Supporting information

for the manuscript

Thermal desorption of hydrogen from ammonia borane: unexpected role of homopolar B-H···H-B interactions

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S1 Experimental Methods

S1.1 General Considerations

All manipulations were carried out under an inert atmosphere in a nitrogen filled drybox or using an argon Schlenk line. Unless otherwise noted, all reagents were purchased from commercial sources (Sigma Aldrich) and used without further purification. The THF was purified using a Seca Solvent Dispensing System, followed by vigorous sparging with argon, and stored over molecular sieves (4 A). Solution ^{1}H and ^{2}H NMR spectra were acquired using Varian Unity INOVA (300 MHz or 400 MHz) spectrometers at 298 K. The reported chemical shifts are presented in parts per million (ppm); in which the ^{1}H NMR spectra were referenced to residual ^{1}H nuclei in the deuteriated solvent, while the ^{2}H NMR spectra were referenced to residual ^{2}H nuclei in the non-deuteriated solvent. The TGA plots were acquired using a TGAQ_{50} instrument.

S1.2 Synthesis of ND_3BH_3 and NH_3BD_3

ND_3BH_3 (0.10 g, 3.0 mmol) was prepared according to literature methods,[1] in which a sample of NH_3BH_3 (0.10 g, 3.24 mmol) was washed in excess D_2O. The NH_3BD_3 derivative (0.47 g, 13.9 mmol) was synthesized through a direct 1:1 reaction between $NaBD_4$ (0.62 g, 14.8 mmol) and $(NH_4)_2SO_4$ (1.95 g, 14.8 mmol).[2] These reactions were allowed to stir until no residual NH_3 or BH_3 peaks were observed in the corresponding ^{1}H NMR spectra (Figure S1).

1. A.T. Luedtke, T. Autrey, *Inorg. Chem.*, 2010, **49**, 3905-3910.
2. P.V. Ramachandran, P. Gagare, *Inorg. Chem.*, 2007, **46**, 7810-7817.

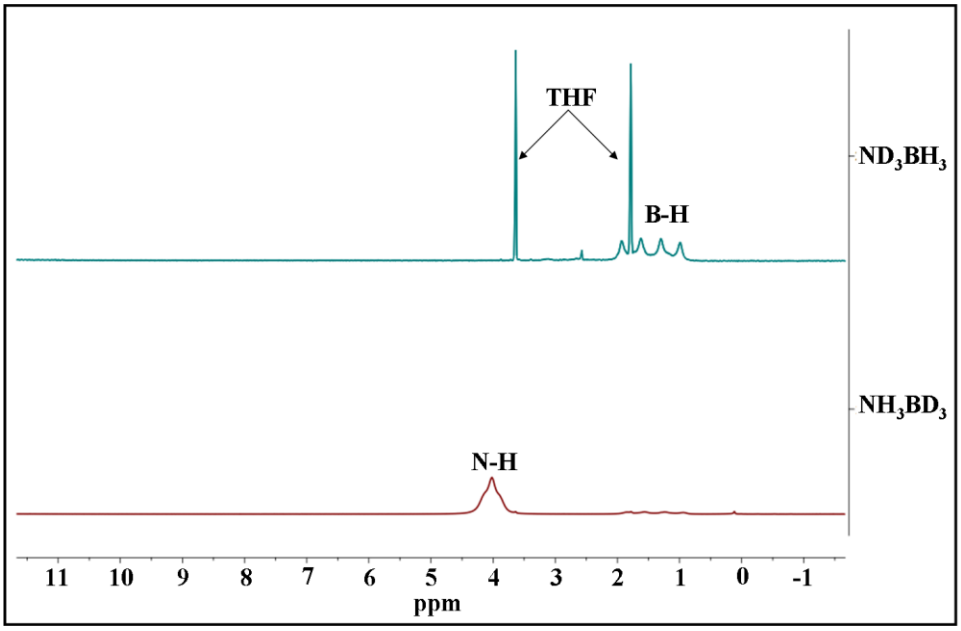

Figure S1. ^{1}H NMR spectrum of ND_3BH_3 (top) and NH_3BD_3 (bottom) in THF-d_8

S1.3 Hydrogen desorption experiments

Small amounts of solid ND_3BH_3 and NH_3BD_3 (~10-20 mg) were placed in separate 5 mm NMR tube each equipped with a Teflon valve (J. Young), followed by the addition of toluene-d_8 (1 mL) for ND_3BH_3 and non-deuteriated toluene (1 mL) for NH_3BD_3. The NMR tube was then placed into an oil bath and heated in 20 °C increments (60-120 °C) in 20 min stages. The ^{1}H and ^{2}D NMR spectra were recorded after each increment.

S1.4 Thermogravimetric analysis (TGA) experiments

TGA plots were obtained by loading separate sample holders with 2.5-7 mg of ND_3BH_3 and NH_3BD_3 in a nitrogen-filled drybox. NH_3BD_3 in particular displayed a high tendency to plume on account of the exothermic nature of hydrogen desorption. Accordingly, the lower limit used for this sample was ~2.5 mg. These samples were each heated to 300 °C at a ramping rate of 2 °C/min.