

Amine–Boranes Reactions Promoted by Lanthanide(II) Ions

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Supplementary Information

General Procedures.	S4
X-ray diffraction.	S4
Table S1. Crystal data and structure refinement parameters for 2_Sm ^{DMAB} and 3_Yb ^{DMAB} ·DME.	S4
Synthetic procedures.	S4
Table S2. Selected ¹ H and ¹¹ B NMR parameters of complexes 1-4, their ligands and amine-boranes.	S6
Scheme S1. Synthesis of 3_Yb·DME.	S6
Volumetric studies of amine boranes dehydrogenation.	S7
Figure S1. ¹¹ B NMR spectrum of the reaction mixture for 3_Yb (<i>c</i> = 0.01 M) and 30 equiv. of Me ₂ NHBH ₃ (DMAB) after 14 days in toluene- <i>d</i> ₈ , 128.34 MHz, 290 K.	S7
Figure S2. IR spectra in the ν _{NH} region of amine-boranes (blue - NH ₃ BH ₃ 0.01 M, green – <i>t</i> BuNH ₂ BH ₃ 0.01 M, red – Me ₂ NHBH ₃ 0.02 M) in THF and of complexes 2 ^{DMAB} (bold red line), 4 ^{TBAB} (bold green line) and 4 ^{AB} (bold blue line) as the products of the amine-boranes reaction with (TBDM) ₂ Yb(DME) ₂ (1_Yb·DME, 0.01 M). Dashed lines – addition of one more equivalent of amine-borane (two more in case of DMAB) to the corresponding reaction mixture. <i>l</i> = 0.2 cm, 298 K.	S8
Figure S3. IR spectra in the ν _{NH} region of 0.02 M amine-boranes (green – <i>t</i> BuNH ₂ BH ₃ , red – Me ₂ NHBH ₃) and of complexes 2_Yb ^{TBAB} (bold green line) and 2_Yb ^{DMAB} (bold red line) as the products of their reaction with (TBDM) ₂ Yb(TMEDA) (1_Yb·TMEDA, 0.01 M). Dashed lines – addition of two more equivalent of amine-borane to the corresponding reaction mixture. Toluene, <i>l</i> = 0.2 cm, 298 K.	S8
Figure S4. IR spectra in the ν _{NH} region of Me ₂ NHBH ₃ (<i>c</i> = 0.02 M, thin solid line) and of complex (TBDM) ₂ Sm(TMEDA) (2_Sm ^{DMAB} , bold line) as the product of its reaction with (TBDM) ₂ Sm(TMEDA) (0.01 M). Dashed line – addition of two more equivalents of DMAB to the corresponding reaction mixture. Toluene, <i>l</i> = 0.2 cm, 298 K.	S9
Figure S5. IR spectra in the ν _{BH} region of amine-boranes (blue - NH ₃ BH ₃ 0.01 M, green – <i>t</i> BuNH ₂ BH ₃ 0.01 M, red – Me ₂ NHBH ₃ 0.02 M) in THF and the products of their interaction with 0.01 M (TBDM) ₂ Yb(DME) ₂ (bold lines), <i>l</i> = 0.2 cm, 298 K. Region of terminal ν _{BH} – left box, noncovalently bonded ν _{BH} – right box.	S9
Figure S6. IR spectra in the ν _{BH} region of complexes 2'_Yb ^{TBAB} (dotted green line), 2'_Yb ^{DMAB} (dotted red line), 2_Yb ^{TBAB} (bold green line), and 2_Yb ^{DMAB} (bold red line) measured for the reaction mixtures of 0.01 M (TBDM) ₂ Yb(TMEDA) (1_Yb·TMEDA) with 0.01 M (dotted lines) and 0.02 M (bold lines) of the corresponding amine-	

borane. Toluene, $l = 0.2$ cm, 298 K. IR spectra of amine-boranes in toluene ($c = 0.02$ M; thin solid lines; green – $t\text{BuNH}_2\text{BH}_3$, red – Me_2NHBH_3) are given for comparison.	S10
Figure S7. IR spectra in the ν_{BH} region of complexes $2'_{\text{Sm}}^{\text{DMAB}}$ (dotted line), and $2_{\text{Sm}}^{\text{DMAB}}$ (bold line) measured for the reaction mixtures of 0.01 M $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ ($1_{\text{Sm}}\text{-TMEDA}$) with 0.01 M (dotted lines) and 0.02 M (bold lines) in toluene. $l = 0.2$ cm, 298 K. IR spectrum of Me_2NHBH_3 ($c = 0.02$ M; thin solid line) and after addition of two more equivalents of DMAB to $2_{\text{Sm}}^{\text{DMAB}}$ (dashed lines) are given for comparison. Region of terminal ν_{BH} – left box, noncovalently bonded ν_{BH} – right one.	S11
Figure S8. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of $t\text{BuNH}_2\text{BH}_3$ (TBAB, $c = 0.02$ M) and its 1:2 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ ($1_{\text{Yb}}\text{-TMEDA}$, $c = 0.01$ M) showing the formation of complex 2_{Yb} in toluene- d_8 , 128.34 MHz, 290 K.	S11
Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of Me_2NHBH_3 (DMAB, $c = 0.02$ M) and its 1:2 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M) in THF- d_6 , 128.34 MHz, 290 K.	S12
Figure S10. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of $t\text{BuNH}_2\text{BH}_3$ (TBAB, $c = 0.01$ M) and its 1:1 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M) in THF- d_6 , 128.34 MHz, 290 K.	S12
Figure S11. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of NH_3BH_3 (AB, $c = 0.01$ M) and its 1:1 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M) in THF- d_6 , 128.34 MHz, 290 K.	S13
Figure S12. ^1H NMR spectra of $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M, blue) and its reaction mixture with amine-boranes (NH_3BH_3 (AB, $c = 0.01$ M) – green, $t\text{BuNH}_2\text{BH}_3$ (TBAB, $c = 0.01$ M) – red, Me_2NHBH_3 (DMAB, $c = 0.02$ M) – purple) in THF- d_6 . Highlighted signals: ● – $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$, ● – 1_{Yb}-DME . 400 MHz, 290 K.	S13
Figure S13. ^1H NMR spectra of $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ ($1_{\text{Yb}}\text{-TMEDA}$, $c = 0.01$ M, blue) and its 1:2 ($c = 0.02$ M) reaction mixture with amine-boranes ($t\text{BuNH}_2\text{BH}_3$ (TBAB) – red, Me_2NHBH_3 (DMAB) – purple) in toluene- d_8 . Highlighted signals: ● – $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$, ● – $1_{\text{Yb}}\text{-TMEDA}$, 400 MHz, 290 K.	S14
Figure S14. ^1H NMR spectrum of the 1:1 mixture of 0.01 M complex $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ and 0.01 M amine-borane (Me_2NHBH_3 –bottom, $t\text{BuNH}_2\text{BH}_3$ –top). Highlighted signals: ● – $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$, ● – $2'_{\text{Yb}}^{\text{DMAB}}$, ● – $2'_{\text{Yb}}^{\text{TBAB}}$. 400 MHz, toluene- d_8 , 290 K.	S15
Figure S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 0.01 M Me_2NHBH_3 (blue) and its 2:1 mixture with 0.01 M $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (after 30 min – green, after 24 h – red). 128.34 MHz, toluene- d_8 , 290 K.	S15
Figure S16. General view of a fragment of the crystal packing in $2_{\text{Sm}}^{\text{DMAB}}$ obtained from the mixture of $1_{\text{Sm}}\text{-TMEDA}$ and 2 equiv. DMAB in toluene.	S16
Figure S17. ^{11}B NMR spectrum of the reaction mixture of DMAB (0.04 M) with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (0.01 M) after 24 h. Toluene- d_8 , 128.34 MHz, 290 K.	S16
Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (128.34 MHz) of DMAB (0.01 M, blue) and its 4:1 mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (red). Toluene- d_8 , 290 K.	S17
Figure S19. The plot of H_2 pressure changes measured by Man on the Moon kit for the 1 : 2 mixture of $2_{\text{Yb}}^{\text{DMAB}}$ with DMAB in toluene, 295 K.	S17
Figure S20. Time-evolution of IR spectra in the ν_{BH} region for the mixture of DMAB (0.02 M) and $2_{\text{Yb}}^{\text{DMAB}}$ (0.01 M) in toluene; $t = 0$ (blue) -20 h (green). Spectra of DMAB (0.02 M; black) and $2_{\text{Yb}}^{\text{DMAB}}$ (0.01 M; red) are given for the reference. 298 K, $l = 0.2$ cm.	S18
Figure S21. The second-order kinetic curve built on the base of IR-spectra analysis (ν_{NH}) for 1:2 mixture $2_{\text{Yb}}^{\text{DMAB}}$ /DMAB in toluene, 295 K.	S18
Figure S22. The second-order kinetic curve built on the base of volumetric data for 1:2 mixture $2_{\text{Yb}}^{\text{DMAB}}$ /DMAB in toluene, 295 K.	19
Figure S23. ^1H NMR spectra of 4:1 mixture of Me_2NHBH_3 (0.04 M) and 0.01 M $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ ($1_{\text{Sm}}\text{-TMEDA}$, 0.01 M). 300 MHz, toluene- d_8 , 190 K.	S19

Figure S24. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 mixture of Me_2NHBH_3 (0.04 M) and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M). 128.34 MHz, toluene- d_8 , 290 K. * - signal of DMAB influenced by paramagnetic Sm(II)	S20
Figure S25. ^{11}B NMR spectra of 2:1 (blue) and 4:1 (green, red) mixtures of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ (0.01 M) after 5 h (blue, green) and after 30 h (red) of the reaction. 128.34 MHz, toluene- d_8 , 290 K.....	S20
Figure S26. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 (blue), 6:1 (green) and 8:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ ($c = 0.01$ M) after 1 h of the reaction. 128.34 MHz, toluene- d_8 , 290 K.....	S21
Figure S27. ^{11}B NMR spectra of 6:1 mixture of $t\text{BuNH}_2\text{BH}_3$ (0.06 M) and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M) in 1h and 22 h after mixing. 128.34 MHz, toluene- d_8 , 290 K.....	S21
Figure S28. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 (blue), 6:1 (green) and 8:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ ($c = 0.01$ M) after 30 h. 128.34 MHz, toluene- d_8 , 290 K.	S22
Figure S29. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 8:1 mixture of $t\text{BuNH}_2\text{BH}_3$ (0.08 M) and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ (0.01 M) in 75 h after mixing. 128.34 MHz, toluene- d_8 , 290 K.....	S22
Table S3. Comparison of $2_Yb^{TBAB}/2TBAB$ and $1_Yb\cdot\text{TMEDA}/4TBAB$ systems kinetic parameters.	S23
Figure S30. The plot of H_2 pressure changes measured by Man on the Moon kit for 1 : 2 mixture of 2_Yb^{TBAB} with TBAB (blue) and 1 : 4 mixture of $1_Yb\cdot\text{TMEDA}$ with TBAB (red) in toluene, 295 K.....	S23
Figure S31. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 1:1 (blue), 2:1 (green) and 4:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M) after 1 h of the reaction. 128.34 MHz, toluene- d_8 , 290 K.....	S23
Figure S32. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 1:1 (blue), 2:1 (green) and 4:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M) after 22 h of the reaction. 128.34 MHz, toluene- d_8 , 290 K.....	S24

General Procedures.

All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or in a nitrogen filled glovebox. Solvents (including deuterated solvents used for NMR) were dried over appropriate drying agent and distilled prior to use. FTIR spectra were measured on Nicolet iS50 FTIR spectrometer. NMR spectra were recorded on a Bruker Avance II 400 MHz and 600 MHz and Varian Inova FT-NMR 400 MHz spectrometers. ^1H chemical shifts are reported in parts per million (ppm) downfield to tetramethylsilane (TMS) and were calibrated against the residual solvent resonance, while ^{11}B signals were referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$.

X-ray diffraction.

Single crystals of $2\text{-Sm}^{\text{DMAB}}\cdot\text{TMEDA}$ and $3\text{-Yb}\cdot\text{DME}$ were grown by slow diffusion of hexane into a solution of the $2\text{-Sm}^{\text{DMAB}}\cdot\text{TMEDA}$ in a THF-TMEDA mixture or by direct crystallization from the reaction mixture for $3\text{-Yb}\cdot\text{DME}$. X-ray diffraction data were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using the graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Using Olex2 [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, 42, 339-341], the structures were solved with the ShelXT structure solution program [G. M. Sheldrick, *Acta Cryst. A* 2015, 71, 3-8] using Intrinsic Phasing and refined using Least-Squares minimisation. Hydrogen atoms of BH groups were located in difference Fourier synthesis. Positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation in the riding model. Crystal data and structure refinement parameters are given in Table S1. Full crystallographic data have been deposited with the CCDC as 2117456 and 2117457 contain the supplementary crystallographic data for $2\text{-Sm}^{\text{DMAB}}\cdot\text{TMEDA}$ and $3\text{-Yb}\cdot\text{DME}$, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Table S1. Crystal data and structure refinement parameters for $2\text{-Sm}^{\text{DMAB}}$ and $3\text{-Yb}^{\text{DMAB}}\cdot\text{DME}$.

	$2\text{-Sm}^{\text{DMAB}}\cdot\text{TMEDA}$	$3\text{-Yb}\cdot\text{DME}$
Formula unit	$\text{C}_{28}\text{H}_{104}\text{B}_8\text{N}_{12}\text{Sm}_4$	$\text{C}_{12}\text{H}_{44}\text{B}_4\text{N}_4\text{O}_2\text{Yb}$
Formula weight	1297.11	492.79
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pccn
Z	1	4
a, \AA	9.7159(17)	10.3781(4)
b, \AA	13.065(2)	12.5474(4)
c, \AA	13.542(2)	17.7027(6)
α , $^\circ$	104.319(4)	90
β , $^\circ$	107.514(4)	90
γ , $^\circ$	108.505(3)	90
V, \AA^3	1438.6(4)	2305.21(14)
D_{calc} (g cm^{-3})	1.497	1.420
Linear absorption, $\text{m}(\text{cm}^{-1})$	40.51	40.66
F(000)	644	1000
$2\theta_{\text{max}}$, $^\circ$	52	58
Reflections measured	5650	26967
Independent reflections	5650	3063
Observed reflections [$I > 2s(I)$]	3809	2129
Parameters	247	110
R1	0.0815	0.0164
wR2	0.2077	0.0418
GOF	1.062	1.066
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e \AA^{-3})	1.777/-1.465	0.595/-0.282

Synthetic procedures.

Complexes 1-TMEDA have been synthesized as reported before [A. N. Selikhov, G. S. Plankin, A. V. Cherkasov, A. S. Shavyrin, E. Louyriac, L. Maron and A. A. Trifonov, *Inorg. Chem.*, 2019, 58, 5325-5334.], and $1\text{-Yb}\cdot\text{DME}$ was obtained similarly to the reported isostructural samarium complex.

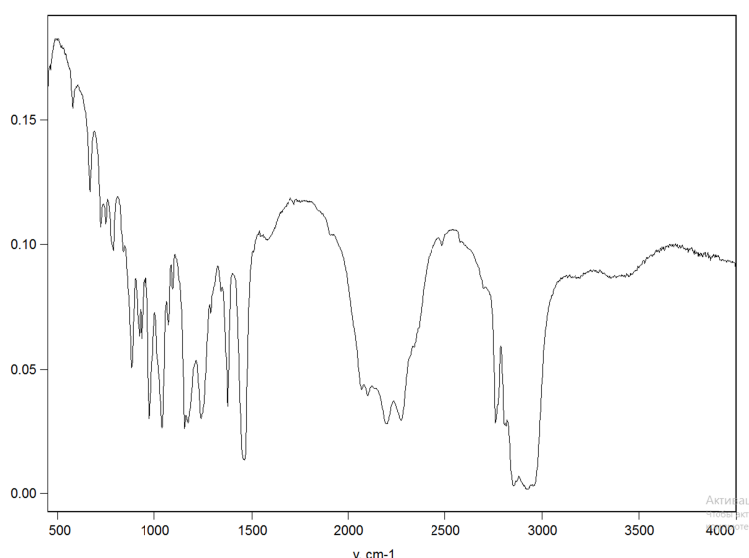
Synthesis of $[(p\text{-tBu-C}_6\text{H}_4)_2\text{CH}]_2\text{Yb}(\text{TMEDA})$ ($1\text{-Yb}\cdot\text{TMEDA}$). ($p\text{-tBu-C}_6\text{H}_4$) $_2\text{CH}_2$ (1.18 g, 4.20 mmol) was dissolved in hexane (5 mL), the solution was cooled to 0°C and 1 mL of TMEDA (6.70 mmol) was added. n-BuNa (0.36 g, 4.4 mmol) was added to the

solution under vigorous stirring. The suspension was stirred at 0° C for 2 h, then brought to room temperature and stirred for an additional hour. A yellow precipitate of [(*p*-*t*Bu-C₆H₄)₂CH]Na(TMEDA) was formed. Hexane was removed in vacuum, and toluene (10 mL) was added. The resulting suspension was slowly added to the suspension of YbI₂ (0.90 g, 2.10 mmol) in TMEDA (3 mL) at room temperature and the resulting dark red solution which was stirred at 50 °C for 4 h and at room temperature for 24 h. The solution was centrifuged from the insoluble precipitate of NaI, the precipitate was once extracted with toluene (5 mL). The toluene extracts were combined, complex 3 was obtained as dark red crystals by cooling the solution of the complex in toluene to -35 °C. The yield was 1.27 g (71%). Melting point with decomposition 156-159 °C. ¹H NMR (400 MHz, C₆D₆, 293 K): δ 1.33-1.40 (compl m, 52 H, CCH₃, -CH₂CH₂- and NMe₂, TMEDA), 4.10 (s, 2 H, CH), 7.01 (d, 8 H, *o*-CH, C₆H₄, ³J_{HH} = 5.9 Hz), 7.19 (d, 8 H, *m*-CH, C₆H₄, ³J_{HH} = 8.4 Hz). ¹³C{¹H} NMR (100 MHz, C₆D₆, 293 K): δ 31.8 (s, C(CH₃)₃), 34.0 (s, C(CH₃)₃), 45.7 (s, NMe₂, TMEDA), 56.5 (s, -CH₂CH₂-, TMEDA), 71.2 (s, CH), 117.8 (s, *o*-CH, C₆H₄), 127.9 (s, *m*-CH, C₆H₄), 136.9 (s, *ipso*-C), 143.1 (s, *ipso*-C). IR (KBr): 1790 (s), 1264 (m), 1175 (s), 1128 (w), 1030 (m), 811 (s), 661 (m), 623 (w), 547 (m). Anal. CalcTd. for C₄₈H₇₀N₂Yb (848.16 g/mol): C 67.97; H 8.32; N 3.30; Yb 20.40. Found: C 67.69; H 8.06; N 3.00; Yb 21.25.

Synthesis of [(*p*-*t*Bu-C₆H₄)₂CH]₂Sm(TMEDA) (1_SmzTMEDA). (*p*-*t*Bu-C₆H₄)₂CH₂ (2.00 g, 7.10 mmol) was dissolved in hexane (15 mL), the solution was cooled to 0° and TMEDA (1.80 mL, 12.00 mmol) was added. *n*-BuNa (0.62, g 7.80 mmol) was added at 0°. The solution was stirred for 2 h, then was brought to room temperature and stirred for an additional hour. A yellow precipitate of [(*p*-*t*Bu-C₆H₄)₂CH]Na(TMEDA) was formed. Hexane was removed in vacuum and toluene (10 mL) was added. A suspension of [(*p*-*t*Bu-C₆H₄)₂CH]Na(TMEDA) in toluene was added to a green suspension of SmI₂(THF)₂ (1.94 g, 3.55 mmol) in TMEDA (3 mL, 20 mmol) and a resulting dark brown solution was stirred at room temperature for 24 h. The solution was centrifuged from the insoluble precipitate of NaI and the precipitate was once extracted with toluene (15 mL). The toluene extracts were combined, the volatiles were removed in vacuum and black solid residue was dried in vacuum for 1 h and was recrystallized from fresh toluene (20 mL) by slow concentration of mother liquor. The yield of complex 2 was 1.60 g (55%). Melting point with decomposition 151-153 °C. ¹H NMR (200 MHz, C₆D₆, 293 K): δ 2.05 (br s, 12 H, NMe₂, TMEDA), 2.26 (br s, 4 H, -CH₂CH₂-, TMEDA), 3.52 (br s, 36 H, *t*Bu), 6.13 (br s, 8 H, *o*-CH, C₆H₄), 10.14 (br s, 8 H, *m*-CH, C₆H₄), 14.10 (br s, 2 H, CH). IR (KBr): 1792 (s), 1260 (m), 1175 (s), 1130 (w), 1032 (m), 811 (s), 665 (m), 630 (w), 544 (m). Anal. CalcTd. for C₄₈H₇₀N₂Sm (825.46 g/mol): C 69.84; H 8.55; N 3.39; Sm 18.22. Found: C 69.59; H 8.23; N 3.07; Sm 19.11.

Synthesis of [(*p*-*t*Bu-C₆H₄)₂CH]₂Yb(DME)₂ (1_YbzDME). Complex [(*p*-*t*Bu-C₆H₄)₂CH]₂Yb(TMEDA) (3) (0.579g, 0.69 mmol) was dissolved in toluene (10 mL) and excess of DME (1 mL) was added. Bright-yellow powder of 4 formed instantly. The suspension was stirred at room temperature for 20 min and then centrifuged. The bright yellow precipitate of complex 4 was separated by decantation from the mother liquor and dried in vacuum for 3 hours at 50 °C. The complex yield was 0.565 g (90%). IR (KBr): 1595 (s), 1511 (s), 1270 (w), 1189 (m), 1107 (s), 1057 (s), 1020 (s), 858 (s), 827 (s), 799 (s), 672 (m), 632 (m), 548 (s). Anal. CalcTd. for C₅₀H₇₄O₄Yb (912.19 g/mol): C, 65.84; H, 8.18; Yb, 18.97. Found: C, 65.60; H, 8.25; Yb, 19.08.

Synthesis of [(Me₂NBH₃)Sm(TMEDA)]₂²⁺{(Me₂NBH₃)₃Sm}₂²⁻ (2_Sm^{DMAB}zTMEDA). To a solution of [(*p*-*t*Bu-C₆H₄)₂CH]₂Sm(TMEDA) (1.0 g, 1.2 mmol) in toluene (8 ml) was added DMAB (0.14 g, 2.4 mmol), instantly the solution turned black. After 2 hours at RT, all volatiles were removed in vacuo, the black residue was washed with hexane and dissolved in a TMEDA-THF (2:1) mixture. Black crystals suitable for X-ray structural analysis were obtained by slow diffusion of hexane into a solution of the complex in a THF-TMEDA mixture (1 ml) (0.263g, 67%). IR (KBr): 2761 (s), 2400-2000 (s, BH), 1244 (s), 1159 (s), 1098 (w), 1074 (w), 1040 (s), 976 (s), 935 (w), 920 (w), 879 (s) (see figure below). Anal. Calc. for C₂₈H₁₀₄B₈N₁₂Sm₄ (1297.14 g/mol): C, 25.93; H, 8.08; N, 12.96; Sm, 46.37. Found: C, 26.14; H, 7.98; N, 13.10; Sm, 45.99.



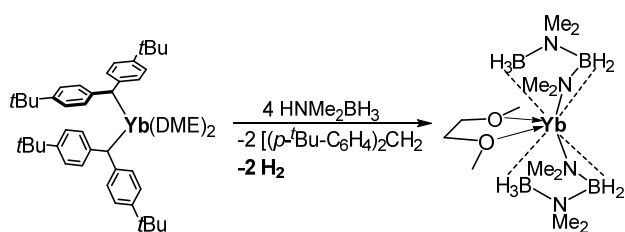
IR spectrum (KBr pellets) of complex [(Me₂NBH₃)Sm(TMEDA)]₂²⁺{(Me₂NBH₃)₃Sm}₂²⁻..

Table S2. Selected ^1H and ^{11}B NMR parameters of complexes 1-4, their ligands and amine-boranes.

	δ_{H} , ppm					δ_{B} , ppm		
	L		TBDM/(TBDM)H			-BH ₃	-BH/BH ₂ -	
	-CH ₃	-CH ₂ -	- <i>t</i> Bu	-CH/CH ₂ -	-C ₆ H ₄ -			
THF								
L = DME	3.28	3.43						
L = TMEDA	2.15	2.30						
(TBDM)H			1.28	3.86	7.09	7.27		
DMAB							-13.5	
TBAB							-23.3	
AB							-22.34	
1_Yb·DME	^a	^a	1.21	3.66	6.76	6.91		
1_Yb·TMEDA	^a	^a						
2_Yb^{DMAB}							-13.5	
4_Yb^{TBAB}							-23.0	
4_Yb^{AB}							-18.9	
toluene								
DME	3.12	3.31						
TMEDA	2.12	2.33						
(TBDM)H			1.22	3.81	7.05	7.19		
DMAB	1.7						-12.7	
TBAB							-22.4	
1_Yb·DME	3.07	3.23	1.34	4.02	6.92	7.13		
1_Yb·TMEDA	1.39	^b						
2'_Yb^{DMAB}			1.29	3.90	7.25	7.50	-10.6 (w)	
			1.31	3.94	7.27	7.53		
2'_Yb^{TBAB}			1.19 (w)	3.86 (w)	^b	7.37	-7.07 (w)	
					7.27	7.46		
2_Yb^{DMAB}							-12.0	
2_Yb^{TBAB}							-18.5	
3_Yb·DME							-10.2	1.7
3_Yb·TMEDA							-9.7	3.5

^a In THF both DME and TMEDA are dissociated

^b These resonances are overlapped with free (TBDM)H resonances



Scheme S1. Synthesis of 3_Yb·DME.

Volumetric studies of amine boranes dehydrogenation.

Hydrogen evolution during dehydrogenation of amine-boranes was monitored using the *Man on the Moon X103* kit developed for monitoring the progress of reactions that evolve gases by measuring the pressure variation vs. time in closed reaction systems. More information about the features of the kit can be found at the following link: <http://www.manonthemoontech.com/x102-gas-evolution.html>. The systems' volumes were 19 and 32 ml (two-necked round-bottom flask – 17 or 30 ml, three-way valve – 2 ml).

The monitored solutions were prepared via two methods:

Method I: in the nitrogen filled glovebox the toluene or toluene- d_8 solution of complex 1 ($c = 0.01$ M) was put in the flask of the device connected to a three-way valve. The valve was opened to the pressure sensor. The chosen amount of amine-borane solution in toluene or toluene- d_8 ($c = 0.5$ -1 M) was quickly added to the flask. Then the flask was tightly closed with a septum cap.

Method II: complex 2 ($c = 0.01$ M) was generated *in situ* by mixing the solutions of complex 1 in toluene or toluene- d_8 ($c = 0.01$ M, 1 equiv) and 2 equiv. amine-borane (stock solution with $c = 0.5$ -1 M was used). Resulting solution was put in the flask of the device connected to a three-way valve. The valve was opened to the pressure sensor. The chosen amount of amine-borane solution in toluene or toluene- d_8 ($c = 0.5$ -1 M) was quickly added to the flask. Then the flask was tightly closed with a septum cap.

The resulting mixture was stirred at 295-300 K. Data from a pressure sensor connected via a wireless network to a computer were recorded as a function of pressure versus time for 3-120 hours. The values accumulated were referenced by the pressure of toluene in a blank experiment at 295-300 K and used for calculations of the H_2 equivalents evolved. The calculations were performed in the ideal gas approximation ($pV = nRT$).

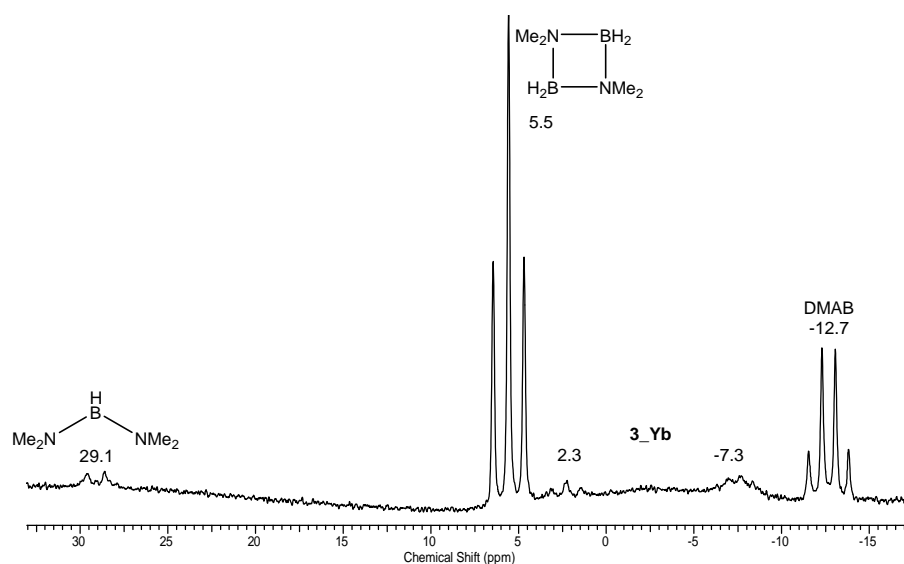


Figure S1. ^{11}B NMR spectrum of the reaction mixture for 3_Yb ($c = 0.01$ M) and 30 equiv. of Me_2NHBH_3 (DMAB) after 14 days in toluene- d_8 , 128.34 MHz, 290 K

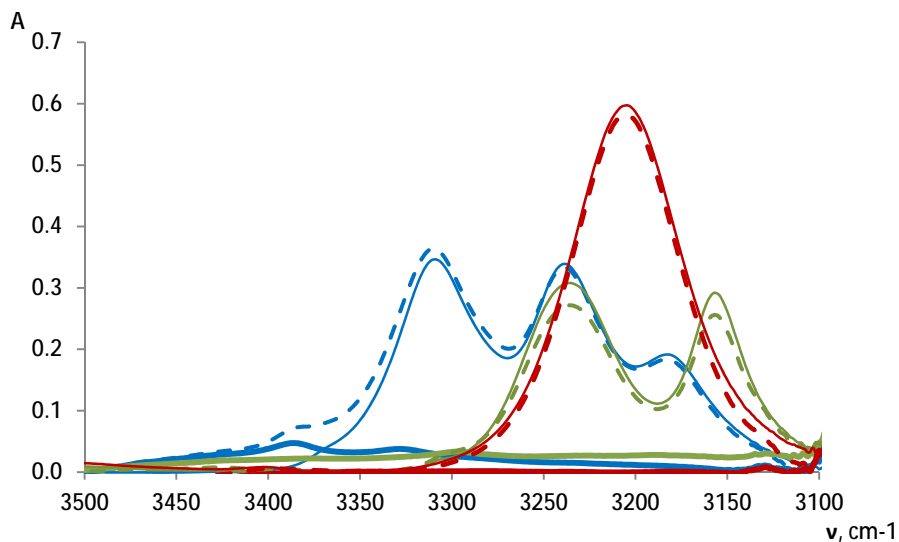


Figure S2. IR spectra in the ν_{NH} region of amine-boranes (blue - NH_3BH_3 0.01 M, green - $t\text{BuNH}_2\text{BH}_3$ 0.01 M, red - Me_2NHBH_3 0.02 M) in THF and of complexes 2^{DMAB} (bold red line), 4^{TBAB} (bold green line) and 4^{AB} (bold blue line) as the products of the amine-boranes reaction with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_Yb-DME, 0.01 M). Dashed lines – addition of one more equivalent of amine-borane (two more in case of DMAB) to the corresponding reaction mixture. $l = 0.2 \text{ cm}$, 298 K.

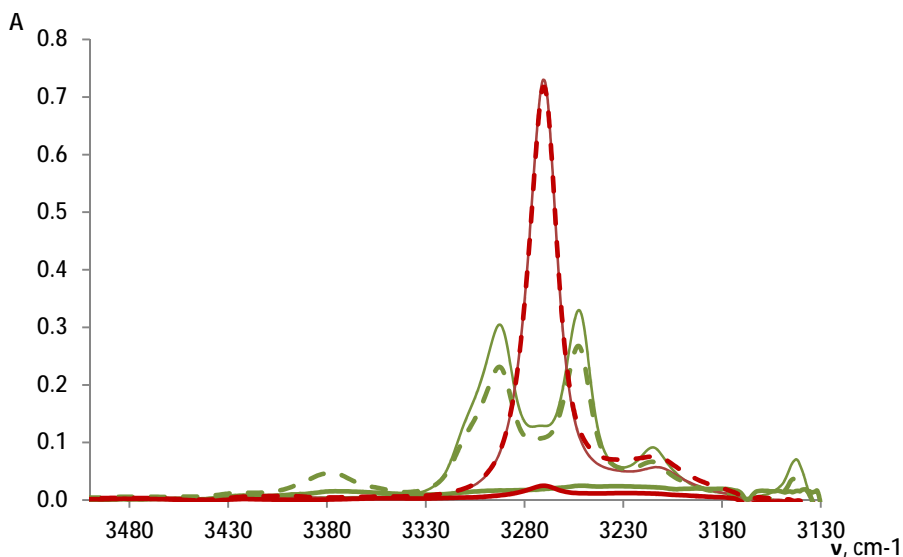


Figure S3. IR spectra in the ν_{NH} region of 0.02 M amine-boranes (green - $t\text{BuNH}_2\text{BH}_3$, red - Me_2NHBH_3) and of complexes $2_{\text{Yb}}^{\text{TBAB}}$ (bold green line) and $2_{\text{Yb}}^{\text{DMAB}}$ (bold red line) as the products of their reaction with $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ (1_Yb-TMEDA, 0.01 M). Dashed lines – addition of two more equivalent of amine-borane to the corresponding reaction mixture. Toluene, $l = 0.2 \text{ cm}$, 298 K.

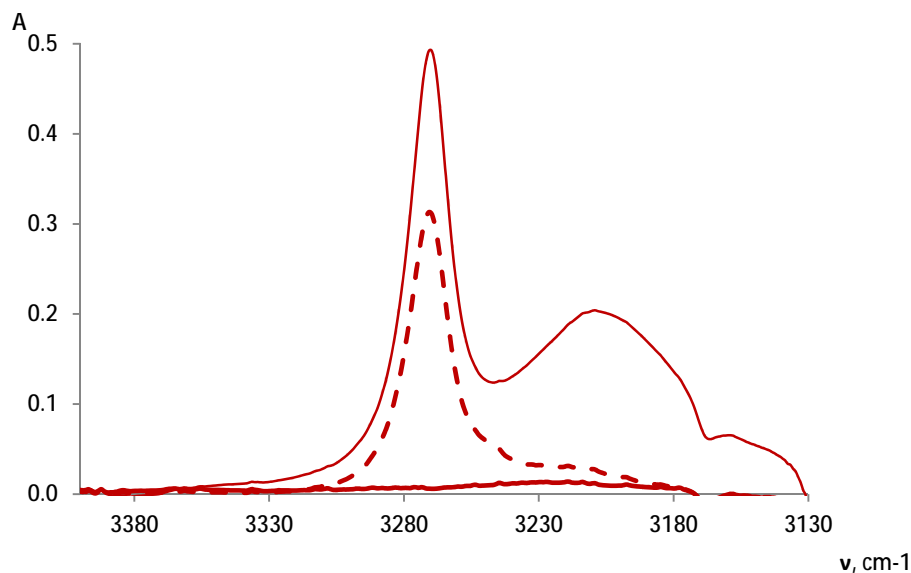


Figure S4. IR spectra in the ν_{NH} region of Me_2NHBH_3 ($c = 0.02$ M, thin solid line) and of complex $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ ($2_{\text{Sm}}^{\text{DMAB}}$, bold line) as the product of its reaction with $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M). Dashed line – addition of two more equivalents of DMAB to the corresponding reaction mixture. Toluene, $l = 0.2$ cm, 298 K.

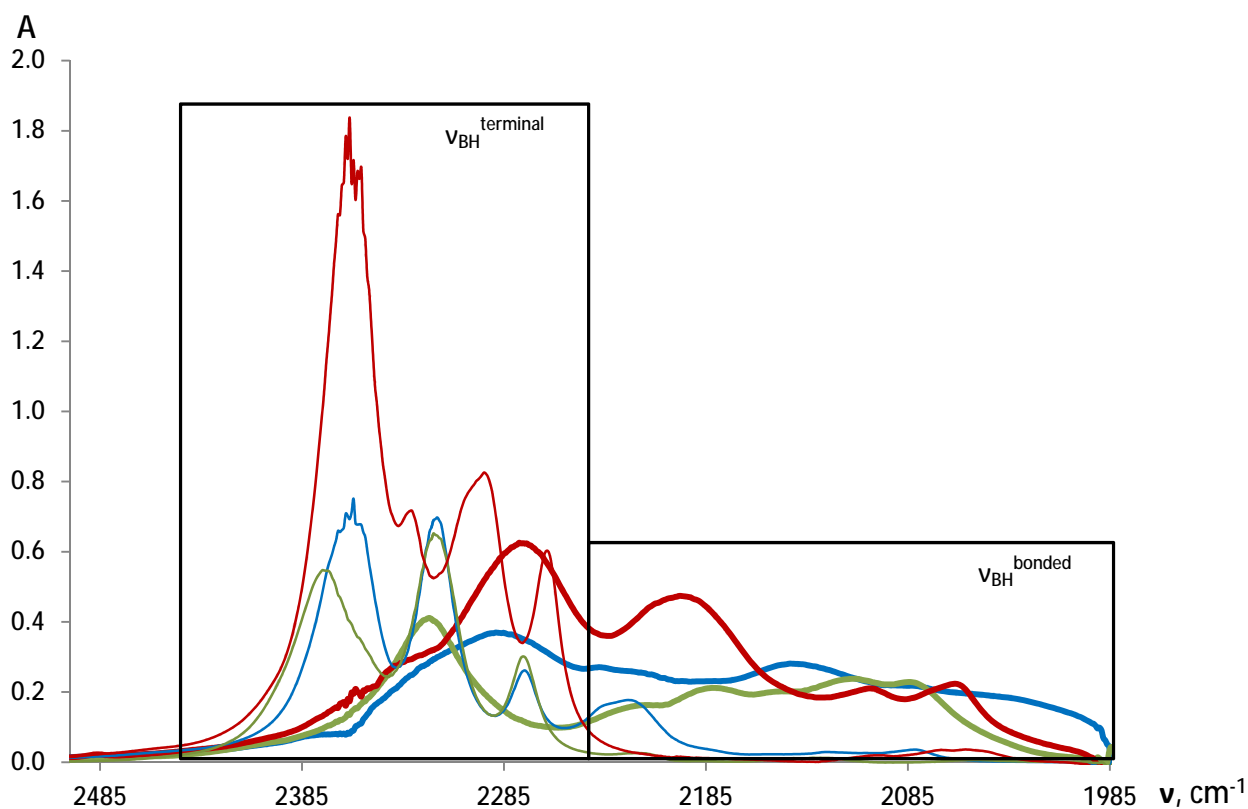


Figure S5. IR spectra in the ν_{BH} region of amine-boranes (blue - NH_3BH_3 0.01 M, green - ${}^t\text{BuNH}_2\text{BH}_3$ 0.01 M, red - Me_2NHBH_3 0.02 M) in THF and the products of their interaction with 0.01 M $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (bold lines), $l = 0.2$ cm, 298 K. Region of terminal ν_{BH} – left box, noncovalently bonded ν_{BH} – right box

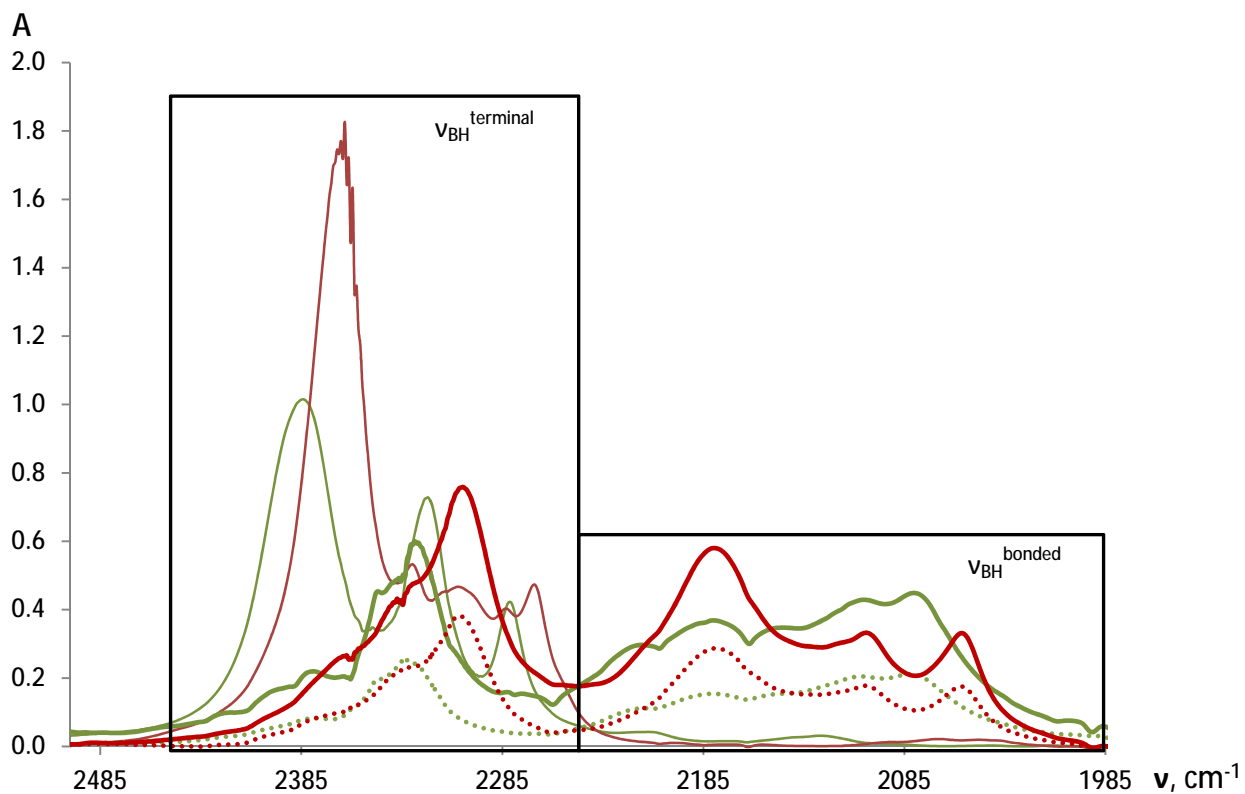


Figure S6. IR spectra in the ν_{BH} region of complexes $2'_\text{Yb}^{\text{TBAB}}$ (dotted green line), $2'_\text{Yb}^{\text{DMAB}}$ (dotted red line), $2_\text{Yb}^{\text{TBAB}}$ (bold green line), and $2_\text{Yb}^{\text{DMAB}}$ (bold red line) measured for the reaction mixtures of 0.01 M $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ ($1_\text{Yb}\cdot\text{TMEDA}$) with 0.01 M (dotted lines) and 0.02 M (bold lines) of the corresponding amine-borane. Toluene, $l = 0.2$ cm, 298 K. IR spectra of amine-boranes in toluene ($c = 0.02$ M; thin solid lines; green – $t\text{BuNH}_2\text{BH}_3$, red – Me_2NHBH_3) are given for comparison.

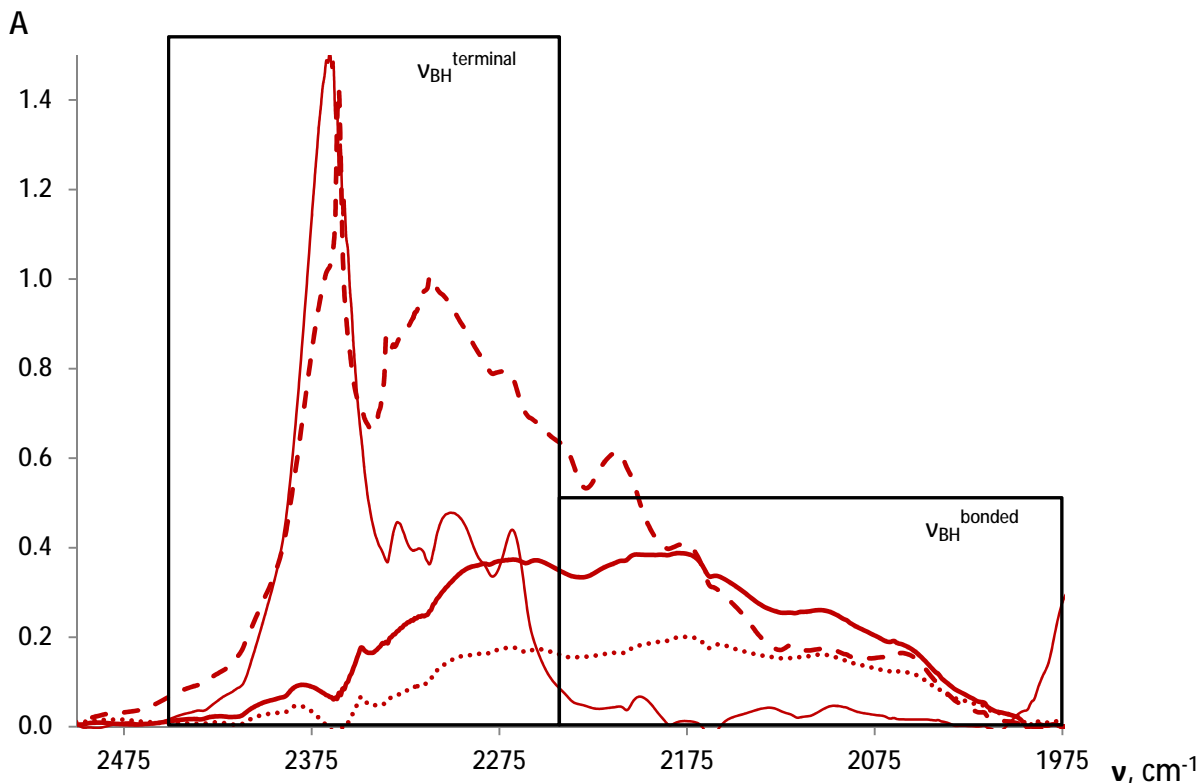


Figure S7. IR spectra in the ν_{BH} region of complexes 2'_Sm^{DMAB} (dotted line), and 2_Sm^{DMAB} (bold line) measured for the reaction mixtures of 0.01 M (TBDM)₂Sm(TMEDA) (1_Sm-TMEDA) with 0.01 M (dotted lines) and 0.02 M (bold lines) in toluene. $l = 0.2 \text{ cm}$, 298 K. IR spectrum of Me₂NHBH₃ ($c = 0.02 \text{ M}$; thin solid line) and after addition of two more equivalents of DMAB to 2_Sm^{DMAB} (dashed lines) are given for comparison. Region of terminal ν_{BH} – left box, noncovalently bonded ν_{BH} – right one.

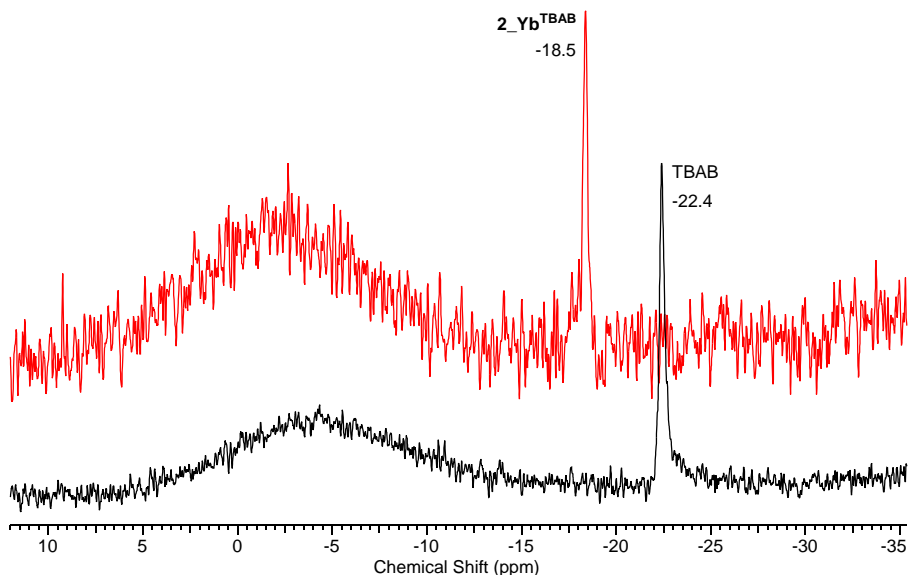


Figure S8. ¹¹B{¹H} NMR spectra of *t*BuNH₂BH₃ (TBAB, $c = 0.02 \text{ M}$) and its 1:2 reaction mixture with (TBDM)₂Yb(TMEDA) (1_Yb-TMEDA, $c = 0.01 \text{ M}$) showing the formation of complex 2_Yb in toluene-*d*₈, 128.34 MHz, 290 K

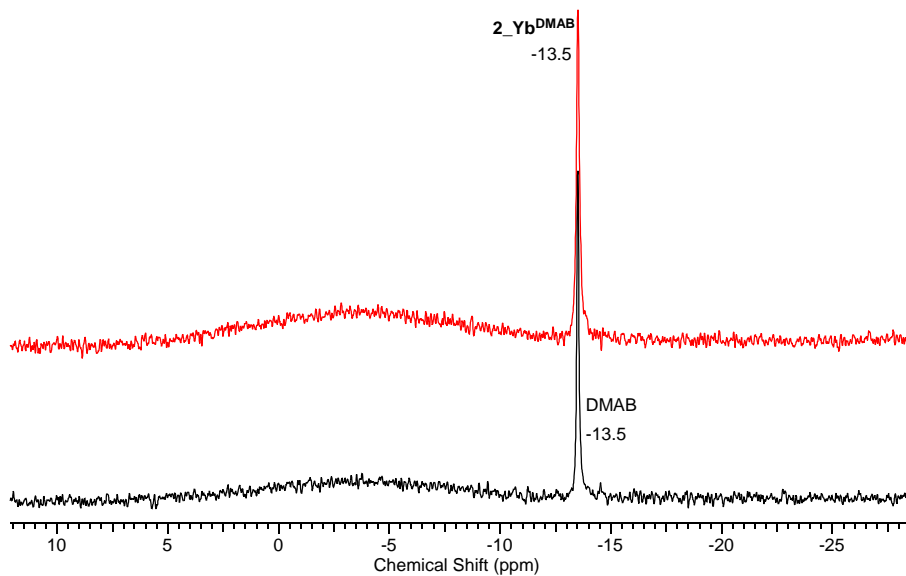


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of Me_2NHBH_3 (DMAB, $c = 0.02$ M) and its 1:2 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M) in $\text{THF-}d_8$, 128.34 MHz, 290 K

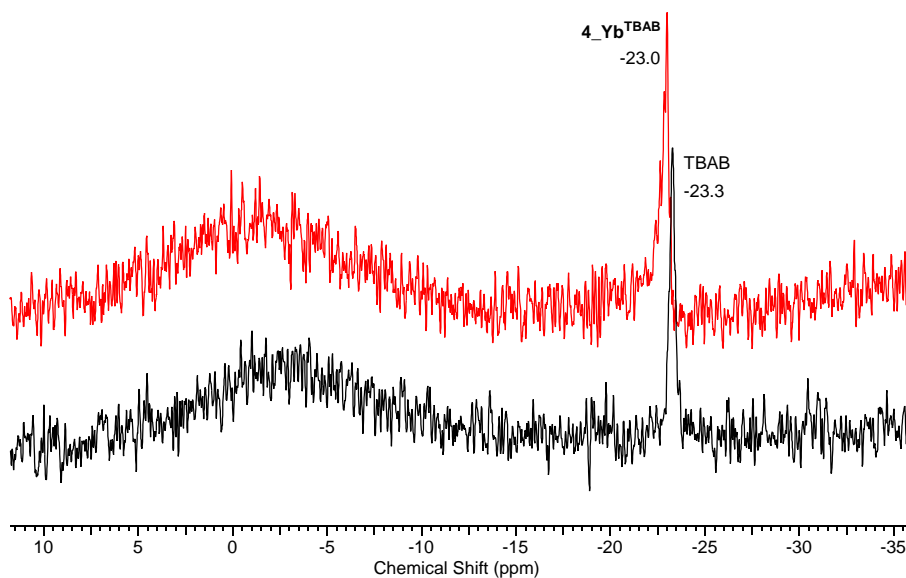


Figure S10. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of $t\text{BuNH}_2\text{BH}_3$ (TBAB, $c = 0.01$ M) and its 1:1 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_{Yb}-DME , $c = 0.01$ M) in $\text{THF-}d_8$, 128.34 MHz, 290 K

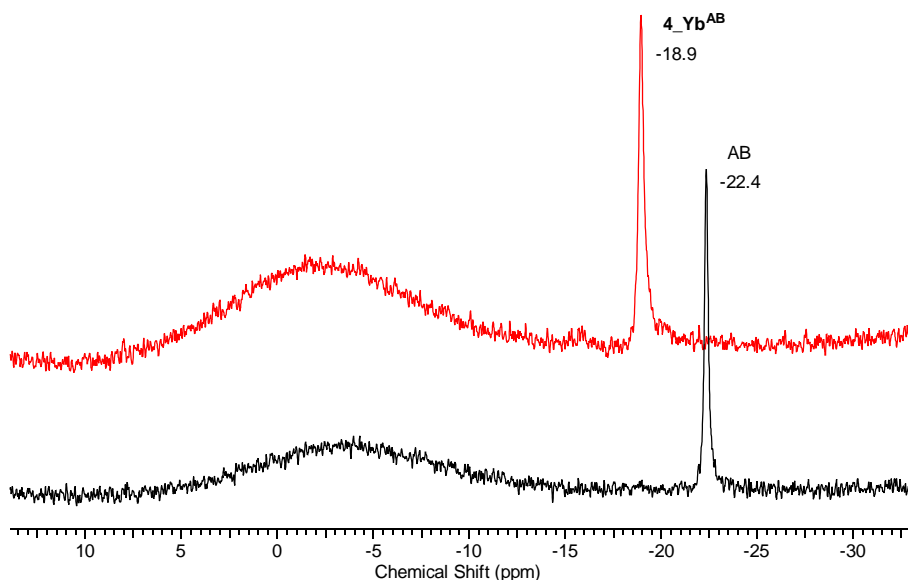


Figure S11. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of NH_3BH_3 (AB, $c = 0.01$ M) and its 1:1 reaction mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_Yb-DME , $c = 0.01$ M) in $\text{THF-}d_8$, 128.34 MHz, 290 K

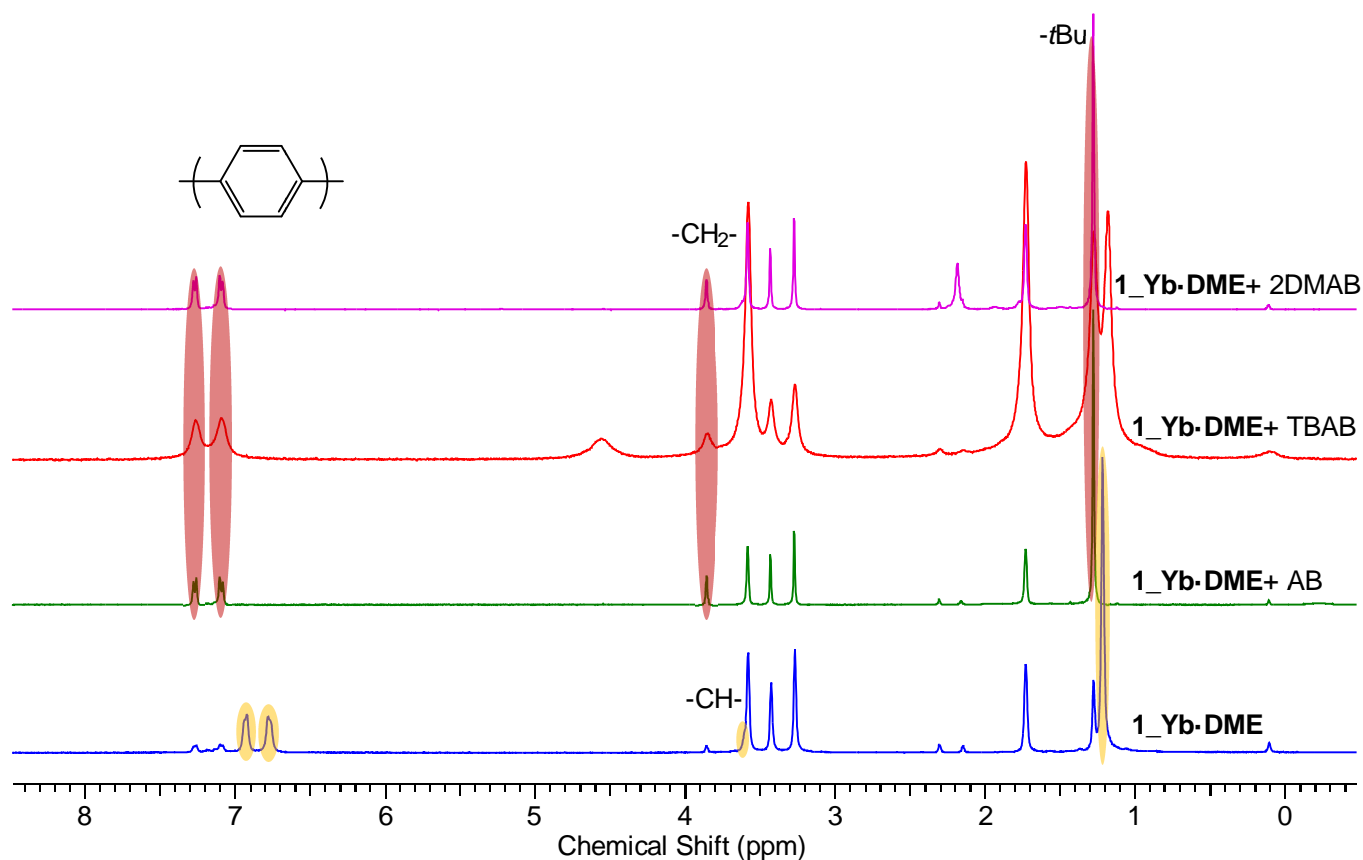


Figure S12. ^1H NMR spectra of $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (1_Yb-DME , $c = 0.01$ M, blue) and its reaction mixture with aminoboranes (NH_3BH_3 (AB, $c = 0.01$ M) – green, $t\text{BuNH}_2\text{BH}_3$ (TBAB, $c = 0.01$ M) – red, Me_2NHBH_3 (DMAB, $c = 0.02$ M) – purple) in $\text{THF-}d_8$. Highlighted signals: ● – $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$, ● – 1_Yb-DME . 400 MHz, 290 K.

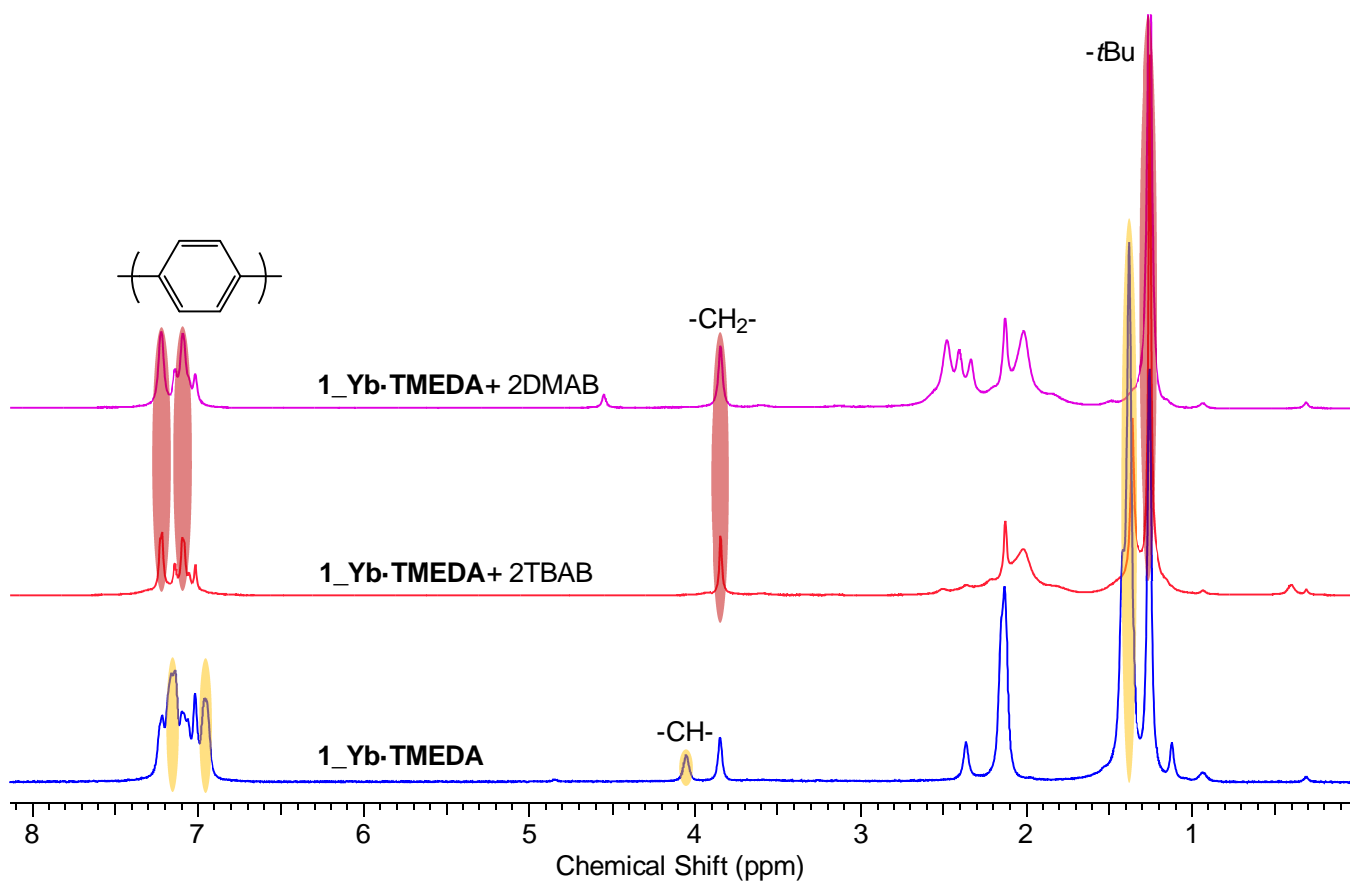


Figure S13. ¹H NMR spectra of (TBDM)₂Yb(TMEDA) (1_Yb-TMEDA, *c* = 0.01 M, blue) and its 1:2 (*c* = 0.02 M) reaction mixture with amine-boranes (*t*BuNH₂BH₃ (TBAB) – red, Me₂NHBH₃ (DMAB) – purple) in toluene-*d*₈. Highlighted signals: ● – (*p*-*t*Bu-C₆H₄)₂CH₂, ● – 1_Yb-TMEDA, 400 MHz, 290 K

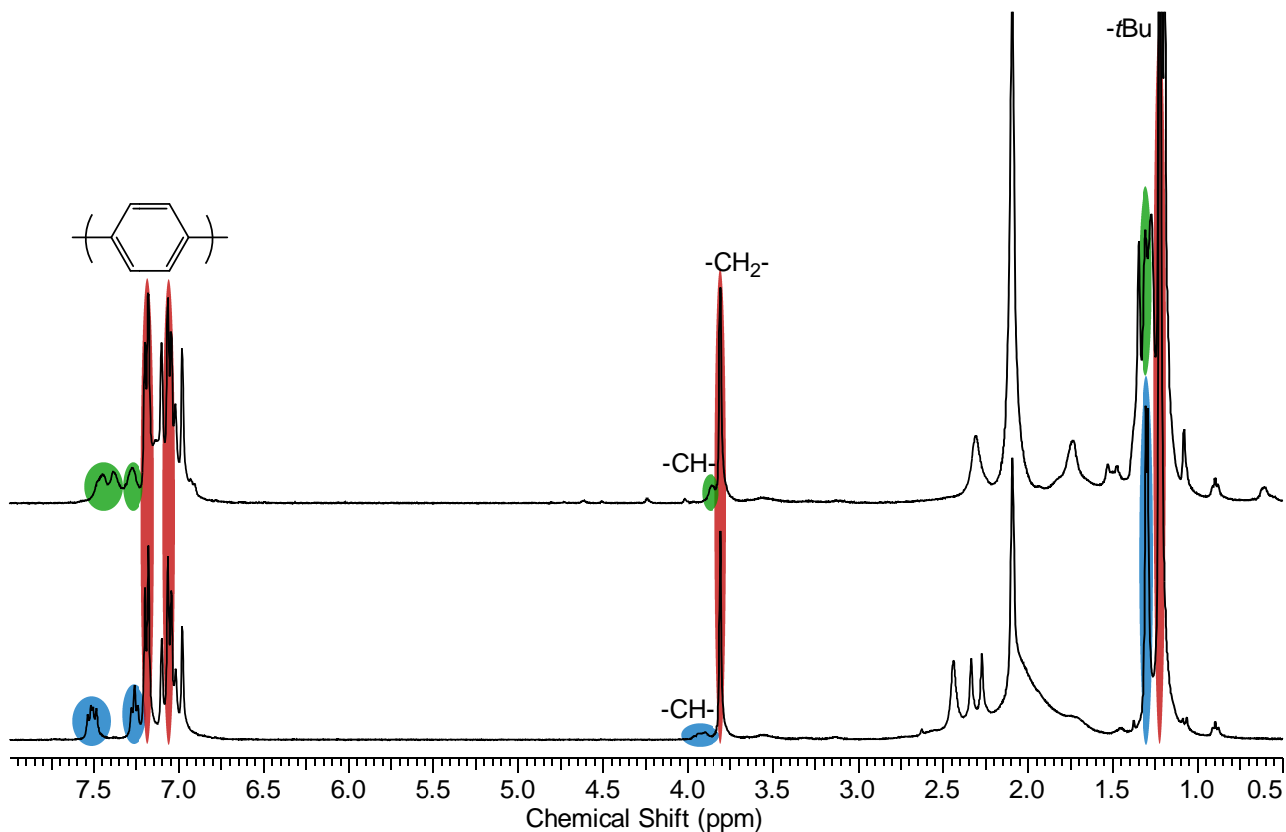


Figure S14. ^1H NMR spectrum of the 1:1 mixture of 0.01 M complex $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ and 0.01 M amine-borane (Me_2NHBH_3 –bottom, $t\text{BuNH}_2\text{BH}_3$ –top). Highlighted signals:
 ● – $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$, ● – $2'\text{-Yb}^{\text{DMAB}}$, ● – $2'\text{-Yb}^{\text{TBAB}}$. 400 MHz, toluene- d_8 , 290 K

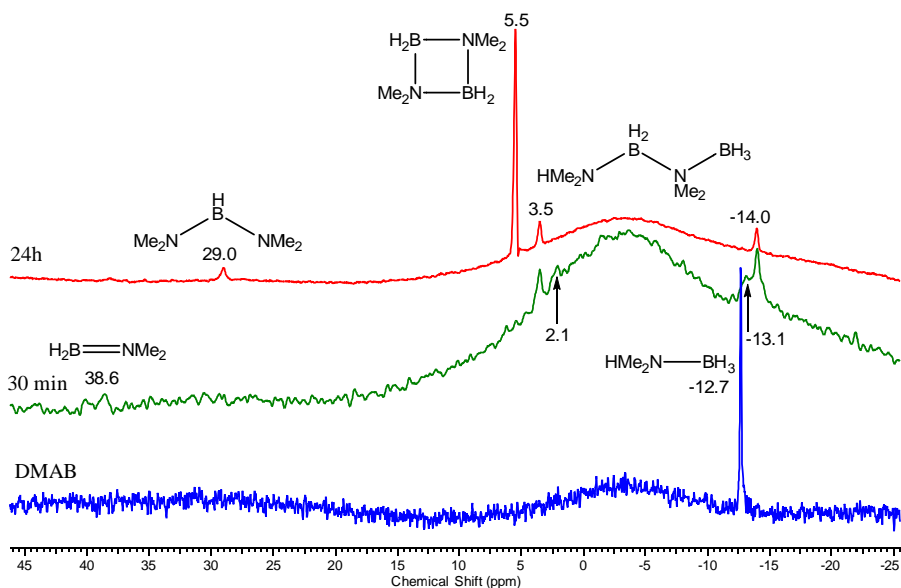


Figure S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 0.01 M Me_2NHBH_3 (blue) and its 2:1 mixture with 0.01 M $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (after 30 min – green, after 24 h – red). 128.34 MHz, toluene- d_8 , 290 K

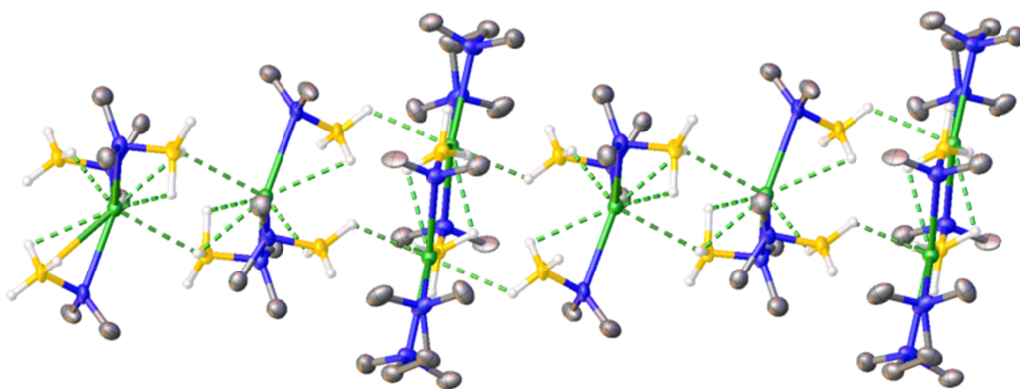


Figure S16. General view of a fragment of the crystal packing in 2_Sm^{DMAB} obtained from the mixture of 1_Sm -TMEDA and 2 equiv. DMAB in toluene. Hydrogen atoms except those of BH groups are omitted for clarity, and only labels for symmetry-independent heteroatoms are given. Selected distances (Å): Sm(1)-N(1) 2.643(15), Sm(1)-N(5) 2.821(14), Sm(1)-N(6) 2.843(14), Sm(2)-N(2) 2.621(14), Sm(2)-N(3) 2.566(14), Sm(2)-N(4) 2.622(14), Sm(1)-B(1) 2.925(17) and 2.934(18), Sm(1)-B(2) 3.045(18), Sm(2)-B(2) 2.89(2), Sm(2)-B(3) 2.920(18), Sm(2)-B(4) 2.851(17) and 2.974(19), N(1)-B(1) 1.53(2), N(2)-B(2) 1.60(2), N(3)-B(3) 1.53(2), N(4)-B(4) 1.54(2), B(1)-H 1.20 – 1.23, B(2)-H 1.06 – 1.15, B(3)-H 1.04 – 1.23, B(4)-H 1.19 – 1.22.

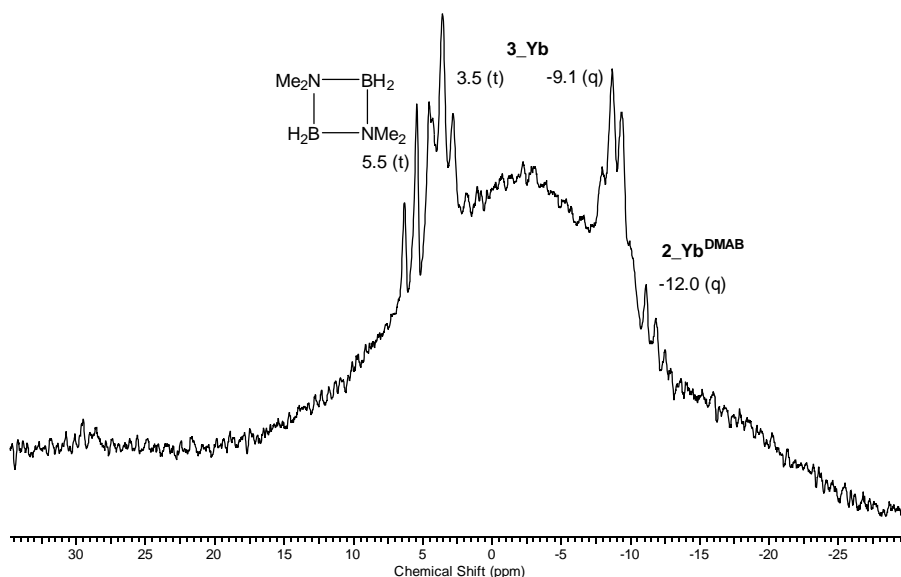


Figure S17. ^{11}B NMR spectrum of the reaction mixture of DMAB (0.04 M) with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (0.01 M) after 24 h. Toluene- d_8 , 128.34 MHz, 290 K

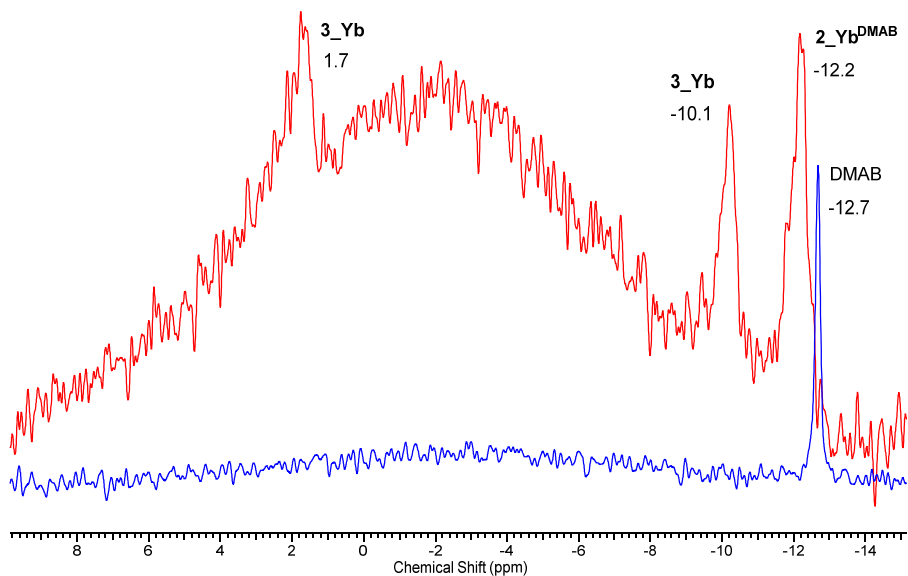


Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (128.34 MHz) of DMAB (0.01 M, blue) and its 4:1 mixture with $(\text{TBDM})_2\text{Yb}(\text{DME})_2$ (red). Toluene- d_8 , 290 K

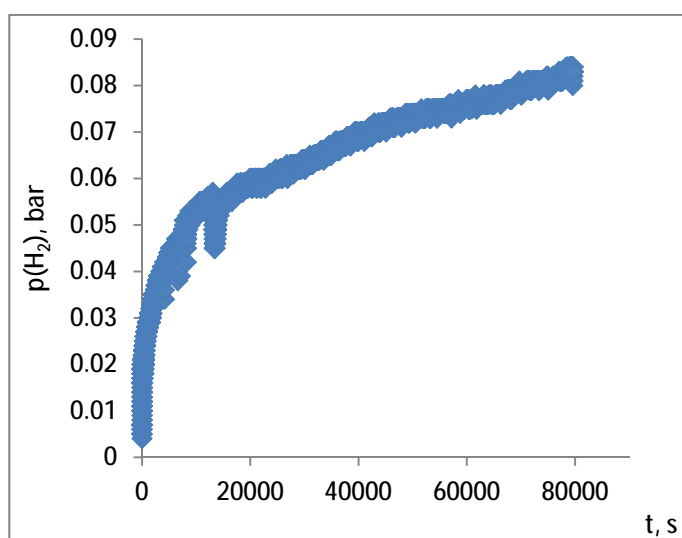


Figure S19. The plot of H_2 pressure changes measured by Man on the Moon kit for the 1 : 2 mixture of 2_Yb^{DMAB} with DMAB in toluene, 295 K

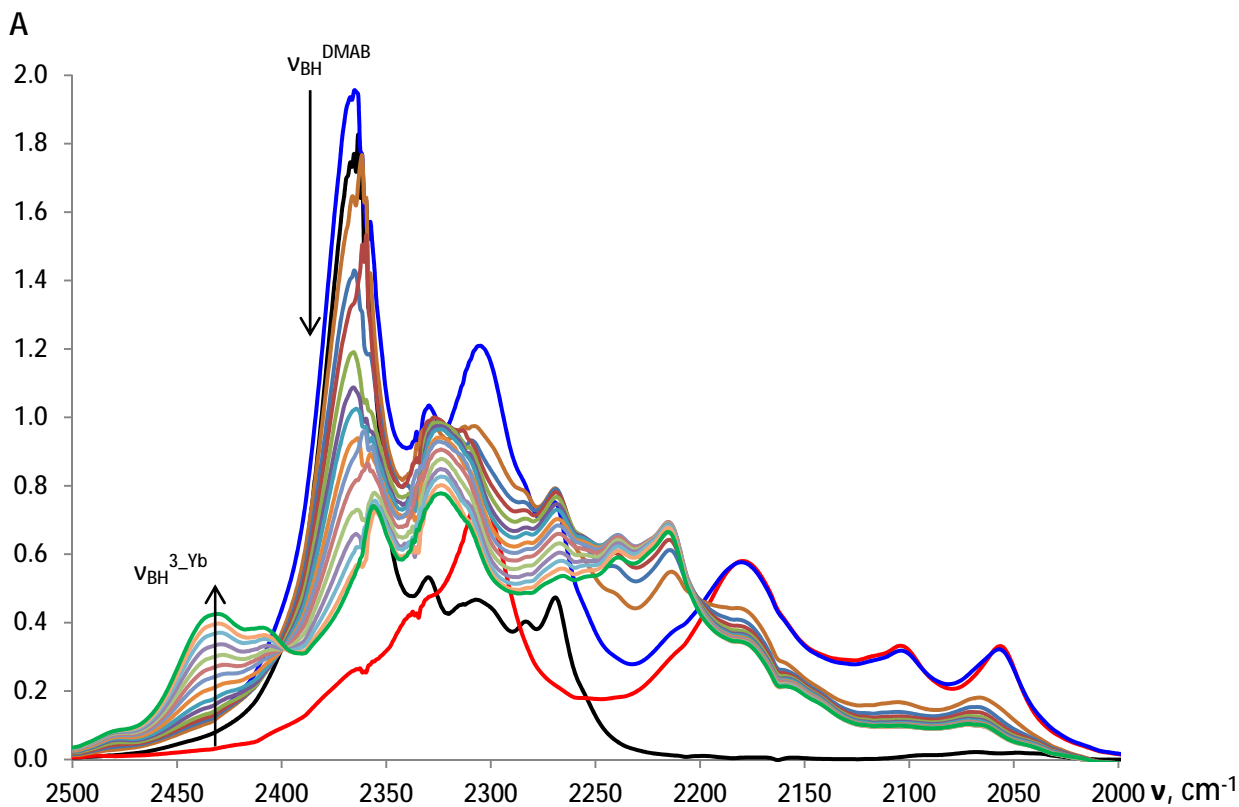


Figure S20. Time-evolution of IR spectra in the ν_{BH} region for the mixture of DMAB (0.02 M) and $2\text{-Yb}^{\text{DMAB}}$ (0.01 M) in toluene; $t = 0$ (blue) -20 h (green). Spectra of DMAB (0.02 M; black) and $2\text{-Yb}^{\text{DMAB}}$ (0.01 M; red) are given for the reference. 298 K, $l = 0.2$ cm.

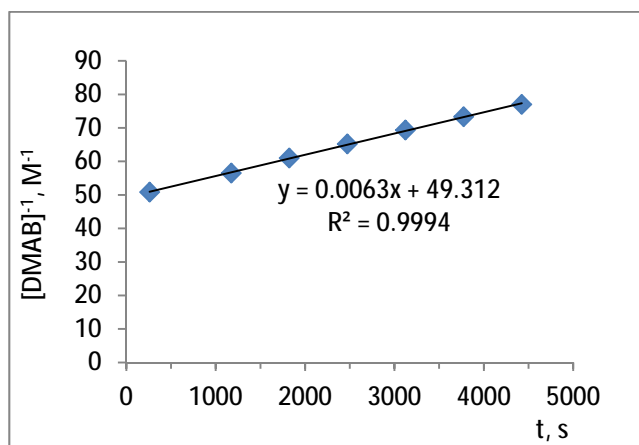


Figure S21. The second-order kinetic curve built on the base of IR-spectra analysis (ν_{NH}) for 1:2 mixture $2\text{-Yb}^{\text{DMAB}}$ / DMAB in toluene, 295 K

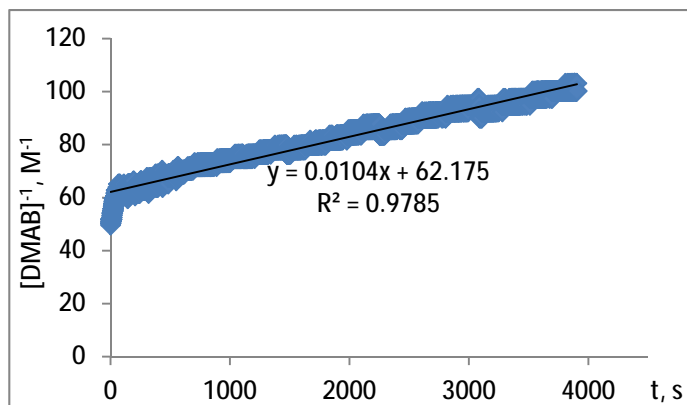


Figure S22. The second-order kinetic curve built on the base of volumetric data for 1:2 mixture 2_Yb^{DMAB} / DMAB in toluene, 295 K

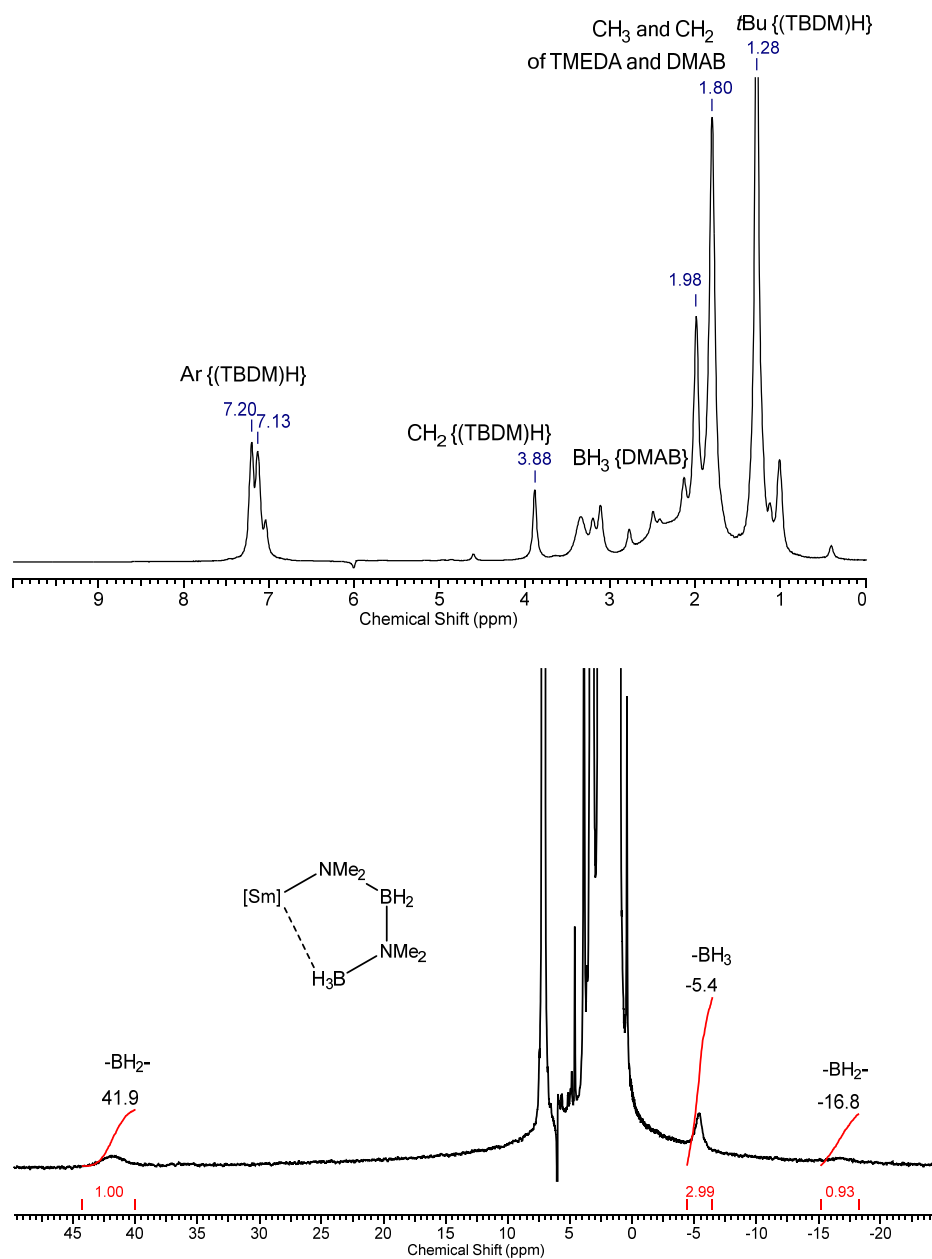


Figure S23. Top: 1H NMR spectrum of 4:1 mixture of Me_2NHBH_3 (0.04 M) and 0.01 M $(TBDM)_2Sm(TMEDA)$ ($1_Sm-TMEDA$, 0.01 M). 300 MHz, toluene- d_8 , 190 K. Bottom: enlarged spectrum showing the BH- signals of 3_Sm^{DMAB} .

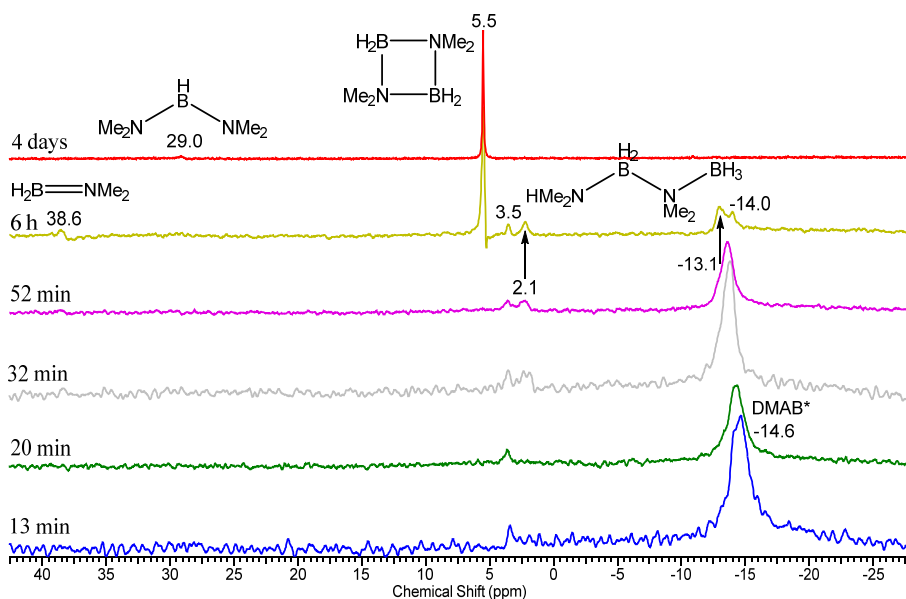


Figure S24. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 mixture of Me_2NHBH_3 (0.04 M) and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M). 128.34 MHz, $\text{toluene-}d_8$, 290 K. * - signal of DMAB influenced by paramagnetic $\text{Sm}(\text{II})$

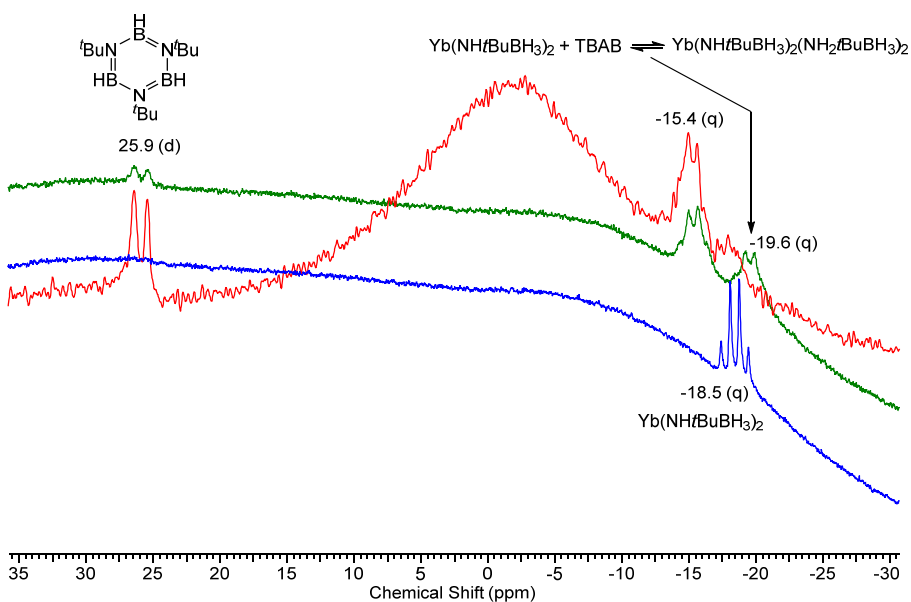


Figure S25. ^{11}B NMR spectra of 2:1 (blue) and 4:1 (green, red) mixtures of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ (0.01 M) after 5 h (blue, green) and after 30 h (red) of the reaction. 128.34 MHz, $\text{toluene-}d_8$, 290 K.

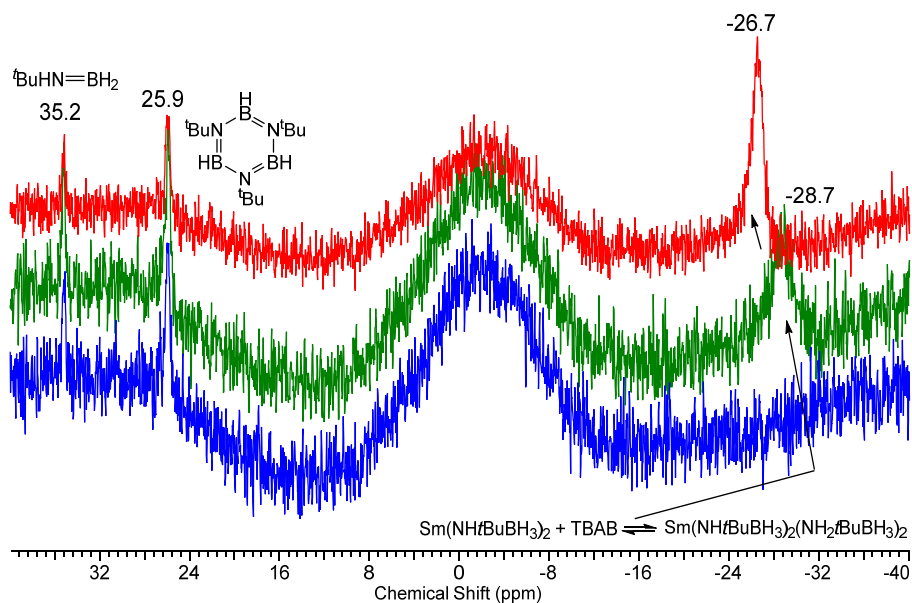


Figure S26. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 (blue), 6:1 (green) and 8:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (c = 0.01 M) after 1 h of the reaction. 128.34 MHz, toluene- d_8 , 290 K.

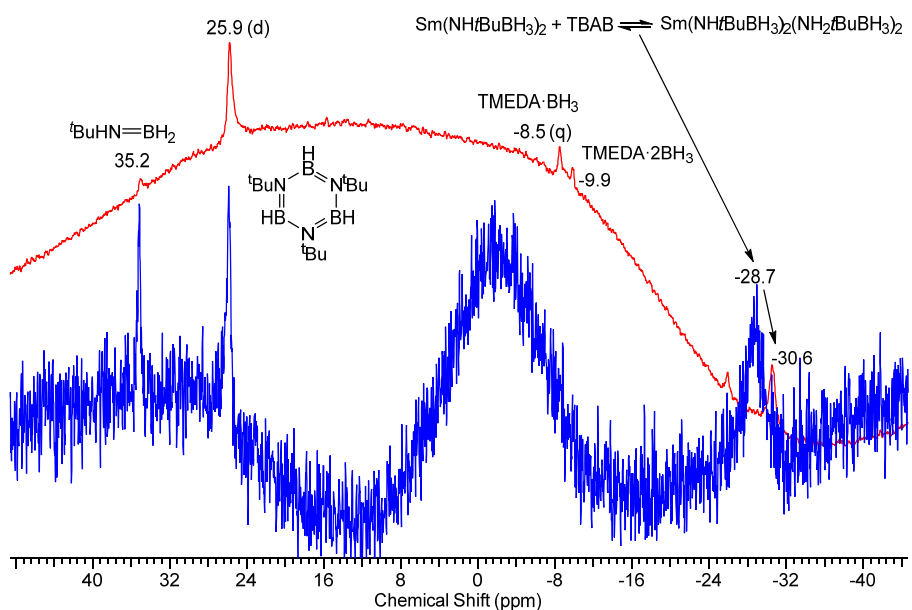


Figure S27. ^{11}B NMR spectra of 6:1 mixture of $t\text{BuNH}_2\text{BH}_3$ (0.06 M) and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M) in 1h and 22 h after mixing. 128.34 MHz, toluene- d_8 , 290 K.

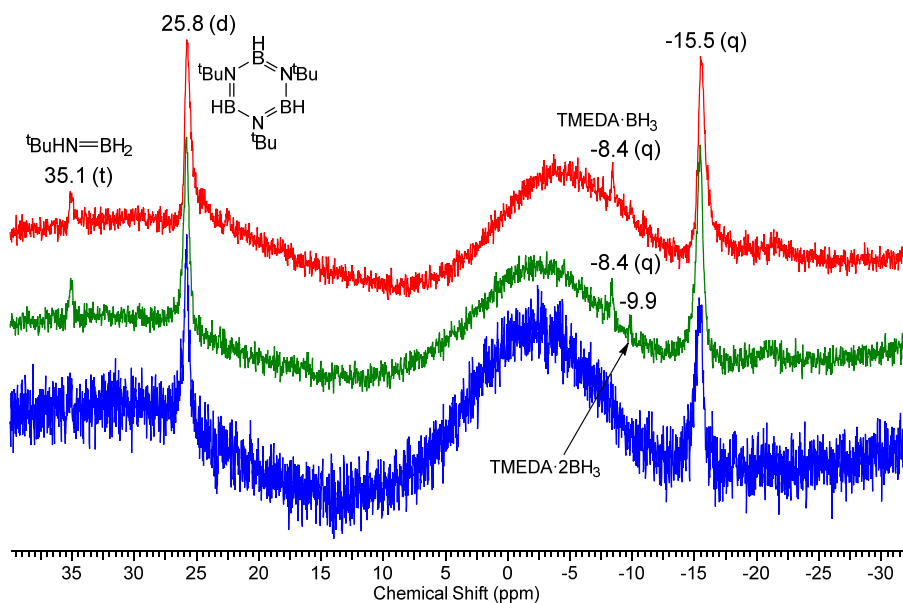


Figure S28. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 4:1 (blue), 6:1 (green) and 8:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ ($c = 0.01 \text{ M}$) after 30 h. 128.34 MHz, $\text{toluene-}d_6$, 290 K.

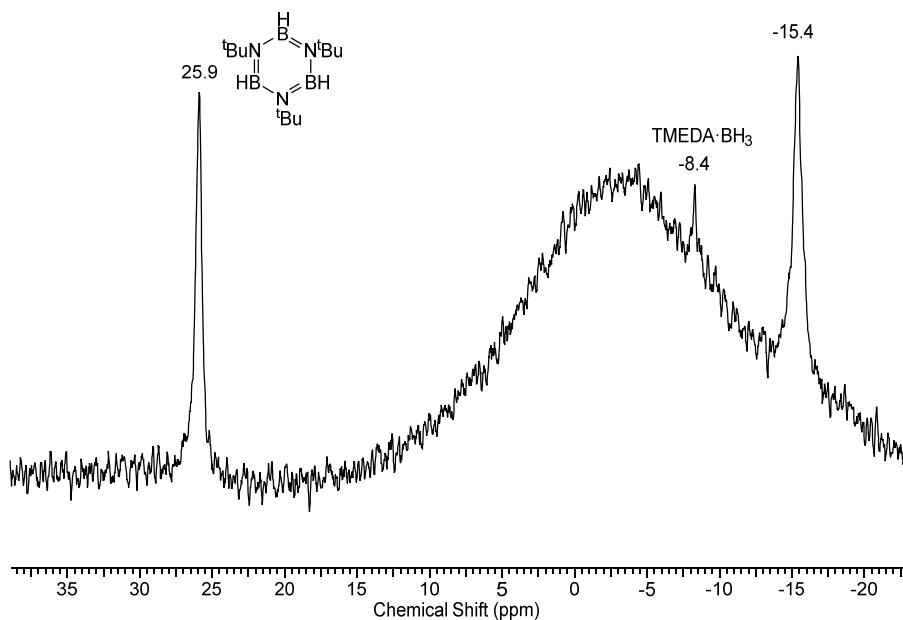


Figure S29. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 8:1 mixture of $t\text{BuNH}_2\text{BH}_3$ (0.08 M) and $(\text{TBDM})_2\text{Yb}(\text{TMEDA})$ (0.01 M) in 75 h after mixing. 128.34 MHz, $\text{toluene-}d_6$, 290 K.

Table S3. Comparison of 2_Yb^{TBAB}/2TBAB and 1_Yb-TMEDA/4TBAB systems kinetic parameters.

	Addition of 2 eq. of TBAB to 2_Yb ^{TBAB}	Addition of 4 eq. of TBAB to 1_Yb-TMEDA
Reaction time, h	20	23
H ₂ ↑, equiv	2.8	2.9
υ ₀ (H ₂), bar s ⁻¹	0.73·10 ⁻⁵	0.55·10 ⁻⁵
υ ₀ (TBAB), M s ⁻¹	-1.7·10 ⁻⁶	-1.3·10 ⁻⁶
τ _{1/2} , h	6.5	6

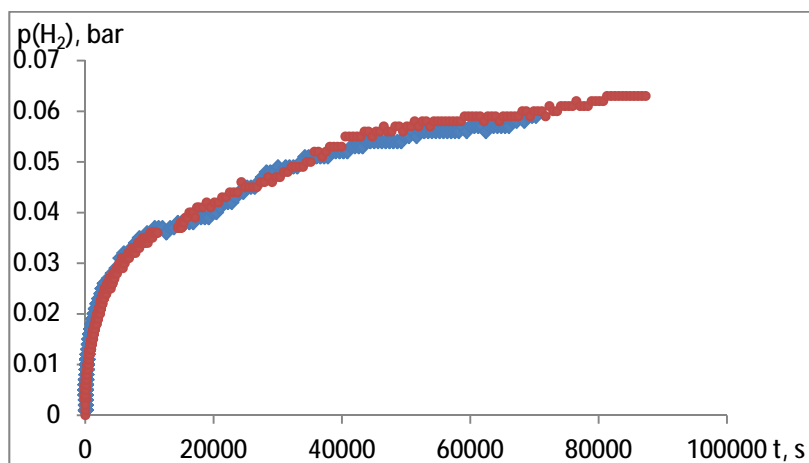


Figure S30. The plot of H₂ pressure changes measured by Man on the Moon kit for 1 : 2 mixture of 2_Yb^{TBAB} with TBAB (blue) and 1 : 4 mixture of 1_Yb-TMEDA with TBAB (red) in toluene, 295 K

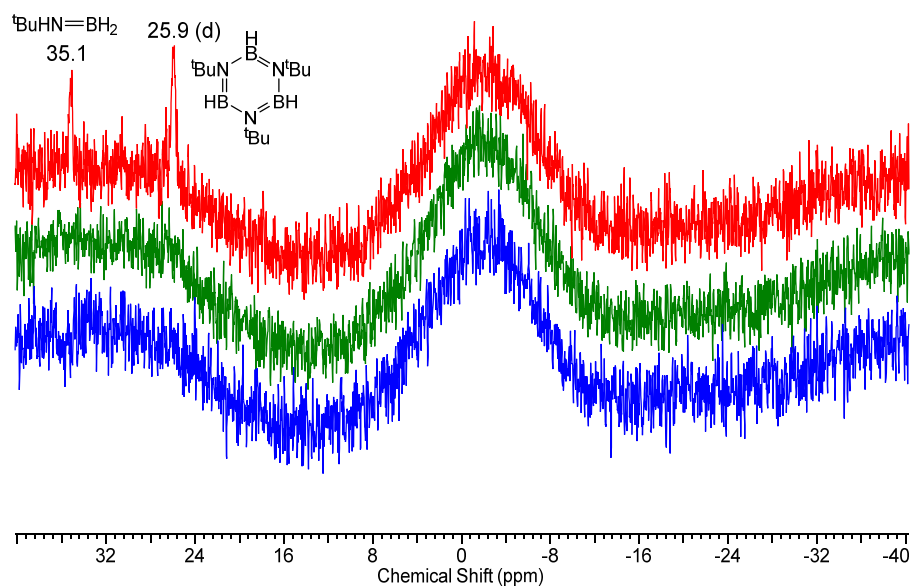


Figure S31. ¹¹B{¹H} NMR spectra of 1:1 (blue), 2:1 (green) and 4:1 (red) mixture of *t*BuNH₂BH₃ and (TBDM)₂Sm(TMEDA) (0.01 M) after 1 h of the reaction. 128.34 MHz, toluene-*d*₈, 290 K

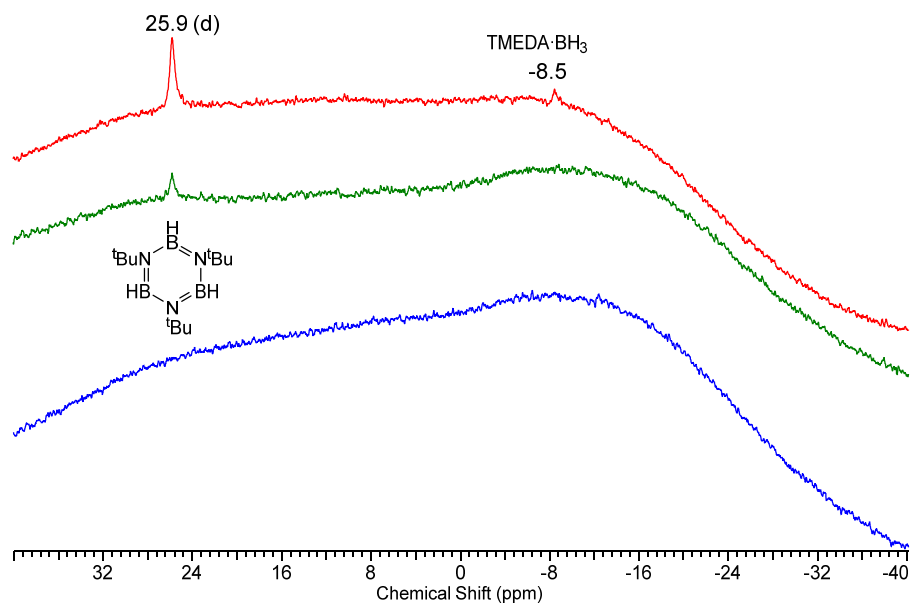


Figure S32. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of 1:1 (blue), 2:1 (green) and 4:1 (red) mixture of $t\text{BuNH}_2\text{BH}_3$ and $(\text{TBDM})_2\text{Sm}(\text{TMEDA})$ (0.01 M) after 22 h of the reaction. 128.34 MHz, toluene- d_8 , 290 K