

Supplementary Data

Encapsulation of hydride by molecular main group metal clusters: manipulating the source and coordination sphere of the interstitial ion.

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*Synthesis of $[\{Me-4-C_6H_4(2-C_5H_4N)N\}_6HLi_8]^+ [(Bu^t_2AlMe_2)_2Li]^- \cdot PhMe$ **5**.*

Me_3Al (0.5 ml, 2.0 M in toluene, 1.0 mmol) was added to a solution of (*N*-2-pyridyl)-4-methylaniline (0.18 g, 1.0 mmol) in toluene (2 ml) at room temperature under N_2 and the mixture was stirred until reaction subsided. Bu^tLi (0.88 ml, 1.7 M in pentane, 1.5 mmol) was added at $-78^\circ C$ and the mixture allowed to warm to room temperature whereupon a yellow solution formed. Crystals of **5** deposited after 24 h. at this temperature. Yield 48 mg, 19 % (based on Bu^tLi), m. p. 256-258 $^\circ C$. Found, C 72.84, H 7.66, N 11.52 %. Calcd. for $C_{92}H_{115}Al_2Li_9N_{12}$ C 73.40, H 7.70, N 11.16 %. 1H NMR spectroscopy (400 MHz, d_8 -thf), δ 7.66 (m, 6H, 6- C_5H_4N), 6.98 (m, 6H, 4- C_5H_4N), 6.90 (d, 12H, 3,5- C_6H_4), 6.87 (d, 12H, 2,6- C_6H_4), 6.57 (dd, 6H, 3- C_5H_4N), 5.92 (ddd, 6H, 5- C_5H_4N), 2.20 (s, 18H, 4-Me), 0.77 (m, 36H, Bu^t), -1.32 (sext., 12H, $^2J_{HAl} = 5.9$ Hz, AlMe). ^{13}C NMR spectroscopy (100 MHz, d_8 -thf), δ 166.6 (2- C_5H_4N), 150.7 (1-Ph), 148.5 (6- C_5H_4N), 136.9 (4- C_5H_4N), 129.7 (3,5- C_6H_4), 126.8 (2,6- C_6H_4), 121.8 (4- C_6H_4), 107.2 (3- C_5H_4N), 106.7 (5- C_5H_4N), 33.3 (Bu^t), 20.9 (C_6H_4Me). 7Li NMR spectroscopy (155 MHz, d_8 -thf), δ -0.65 (s).

Crystal data for 5.

$C_{95}H_{118.5}Al_2Li_9N_{12}$, $M = 1544.94$, triclinic, space group $P\bar{1}$, $a = 15.288(3)$, $b = 17.861(4)$, $c = 18.576(4)$ Å, $\alpha = 89.91(3)$, $\beta = 79.01(3)$, $\gamma = 71.23(3)^\circ$, $V = 4704.8(17)$ Å³, $Z = 2$, $\rho_{calcd} = 1.091$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71073$ Å, $\mu = 0.080$ mm⁻¹, $T = 150(2)$ K. 53192 data (16488 unique, $R_{int} = 0.0347$, $\theta < 25.04^\circ$) were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, 1997) to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} = 0.1745$, conventional $R = 0.0611$ on F values of 13943 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.082, 1090 parameters. Residual electron density extrema ± 0.98 eÅ⁻³. The asymmetric unit contains a $[(Bu^t_2AlMe_2)_2Li]^-$ anion and two structurally similar half molecules of the $[\{Me-4-C_6H_4(2-C_5H_4N)N\}_6HLi_8]^+$ cation, each sitting on a crystallographic centre of symmetry coincident with the interstitial hydride, and also a disordered toluene molecule.

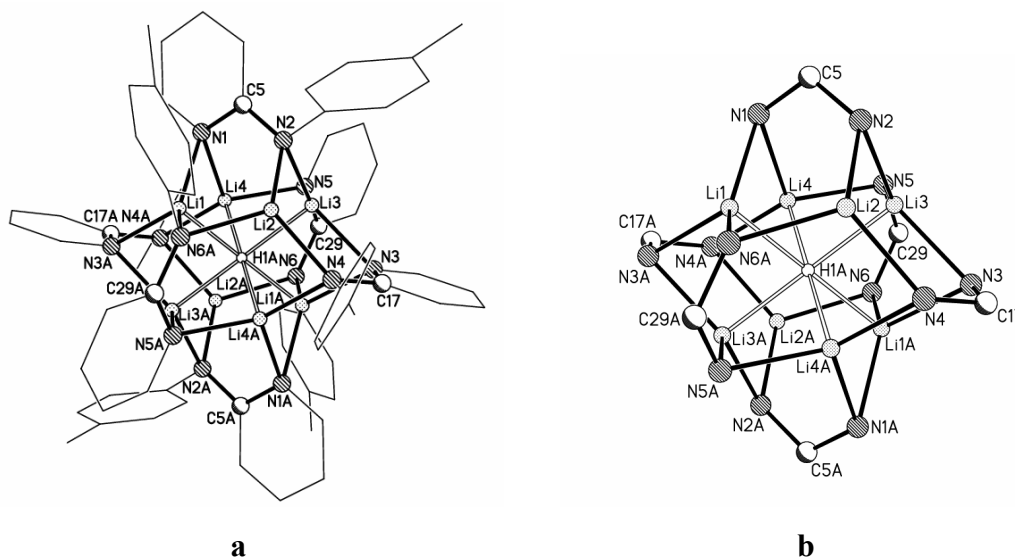


Figure S1 Structure of a) the $[\{\text{Me-4-C}_6\text{H}_4(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ ion in **5**, and b) the cation core. H-atoms (except H1A) and lattice toluene molecule omitted.

Table S1 Selected bond lengths (Å) and angles (°) for **5**.

H1A–Li1	2.007(4)	N3–Li3	2.053(4)
H1A⋯Li2	2.861(4)	N5–Li3	2.144(4)
H1A–Li3	2.024(4)	N1–Li4	2.129(4)
H1A–Li4	2.008(4)	N4A–Li4	2.018(4)
N1–Li1	2.058(4)	N5–Li4	2.042(4)
N3A–Li1	2.131(4)	Li1–N1–Li4	73.35(16)
N6A–Li1	2.005(4)	Li2–N2–Li3	82.73(17)
N2–Li2	2.058(4)	Li1A–N3–Li3	74.38(16)
N4–Li2	2.053(4)	Li2–N4–Li4A	83.11(17)
N6A–Li2	2.065(4)	Li3–N5–Li4	74.06(16)
N2–Li3	2.000(4)	Li1A–N6–Li2A	82.75(17)

Crystal data for 8.

$C_{104}H_{194}B_2Li_{16}N_{36}$, $M = 2081.61$, monoclinic, space group $P2(1)/n$, $a = 17.486(4)$, $b = 15.323(3)$, $c = 23.014(5)$ Å, $\beta = 97.66(3)^\circ$, $V = 6111(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.131$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71073$ Å, $\mu = 0.068$ mm⁻¹, $T = 180(2)$ K. 19728 data (5990 unique, $R_{\text{int}} = 0.0761$, $\theta < 20.50^\circ$) were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, 1997) to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]\}^{1/2} = 0.2370$, conventional $R = 0.0783$ on F values of 3796 reflections with $F^2 > 2\sigma(F^2)$, GoF = 1.044, 720 parameters. Residual electron density extrema ± 0.57 eÅ⁻³.

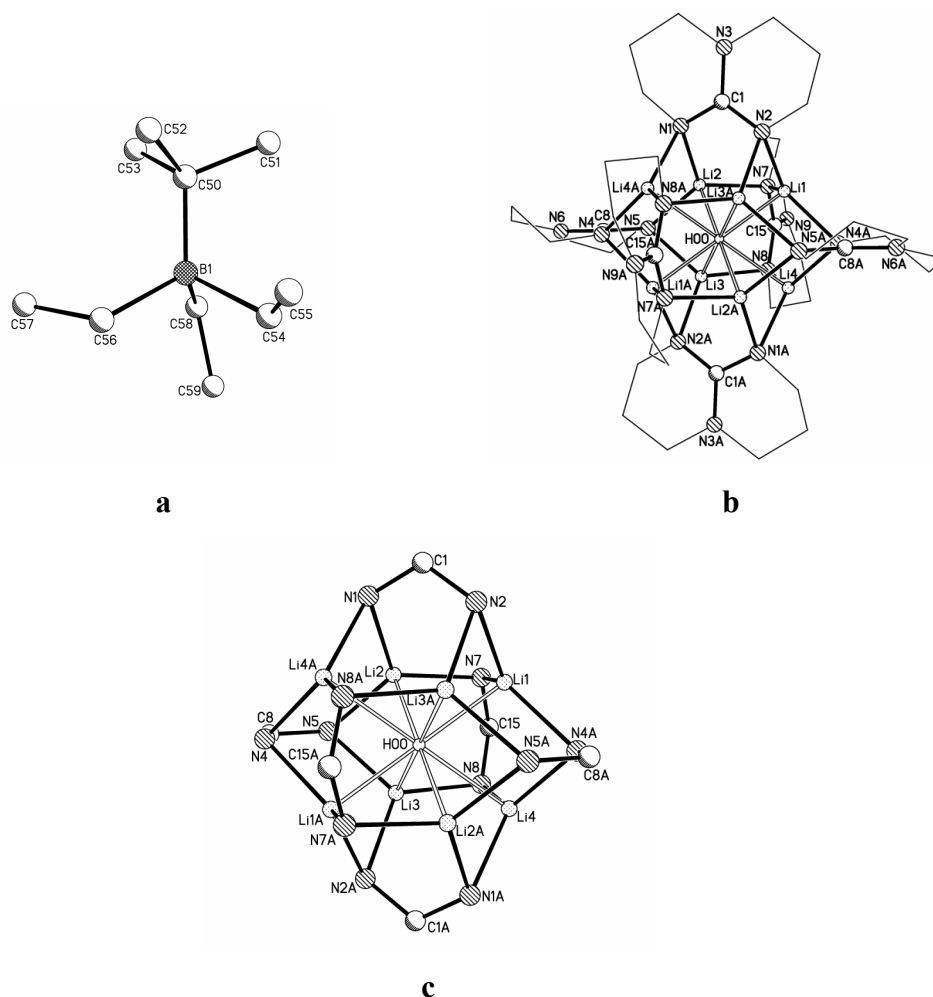


Figure S2 Structure of a) the borate anion and b) the $[hpp_6HLi_8]^+$ ion in **8**, and c) the cation core. H-atoms (except H00) omitted.

Table S2 Selected bond lengths (Å) and angles (°) for **8**.

H00–Li1	2.135(9)	N5–Li3	2.034(9)
H00–Li2	2.101(9)	N8–Li3	2.025(10)
H00–Li3	2.065(8)	N1A–Li4	2.023(10)
H00–Li4	2.332(9)	N4A–Li4	1.997(10)
N2–Li1	2.010(9)	N8–Li4	2.000(9)
N4A–Li1	2.048(10)	Li2–N1–Li4A	76.9(4)
N7–Li1	1.971(9)	Li1–N2–Li3A	75.6(4)
N1–Li2	2.023(9)	Li1A–N4–Li4A	78.1(4)
N5–Li2	2.026(10)	Li2–N5–Li3	74.8(4)
N7–Li2	2.047(10)	Li1–N7–Li2	75.5(4)
N2A–Li3	2.007(9)	Li3–N8–Li4	77.5(4)

*Synthesis of [tmeda₂Li]⁺[Et₃BH][−] **9**.*

A solution of hppH (0.139 g, 1.0 mmol) in toluene (1.2 ml) was treated with Et₃B (1.0 ml, 1.0 M in toluene, 1.0 mmol) under N₂ at −78 °C. Reaction with Bu^tLi (0.88 ml, 1.7 M in hexanes, 1.5 mmol) gave a suspension that was left to reach room temperature. The addition of tmeda (0.3 ml, 2.0 mmol) afforded a thick white slurry, which was heated to reflux and filtered hot. Storage of the resultant solution at +5 °C for 2 d yielded **9** as colourless crystals. Yield 46 mg, 14 % (based on tmeda), m. p. decomp. from 60 °C (trace solid residue melts at 160-164 °C). Satisfactory elemental analysis not possible, presumably due to unidentified [hpp][−] contamination (see NMR, below). ¹H NMR spectroscopy (500 MHz, *d*₆-dmsO), δ 3.04 (t, 2H, trace [hpp][−] NCH₂), 2.99 (t, 2H, trace [hpp][−] NCH₂), 2.28 (s, 8H, tmeda NCH₂), 2.12 (s, 24H, tmeda NMe), 1.74 (quint., 2H, trace [hpp][−] CH₂), 0.61 (m, 9H, BCH₂Me), −0.14 (m, 6H, MeCH₂B). ¹¹B NMR spectroscopy (160 MHz, *d*₆-dmsO, ref. F₃B·OEt₂/*d*-chloroform) δ −13.09 (d, ¹J_{BH} = 74.6 Hz). {¹H} ¹¹B NMR spectroscopy (160 MHz, *d*₆-dmsO, ref. F₃B·OEt₂/*d*-chloroform) δ −13.06 (s). ⁷Li NMR spectroscopy (194 MHz, *d*-dmsO, ref. ClLi/D₂O) δ −1.17 (s).

Crystal data for **10** (see Table 4).

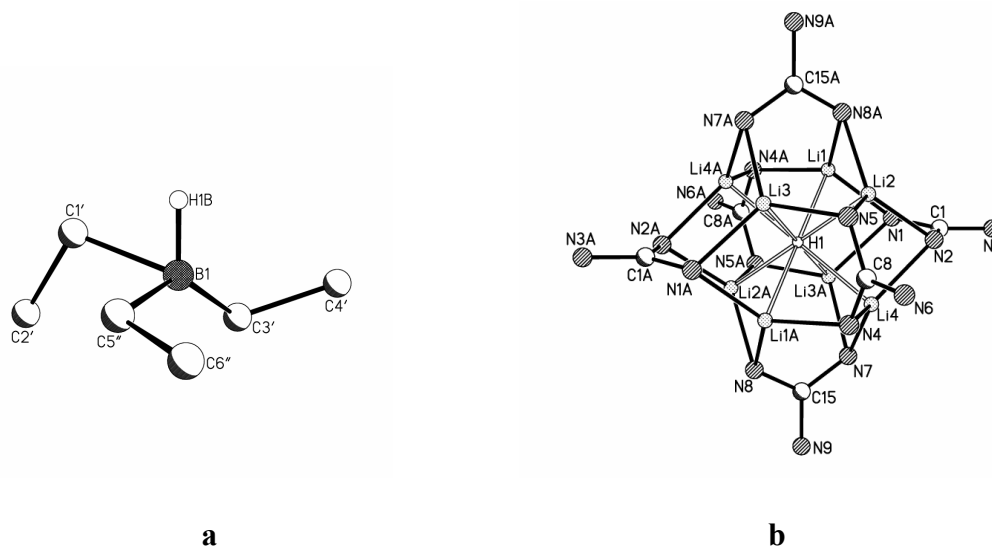


Figure S3 Structure of a) the borate anion and b) core of the $[\text{hpp}_6\text{HLi}_8]^+$ ion in **10**. H-atoms (except H1B and H1), CH_2 components of the $[\text{hpp}]^-$ ligands and Et-disorder in the borate anion omitted.

Table S3 Selected bond lengths (Å) and angles (°) for **10**.

H1–Li1	2.242(7)	N5–Li3	2.002(7)
H1–Li2	2.072(6)	N7A–Li3	2.015(7)
H1–Li3	2.190(6)	N2–Li4	2.025(6)
H1–Li4	2.150(6)	N4–Li4	2.025(6)
N1–Li1	2.003(6)	N7–Li4	1.991(7)
N4A–Li1	2.011(7)	Li1–N1–Li3A	78.2(3)
N8A–Li1	2.018(7)	Li2–N2–Li4	75.9(3)
N2–Li2	1.997(6)	Li1A–N4–Li4	77.5(3)
N5–Li2	2.023(6)	Li2–N5–Li3	75.3(3)
N8A–Li2	2.010(6)	Li3A–N7–Li4	77.3(3)
N1A–Li3	2.045(7)	Li1A–N8–Li2A	76.1(3)

Crystal data for **12** (see Table 4).

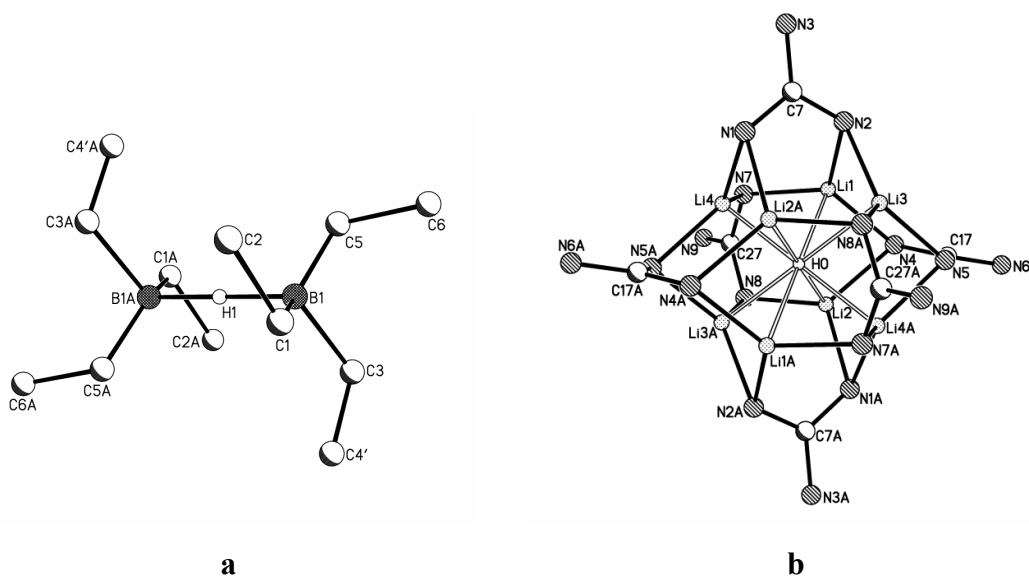


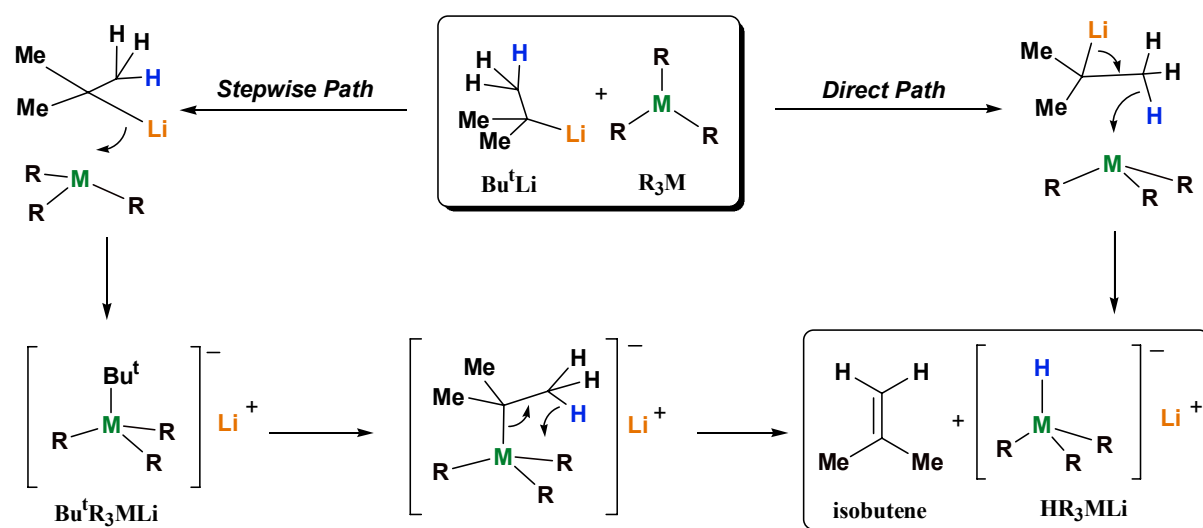
Figure S4 Structure of a) the borate anion and b) core of the $[\text{hpp}_6\text{HLi}_8]^+$ ion in **12**. H-atoms (except H1 and H0), CH_2 components of the $[\text{hpp}]^-$ ligands and Et-disorder in the anion omitted for clarity.

Table S4 Selected bond lengths (Å) and angles (°) for **12**.

H0–Li1	2.325(7)	N5–Li3	1.996(7)
H0–Li2	2.073(6)	N8A–Li3	2.048(7)
H0–Li3	2.165(5)	N1–Li4	2.038(7)
H0–Li4	2.068(6)	N5A–Li4	2.027(7)
N2–Li1	2.003(7)	N7–Li4	2.015(7)
N4–Li1	1.994(7)	Li2A–N1–Li4	74.8(3)
N7–Li1	2.011(7)	Li1–N2–Li3	77.8(3)
N1A–Li2	2.006(7)	Li1–N4–Li2	76.4(3)
N4–Li2	2.027(7)	Li3–N5–Li4A	76.9(3)
N8–Li2	1.993(7)	Li1–N7–Li4	77.4(3)
N2–Li3	2.024(7)	Li2–N8–Li3A	75.6(3)

Theoretical Study

As a preliminary study, the effects of amine ligands were neglected and the reaction of Bu^tLi with Lewis acid was considered. Two possibilities were tested: direct hydride formation from Bu^tLi and Lewis acids, and stepwise hydride formation *via* an intermediary *tert*-butyl 'ate complex (Scheme S1).



Scheme S1

Trimethylborane was employed as a model Lewis acid and its reaction with Bu^tLi was tested at the B3LYP/6-31G* level of theory. Though the potential energy surfaces were calculated in terms of all electron energy (ΔE), frequency analysis was conducted for all the stationary and transition points to consider Gibbs free energy (ΔG). Because the number of molecules changes in the course of the reactions, relative ΔG was considered for discussions.

Two pathways for direct hydride formation and a single pathway was located for the stepwise route (Scheme S1 and Scheme 5). Energy diagrams for these pathways are shown in Figures S5 (plotted in ΔE) and S6 (plotted in ΔG). Optimized molecular structures are shown in Figure S7.

The optimized structure of the stationary point in [(Me₃B)₂H]⁻ (*viz.* **12**) is shown in Fig. S8.

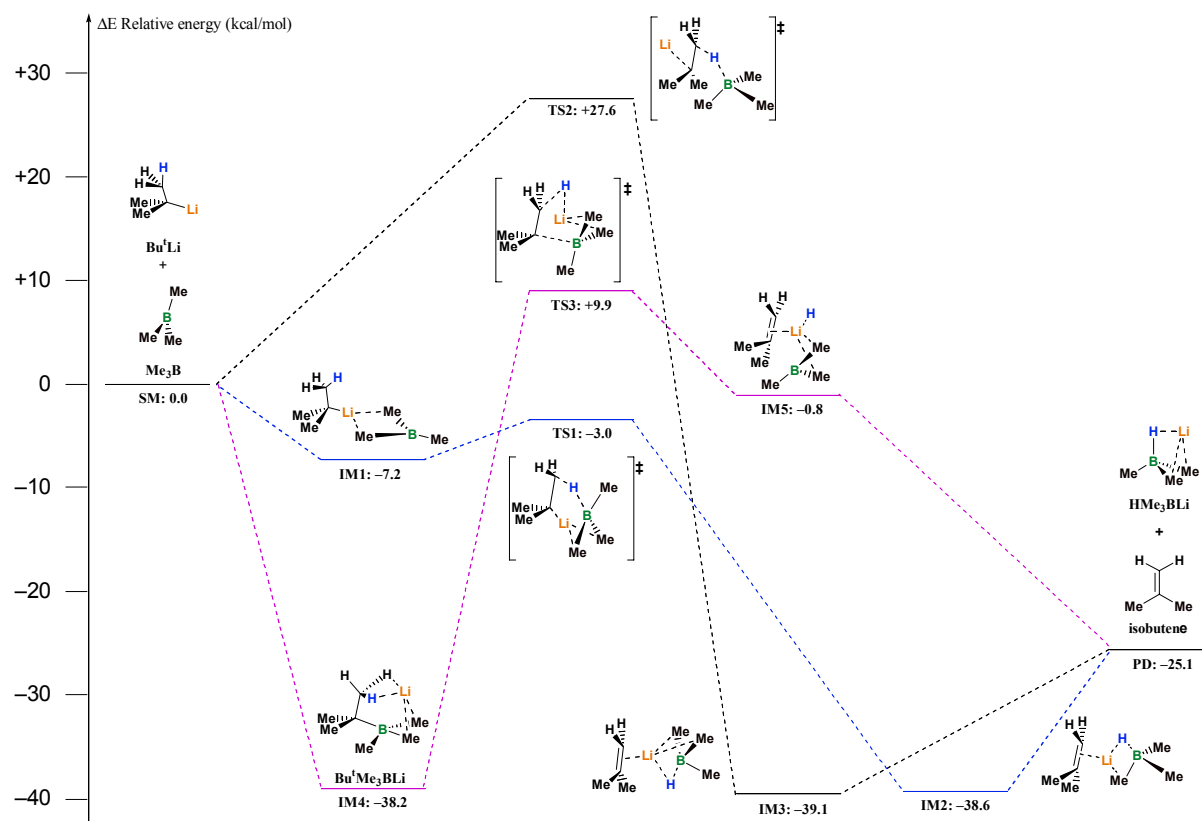


Figure S5 Reaction coordinates for borohydride formation from *t*-butyllithium and trimethylborane. Energy values (ΔE) are relative to SM and are shown in kcal/mol.

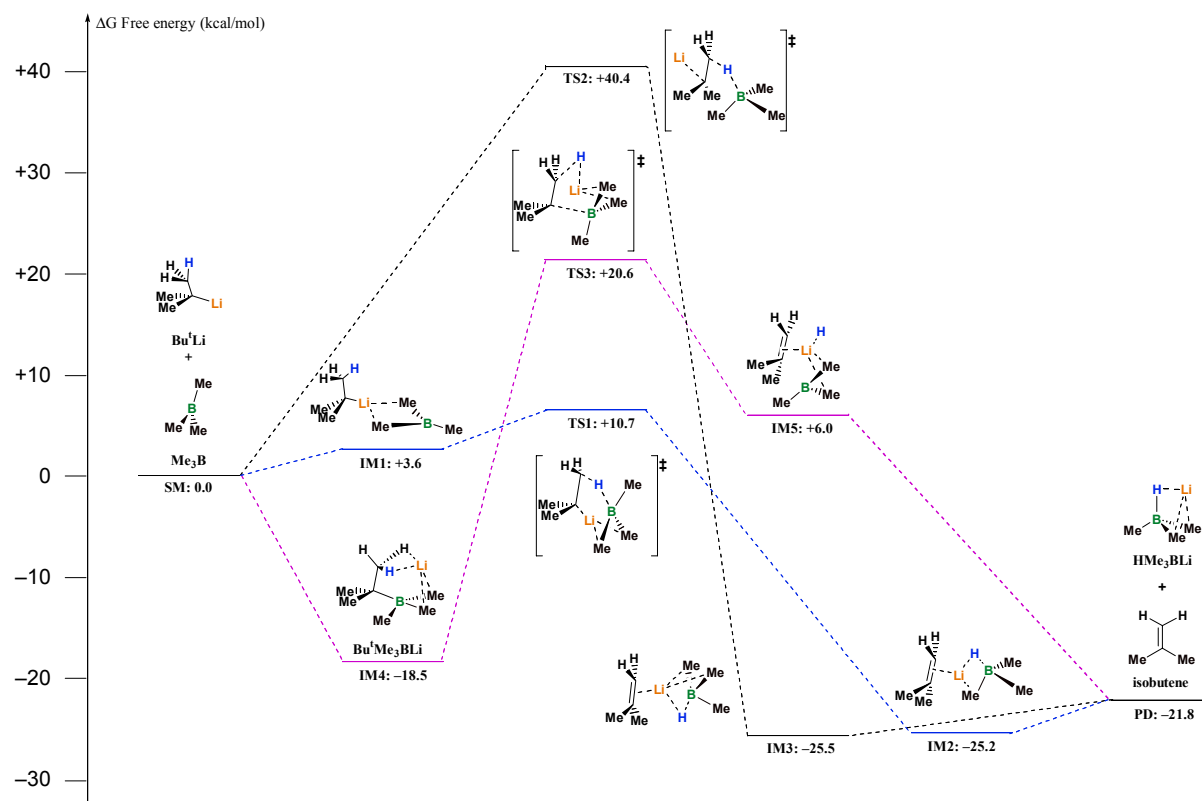


Figure S6 Reaction coordinates for borohydride formation from *t*-butyllithium and trimethylborane. Gibbs free energy values (ΔG) are relative to SM and are shown in kcal/mol.

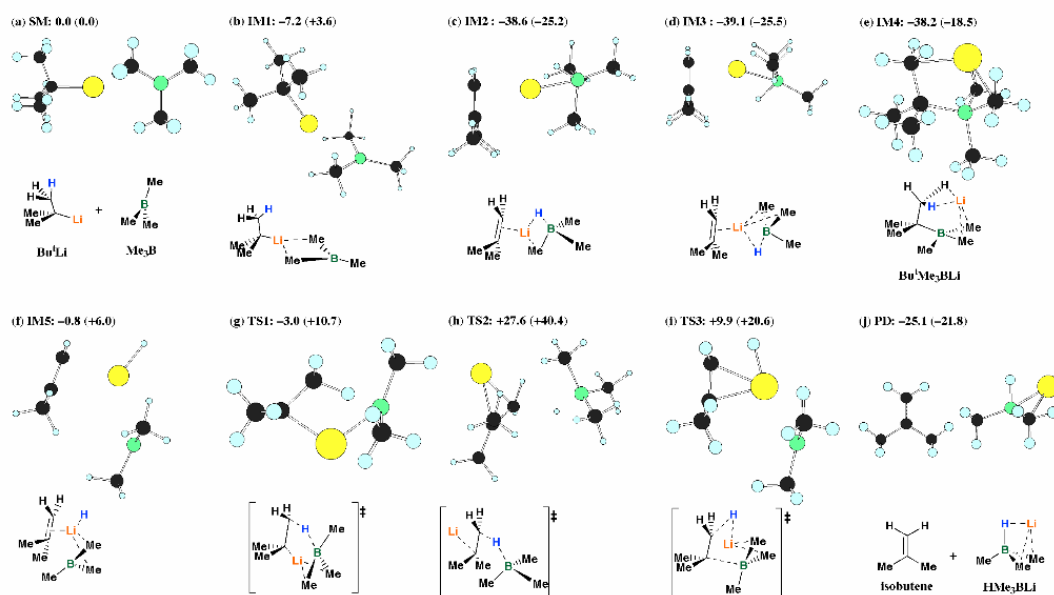


Figure S7 Optimized structures of the stationary points and transition states. Energy values (ΔE) and Gibbs free energy values (ΔG) (in parenthesis) are relative to SM and are shown in kcal/mol.

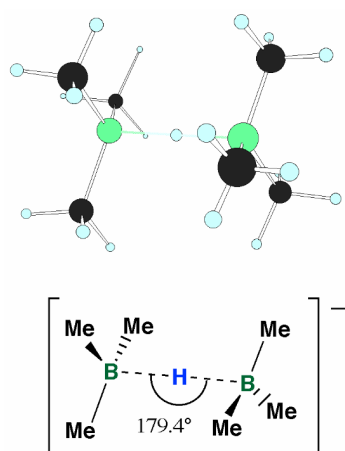


Figure S8 Optimized structure of the stationary point in $[(\text{Me}_3\text{B})_2\text{H}]^-$. This structure was found to be 6.3 kcal/mol more stable than that modeled with a frozen B–H–B angle of 127° .

Calculations were carried out with a Gaussian 03 (G03) program package (M. J. Frish, *et al.* *Gaussian 03*, revision c.01; Gaussian, Inc.; Wallingford, CT, 2004) using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-Yang-Parr non-local correlation functional (B3LYP) (A. D. Becke, *Phys. Rev.*, 1998, **A38**, 3098; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C.

Lee, W. Yang, R. G. Parr, *Phys. Rev.*, 1998, **B37**, 785). The 6-31G* basis set was used for all atoms. Geometry optimizations and vibrational analyses were performed at the same level. All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAGs, was 0 for minima and 1 for transition states, TSs).