Acid Initiation of Ammonia-Borane Dehydrogenation for Hydrogen Storage

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General experimental considerations: Reactions were carried out in an inert atmosphere using anhydrous solvents. Ammonia-borane was synthesized according to literature procedures. \(^1\) \(^1\)H and \(^13\)C NMR spectra are referenced to residual solvent: CD\(_2\)Cl\(_2\) (5.3 ppm, 54.0 ppm). \(^{19}\)F NMR spectra are referenced to external \(\alpha,\alpha,\alpha\)-trifluorotoluene (−63.7 ppm). Hydrogen quantification was completed using either a gas buret or a Toepler pump.

Synthesis of [BH\(_2\)(NH\(_3\))(OEt\(_2\))][B(3,5-(CF\(_3\))C\(_6\)H\(_3\))]\(_4\)]. A solution of [H(OEt\(_2\))\(_2\)][B(3,5-(CF\(_3\))C\(_6\)H\(_3\))]\(_4\)] (0.70 g, 0.69 mmol) was prepared in 5 mL Et\(_2\)O and was placed in a round bottom flask. A solution of H\(_3\)NBH\(_3\) (0.02 g, 0.71 mmol) was prepared in 10 mL Et\(_2\)O and placed in a pressure equalizing dropping funnel. While stirring the solution of acid, the solution of H\(_3\)NBH\(_3\) was added dropwise (ca. 2 drops/s). Bubbling was observed immediately. After 2 h, the reaction mixture was filtered through Celite and the solvent was removed in vacuo. Isolated yield: 0.565 g, 84%. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300 MHz): 7.72 (ortho, 8H), 7.57 (para, 4H), 4.34 (q, O(CH\(_2\)Me\(_2\)), 4H), 4.20 (broad multiplet, NH\(_3\)), 3H), 2.70 (broad q, BH\(_2\)), 2H), 1.49 (t, O(CH\(_2\)Me\(_2\))), 6H) ppm. \(^13\)C NMR (CD\(_2\)Cl\(_2\), 75 MHz): 162.3 (q, \(J_{BC} = 50\) Hz, ipso), 135.4 (ortho), 129.4 (q, \(J_{CF} = 29\) Hz, meta), 125.2 (q, \(J_{CF} = 272\) Hz, CF\(_3\)), 118.1 (para), 79.7 (O(CH\(_2\)Me)), 13.3 (O(CH\(_2\)Me)), ppm. \(^{11}\)B NMR (CD\(_2\)Cl\(_2\), 96 MHz): 0.19 (t, \(J_{BH} = 125\) Hz, BH\(_2\)), −7.05 (s, B(3,5-(CF\(_3\))C\(_6\)H\(_3\)))), ppm. \(^{19}\)F NMR (CD\(_2\)Cl\(_2\), 282 MHz): −64.2 ppm.

Scheme S1. Energy level diagram depicting calculated structures as ball-and-stick models. Energies are given in kJ mol\(^{-1}\).
Scheme S2. Variable temperature $^{11}$B NMR spectra of $\mu$-(NH$_2$)$_2$B$_2$H$_6$ (7) generated in the acid-initiated dehydropolymerization of H$_2$NBH$_3$ (1): blue, 25 °C; pink, 40 °C; yellow, 60 °C; aqua, 80 °C. Doublet centered at ca. -27 ppm is attributed to the anion [HB(C$_6$F$_5$)$_3$]$^-$. The broad triplet at ca. -29 ppm is resolved into a sextet at 80 °C, consistent with 7. $^{11}$B($^1$H) NMR spectra reveal two peaks in this region (assigned to [HB(C$_6$F$_5$)$_3$]$^-$ and 7), indicating that compounds 4 and 6 do not significantly build up during the reaction.