A synergistic strategy established by the combination of two H-enriched B-N based hydrides towards superior dehydrogenation

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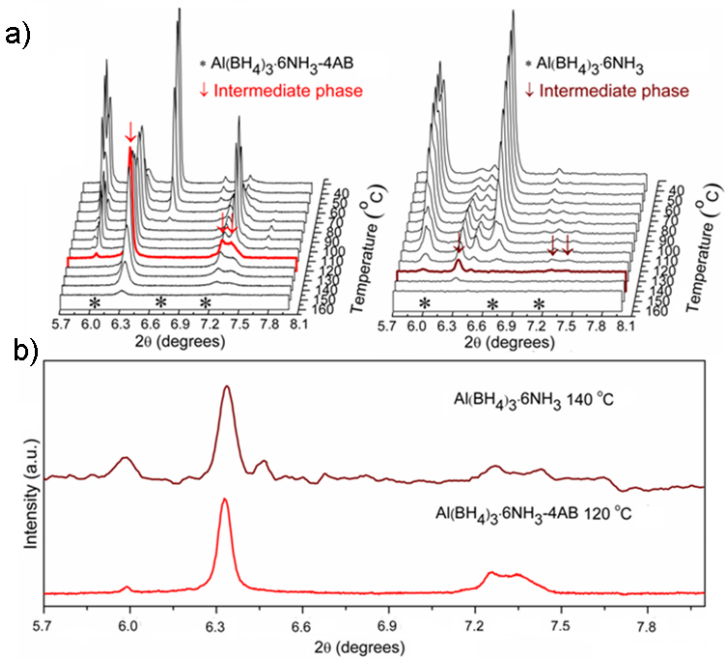

Fig. S1 a) Selected parts of the in-situ XRD patterns for $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Al(BH_4)_3 \cdot 6NH_3$; b) XRD patterns for $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Al(BH_4)_3 \cdot 6NH_3$ at 120 ^{o}C and 140 ^{o}C, respectively. The data is collected at a wavelength of 0.688702 Å.

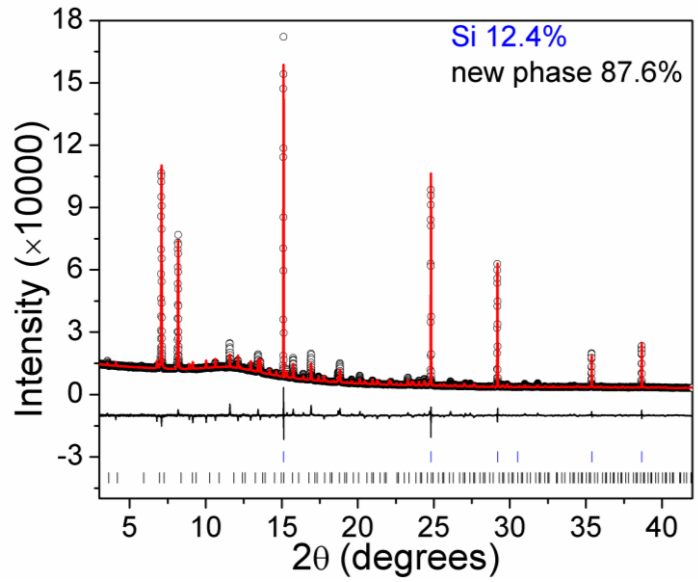

Fig. S2 Rietveld refinement profile for as-prepared $Li_2Al(BH_4)_5(NH_3BH_3)_3{\cdot}6NH_3$ sample with Si (spiked 10 wt.%) as internal reference showing observed (black circles), calculated (red line), and difference (black line) plots. The positions of Bragg reflections (tick marks) are shown for $Li_2Al(BH_4)_5(NH_3BH_3)_3{\cdot}6NH_3$ (black) and Si (blue). The refined proportions of $Li_2Al(BH_4)_5(NH_3BH_3)_3{\cdot}6NH_3$ and Si were 87.6 wt. % and 12.4 wt. %, respectively. The data is collected at a wavelength of 0.8250 Å.

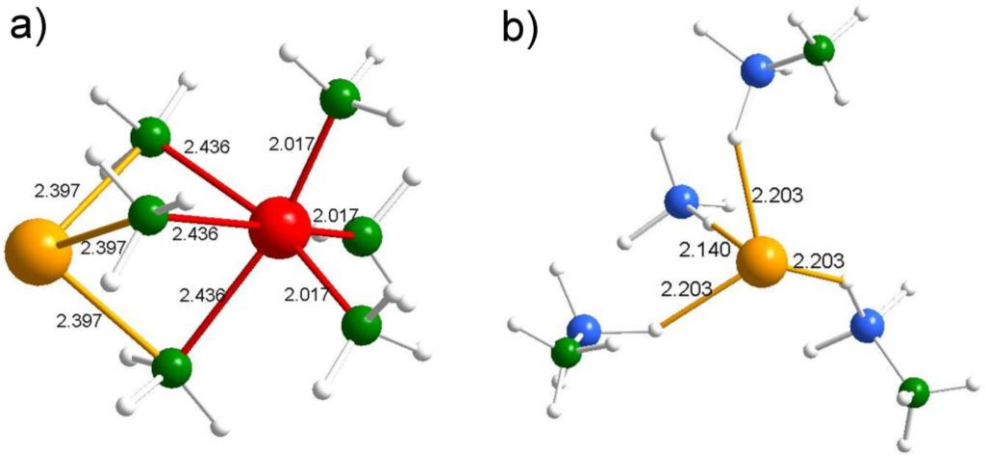

Fig. S3 Illustrations of the $Li_2Al(BH_4)_5(NH_3BH_3)_3 \cdot 6NH_3$ structure.

In $Li_2Al(BH_4)_5(NH_3BH_3)_3 \cdot 6NH_3$ structure, one Li atom connects to three NH_3 molecules with a Li-N distance of 2.397 Å, which induces extend the distance of Al-N *via* the Li-N bonds, and Al atoms centered distorted octahedron coordinated exclusively by six NH_3 molecules with a Al-N distance of 2.017 Å and 2.436 Å. Another Li atom is tetrahedrally coordinated with three AB and one BH_4^- units *via* Li-H ionic bonds. The distances between the Li and the nearby hydridic H^- are 2.141 Å and 2.203 Å, comparable to those between Li and H in the $LiBH_4$ (2.023-2.246 Å).

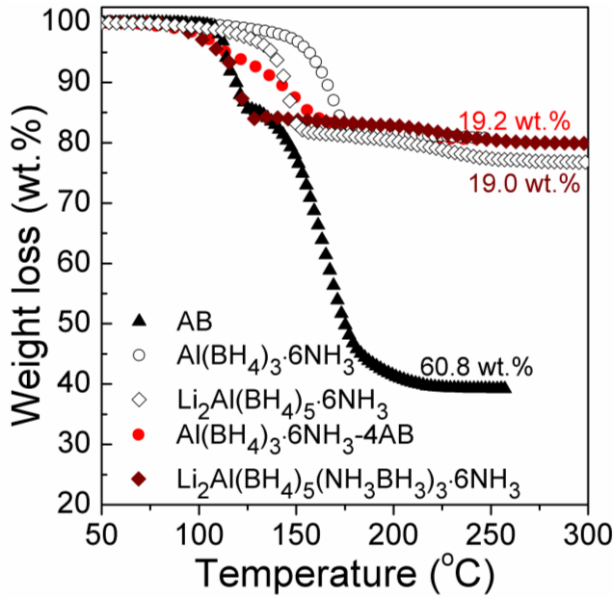

Fig. S4 TG results for neat AB, $Al(BH_4)_3 \cdot 6NH_3$, $Li_2Al(BH_4)_5 \cdot 6NH_3$, $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Li_2Al(BH_4)_5 \cdot 6NH_3$-3AB.

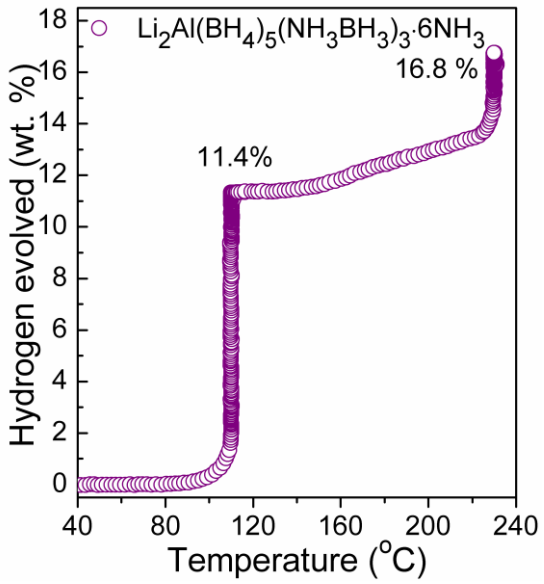

Fig. S5 (a) TPD result for $Li_2Al(BH_4)_5 \cdot 6NH_3$-3AB with a heating rate of 5 $^oC \cdot min^{-1}$. For TPD measurement, the sample was hold at 110 and 230 ^oC for 180 min, respectively, during heating.

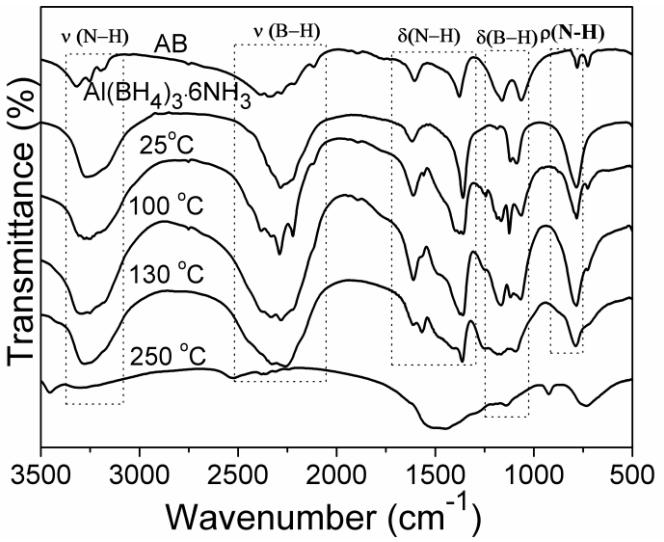

Fig. S6 FTIR spectra for $Al(BH_4)_3 \cdot 6NH_3$-4AB at 25 ^oC and its products after heating to 100 ^oC, 130 ^oC and 250 ^oC. Neat AB and $Al(BH_4)_3 \cdot 6NH_3$ were also measured for comparison.

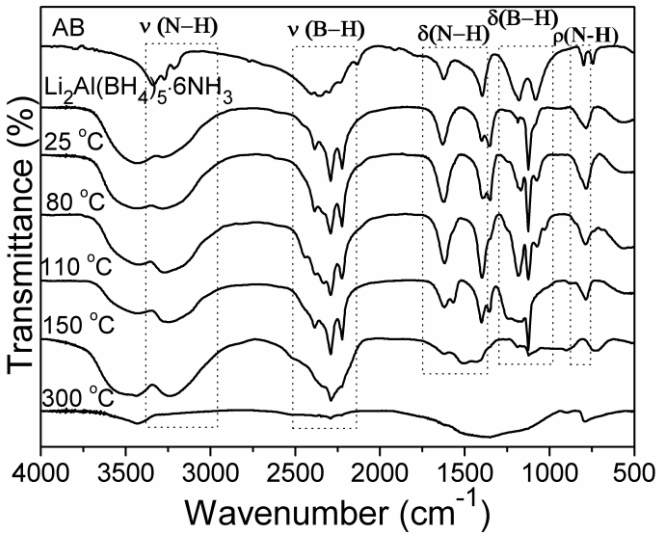

Fig. S7 FTIR spectra for $Li_2Al(BH_4)_5 \cdot 6NH_3$-3AB at 25 ^oC and its products after heating to 80 ^oC, 110 ^oC, 150 ^oC and 300 ^oC. Neat AB and $Li_2Al(BH_4)_5 \cdot 6NH_3$ were also measured for comparison.

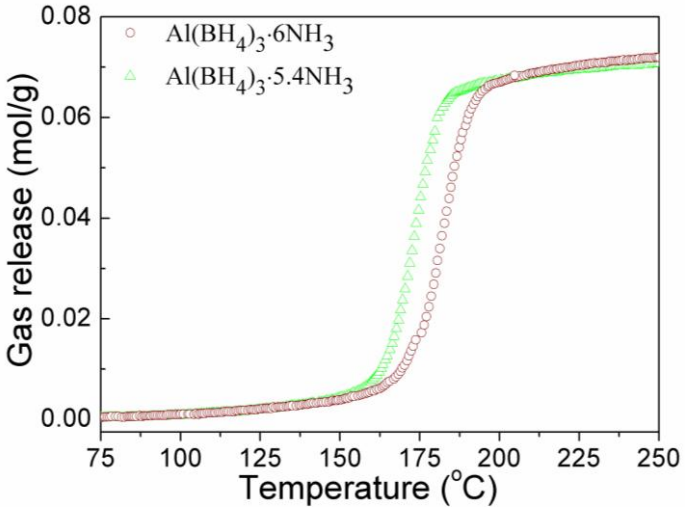

Fig. S8 TPD results of hydrogen release from $Al(BH_4)_3 \cdot 6NH_3$ and $Al(BH_4)_3 \cdot 5.4NH_3$ with a heating rate of 5 $^oC\ min^{-1}$.

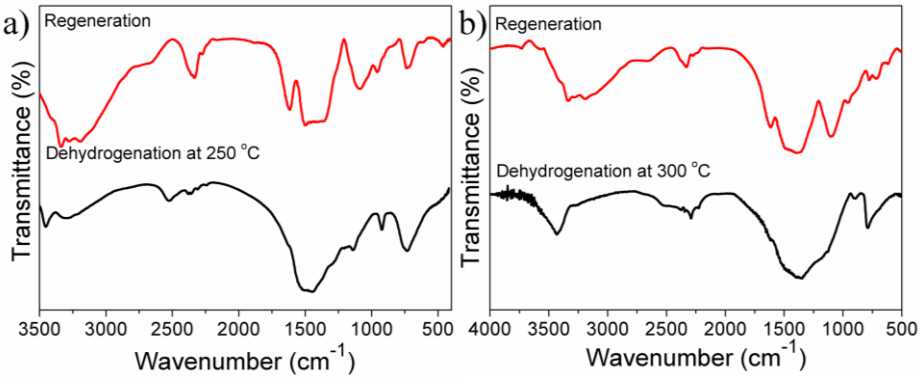

Fig. S9 FTIR spectra for dehydrogenated and regenerated a) $Al(BH_4)_5 \cdot 6NH_3$-4AB and b) $Li_2Al(BH_4)_5(NH_3BH_3)_3 \cdot 6NH_3$.

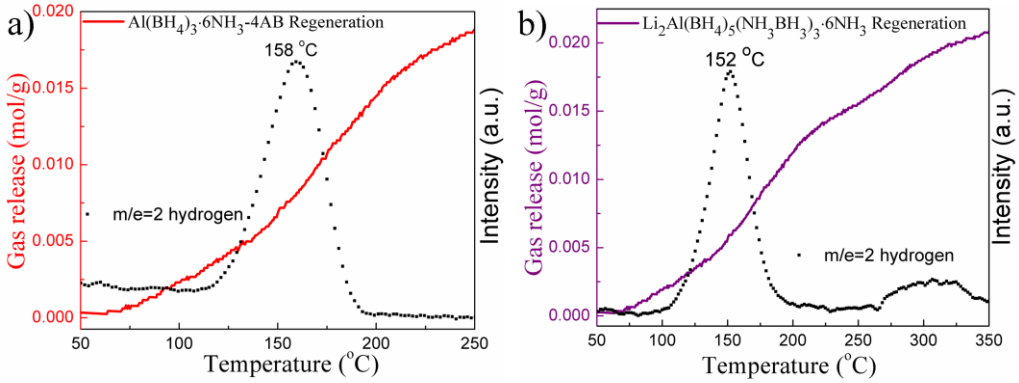

Fig. S10 TPD/MS profiles for a) $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Li_2Al(BH_4)_5(NH_3BH_3) \cdot 6NH_3$, with a heating rate of 5 °C min^{-1} in nitrogen.

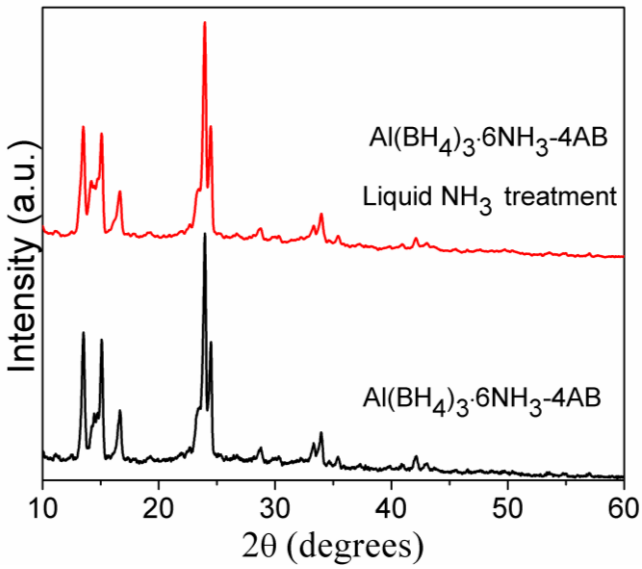

Fig. S11 XRD patterns of $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Al(BH_4)_3 \cdot 6NH_3$-4AB after treatment with ammonia. The data is collected at a wavelength of 1.5406 Å.

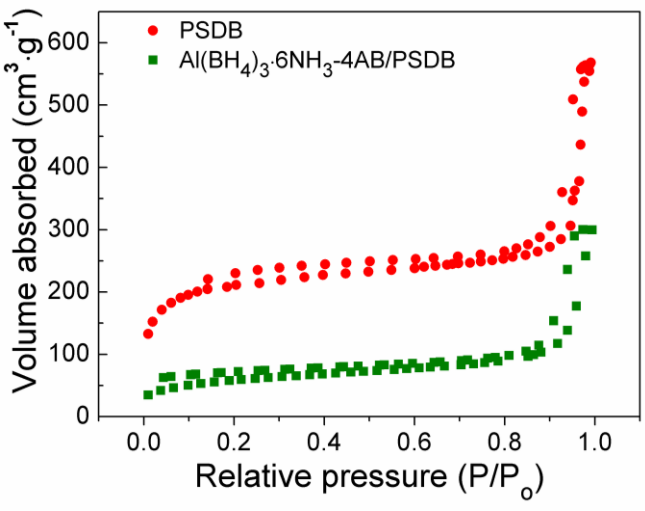

Fig. S12 Pore size distributions for PSDB and PSDB-confined $Al(BH_4)_3 \cdot 6NH_3$-4AB. The inset shows the corresponding N_2 absorption-desorption isotherms at 77 K.

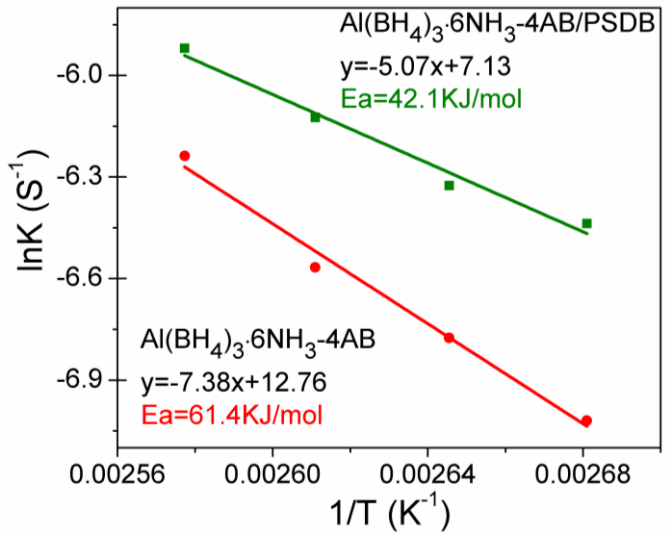

Fig. S13 Arrhenius treatment of the temperature-dependent rate data giving the activation energy of $Al(BH_4)_3 \cdot 6NH_3$-4AB and $Al(BH_4)_3 \cdot 6NH_3$-4AB/PSDB.

Table S1 Experimental and calculated structural parameters of $Li_2Al(BH_4)_5(NH_3BH_3)_3 \cdot 6NH_3$ (space group F23, no. 196, a = b = c =23.1220(3) Å)

Atom	site	x		y		z	
		Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
B11	48h	0.25727	0.25727	0.11806	0.11806	0.32779	0.32779
H11a	48h	0.23545	0.23543	0.07065	0.06930	0.32133	0.32023
H11b	48h	0.23170	0.23173	0.15244	0.15076	0.35685	0.36084
H11c	48h	0.30980	0.31103	0.11817	0.11771	0.32598	0.32559
H11d	48h	0.25481	0.25513	0.14043	0.14383	0.27017	0.27209
H12a	48h	0.35608	0.35518	0.36740	0.36760	0.42381	0.42484
H13a	48h	-0.19460	-0.19539	-0.12869	-0.12681	-0.13843	-0.14019
N21	48h	-0.32157	-0.32157	-0.09793	-0.09793	0.79711	0.79711
H21a	48h	-0.32125	-0.31995	-0.05295	-0.05189	0.79767	0.79749
H21b	48h	-0.27827	-0.27762	-0.11050	-0.11213	0.79847	0.79826
H21c	48h	-0.33744	-0.33808	-0.11052	-0.11065	0.75619	0.75526
N22	48h	-0.07724	-0.07724	0.65524	0.65524	-0.04536	-0.04536
H22a	48h	-0.03255	-0.03156	0.65202	0.65202	-0.04964	-0.05004
H22b	48h	-0.08288	-0.08278	0.69949	0.70059	-0.03727	-0.03659
H22c	48h	-0.08886	-0.08908	0.63754	0.63712	-0.00505	-0.00405
B1	48h	0.31729	0.31729	0.48686	0.48686	-0.91647	-0.91647
H1a	48h	0.32047	0.32056	0.49501	0.49616	-0.86481	-0.86378
H1b	48h	0.35294	0.35313	0.51782	0.51911	-0.94222	-0.94304
H1c	48h	0.26889	0.26769	0.49779	0.49862	-0.93516	-0.93538
N2	48h	0.33377	0.33377	0.42164	0.42164	-0.93088	-0.93088
H2a	48h	0.32468	0.32458	0.39501	0.39434	-0.89482	-0.89370
H2b	48h	0.30889	0.30809	0.40512	0.40428	-0.96407	-0.96445
H2c	48h	0.37557	0.37626	0.41675	0.41666	-0.94568	-0.94675
Li1	16e	0.94292	0.94292	0.94292	0.94292	0.94292	0.94292

Li2	16e	0.55237	0.55237	0.55237	0.55237	0.55237	0.55237
Al1	16e	0.63435	0.63435	0.63435	0.63435	0.63435	0.63435
B12	16e	0.39021	0.39021	0.39021	0.39021	0.39021	0.39021
H12b	16e	0.42302	0.42397	0.42302	0.42397	0.42302	0.42397
B13	16e	-0.14265	-0.14265	-0.14265	-0.14265	-0.14265	-0.14265
H13b	16e	-0.11233	-0.11175	-0.11233	-0.11175	-0.11233	-0.11175

Table S2 Purity of hydrogen released in all the samples.

Samples	Wt % H_2 capacity	mol % H_2	Mol H_2
$Al(BH_4)_3 \cdot 6NH_3$	13.3	93.7	11.5
$Al(BH_4)_3 \cdot 6NH_3$-AB	13.8	96.4	14.1
$Al(BH_4)_3 \cdot 6NH_3$-2AB	14.2	97.3	16.6
$Al(BH_4)_3 \cdot 6NH_3$-3AB	14.4	98.1	19.0
$Al(BH_4)_3 \cdot 6NH_3$-4AB	14.5	98.3	21.3
$Al(BH_4)_3 \cdot 6NH_3$-5AB	14.7	98	23.9
$Al(BH_4)_3 \cdot 6NH_3$-6AB	14.8	97.8	26.4
$Li_2Al(BH_4)_5 \cdot 6NH_3$	15.1	94.3	16.2
$Li_2Al(BH_4)_5 \cdot 6NH_3$-AB	16.5	97.6	20.2
$Li_2Al(BH_4)_5 \cdot 6NH_3$-2AB	16.6	98.0	23.0
$Li_2Al(BH_4)_5 \cdot 6NH_3$-3AB	16.9	98.6	26.0
$Li_2Al(BH_4)_5 \cdot 6NH_3$-4AB	16.8	97.1	28.3
$Li_2Al(BH_4)_5 \cdot 6NH_3$-5AB	16.6	96.9	30.5
$Li_2Al(BH_4)_5 \cdot 6NH_3$-6AB	16.4	95.0	32.7