Electronic Supporting Information

Facile ring-opening of THF at lithium induced by a pendant Si-H bond and BPh₃

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General remarks

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Prior to use, glasswares were dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. (Me₃TA CD)H,^{S1} Me₄TACD,^{S2} [M{N(SiHMe₂)₂],^{S3} and B(C₆F₅)₃^{S4} were synthesized following literature procedures. BPh₃ (95%) was purchased from abcr and purified by sublimation. NMR measurements were performed on a Bruker DRX 400 at ambient temperature unless otherwise mentioned. The chemical shifts (δ ppm) in the ¹H and ¹³C{¹H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane.^{S5} Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), sep (septet), br (broad), IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra: w (weak), m (medium), s (strong), br (broad). Elemental analyses were performed on an *elementar vario EL* machine. X-ray diffraction data were collected on a Bruker APEX II diffractometer. Single crystal diffraction data of **3** and **7** are reported in crystallographic information file (cif) accompanying this document.

Synthetic Procedures and spectroscopic data for 1-5 and 7

$[\{(Me_3TACD)H\}Li\{N(SiHMe_2)_2\}] (1)$

A mixture of [Li{(N(SiHMe₂)₂}] (0.100 g, 0.718 mmol) and LH (0.154 g, 0.718 mmol) in *n*-pentane (5 mL) was stirred for 0.5 h at room temperature. Removal of the volatiles under reduced pressure afforded analytically pure **1** (0.240 g, 0.679 mmol, 95%) as a colorless powder. ¹H NMR (400 MHz, benzene-*d*₆): δ 5.07 (sept, ¹*J*_{SiH} = 167 Hz, 2 H, Si*H*Me₂), 2.36-2.24 (m, 2 H, *CH*₂), 2.25 (s, 6 H, *NMe*), 2.19 (s, 3 H, *NMe*), 1.93-1.74 (m, 14 H, *CH*₂), 1.37

(br, m, 1 H, N*H*), 0.59 (d, ${}^{3}J_{HH} = 3.0$ Hz, 12 H, SiH*Me*₂). ${}^{13}C\{{}^{1}H\}$ NMR (100 MHz, benzene*d*₆): δ 56.0 (*C*H₂), 54.5 (*C*H₂), 53.4 (*C*H₂), 45.2 (*C*H₂), 44.4 (N*Me*), 44.4 (N*Me*), 7.3 (SiH*Me*₂). ${}^{29}Si\{{}^{1}H\}$ NMR (80 MHz, benzene-*d*₆): δ -28.5. IR (KBr, cm⁻¹): 2039 (s, v_{SiH}). Anal. Calcd. for C₁₅H₄₀N₅Si₂Li: C, 50.90; H, 11.40; N, 19.80. Found: C, 50.45; H, 11.15; N, 19.69.





Figure S2. ¹³C{¹H} NMR spectrum of **1** in benzene- d_6 .



Figure S3. ²⁹Si{¹H} NMR spectrum of **1** in benzene- d_6 .



 $v(cm^{-1})$

2000

2500

1500

1000

3000

3500

Figure S5. Solid-state IR (KBr) spectrum of 1.

$[\{(Me_3TACD)H\}Na\{N(SiHMe_2)_2\}] (2)$

A mixture of $[Na\{(N(SiHMe_2)_2\}]$ (0.029 g, 0.187 mmol) and LH (0.040 g, 0.187 mmol) in *n*-pentane (5 mL) was stirred for 0.5 h at room temperature. Removal of the volatiles under reduced pressure afforded analytically pure **2** (0.065 g, 0.176 mmol, 94%) as a colorless powder. ¹H NMR (400 MHz, benzene-*d*₆): δ 5.37 (sept, ¹*J*_{SiH} = 164 Hz, 2 H, Si*H*Me₂), 2.17 (br, m, 2 H, C*H*₂), 2.10 (s, 6 H, N*Me*), 2.07 (s, 3 H, N*Me*), 1.87-1.59 (br, m, 14 H, C*H*₂), 0.69 (br, s, 1 H, N*H*), 0.61 (d, ³*J*_{HH} = 2.8 Hz, 12 H, SiH*Me*₂). ¹³C{¹H} NMR (100 MHz, benzene-*d*₆): δ 55.4 (*C*H₂), 53.9 (*C*H₂), 53.2 (*C*H₂), 44.5 (*C*H₂), 44.1 (N*Me*), 44.0 (N*Me*), 7.4 (SiH*Me*₂). ²⁹Si{¹H} NMR (80 MHz, benzene-*d*₆): δ -31.9. IR (KBr, cm⁻¹): 1990 (s, v_{SiH}). Anal. Calcd. for C₁₅H₄₀N₅Si₂Na: C, 48.74; H, 10.91; N, 18.94. Found: C, 48.56; H, 10.43; N, 19.22.





Figure S7. ¹³C $\{^{1}H\}$ NMR spectrum of **2** in benzene- d_{6} .



Figure S9. Solid-state IR (KBr) spectrum of 2.

$[\{(Me_3TACD)H\}K\{N(SiHMe_2)_2\}] (3)$

A mixture of $[K\{(N(SiHMe_2)_2\}]$ (0.040 g, 0.233 mmol) and LH (0.050 g, 0.233 mmol) in *n*-pentane (5 mL) was stirred for 0.5 h at room temperature. Removal of the volatiles under reduced pressure afforded analytically pure **3** (0.085 g, 0.220 mmol, 94%) as a colorless powder. ¹H NMR (400 MHz, benzene-*d*₆): δ 5.34 (sept, ¹*J*_{SiH} = 161 Hz, 2 H, Si*H*Me₂), 2.26-2.22 (m, 4 H, C*H*₂), 2.09 (s, 6 H, N*Me*), 2.05 (s, 3 H, N*Me*), 1.98-1.91 (m, 12 H, C*H*₂), 1.21 (m, 1 H, N*H*), 0.49 (d, ³*J*_{HH} = 2.8 Hz, 12 H, SiH*Me*₂). ¹³C{¹H} NMR (100 MHz, benzene-*d*₆): δ 55.7 (*C*H₂), 54.6 (*C*H₂), 53.7 (*C*H₂), 45.1 (N*Me*), 44.5 (N*Me*), 44.1 (*C*H₂), 7.0 (SiH*Me*₂). ²⁹Si{¹H} NMR (80 MHz, benzene-*d*₆): δ -33.5. IR (KBr, cm⁻¹): 2032 (v_{SiH}), 1964 (v_{SiH}). Anal. Calcd. for C₁₅H₄₀N₅Si₂K: C, 46.70; H, 10.45; N, 18.15. Found: C, 46.36; H, 10.17; N, 18.19.



Figure S12. ²⁹Si{¹H} NMR spectrum of **3** in benzene- d_6 .



Figure S13. Solid-state IR (KBr) spectrum of 3.

[Li{(Me₃TACD)SiMe₂N(SiHMe₂)}] (4)

A solution of **1** (0.100 g, 0.283 mmol) in 0.5 mL of benzene- d_6 was heated to 60 °C for 12 h. Progress of the reaction was monitored time to time by ¹H NMR spectroscopy. After completion, all the volatiles were removed under reduced pressure to obtain a colorless solid. The solid was recrystallized from a concentrated *n*-pentane solution at -35 °C overnight and dried under vacuum to give analytically pure **4** (0.086 g, 0.244 mmol, 86%) as a white powder. ¹H NMR (400 MHz, benzene- d_6): δ 5.46 (sept, ¹ J_{SiH} = 169 Hz, 1 H, SiHMe₂), 3.47 (m, 2 H, CH₂), 2.30-2.26 (br, m, 2 H, CH₂), 2.14-2.07 (br, m, 11 H, NMe and CH₂), 1.92-1.70 (br, m, 10 H, CH₂), 0.50 (s, 6 H, SiMe₂), 0.48 (d, ³ J_{HH} = 2.8 Hz, 6 H, SiHMe₂). ¹³C {¹H} NMR (100 MHz, benzene- d_6): δ 61.5 (CH₂), 56.8 (CH₂), 50.5 (CH₂), 44.9 (NMe), 42.2 (NMe), 6.6 (SiHMe₂), 5.5 (SiMe₂). ²⁹Si {¹H} NMR (80 MHz, benzene- d_6): δ -16.4 (SiMe₂), -35.2 (SiHMe₂). IR (KBr, cm⁻¹): 2000 (s, v_{SiH}). Anal. Calcd. for C₁₅H₃₈N₅Si₂Li: C, 51.24; H, 10.89; N, 19.92. Found: C, 50.96; H, 10.77; N, 19.69.



Figure S16. ²⁹Si $\{^{1}H\}$ NMR spectrum of **4** in benzene- d_{6} .



Figure S18. Solid-state IR (KBr) spectrum of 4.

[Na{(Me₃TACD)SiMe₂N(SiHMe₂)}] (5)

A solution of **2** (0.150 g, 0.406 mmol) in 0.5 mL of benzene- d_6 was heated to 80 °C for 48 h. Progress of the reaction was monitored time to time by ¹H NMR spectroscopy. After completion, all the volatiles were removed under reduced pressure to obtain a light brown colored solid. The solid was recrystallized from a concentrated *n*-pentane solution at -35 °C overnight and dried under vacuum to give analytically pure **5** (0.095 g, 0.258 mmol, 64%) as a white powder. ¹H NMR (400 MHz, benzene- d_6): δ 5.76 (sept, ¹ J_{SiH} = 167 Hz, 1 H, SiHMe₂), 3.21-3.15 (m, 2 H, CH₂), 2.27-2.21 (m, 2 H, CH₂), 2.14-2.08 (m, 2 H, CH₂), 2.0 (br, m, 8 H,

NMe and CH₂), 1.84-1.76 (m, 4 H, CH₂), 1.67-1.61 (m, 2 H, CH₂), 1.54-148 (m, 5 H, NMe and CH₂), 0.61 (d, ${}^{3}J_{HH} = 2.8$ Hz, 6 H, SiHMe₂), 0.54 (s, 6 H, SiMe₂). ${}^{13}C{}^{1}H{}$ NMR (100 MHz, benzene-d₆): δ 57.5 (CH₂), 54.4 (CH₂), 53.7 (CH₂), 48.1 (CH₂), 43.5 (NMe), 42.8 (NMe), 7.0 (SiHMe₂), 5.2 (SiMe₂). ${}^{29}Si{}^{1}H{}$ NMR (80 MHz, benzene-d₆): δ -19.0 (SiMe₂), -37.6 (SiHMe₂). IR (KBr, cm⁻¹): 2000 (s, v_{SiH}). Anal. Calcd. for C₁₅H₃₈N₅Si₂Na: C, 49.00; H, 10.42; N, 19.05. Found: C, 48.67; H, 10.08; N, 19.26.



Figure S19. ¹H NMR spectrum of **5** in benzene- d_6 .



Figure S20. ¹³C{¹H} NMR spectrum of 5 in benzene- d_6 .





Figure S22. Solid-state IR (KBr) spectrum of 5.

[Li{(Me₃TACD)SiMe₂N(SiMe₂OnBu)BPh₃}] (7)

Slow *n*-pentane diffusion into a solution of BPh₃ (0.071 g, 0.293 mmol) and **4** (0.103 g, 0.293 mmol) in 1 mL of THF at -35 °C over two days precipitated a white solid. The solid was isolated by decantation and dried under vacuum to obtain analytically pure **7** (0.172 g, 0.258 mmol, 88%) as a white powder. X-ray quality single crystals were also obtained in a similar fashion. ¹H NMR (400 MHz, benzene-*d*₆): δ 7.69-7.66 (m, 6 H, *o*-Ph), 7.33-7.29 (m, 3 H, *p*-Ph), 7.27-7.23 (m, 6 H, *m*-Ph), 3.91 (m, 2 H, OCH₂CH₂CH₂CH₃), 3.47 (m, 2 H, CH₂), 2.28-2.25 (m, 2 H, CH₂), 2.18 (br, s, 6 H, NMe), 2.13 (br, s, 3 H, NMe), 2.10-2.06 (m, 2 H, CH₂), 1.94-1.55 (br, m, 12 H, CH₂ and OCH₂CH₂CH₂CH₃), 1.02 (t, ³J_{HH} = 7.3 Hz, 3 H, OCH₂CH₂CH₂CH₂CH₃), 0.52 (s, 6 H, SiMe₂), 0.41 (s, 6 H, SiMe₂). ¹³C{¹H} NMR (100 MHz, benzene-*d*₆): δ 139.3 (*Ph*), 131.7 (*Ph*), 128.1 (*Ph*), 68.2 (OCH₂CH₂CH₂CH₂CH₃), 61.4 (*C*H₂), 56.6

(CH₂), 53.5 (CH₂), 50.4 (CH₂), 44.7 (NMe), 42.5 (NMe), 36.8 (OCH₂CH₂CH₂CH₂CH₃), 20.4 (OCH₂CH₂CH₂CH₃), 14.9 (OCH₂CH₂CH₂CH₃), 5.6 (SiMe₂), 4.0 (SiMe₂). ¹¹B NMR (128 MHz, THF- d_8): δ 67.9 (br, s). ²⁹Si{¹H} NMR (80 MHz, THF- d_8): δ -18.6 (SiMe₂), -22.1 (SiMe₂). Anal. Calcd. for C₃₇H₆₁N₅OSi₂BLi: C, 66.74; H, 9.23; N, 10.52. Found: C, 66.66; H, 9.22; N, 10.67.



Figure S23. ¹H NMR spectrum of **7** in benzene- d_6 .



Figure S24. ¹³C $\{^{1}H\}$ NMR spectrum of **7** in benzene-*d*₆.









Figure S27. Solid-state IR (KBr) spectrum of 7.

An NMR-scale reaction between BPh₃ and **4** in THF- d_8 showed immediate completion of ring-opening within <5 min to give Li[(Me₃TACD)SiMe₂NSiMe₂{O(CD₂)₃CD₂H}BPh₃] (**7**- d_8). NMR spectroscopic characterization indicates the presence of free BPh₃. ¹H NMR (400 MHz, THF- d_8): δ 7.55-7.52 (m, 6 H, *o*-Ph), 7.34-7.32 (m, 9 H, *m*-Ph and *p*-Ph), 3.51-3.44 (m, 2 H, CH₂), 2.79-2.72 (m, 2 H, CH₂), 2.62-2.46 (m, 8 H, CH₂), 2.40 (s, 3 H, NMe), 2.34 (s, 6 H, NMe), 2.40-2.34 (m, 2 H, CH₂), 2.12-2.06 (m, 2 H, CH₂), 0.91-0.84 (m, 1 H, OCD₂CD₂CD₂CD₂H), 0.04 (s, 6 H, SiMe₂), -0.18 (s, 6 H, SiMe₂). ¹³C{¹H} NMR (100 MHz, THF- d_8): δ 147.0 (*ipso-Ph*), 138.1 (*Ph*), 130.0 (*Ph*), 128.0 (*Ph*), 61.9 (CH₂), 57.3 (CH₂), 54.3 (CH₂), 50.9 (CH₂), 45.0 (NMe), 42.8 (NMe), 5.2 (SiMe₂), 3.5 (SiMe₂). ¹¹B NMR (128 MHz, THF- d_8): δ 48.3 (br, s). ²⁹Si{¹H} NMR (80 MHz, THF- d_8): δ -18.5 (*Si*Me₂), -22.1 (*Si*Me₂).







Figure S30. ¹¹B NMR spectrum of **7**- d_8 in THF- d_8 . The borate peaks (1.2 and -2.4 ppm) of low intensities could from impurities or intermediates in the exchange process.



Figure S31. ²⁹Si $\{^{1}H\}$ NMR spectrum of 7-*d*₈ in THF-*d*₈.

Variable temperature NMR spectroscopic analysis of 7 and 7- d_8

NMR spectroscopic characterization of 7 and 7- d_8 in benzene- d_6 and THF- d_8 , respectively suggests that the BPh₃ exists as a 'free' borane in solution at room temperature, contrary to the solid-state structure. 7- d_8 is generated in situ by mixing 4 and BPh₃ in 1:1 ratio in THF- d_8 . A variable temperature NMR spectroscopic analysis of 7 in toluene- d_8 and of 7- d_8 in THF- d_8 shows that the species undergoes temperature-dependent reversible association/dissociation between the zwitterionic 7 and a mixture of neutral 7' and BPh₃.



Figure S32. Variable temperature ¹¹B NMR spectra of 7 in toluene- d_8 .



Figure S33. Variable temperature ⁷Li{¹H} NMR spectra of **7** in toluene- d_8 .



Figure S34. Variable temperature ¹H NMR spectra of **7** in toluene- d_8 .



Figure S35. Variable temperature ¹¹B NMR spectra of a 1:1 mixture of **4** and BPh₃ in THF- d_8 .



Figure S36. Variable temperature ⁷Li{¹H} NMR spectra of a 1:1 mixture of **4** and BPh₃ in THF- d_8 .



Figure S37. Variable temperature ¹H NMR spectra of a 1:1 mixture of 4 and BPh₃ in THF- d_8 .

Kinetic plots for the transformation of 1 to 4

The kinetic measurement for the conversion of **1** to **4** (dehydrogenative Si–N bond formation) was conducted by monitoring the reaction with ¹H NMR spectroscopy. A 0.6 mL of benzened₆ solution containing **1** (0.020 M) and 1,3,5-trimethoxybenzene (0.042 M) as an internal standard) was taken in a Teflon-sealed NMR tube. The NMR tube was placed in an oil bath preheated to 75 °C. Progress of the reaction was examined by removing the tube from the oil bath time to time and measuring the ¹H NMR spectrum at room temperature. No reaction at room temperature ensured that there is no elapsed time during the spectral acquisition. The concentrations of **1** and **4** were determined by comparison of corresponding integrated resonances to the known concentration of 1,3,5-trimethoxybenzene. A first order rate constant (*k*) was obtained by a non-weighted linear least square fit of the data to the first order rate law, $\ln[\mathbf{1}] = \ln[\mathbf{1}]_0 + kt$. A value of $k = 5.9 \pm 0.1 \times 10^{-3} \text{ min}^{-1}$ was derived from the slope.



Figure S38. Plot of [1] vs. time (min) at 75 °C in benzene- d_6 which shows an exponential decay.



Figure S39. Plot of $\ln[1]$ vs. time (min) at 75 °C in benzene- d_6 .

4. X-ray crystallography

Single-crystal X-ray diffraction measurements of 3 and 7 were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoK α radiation ($\lambda = 0.71073$ Å), multilayer optics and ω -scans. Temperature control was achieved with an Oxford cryostream 700. The SMART program was used for data collection and unit cell determination; processing of the raw data frame was performed using SAINT+,^{S6} multi scan absorption corrections were applied with SADABS.^{S7} Both compounds are extremely sensitive towards air and moisture and decompose quickly. The structures were solved by direct methods (SIR-92).^{S8} The molecule of **3** shows crystallographic inversion symmetry. The packing of 7 contains THF molecules within the crystal lattice. Within the molecule of 3, the CH_2 carbon atoms of the Me₃TACD ligands C1 – C8 are disordered. The disorder could be modeled with split positions. Within the molecule of 7, the CH_2 carbon atom C14 and the CH₃ carbon atom C15 of the n-butyl group are disordered. This disorder could also be modeled with split positions. The Refinements were performed against F^2 with the program SHELXL-2013 using all reflections.⁵⁹ Hydrogen atoms were included as riding on calculated positions with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(non-H)$, except for the atoms bound to silicon (H1 and H2 in 3) that were localized in difference Fourier maps and refined in their position with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(Si)$. All nonhydrogen atoms were refined anisotropically, except for the atoms C1-C8 in 3 and O3 as well as C42-C47 (of the solvent molecule thf in 7) that were refined with split positions. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.^{S10} CCDC-1544769 (3), -1544770 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

 Table S1. Crystal data and structure refinement.

	3	7
chemical formula	$C_{30}H_{80}N_{10}K_2Si_4$	C ₃₇ H ₆₁ N ₅ BLiOSi ₂ , 2(C ₄ H ₈ O)
fw (g·mol ⁻¹)	771.60	810.04
space group	$P2_{1}/n$	Pī
crystal size (mm)	0.25×0.20×0.08	0.31×0.27×0.11
unit cell parameters		
<i>a</i> (Å)	9.338(6)	11.063(4)
<i>b</i> (Å)	16.547(11)	11.919(7)
<i>c</i> (Å)	14.617(9)	19.901(11)
α (°)		87.199(12)
β (°)	90.829(15)	77.299(12)
γ (°)		65.471(11)
$V(\text{\AA}^3)$	2258(3)	2326(2)
Z	2	2
<i>T</i> (K)	100(2)	100(2)
$\mu(Mo K_{\alpha}) (mm^{-1})$	0.348	0.120
reflns	12450	22016
independent reflns $(R_{int.})$	3985 (0.2175)	9958 (0.1852)
observed reflns	1736	3277
parameters	214	536
goodness of fit on F^2	0.887	0.835
final R indices		
$R1, wR2$ $[I \ge 2\sigma(I)]$	0.0717, 0.1415	0.0841, 0.1721
R1, wR2 (all data)	0.1809, 0.1783	02292, 0.2000

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