Supporting Information

for

Soluble, reactive and stable – unique alumosilicate ligands and a heterobimetallic derivative $[LAl(SLi)(\mu\text{-}O)Si(OLi\cdot 2thf)(O^tBu)_2]_2$†

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Preparation of complexes 1–3:

General. All preparations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified prior to use by distillation over the appropriate drying agents under nitrogen. $LAl(SH)_2$, $(^tBuO)_2Si(OH)_2$ were prepared using literature procedures,[1,2] and $[(Me_3Si)_2NLi\cdot OEt_2]_2$ was prepared freshly from $(Me_3Si)_2NH$ and ^{n}BuLi in diethylether. Infrared spectra were recorded as CsI pellets in the range 4000–250 cm^{-1} on a Bruker Tensor 27 Fourier-transform spectrometer; ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded using a JEOL ECLIPSE 300 NMR spectrometer. Mass spectra (EI-MS) were recorded using a JEOL JMS-AX505HA mass-spectrometer. Elemental analyses (C, H, N) were carried out by Galbraith Laboratories Inc. (Knoxville, TN).

LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$ (1). A Schlenk flask charged with LAl(SH)$_2$ (2.00 g, 3.92 mmol) and (^{t}BuO)$_2$Si(OH)$_2$ (0.82 g, 3.92 mmol) was placed in liquid nitrogen and then THF (40 mL) was added in such rate, that nearly all solidified during the addition. The reaction mixture was allowed to thaw, and warmed to ambient temperature under rapid stirring. The colorless solution was stirred for 16 hours, all volatiles were removed under vacuum and the essentially white product was recrystallized from a hexane/toluene mixture to give **1** in a form of large rhombohedral crystals. Yield: 2.28 g (85 %); M.p. 152 ºC (dec.); Elemental analysis (%) calcd. for $C_{37}H_{61}AlN_2O_4SSi$ (685.03 g·mol^{-1}): C 64.87, H 8.98, N 4.09; found: C 64.8, H 9.1, N 4.0; IR (CsI): $\tilde{\nu}$ 3462 (w, vbr, ν OH), 2560 cm^{-1} (vw, b, ν SH). ^{1}H NMR (300.53 MHz, C_6D_6, 20 ºC, TMS): $\delta = -0.45$ (s, 1 H, S*H*), 1.05 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.12 (s, 18 H, C(C*H*$_3$)$_3$), 1.13 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.18 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.51 (s, 6 H, C*H*$_3$), 1.53 (s, 1 H, O*H*), 1.53 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 3.37 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.60 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.84 (s, 1 H, γ-C*H*), 7.14–7.15 ppm (m, 6H, *H* of Ar); ^{13}C{^{1}H} NMR (75.57 MHz, C_6D_6, 20 ºC, TMS): δ = 23.3, 24.0, 24.6, 24.8 (CH(*C*H$_3$)$_2$), 27.0, 28.0 (*C*H(CH$_3$)$_2$), 28.9 (*C*H$_3$), 31.2 (C(*C*H$_3$)$_3$), 71.4 (*C*(CH$_3$)$_3$), 97.8 (γ-*C*), 124.1, 124.5, 125.0, 139.4, 144.0, 145.3 (*C* of Ar), 170.8 ppm (*C*=N); ^{29}Si{^{1}H} NMR (29.94 MHz, C_6D_6, 20 ºC, TMS): $\delta = -111$ ppm. Mass Spec (EI-MS): m/z 684 [M]$^+$, 651 [M – SH]$^+$, 595 [M – SH – C_4H_8]$^+$, 539 [M – SH – 2C_4H_8]$^+$, 523 [M – SH – C_4H_8 – O^{t}Bu + H]$^+$.

LAl(OH·thf)(μ-O)Si(OH)(O^{t}Bu)$_2$ (2). Solution of **1** (1.00 g, 1.46 mmol) in THF (20 mL) was cooled to –78 °C and 1M solution of H_2O in THF (1.46 mL, 1.46 mmol) was added quickly. The reaction mixture was stirred at this temperature for 30 min and let to warm to ambient temperature over a period of one hour. The colorless solution was stirred for 16 hours, all volatiles were removed under vacuum and the essentially white product was recrystallized from a hexane/toluene mixture with addition of 0.5 mL of THF to give **2** in a form of large prismatic crystals, which were rinsed with cold hexane. Yield: 0.81 g (75 %); M.p. 134 ºC (dec.) ; Elemental analysis (%) calcd. for $C_{41}H_{69}AlN_2O_6Si$ (741.08 g·mol^{-1}): C 66.45, H 9.38, N 3.78; found: C 66.5, H 9.3, N 3.9; IR (CsI): $\tilde{\nu}$ 3541 (w, br, ν(Al)OH), 3357 cm^{-1} (w, vbr, ν(Si)OH). ^{1}H NMR (300.53 MHz, C_6D_6, 20 ºC, TMS): δ = 0.95 (s, 1 H, Al–O*H*), 1.10 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.13 (s, 18 H, C(C*H*$_3$)$_3$), 1.17 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.38 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.40 (m, 4 H, (O(CH$_2$C*H*$_2$)$_2$)), 1.51 (s, 6 H, C*H*$_3$), 1.53

(d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 2.76 (s, 1 H, Si–O*H*), 3.25 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.37 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.56 (m, 4 H, (O(C*H*$_2$CH$_2$)$_2$)), 4.86 (s, 1 H, γ-C*H*), 7.00–7.20 ppm (m, 6H, *H* of Ar); ^{13}C{^{1}H} NMR (75.57 MHz, C$_6$D$_6$, 20 ºC, TMS): δ = 22.9, 23.2, 24.2, 24.4 (CH(*C*H$_3$)$_2$), 25.6 (O(*C*H$_2$CH$_2$)$_2$), 27.8 (*C*H$_3$), 28.4, 28.7 (*C*H(CH$_3$)$_2$), 31.8 (C(*C*H$_3$)$_3$), 67.6 (O(CH$_2$*C*H$_2$)$_2$), 71.1 (*C*(CH$_3$)$_3$), 96.8 (γ-*C*), 124.2, 124.4, 127.2, 139.5, 144.0, 144.6 (*C* of Ar), 170.6 ppm (*C*=N); ^{29}Si{^{1}H} NMR (29.94 MHz, C$_6$D$_6$, 20 ºC, TMS): δ = –111 ppm. Mass Spec (EI-MS): m/z 668 [M – THF]$^+$, 651 [M – THF – OH]$^+$, 612 [M – THF – C$_4$H$_8$]$^+$, 595 [M – THF – O^{t}Bu]$^+$, 539 [M – THF – O^{t}Bu –C$_4$H$_8$]$^+$, 523 [M – THF – 2 O^{t}Bu + H]$^+$.

[LAl(SLi)(μ-O)Si(OLi·2thf)(O^{t}Bu)$_2$]$_2$ (3). A Schlenk flask with **1** (1.00 g, 1.46 mmol) and [(Me$_3$Si)$_2$NLi·OEt$_2$]$_2$ (0.72 g, 1.48 mmol) was cooled to –78 °C and THF (25 mL) was added. The reaction mixture was allowed to warm to ambient temperature under rapid stirring. A white precipitate was formed after adding the THF. The suspension was stirred for additional 2 hours, all volatiles were removed under vacuum and the essentially white product was recrystallized from a hot THF to give **3** in a form of prismatic crystals. Yield: 1.11 g (90 %); M.p. 212 ºC (dec.); Elemental analysis (%) calcd. for $C_{90}H_{150}Al_2Li_4N_4O_{12}S_2Si_2$ (1682.22 g·mol^{-1}): C 64.26, H 8.99, N 3.33; found: C 64.1, H 8.9, N 3.3. ^{1}H NMR (300.53 MHz, CDCl$_3$, 20 ºC, TMS): δ= 0.81 (s, 36 H, C(C*H*$_3$)$_3$), 1.04 (d, 12 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.05 (d, 12 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.15 (d, 12 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.31 (d, 12 H, $^3J_{H-H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.69 (s, 12 H, C*H*$_3$), 1.85 (m, 16 H, (O(CH$_2$C*H*$_2$)$_2$)), 3.28 (sept, 4 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.75 (m, 16 H, (O(C*H*$_2$CH$_2$)$_2$)), 4.38 (sept, 4 H, $^3J_{H-H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.23 (s, 2 H, γ-C*H*), 7.00–7.30 ppm (m, 12 H, *H* of Ar); ^{13}C{^{1}H} NMR (75.57 MHz, CDCl$_3$, 20 ºC, TMS): δ = 23.7, 23.7, 23.9, 24.8 (CH(*C*H$_3$)$_2$), 25.6 (O(CH$_2$*C*H$_2$)$_2$), 27.1 (*C*H$_3$), 28.5, 28.6 (*C*H(CH$_3$)$_2$), 30.9 (C(*C*H$_3$)$_3$), 68.0 (O(*C*H$_2$CH$_2$)$_2$), 71.3 (*C*(CH$_3$)$_3$), 98.7 (γ-*C*), 123.7, 124.4, 126.2, 141.2, 144.0, 145.3 (*C* of Ar), 169.8 ppm (*C*=N); ^{7}Li{^{1}H} NMR (116.80 MHz, CDCl$_3$, 20 ºC, TMS): δ= 4.16 ppm; ^{29}Si{^{1}H} NMR (29.94 MHz, CDCl$_3$, 20 ºC, TMS): δ= –110 ppm.

X-Ray structure Determination. Crystals were mounted on nylon loops and rapidly placed in a stream of cold nitrogen. Diffraction data were collected on a Bruker-APEX three-circle diffractometer using Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) at –100 ºC. The structures were solved by direct methods (SHELXS-97)[3] and refined against all data by full-matrix least-squares on F^2.[4] The hydrogen atoms of C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the OH and SH moieties were localized from the difference electron-density map and refined isotropically with distance restraints (SADI) when applicable. The disordered hexane (in the crystal of **1**) and THF (in the crystals of **2** and **3**) molecules as well as the disordered ^{t}Bu moieties (in the crystal of **1**) were refined using geometry and distance restraints (SAME, SADI) together with the restraints for the U_{ij} values (SIMU, DELU). The twin law for **2** was determined as 1 0 0 0 –1 0 0 0 –1 and the ratio of the twin domains was refined to 85:15. The hexane content in the crystal of **1** was refined to 2 hexane molecules per a cavity centered around the $\overline{3}$ axis. Thus there is 1/3 of hexane in the asymmetric unit, which is disordered over 3 independent positions (18 for the whole cavity and 2 hexane molecules). The sum of the occupancies was controlled using the SUMP command implemented in the in SHELXL program.[4] For the refinement of **1**, the number of formulas per asymmetric unit Z was based on the silicon complex and not on the hexane as implemented in cifCheck, which led to two alerts level C: Calc. and Rep. SumFormula Strings Differ and Calculated and Reported Z Differ by 0.17 Ratio. CCDC-628448 (**1**), CCDC-628449 (**2**) and CCDC-628450 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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