Release of pure H_2 from $Na[BH_3(CH_3NH)BH_2(CH_3NH)BH_3]$ by introduction of methyl substituents

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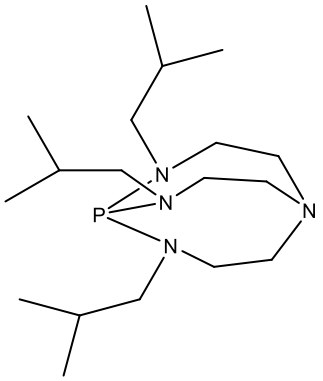

$C_{18}H_{39}N_4P$, VB

Figure S1. Chemical formula of VB.

Table S1. H-contents, mass losses and by-products formed during thermal treatment of several $M[B_3N_2]$ compounds.

Compound[reference]	**H-content (wt. %, excluding hydrogen on carbon)**	**Mass loss below 200 °C (%)**	**By-products**
$[Bu_4N][B_3N_2]$[35]	3.8	3.0	None
$[Et_4N][B_3N_2]$[35]	6.0	6.0	None
$[C(N_3H_6)][B_3N_2]$[35]	13.7	18.5	NH_3, CH_4
$[C(N_3H_5CH_3)][B_3N_2]$[35]	11.7	8.0	NH_3, CH_4
$[NH4][B_3N_2]$: $NH_3BH_2NH_2BH_2NH_2BH_3$ (1 : 3) [38]	16.4	~ 45	$B_3N_3H_6$, B_2H_6, NH_3
$Li[B_3N_2]$[33]	15.2	~ 5	None
$Na[B_3N_2]$[33]	12.7	~ 20	NH_3, BNH_5, B_2NH_7

$K[B_3N_2]$[34]	10.8	~ 36	NH_3, B_2H_6
$Rb[B_3N_2]$[34]	7.6	~ 23	NH_3, B_2H_6
$Cs[B_3N_2]$[34]	5.9	~ 19	NH_3, B_2H_6

Table S2. H-content in $NaNH_2BH_3$, $NaBH_3NH_2BH_3$, $NaBH_3NH_2BH_2NH_2BH_3$, $NaBH_3NH_2BH_2NH_2BH_2NH_2BH_3$ and $NaBH_3NH_2BH(NH_2BH_3)_2$.

Compound	Molar mass (g/mol)	H-content (wt. %)
$NaNH_2BH_3$	52.85	9.54
$NaBH_3NH_2BH_3$	66.68	12.09
$NaBH_3NH_2BH_2NH_2BH_3$	95.53	12.66
$NaBH_3NH_2BH_2NH_2BH_2NH_2BH_3$	124.38	12.97
$NaBH_3NH_2BH(NH_2BH_3)_2$	124.38	12.97

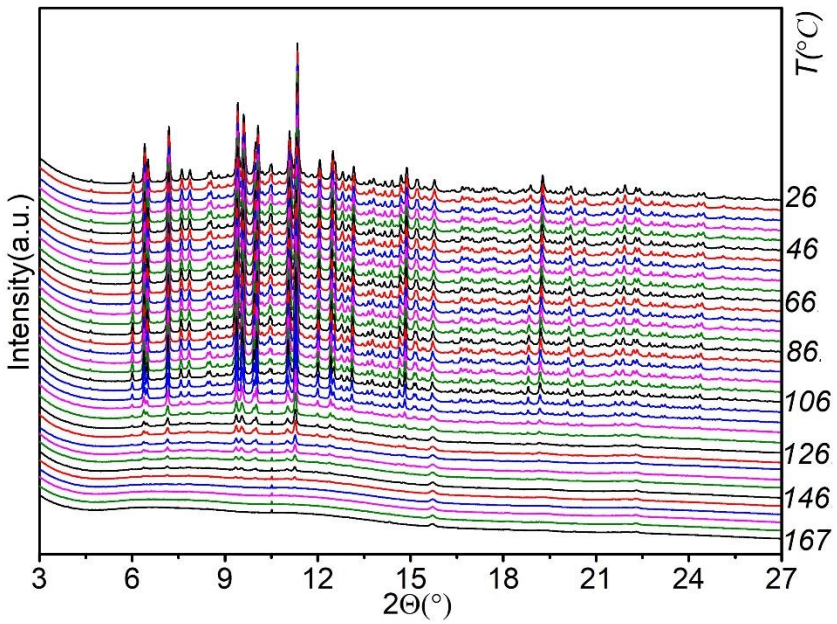

Figure S2. Synchrotron PXRD patterns of $Na[B_3(MeN)_2]$ (λ = 0.77509 Å)

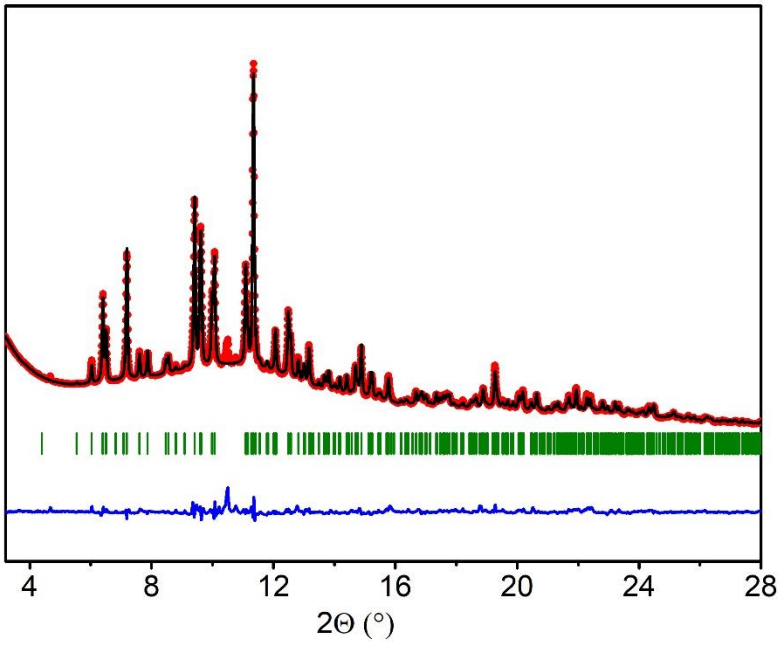

Figure S3. Rietveld refinement of the synchrotron PXRD pattern of $Na[B_3(MeN)_2]$ (λ = 0.77509 Å, T = 300 K). Observed data (Yobs) are displayed in red, the Rietveld refinement profile (Ycalc) in black and the difference plot (Yobs – Ycalc) in blue. Agreement factors, with background correction, are R_B = 7.9 %, R_p = 14.2, R_{wp} = 12.5, χ^2 = 424.

Table S3. Inter-anion dihydrogen bond lengths and angles in $Na[B_3(MeN)_2]$.

N-H$^{\delta+}$…H$^{\delta-}$-B	D(H···H) / Å	∠(N-H···H) / °
N(12)-H(121) …H(212)-B(21) (terminal B)	2.37	135.6
N(22)-H(221) …H(131)-B(13) (central B)	2.13	173.8
N(14)-H(141) …H(251)-B(25) (terminal B)	2.28	124.0
N(24)-H(241) …H(151)-B(15) (terminal B)	2.46	159.4
N(24)-H(241) …H(232)-B(23) (central B)	2.49	136.6

Table S4. B-N bond lengths in $CH_3NH_2BH_3$, $M[B_3N_2]$ (M = Li – Cs), and $Na[B_3(MeN)_2]$ (Because of the significant disorder and presence of peaks from unidentified impurities, they modeled the structure of $Na/Li[B_3N_2]$ in Jana2006. And B–N distances in $Na[B_3N_2]$ were restrained to 1.60(1) Å).

Compound	Identification of B-N bond	Bond length (Å)
$CH_3NH_2BH_3$[43]	B-N	1.587(3)
$Li[B_3N_2]$[33]	B-N	-
$Na[B_3N_2]$ [33]	B-N	1.60(1)
$K[B_3N_2]$[34]	B-N (terminal B)	1.609(1)
	B-N (central B)	1.551(1)
$Rb[B_3N_2]$[34]	B-N (terminal B)	1.62(2) – 1.65(2)
	B-N (central B)	1.60(2)
$Cs[B_3N_2]$[34]	B-N	1.56(7) – 1.57(7)
	B11-N12 (terminal B)	1.638(9)

$Na[B_3(MeN)_2]$[*(this work)*]	B13-N12 (central B)	1.620(9)
	B13-N14 (central B)	1.626(10)
	B15-N14 (terminal B)	1.592(9)
	B21-N22 (terminal B)	1.603(8)
	B23-N22 (central B)	1.635(11)
	B23-N24 (central B)	1.601(8)
	B25-N24 (terminal B)	1.632(10)

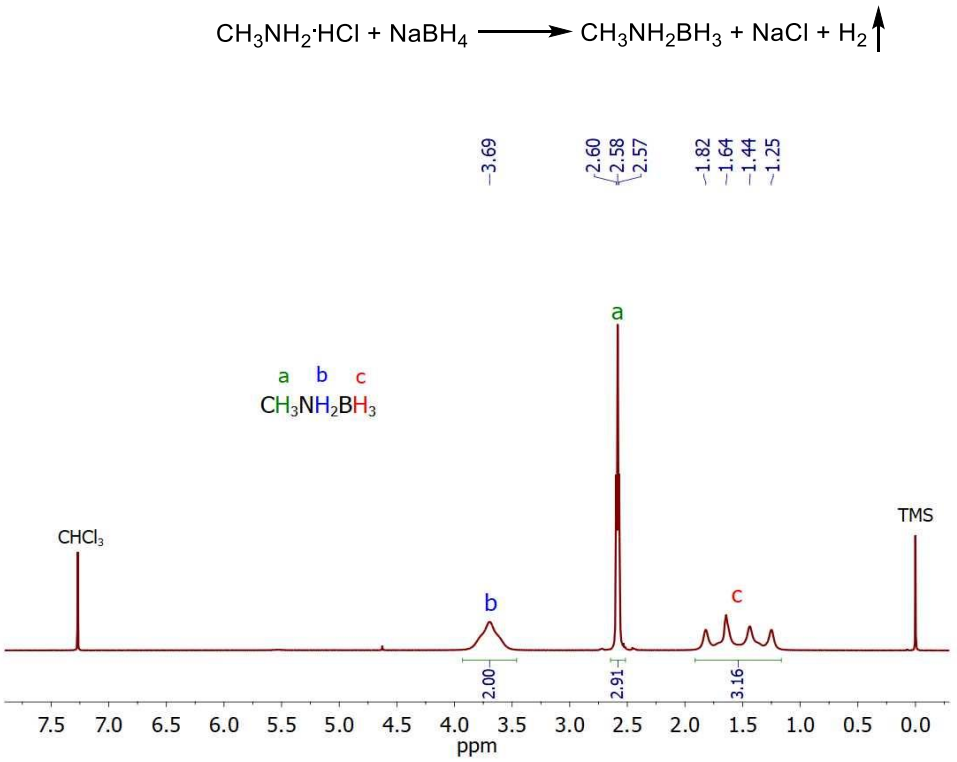

Figure S4 ^{1}H NMR spectrum of $CH_3NH_2BH_3$.

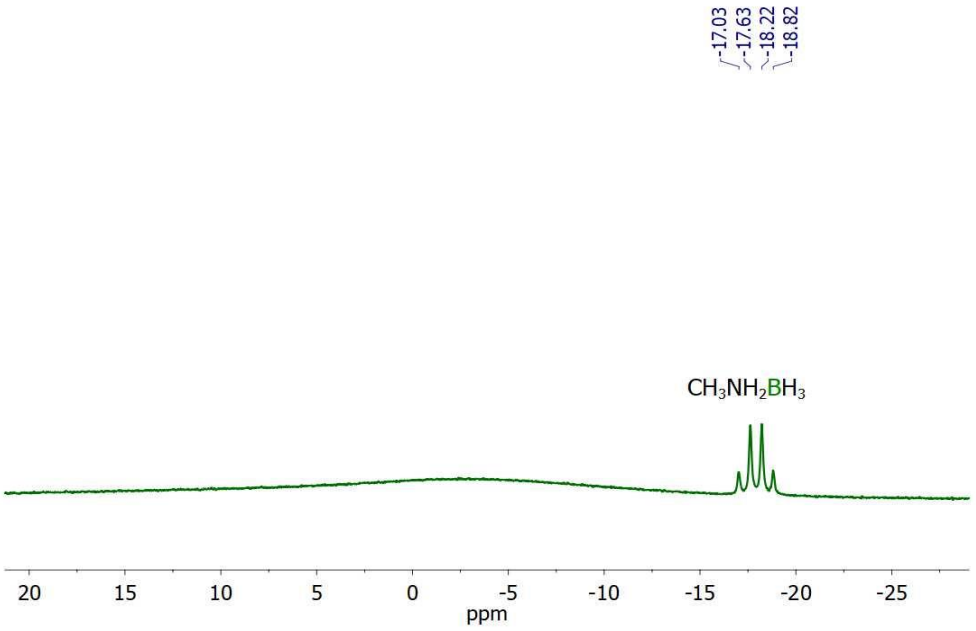

Figure S5 ^{11}B NMR spectrum of $CH_3NH_2BH_3$.

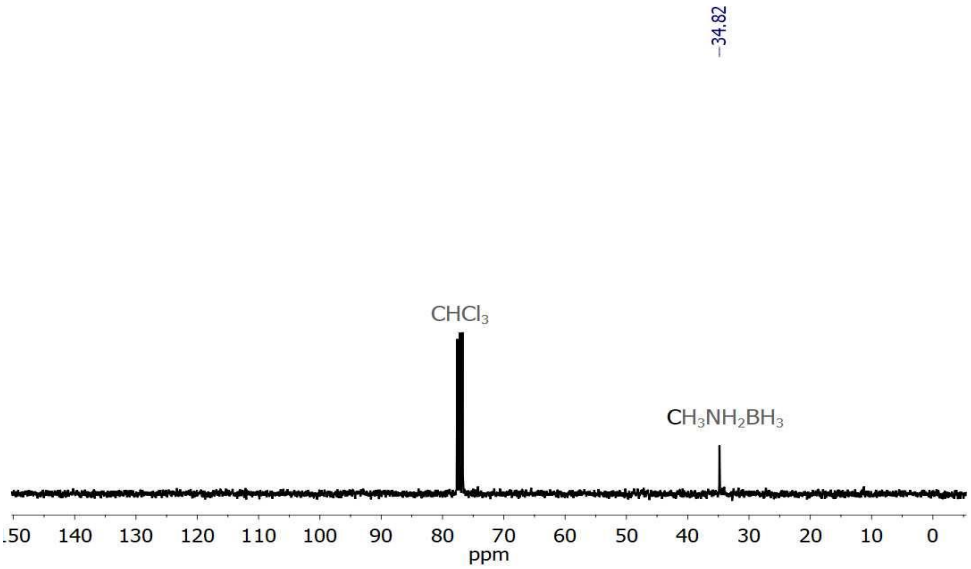

Figure S6 ^{13}C NMR spectrum of $CH_3NH_2BH_3$.

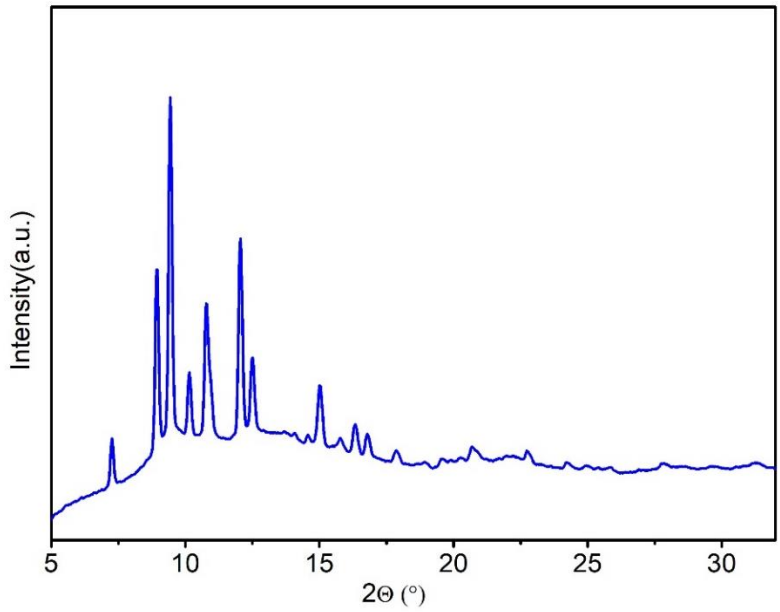

Figure S7. PXRD pattern of $CH_3NH_2BH_3$ (λ = 0.71073 Å).

Table S5. The mole mass, density, gravimetric and volumetric hydrogen density of $Na[B_3(MeN)_2]$

Mole mass	**δ**	**Gravimetric hydrogen density**	**Volumetric hydrogen density**
123.58 g/mol	973 g/L	13.05 %	126 g/L