Supplementary Information

Experimental

Elemental yttrium (ingot, 99.9 %, Sigma–Aldrich), $ZnCl_2$ (anhydrous, beads, 99.99 %, Sigma–Aldrich), $NaBH_4$ (powder, 95%, Katchem) and pressurized H_2 (99.999 %, Messer) are used as received. Yttrium was hydrogenated at 350 °C at 50 bar H_2 to obtain YH₃. $NaZn_2(BH_4)_5$, synthesized by milling a mixture of ZnCl₂ and NaBH₄, was used as diborane source.¹

$$NaZn_2(BH_4)_5 \rightarrow NaH + 2Zn + 5/2B_2H_6 + 2H_2$$

 $Y_2(B_{12}H_{12})_3$ was synthesized in a two-step reaction. First, $Y(BH_4)_3$ was prepared by ball milling of YH_3 in B_2H_6 at room temperature, yielding a product of 75 wt% $Y(BH_4)_3$ with 25 wt% YH_3 remaining.² In a second step, $Y_2(B_{12}H_{12})_3$ was obtained via a gas solid reaction between $Y(BH_4)_3$ and B_2H_6 at 150 °C. In this step, the as-prepared $Y(BH_4)_3$ of 500 mg was filled in a milling vial connected to the diborane source. The whole system was purged with hydrogen and evacuated. Subsequently, the diborane source was heated to 150 °C to fill the system with a B_2H_6/H_2 (5: 4) atmosphere. After the completion of diborane source desorption, the vial containing $Y(BH_4)_3$ was heated to 150 °C using a heating rope. Finally, ball milling was performed and progress of the subsequent reaction was monitored by the pressure change in the milling vial.

The hydrogen desorption behavior was examined by temperature programmed desorption (TPD) measurements. Solution state NMR experiments in D_2O or DMSO-d₆ (dimethylsulfoxide) were performed on a Bruker Avance-400 NMR spectrometer using a 5 mm inverse broadband probe at 25 °C. The ¹¹B NMR spectra were recorded at 128.38 MHz without or with decoupling of the ¹H frequency. ¹H-¹¹B HMQC NMR spectra were recorded selecting a boron hydrogen coupling constant of 150 Hz using the Bruker standard pulse programs and parameter sets. ¹¹B NMR chemical shifts are reported in parts per million (ppm), externally referenced to a 1M B(OH)₃ aqueous solution at 19.6 ppm, and ¹H NMR chemical shifts are referenced to tetramethylsilane at 0 ppm. The deconvolution of ¹¹B NMR spectra was performed applying Gaussian shapes.

Decomposition products of Y(BH₄)₃ under external H₂ pressures of 5 to 10 bar.

Figure S1. Solution state $(D_2O)^{11}B(^{1}H)$ NMR spectra (128.38 MHz) of Y(BH₄)₃ decomposed under external H₂ pressures of 5 to 10 bar at 300 and 400 °C, respectively.



Hydrogen desorption performance of as-synthesized $Y(BH_4)_3$ and $Y_2(B_{12}H_{12})_3$

Figure S2. TPD spectra of as-synthesized $Y(BH_4)_3$ and $Y_2(B_{12}H_{12})_3$, with a heating rate of 2 °C/min and 1 bar H₂ as external atmosphere.



Reference

- 1 D. Ravnsbæk, Y. Filinchuk, Y.Cerenius, H. J. Jakobsen, F. Besenbacher, J. Skibsted and T. R. Jensen, *Angew. Chem. Int. Ed.*, 2009, **48**, 6659.
- 2 A. Remhof, A. Borgschulte, O. Friedrichs, Ph. Mauron, Y. Yan and A. Züttel, Scripta Mater., 2012, 66, 280.