Supporting Information

An improved method for the synthesis and formation mechanism of $\text{M}_2\text{B}_{10}\text{H}_{14}$ based on the reactions of $\text{B}_{10}\text{H}_{14}$ with $\text{MNH}_2\text{BH}_3$ ($\text{M} = \text{Na, K}$)

Xi-Meng Chen, a Xing-Chao Yu, a Jing-Xian Chi, a Yi Jing, b Hongju Wang, c Na Zhang, a Chen Zhang, a Yi-Wen Ge, a and Xuenian Chen*a,b

aSchool of Chemistry and Chemical Engineering, Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, Henan Normal University, Xinxiang, Henan 453007, China

bCollege of Chemistry, Zhengzhou University, Zhengzhou, Henan 450001, China

cSchool of Environment, Henan Normal University, Xinxiang, Henan 453007, China
1. Experimental section:

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

B$_{10}$H$_{14}$ was used as received. NaH and KH was washed with tetrahydrofuran (THF) and n-hexane and then dried in vacuo. NaNH$_2$BH$_3$, KNH$_2$BH$_3$, NaB$_{10}$H$_{13}$, and NaB$_{10}$H$_{15}$ were prepared according to the literature methods.$^{1-3}$ All solvents were distilled from standard drying agents and degassed before use.

1.2. Synthesis of Na$_2$B$_{10}$H$_{14}$. B$_{10}$H$_{14}$ (0.73 g, 6 mmol) and NaNH$_2$BH$_3$ (0.63 g, 12 mmol) were added to a 100 mL Schlenk flask. The flask was connected to a Schlenk line and 50 mL THF was injected. The reaction solution was stirred at room temperature for 30 min. During this time, a small amount of [NH$_2$BH$_2$]$_n$ precipitate was formed and then filtered out (Fig. S1). Then, 1,4-dioxane was added to the filtrate and formed a white precipitate Na$_2$(C$_4$H$_8$O$_2$)$_x$B$_{10}$H$_{14}$ (Fig. S2). After filtration, THF and 1,4-dioxane were removed from the filtrate under a dynamic vacuum to leave a white powder containing the formed NH$_3$BH$_3$ (Fig. S3). And then, the precipitate Na$_2$(C$_4$H$_8$O$_2$)$_x$B$_{10}$H$_{14}$ was washed with CH$_2$Cl$_2$ (3 × 20 mL) and then dried under vacuum to yield a white powder product Na$_2$B$_{10}$H$_{14}$ (0.84 g, 83%). $^{11}$B NMR (193 MHz, (CD$_3$)$_2$SO): $\delta$ $-$7.5 ($d, J = 126$ Hz), $-$22.1 ($d, J = 122$ Hz), $-$34.2 ($t, J = 112$ Hz), $-$40.8 ($d, J = 129$ Hz) ppm (Fig. 2a). $^{11}$B{$^1$H} NMR (193 MHz, (CD$_3$)$_2$SO): $\delta$ $-$7.5 ($s$), $-$22.1 ($s$), $-$34.2 ($s$), $-$40.8 ($s$) ppm (Fig. 2b). $^1$H NMR (600 MHz, (CD$_3$)$_2$SO): $\delta$ 1.44 ($m, 2$H), 0.68 ($m, 4$H), 0.47 ($m, 4$H), $-$2.03 ($m, 2$H), $-$4.96 ($br, 2$H) ppm (Fig. 3a). $^1$H{$^{11}$B} NMR (600 MHz, (CD$_3$)$_2$SO): $\delta$ 1.44 ($s, 2$H), 0.68 ($s, 4$H), 0.47 ($s, 4$H), $-$2.03 ($s, 2$H), $-$4.96 ($s, 2$H) ppm (Fig. 3b). IR: 2520 (m), 2478 (m), 2425 (s), 2369 (s), 2332 (m), 2134 (w), 2034 (w), 1760 (w), 1678 (w), 1534 (w), 1438 (w), 1350 (w), 1250 (w), 1150 (w), 1040 (w) cm$^{-1}$.
1.3. Synthesis of $K_2B_{10}H_{14}$. $B_{10}H_{14}$ (0.73 g, 6 mmol) and $\text{KNH}_2\text{BH}_3$ (0.83 g, 12 mmol) were added to a 100 mL Schlenk flask. The flask was connected to a Schlenk line and 50 mL THF was injected. The reaction solution was stirred at room temperature for 12 hours. During this time, a large amount of white precipitate ($K_2B_{10}H_{14}$ and $[\text{NH}_2\text{BH}_2]_n$) was formed. After the reaction, the reaction solution was examined by $^{11}$B NMR ($\text{NH}_3\text{BH}_3$, Fig. S6) and then a small amount of water (2 mL) was injected into the solution to destroy the formed $[\text{NH}_2\text{BH}_2]_n$. After filtration, the precipitate $K_2B_{10}H_{14}$ was washed with THF ($3 \times 30$ mL) and then dried under vacuum to yield a white powder product $K_2B_{10}H_{14}$ (1.07 g, 89%). $^{11}$B NMR (193 MHz, (CD$_3$)$_2$SO): $\delta$ −7.5 ($d, J = 126$ Hz), −22.1 ($d, J = 117$ Hz), −34.2 ($t, J = 105$ Hz), −40.9 ($d, J = 129$ Hz) ppm (Fig. S7a). $^{11}$B{$^1$H} NMR (193 MHz, (CD$_3$)$_2$SO): $\delta$ −7.5 ($s$), −22.1 ($s$), −34.2 ($s$), −40.9 ($s$) ppm (Fig. S7b). $^1$H NMR (600 MHz, (CD$_3$)$_2$SO): $\delta$ 1.44 ($m, 2H$), 0.68 ($m, 4H$), 0.49 ($m, 4H$), −2.03 ($m, 2H$), −4.97 ($br, 2H$) ppm (Fig. S8a). $^1$H{$^{11}$B} NMR (600 MHz, (CD$_3$)$_2$SO): $\delta$ 1.44 ($s, 2H$), 0.68 ($s, 4H$), 0.49 ($s, 4H$), −2.03 ($s, 2H$), −4.97 ($s, 2H$) ppm (Fig. S8b). IR: 2521 (s), 2481 (s), 2274 (w), 2200 (w), 1411 (w), 1116 (w), 1027 (m), 928 (w), 718 (w) (Fig. S9).

1.4. The reaction of $B_{10}H_{14}$ with 1 equiv. of $\text{NaNH}_2\text{BH}_3$. $B_{10}H_{14}$ (0.24 g, 2 mmol) and $\text{NaNH}_2\text{BH}_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 10 min and then was examined by $^{11}$B NMR spectroscopy (Fig. S10).

1.5. The reaction of $\text{NaB}_{10}H_{13}$ with 1 equiv. of $\text{NaNH}_2\text{BH}_3$. The as-synthesized $\text{NaB}_{10}H_{13}$ (0.29 g, 2 mmol) and $\text{NaNH}_2\text{BH}_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 30 min and then was examined by $^{11}$B NMR spectroscopy (Fig. S11).
1.6. The reaction of NaB$_{10}$H$_{15}$ with 1 equiv. of NaNH$_2$BH$_3$. The as-synthesized NaB$_{10}$H$_{15}$ (0.29 g, 2 mmol) and NaNH$_2$BH$_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 30 min and then was examined by $^{11}$B NMR spectroscopy (Fig. S12).

1.7. The reaction of B$_{10}$H$_{14}$ with 0.5 equiv. of NaNH$_2$BH$_3$. B$_{10}$H$_{14}$ (0.24 g, 2 mmol) and NaNH$_2$BH$_3$ (0.05 g, 1 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 1 hour and then was examined by $^{11}$B NMR spectroscopy (Fig. S13). After filtration, THF was removed from the filtrate under dynamic vacuum to leave an oily product, which was washed with methylbenzene (2 × 30 mL), and then dried under vacuum to yield a white powder product NaB$_{10}$H$_{15}$ which was not very pure (Fig. S14).

2. Supporting results:

![IR spectrum of the formed $[\text{NH}_2\text{BH}_2]_n$ in the reaction of B$_{10}$H$_{14}$ with 2 equiv. of NaNH$_2$BH$_3$.](image_url)

Fig. S1 IR spectrum of the formed $[\text{NH}_2\text{BH}_2]_n$ in the reaction of B$_{10}$H$_{14}$ with 2 equiv. of NaNH$_2$BH$_3$. 
Fig. S2 $^1$H NMR (a) and $^1$H{$^{11}$B} NMR (b) spectra of the 1,4-dioxane-solvated Na$_2$(C$_4$H$_8$O$_2$)$_x$B$_{10}$H$_{14}$ in (CD$_3$)$_2$SO.

Fig. S3 X-ray powder diffraction data of the formed NH$_3$BH$_3$ (*) in the reaction of B$_{10}$H$_{14}$ with 2 equiv. of NaNH$_2$BH$_3$. 

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Fig. S4 The integration of the $^{11}$B NMR spectrum of the prepared Na$_2$B$_{10}$H$_{14}$ in (CD$_3$)$_2$SO.

Fig. S5 The integration of the $^1$H_{($^{11}$B)} NMR spectrum of the prepared Na$_2$B$_{10}$H$_{14}$ in (CD$_3$)$_2$SO.
**Fig. S6** $^{11}$B NMR spectrum of the formed NH$_3$BH$_3$ in the reaction of B$_{10}$H$_{14}$ with 2 equiv. of KNH$_2$BH$_3$.

**Fig. S7** $^{11}$B NMR (a) and $^{11}$B{${}^1$H} NMR (b) spectra of the prepared K$_2$B$_{10}$H$_{14}$ in (CD$_3$)$_2$SO.
Fig. S8 $^1$H NMR (a) and $^1$H$\{(^{11}B)}$ NMR (b) spectra of the prepared K$_2$B$_{10}$H$_{14}$ in (CD$_3$)$_2$SO.

Fig. S9 IR spectrum of the prepared K$_2$B$_{10}$H$_{14}$. 
**Fig. S10** $^{11}$B NMR spectrum of the reaction solution of B$_{10}$H$_{14}$ with 1 equiv. of NaNH$_2$BH$_3$.

**Fig. S11** $^{11}$B NMR spectrum of the reaction solution of NaB$_{10}$H$_{13}$ with 1 equiv. of NaNH$_2$BH$_3$. 
**Fig. S12** $^{11}$B NMR spectrum of the reaction solution of NaB$_{10}$H$_{15}$ with 1 equiv. of NaNH$_2$BH$_3$.

**Fig. S13** $^{11}$B NMR spectrum of the reaction solution of B$_{10}$H$_{14}$ with 0.5 equiv. of NaNH$_2$BH$_3$. 
Fig. S14 $^{11}$B NMR spectrum of the isolated NaB$_{10}$H$_{15}$ which is not very pure.

Fig. S15 IR spectrum of the prepared Na$_2$B$_{10}$H$_{14}$. 
3. References

