

# Supporting Information

## 1-Methyl Boratabenzene Yttrium Alkyl: A Highly Active Catalyst for Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$

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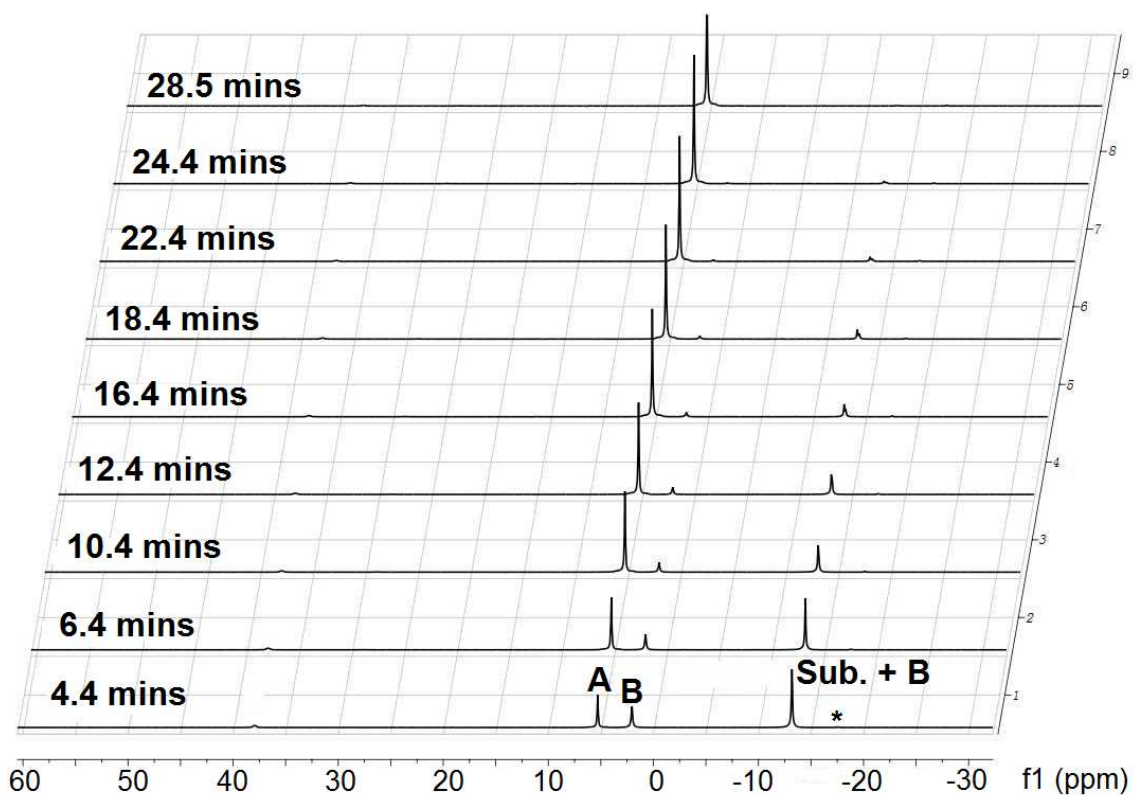
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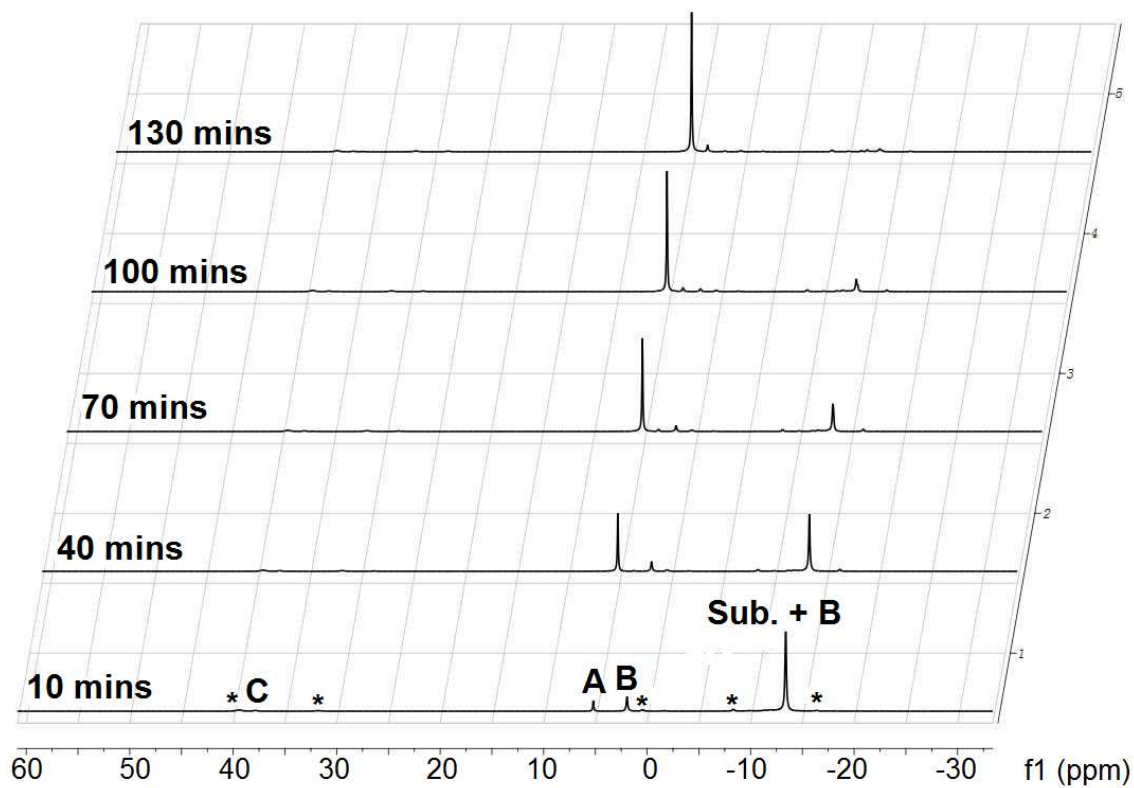
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**General.** All operations were carried out under an atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. C<sub>6</sub>D<sub>6</sub> was dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. Me<sub>2</sub>NH·BH<sub>3</sub> was purchased from Aldrich, sublimed at ambient temperature for three times, and stored in the glovebox at -35 °C. <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer at 128 MHz, and the boron chemical shifts were reported in δ units with reference to external BF<sub>3</sub>·OEt<sub>2</sub>. Boratabenzene rare-earth metal alkyls (**1-4**),<sup>1</sup> rare-earth metal trialkyls (**5-7**),<sup>2</sup> bis(cyclopentadienyl) yttrium alkyl (**8**),<sup>1</sup> and mono(indenyl) yttrium dialkyl (**9**)<sup>3</sup> were prepared according to the published procedures.

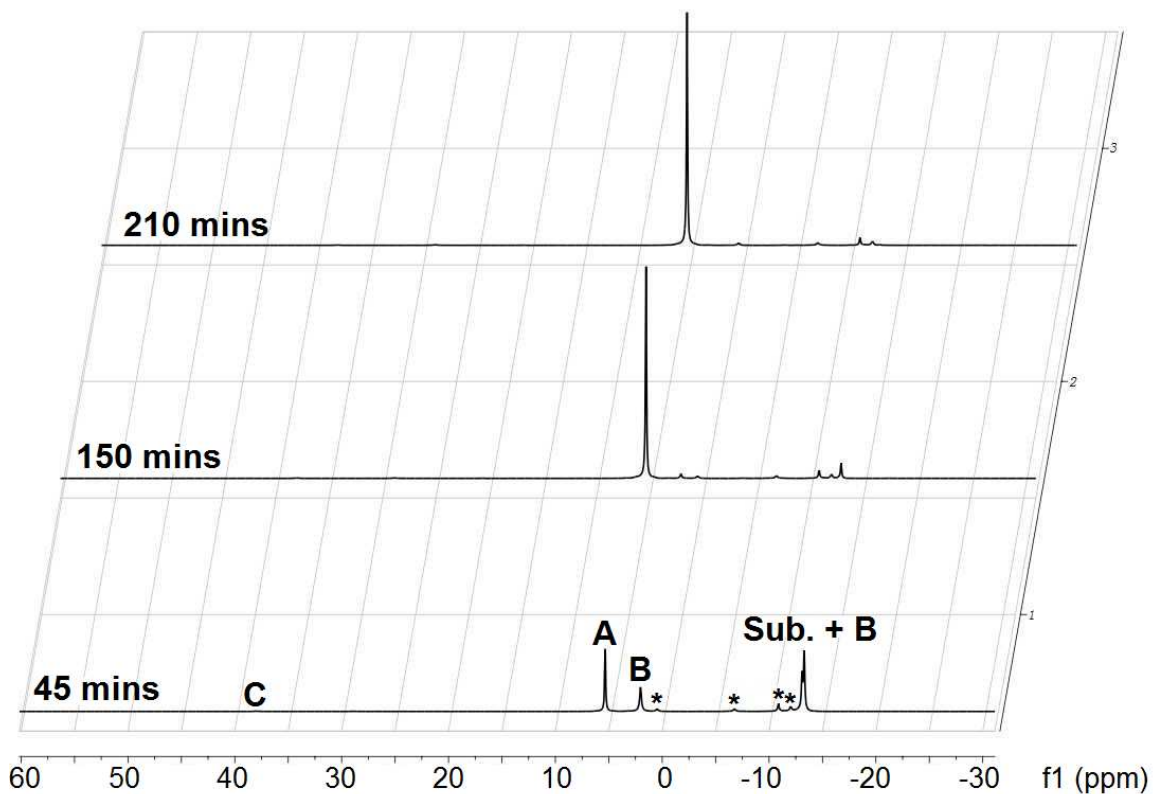
**General procedure of NMR experiments.** Rare-earth metal complex ( $1.7 \times 10^{-3}$  mmol for **1**,  $3.4 \times 10^{-3}$  mmol for **3** and **8**,  $1.7 \times 10^{-2}$  mmol for **2**, **4-7**, and **9**) and Me<sub>2</sub>NH·BH<sub>3</sub> (20 mg, 0.34 mmol) were mixed in 0.5 mL of C<sub>6</sub>D<sub>6</sub> and transferred into a J. Young NMR tube in a glovebox. In all reactions, the initial concentration of substrate is 0.68 M. The mixed reaction solution was immediately frozen in liquid N<sub>2</sub>, and was defrosted just before being inserted into the probe of the Bruker DXP 400 MHz spectrometer, which had been previously set to 50±0.1 °C. The concentrations of **A**, **B** and **Sub.** were obtained from the areas of the signals at 5.1 ppm (for **A**), 2.0 ppm (for **B**) and -13.2 ppm ( $I_{\text{Sub.}} = I_{-13.2 \text{ ppm}} - I_{2.0 \text{ ppm}}$ ).  $I_{\text{Sub.}}$  is the integration area for substrate,  $I_{-13.2 \text{ ppm}}$  is the total integration area for peak at -13.2 ppm,  $I_{2.0 \text{ ppm}}$  is the integration area for peak at 2.0 ppm), respectively. TopSpin<sup>TM</sup> and MestReNova<sup>TM</sup> NMR software package (Version 6.0.3) were used to process the spectrum and obtain accurate integrations. No color change and no precipitate were observed during the reaction.



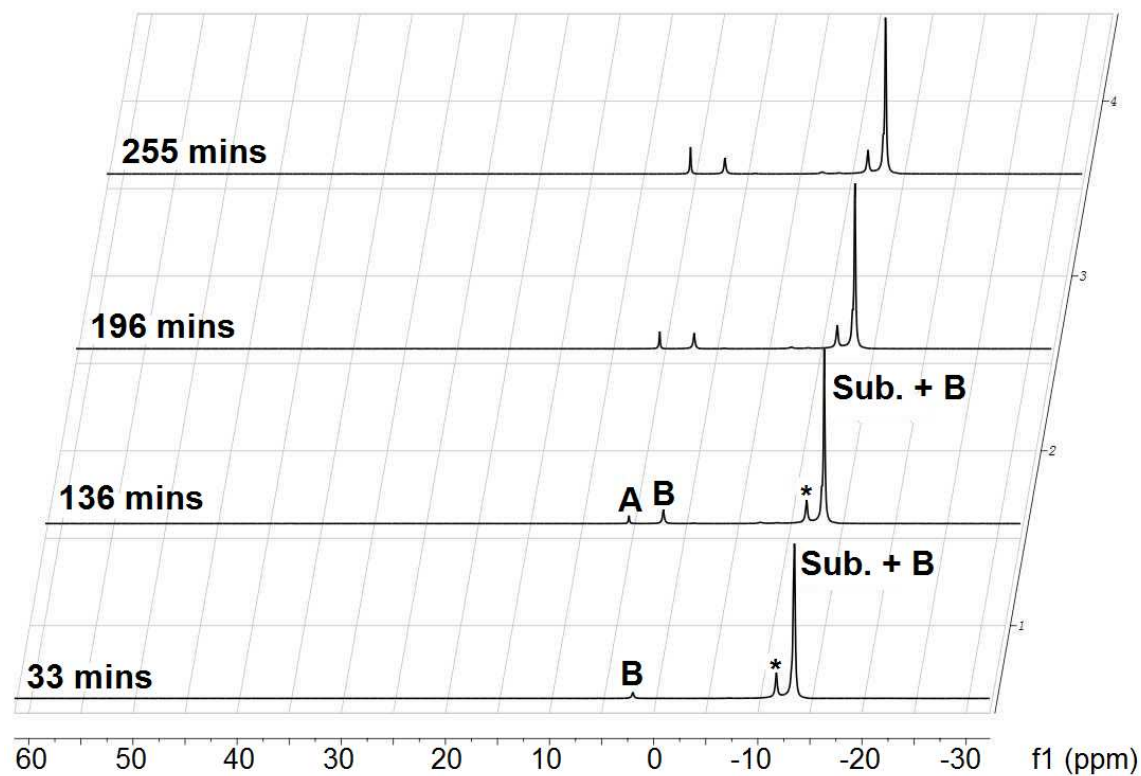
**Figure S1.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 1.0 mol% of **3**. Conditions:  $[\text{Sub.}]_0 = 0.68 \text{ mol/L}$ ,  $\text{C}_6\text{D}_6$  as the solvent,  $50^\circ\text{C}$ . **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



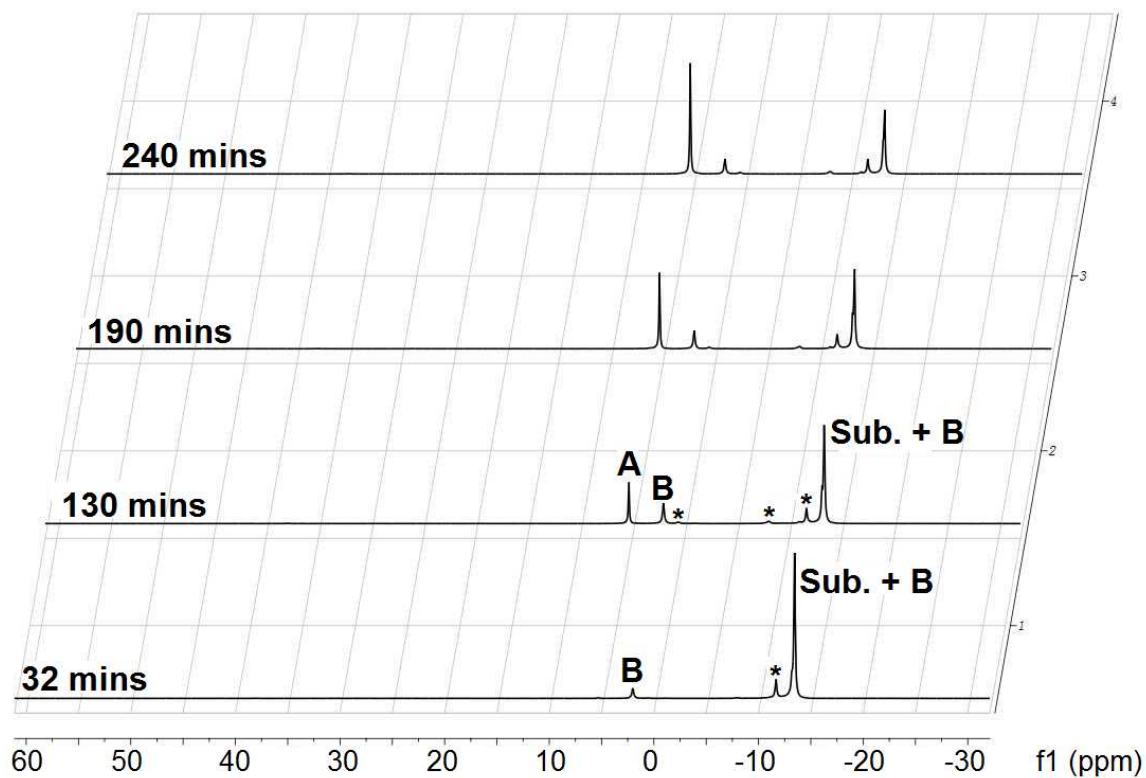
**Figure S2.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 5.0 mol% of **4**. Conditions:  $[\text{Sub.}]_0 = 0.68$  mol/L,  $\text{C}_6\text{D}_6$  as the solvent, 50 °C. **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



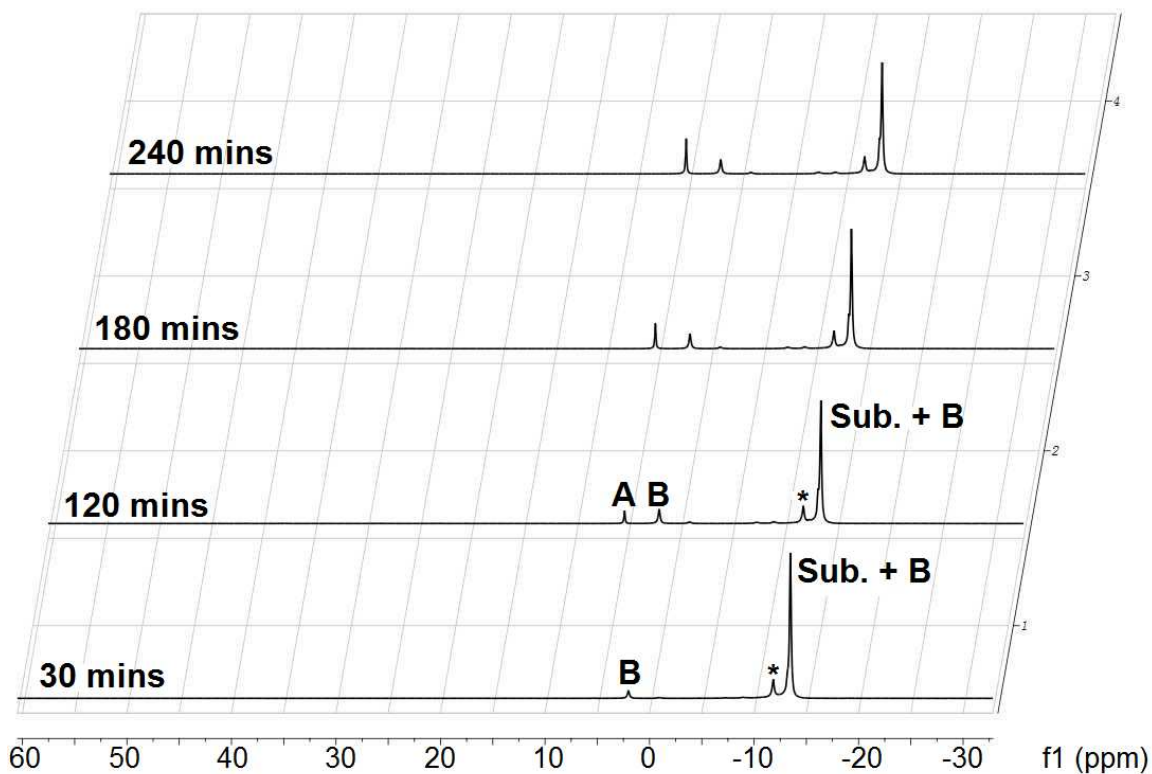
**Figure S3.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 5.0 mol% of **5**. Conditions:  $[\text{Sub.}]_0 = 0.68$  mol/L,  $\text{C}_6\text{D}_6$  as the solvent,  $50^\circ\text{C}$ . **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



**Figure S4.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 5.0 mol% of **6**. Conditions:  $[\text{Sub.}]_0 = 0.68 \text{ mol/L}$ ,  $\text{C}_6\text{D}_6$  as the solvent,  $50^\circ\text{C}$ . **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



**Figure S5.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 5.0 mol% of **7**. Conditions:  $[\text{Sub.}]_0 = 0.68 \text{ mol/L}$ ,  $\text{C}_6\text{D}_6$  as the solvent,  $50^\circ\text{C}$ . **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}\cdot\text{BH}_2-\text{NMe}_2\cdot\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



**Figure S6.**  $^{11}\text{B}\{^1\text{H}\}$  spectra showing the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  catalyzed by 5.0 mol% of **9**. Conditions:  $[\text{Sub.}]_0 = 0.68$  mol/L,  $\text{C}_6\text{D}_6$  as the solvent, 50 °C. **A**:  $[\text{Me}_2\text{N}-\text{BH}_2]_2$ ; **B**:  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ ; **C**:  $\text{Me}_2\text{N}=\text{BH}_2$ ; \*: other boron containing species.



**References:**

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- (3) Xu, X.; Chen, Y. F.; Feng, J.; Zou G.; Sun, J. *Organometallics* **2010**, 29, 549.