation and B<sub>3</sub>H<sub>8</sub><sup>−</sup> anion to construct the 3D molecular structure. The obtained K–B distances are in the range of 3.175 to 3.457 Å, and slightly longer than the Na–B distances of 3.130–3.370 Å in the analogous structure of NaB<sub>3</sub>H<sub>8</sub>.<sup>[12]</sup>

In summary, we have shown that unsolvated MB<sub>3</sub>H<sub>8</sub> (M = K, Rb, and Cs) can be conveniently prepared by reactions of pure alkali metals with THF·BH<sub>3</sub> in THF in very high yield at room temperature without using toxic diborane, electron carriers, or other reaction media, such as mercury, silica gel, or inert salts. The structure of unsolvated KB<sub>3</sub>H<sub>8</sub> was further

determined by synchrotron X-ray powder diffraction. The mechanisms of the reactions were investigated both experimentally and theoretically. The relatively low energy barriers of all elementary steps in the proposed mechanism are consistent with the fact that the reaction can be carried out at room temperature, which is different from the reaction of LiBH<sub>4</sub>/NaBH<sub>4</sub> with THF·BH<sub>3</sub> under reflux. The physical properties of the alkali metals control the reactions. The high sublimation energies of Li and Na prevent them from reacting with THF·BH<sub>3</sub> to produce Li/NaB<sub>3</sub>H<sub>8</sub>. The low melting points of Rb and Cs lead to more vigorous reactions and higher reaction rates.

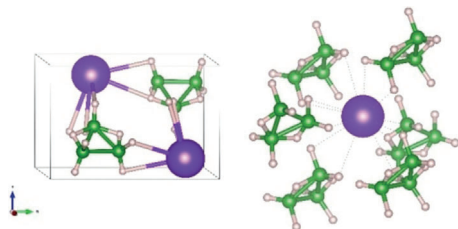
## Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (Grant Nos. U1804253 and 21771057), the Science and Technology Committee of Shanghai (17ZR1402500, 16520721800), and the U.S. National Science Foundation (DMR-1655066 to L.S.W.). Some of the experiments were conducted on the PD beamline, Australian Synchrotron (ANSTO).

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** alkali metals · boron · nucleophilicity · reaction mechanisms · X-ray diffraction



**Figure 4.** Crystal structure of KB<sub>3</sub>H<sub>8</sub> in a unit cell (left) and local coordination of a K cation with six B<sub>3</sub>H<sub>8</sub><sup>−</sup> anions (right). B green, H pink, K purple.

- [1] C. W. Yoon, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2009**, *131*, 855–864.
- [2] Z. Huang, X. Chen, T. Yisgedu, E. A. Meyers, S. G. Shore, J.-C. Zhao, *Inorg. Chem.* **2011**, *50*, 3738–3742.
- [3] G. Kodama, R. W. Parry, J. C. Carter, *J. Am. Chem. Soc.* **1959**, *81*, 3534–3538.
- [4] Z. Huang, M. Eagles, S. Porter, E. G. Sorte, B. Billet, R. L. Corey, M. S. Conradi, J.-C. Zhao, *Dalton Trans.* **2013**, *42*, 701–708.
- [5] D. Y. Kim, Y. Yang, J. Y. Abelson, G. S. Girolami, *Inorg. Chem.* **2007**, *46*, 9060–9066.
- [6] D. M. Goedde, G. S. Girolami, *J. Am. Chem. Soc.* **2004**, *126*, 12230–12231.
- [7] Y. N. Shevchenko, A. V. Fesenko, T. M. Nazarova, O. K. Biryukovich, K. B. Yatsimirskii, U. M. Ogenko, Y. N. Sleasarenko, S. V. Naprasnaya, E. I. Larikov, R. A. Svitsyn, *Otkrytiya Izobret. Prom. Obrabzty Tovarnye Znaki* **1984**, *31*, 78.
- [8] T. G. Hill, R. A. Godfroid, J. P. White, S. G. Shore, *Inorg. Chem.* **1991**, *30*, 2952–2954.
- [9] A. Stock, E. Kuss, *Chem. Ber.* **1923**, *56*, 789–808.
- [10] A. Stock, H. Laudenklos, *Z. Anorg. Allg. Chem.* **1936**, *228*, 178–192.
- [11] A. Stock, E. Pohland, *Chem. Ber.* **1926**, *59*, 2210–2215.
- [12] a) Z. Huang, G. King, X. Chen, J. Hoy, T. Yisgedu, H. K. Lingam, S. G. Shore, P. M. Woodward, J.-C. Zhao, *Inorg. Chem.* **2010**, *49*, 8185–8187; b) M. Chong, M. Matsuo, S. Orimo, T. Autrey, C. M. Jensen, *Inorg. Chem.* **2015**, *54*, 4120–4125; c) M. Chong, A.



- Karkamkar, T. Autrey, S. Orimo, S. Jalisatgi, C. M. Jensen, *Chem. Commun.* **2011**, 47, 1330–1332.
- [13] a) A. C. Dunbar, J. A. Macor, G. S. Girolami, *Inorg. Chem.* **2014**, 53, 822–826; b) M. Büchner, A. M. T. Erle, H. Scherer, I. Krossing, *Chem. Eur. J.* **2012**, 18, 2254–2262; c) O. Palumbo, P. Nguyen, C. M. Jensen, A. Paolone, *Int. J. Hydrogen Energy* **2016**, 41, 5986–5993.
- [14] W. Chen, G. Wu, T. He, Z. Li, Z. Guo, H. Liu, Z. Huang, P. Chen, *Int. J. Hydrogen Energy* **2016**, 41, 15471–15476.
- [15] X. Zheng, Y. Yang, F. Zhao, F. Fang, Y. Guo, *Chem. Commun.* **2017**, 53, 11083–11086.
- [16] J. Huang, Y. Yan, A. Remhof, Y. Zhang, D. Rentsch, Y. S. Au, P. E. Jongh, F. Cuevas, L. Ouyang, M. Zhu, A. Züttel, *Dalton Trans.* **2016**, 45, 3687–3690.
- [17] D. F. Gaines, R. Schaeffer, F. Tebbe, *Inorg. Chem.* **1963**, 2, 526–528.
- [18] J. K. Olson, A. I. Boldyrev, *Comput. Theor. Chem.* **2011**, 967, 1–4.
- [19] a) X.-M. Chen, N. Ma, Q.-F. Zhang, J. Wang, X. Feng, C. Wei, L.-S. Wang, J. Zhang, X. Chen, *J. Am. Chem. Soc.* **2018**, 140, 6718–6726; b) Q. Zhao, R. D. Dewhurst, H. Braunschweig, X. Chen, *Angew. Chem. Int. Ed.* **2019**, <https://doi.org/10.1002/anie.201809733>; *Angew. Chem.* **2019**, <https://doi.org/10.1002/ange.201809733>.
- [20] R. Moury, A. Gigante, H. Hagemann, *Int. J. Hydrogen Energy* **2017**, 42, 22417–22421.
- [21] A. Yu. Bykov, K. Yu. Zhizhin, N. T. Kuznetsov, *Russ. J. Inorg. Chem.* **2014**, 59, 1539–1555.
- [22] H. Fu, X. Wang, Y. Shao, J. Chen, X. Zhang, H. Fu, J. Zheng, X. Li, *Int. J. Hydrogen Energy* **2016**, 41, 384–391.
- [23] M. J. Frisch et al., Gaussian09, Revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.
- [24] R. A. Godfroid, T. G. Hill, T. P. Onak, S. G. Shore, *J. Am. Chem. Soc.* **1994**, 116, 12107–12108.
- [25] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nutall, *J. Phys. Chem. Ref. Data* **1982**, 11, Supplement No. 2.
- [26] S. Pylypko, A. Zadick, M. Chatenet, P. Miele, M. Cretin, U. B. Demirci, *J. Power Sources* **2015**, 286, 10–17.
- [27] G. Kodama, R. W. Parry, *J. Am. Chem. Soc.* **1960**, 82, 6250–6255.
- Manuscript received: November 7, 2018  
Accepted manuscript online: January 21, 2019  
Version of record online: ■■■■■, ■■■■■

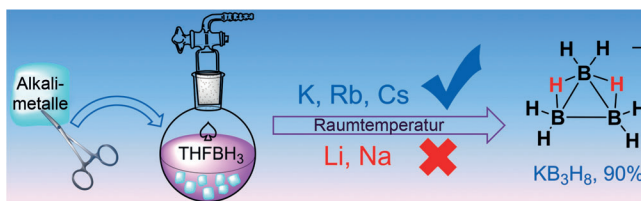
## Zuschriften



## Alkalimetallsalze

X.-M. Chen, N. Ma, R.-X. Liu, C. Wei,  
C.-C. Cui, B.-L. Cao, Y. Guo,\* L. S. Wang,\*  
Q. Gu, X. Chen\* ———— ■■■■-■■■■

Facile Synthesis of Unsolvated Alkali  
Metal Octahydrotriborate Salts  $\text{MB}_3\text{H}_8$   
( $\text{M} = \text{K}, \text{Rb}$ , and  $\text{Cs}$ ), Mechanisms of  
Formation, and the Crystal Structure of  
 $\text{KB}_3\text{H}_8$



**Unsolvatisierte  $\text{MB}_3\text{H}_8$ -Salze** ( $\text{M} = \text{K}, \text{Rb}$  und  $\text{Cs}$ ) wurden ausgehend von den entsprechenden reinen Alkalimetallen und  $\text{THF} \cdot \text{BH}_3$  in hoher Ausbeute bei Raumtemperatur synthetisiert, und die Struktur von unsolvatisiertem  $\text{KB}_3\text{H}_8$

wurde aufgeklärt. Die vorgeschlagenen Reaktionsmechanismen basieren auf experimentellen und theoretischen Untersuchungen. Die physikalischen Eigenschaften der Alkalimetalle spielen hierbei eine entscheidende Rolle.