Supporting Information

The interconversion between THF-B₃H₇ and B₃H₈⁻: an efficient synthetic method for MB₃H₈ (M = Li and Na)

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Scheme S1 The reaction of MBH₄ (M = Li, Na) with THF·B₃H₇. .................................................................................. S15

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1. Experimental Section:


All manipulations were carried out on a Schlenk line or in a glovebox filled with high purity nitrogen. The $^{11}$B NMR spectra were recorded using either a 128 MHz or a 193 MHz spectrometer and externally referenced to BF$_3$·OEt$_2$ in C$_6$D$_6$ (δ = 0.00 ppm). The $^1$H NMR spectra was recorded using either a 400 MHz or a 600 MHz spectrometer. X-ray diffraction (XRD) data were obtained with a Rigaku D/max 2500 diffractometer using Cu/Kα radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA. IR spectra were measured by a Spectrum 400F.

The THF·BH$_3$ tetrahydrofuran (THF) solution, HCl diethyl ether solution, and ammonia borane (NH$_3$BH$_3$) were purchased from United Boron (Zhengzhou) Energy Materials S&T LLC and used as received. K, LiH, NaH, LiBH$_4$, NaBH$_4$, NH$_4$Cl and N(C$_4$H$_9$)$_4$Br were purchased from Sinopharm Chemical Reagents Co., Ltd. NH$_4$Cl was recrystallized from methanol and NBu$_4$Br was recrystallized from tetrahydrofuran (THF). Dichloromethane was dried over calcium hydride, THF and toluene were dried over sodium and freshly distilled prior to use. LiNH$_2$BH$_3$ and NaNH$_2$BH$_3$ were prepared according the literature methods.$^{51}

1.2. Reaction of KB$_3$H$_8$ with HCl.

A solution of KB$_3$H$_8$ (0.40 g, 5 mmol) in 25 mL of THF was added to a 50 mL flask. A solution of 1 M HCl in diethyl ether (5 mL, 5 mmol) was added dropwisely to the flask at room temperature and stirred for 20 min. After KCl was filtered (Fig. S1), the solution of THF·B$_3$H$_7$ was obtained. $^{11}$B NMR (128 MHz, THF): δ -8.23 (br, 2B of BHB), -12.99 (br, BH$_2$) ppm (Fig. 1).

In another batch of reaction, KB$_3$H$_8$ (0.40 g, 5 mmol) was added to a 100 mL flask and then 25 mL of THF was condensed. A solution of 1 M HCl in diethyl ether (5 mL, 5 mmol) was added dropwisely to the flask at room temperature and stirred for 20 min. The $^{11}$B NMR showed the formation of B$_3$H$_7$ (Fig. 2b). Then 5 mL, 10 mL, 15 mL of 1 M HCl diethyl ether solution was added dropwisely to above reaction mixture in turn. Reaction mixture was stirring for 20 min after each addition of HCl and then monitored by $^{11}$B NMR. The results are listed in Fig. 2c, d, and e.

1.3. Reaction of THF·B$_3$H$_7$ with LiNH$_2$BH$_3$.

A THF·B$_3$H$_7$ solution (30 mL, 5 mmol) and LiNH$_2$BH$_3$ (0.19 g, 5 mmol) were added to a 50 mL flask. The mixture was stirred for 20 min at room temperature. The formed precipitate was filtered and dried under dynamic vacuum to give the [NH$_2$BH$_3$]$_n$ white product, which was confirmed by XRD and IR (Figs. S2 and S3). Removal of THF from the filtrate under dynamic vacuum to give
Li(THF)$_{1.5}$B$_3$H$_8$ as a clear oily product (0.64 g, 82%). $^{11}$B NMR (193 MHz, CD$_3$CN): $\delta$ -30.8 (nonet, $J$ = 33 Hz) ppm. $^1$H NMR (600 MHz, CD$_3$CN): $\delta$ 3.64 ($m$, 4$\alpha$-H of THF), 1.79 ($m$, 4$\beta$-H of THF), 0.14 ($dectet$, $J$ = 33 Hz, 8H of B$_3$H$_8$) ppm. $^1$H{[$^{11}$B]} (600 MHz, CD$_3$CN): $\delta$ 3.65 ($m$, 4$\alpha$-H of THF), 1.80 ($m$, 4$\beta$-H of THF), 0.14 ($s$, 8H of B$_3$H$_8$) ppm (Figs. S4, S5 and S6). [NH$_2$BH$_2$]$_n$: IR (cm$^{-1}$): 3300 (s, br), 3248 (w), 2398 (s, br), 1560 (s), 1405 (s), 1209 (s, br), 1081 (m), 846 (w), 708 (w).  

1.4 Reaction of THF·B$_3$H$_7$ with NaNH$_2$BH$_3$.

A THF·B$_3$H$_7$ (30 mL, 5 mmol) solution and NaNH$_2$BH$_3$ (0.27 g, 5 mmol) were added to a 50 mL flask. The reaction was stirred for 30 min at room temperature. The formed precipitate was filtered. Then THF in the filtrate was pumped to give an oily product, which was dissolved in 20 mL CH$_2$Cl$_2$ and converted into suspension under stirring. After filtration, the solid was dried under dynamic vacuum, unsolvated NaB$_3$H$_8$ was obtained (0.24 g, 76%). NaB$_3$H$_8$: $^{11}$B NMR (193 MHz, CD$_3$CN): $\delta$ -30.0 (nonet, $J$ = 33 Hz) ppm. $^1$H NMR (600 MHz, CD$_3$CN): $\delta$ 0.14 ($dectet$, $J$ = 33 Hz) ppm (Figs. S7 and S8).

1.5. Reaction of THF·B$_3$H$_7$ with LiBH$_4$.

In a 50 mL flask, LiBH$_4$ (0.11 g, 5 mmol) was added and then THF·B$_3$H$_7$ (30 mL, 5 mmol) was injected. The reaction was stirred 1 h at room temperature, B$_3$H$_7$ was completely consumed and the formed B$_3$H$_8^-$ and BH$_3$ signals, and a small amount of BH$_4^-$ signal were observed in $^{11}$B NMR (Fig. S9). The THF solvent and the formed THF·BH$_3$ solution was removed under dynamic vaccum to produce a sticky solid, into which 20 mL of THF was added and then 20 $\mu$L of H$_2$O was injected. After stirring 10 min, a small amount of precipitate was formed which was filtered. Removal of THF from the filtrate produced Li(THF)$_{1.5}$B$_3$H$_8$ as a clear oily product (0.61 g, 79%). $^{11}$B NMR (128 MHz, CD$_3$CN): $\delta$ -31.2 (nonet, $J$ = 33 Hz) ppm. $^1$H NMR (600 MHz, CD$_3$CN): $\delta$ 3.64 ($m$, 4$\alpha$-H of THF), 1.80 ($m$, 4$\beta$-H of THF), 0.14 ($dectet$, $J$ = 33 Hz, 8H of B$_3$H$_8$) ppm (Figs. S10 and S11).

1.6. Reaction of THF·B$_3$H$_7$ with NaBH$_4$.

In a 50 mL flask, NaBH$_4$ (0.19 g, 5 mmol) was added and then THF·B$_3$H$_7$ (30 mL, 5 mmol) was injected. The reaction was stirred for 12 h at room temperature, B$_3$H$_7$ was completely consumed and the formed B$_3$H$_8^-$ and BH$_3$ signals, and a small amount of BH$_4^-$ signal were observed in the $^{11}$B NMR (Fig. S12). The formed THF·BH$_3$ and the THF solvent were removed under dynamic vacuum to produce a sticky solid, into which 20 mL of THF was added and then 30 $\mu$L H$_2$O was injected. After stirring 50 min, a small amount of precipitate was formed which was filtered. Removal of THF from the filtrate produced an oily product. The oily product was dissolved in 20 mL CH$_2$Cl$_2$ to convert into
suspension under stirring. After filtration, the solid was dried under dynamic vacuum to produce unsolvated NaB$_3$H$_8$ (0.23 g, 73%).

1.7. Synthesis of NH$_4$B$_3$H$_8$.

The prepared unsolvated KB$_3$H$_8$ (0.80 g, 10 mmol) and NH$_4$Cl (0.54 g, 10 mmol) were added into a 50 mL Schlenk flask and then 30 mL liquid ammonia was condensed at -78 °C. After 50 min stirring, ammonia was removed and the flask was warmed to room temperature. The prepared NH$_4$B$_3$H$_8$ was extracted using dry THF. The KCl residue was washed with THF (3 × 10 mL), which was confirmed by XRD (Fig. S13). The combined filtrate and the wash solution was then evaporated to produce a white solid, which was dried under dynamic vacuum to give the NH$_4$B$_3$H$_8$ white powder (0.57 g, 96%). $^{11}$B NMR (193 MHz, CD$_3$CN): $\delta$ -30.6 (nonet, $J = 33$ Hz) ppm (Fig. S14). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 5.85 (s, 4H of NH$_4$), 0.14 (deacet, $J = 33$ Hz, 8H of B$_3$H$_8$) ppm (Fig. S15).

1.8. Synthesis of NBu$_4$B$_3$H$_8$.

The prepared unsolvated KB$_3$H$_8$ (0.80 g, 10 mmol) and NBu$_4$Br (3.22 g, 10 mmol) were added into a 50 mL flask and then 30 mL of THF was condensed. After the reaction mixture stirring for 6 hours at room temperature, the reaction solution was filtered and the KBr frit was washed with THF (3 × 10 mL), which was confirmed by XRD (Fig. S16). The filtrate was evaporated to produce a sticky solid, which was washed with diethyl ether (3 × 30 mL) and dried under vacuum to give a free-flowing NBu$_4$B$_3$H$_8$ white powder (2.69 g, 95%). $^{11}$B NMR (193 MHz, CD$_3$CN): $\delta$ -31.4 (nonet, $J = 33$ Hz) ppm (Fig. S17). $^1$H NMR (600 MHz, CD$_3$CN): $\delta$ 3.09 (t, 2H of CH$_2$), 1.58 (m, 2H of CH$_2$), 1.35 (m, 2H of CH$_2$), 0.97 ($t, J = 7$ Hz, 3H of CH$_3$), 0.14 (deacet, $J = 33$ Hz, 8H of B$_3$H$_8$) ppm (Fig. S18).
2. Supporting Results:

Fig. S1 X-ray powder diffraction data of KCl.

Fig. S2 X-ray powder diffraction data of the formed [NH₂BH₂]ₙ.
Fig. S3 IR spectrum of the formed \([\text{NH}_2\text{BH}_2]_n\).

Fig. S4 \(^{11}\text{B}\) NMR spectrum of the prepared Li(THF)\(_{1.5}\)B\(_3\)H\(_8\) in CD\(_3\)CN.
**Fig. S5** $^1$H spectrum of the prepared Li(THF)$_{1.5}$B$_3$H$_8$ in CD$_3$CN.

**Fig. S6** $^1$H{$^11$B} spectrum of the prepared Li(THF)$_{1.5}$B$_3$H$_8$ in CD$_3$CN.
Fig. S7 $^{11}$B NMR spectrum of the prepared unsolvated NaB$_3$H$_8$ in CD$_3$CN.

Fig. S8 $^1$H NMR spectrum of the prepared unsolvated NaB$_3$H$_8$ in CD$_3$CN.
**Fig. S9** $^{11}$B NMR spectrum of the reaction solution of LiBH$_4$ and THF·B$_3$H$_7$ in THF at room temperature.

**Fig. S10** $^{11}$B NMR spectrum of the prepared Li(THF)$_{1.5}$B$_3$H$_8$ in CD$_3$CN.
Fig. S11 $^1$H NMR spectrum of the prepared Li(THF)$_{1.5}$B$_3$H$_8$ in CD$_3$CN.

Fig. S12 $^{11}$B NMR spectrum of the reaction solution of NaBH$_4$ and THF·B$_3$H$_7$ in THF at room temperature.
**Fig. S13** X-ray powder diffraction data of the formed KCl.

**Fig. S14** $^{11}$B NMR spectrum of the prepared NH$_4$B$_3$H$_8$ in CD$_3$CN.
**Fig. S15** $^1$H NMR spectrum of the prepared NH$_4$B$_3$H$_8$ in CD$_3$CN.

**Fig. S16** X-ray powder diffraction data of the formed KBr.
Fig. S17 $^{11}$B NMR spectrum of the prepared NBu$_4$B$_3$H$_8$ in CD$_3$CN.

Fig. S18 $^1$H NMR spectrum of the prepared NBu$_4$B$_3$H$_8$ in CD$_3$CN.
3. Supporting Scheme:

Scheme S1 The reaction of MBH₄ (M = Li, Na) with THF·B₃H₇.

4. References: