Supporting Information

Lewis base stabilized lithium TMP – aluminates: an unexpected fragmentation and capture reaction involving cyclic ether 1, 4-dioxane

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Experimental Section

General Methods.

General: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. $^{i}Bu_3Al$ and *n*-Butyllithium were purchased from Aldrich Chemicals as solutions in hexane. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C.

Synthesis of [(dioxane)$_4$.Li][Al^{i}Bu$_4$] (5): In a Schlenk tube, 2 mmol of the complexes [L.Li(μ-TMP)(μ-^{i}Bu)Al(^{i}Bu$_2$)] [(**1**) L = TMPH; (**2**) L = NEt_3] in 10 ml of hexane, were synthesized by following the procedure described above. 1,4-dioxane (8 mmol, 0.68

mL) was added and in both cases a white precipitate formed. Addition of 2mL of toluene and heating the solution until reflux temperature was needed to form a clear solution. Bench cooling of this solution afforded colourless crystals of **5** (0.38g, 30%). ^{1}H NMR (400.13 MHz, d_6-benzene, 300K): 3.29 (s, 32H, 4 dioxane), 2.29 (sept, 4H, C*H*-^{i}Bu), 1.31 (d, 24H, CH_3-^{i}Bu), 0.03 (d, 8H, CH_2-^{i}Bu). ^{13}C{H} NMR (100.63 MHz, d_6-benzene, 300K): 67.64 (*C*H_2 dioxane), 30.12 (*C*H_3 of ^{i}Bu), 28.53 (*C*H of ^{i}Bu). Signal for Al-*C*H_2 of ^{i}Bu was not observed. ^{7}Li NMR (155.50 MHz, d_6-benzene, 300K, reference LiCl in D_2O at 0.00 ppm): -0.73 ppm.

Crystal data for **5**: $C_{32}H_{68}AlLiO_8$, M_r = 614.78, orthorhombic, space group Pbca, a = 19.1742(10), b= 19.4623(9), c= 19.9819(12) Å, V = 7456.7(7) Å^3, Z = 8, λ = 0.71073 Å, μ = 0.097 mm^{-1}, T = 123 K, $2\theta_{max}$ = 44 °; 8504 reflections, 4540 unique, R_{int} 0.0447; final refinement to convergence on F^2 gave R = 0.0666 (F, 3283 obs. data only) and R_w = 0.1501 (F^2, all data), GOF = 1.177.

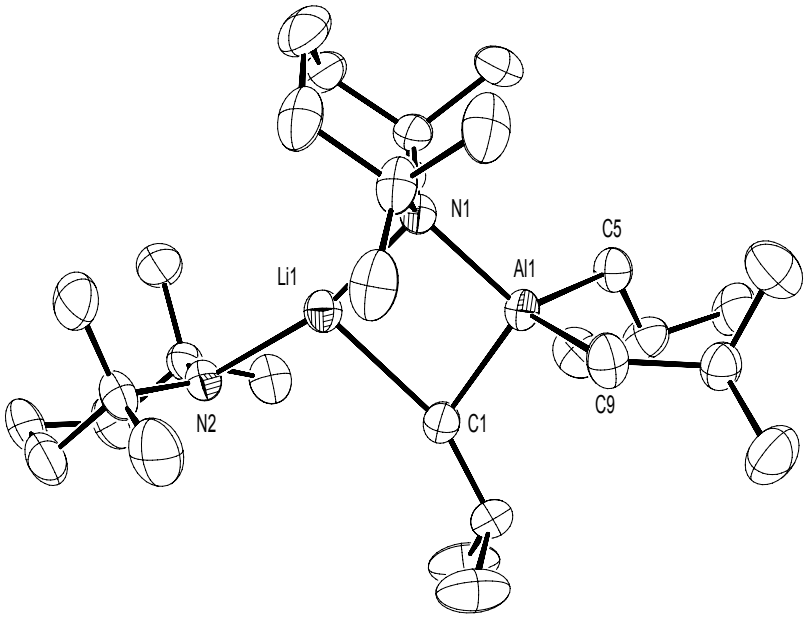

Figure 1. Molecular structure of **1** with 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

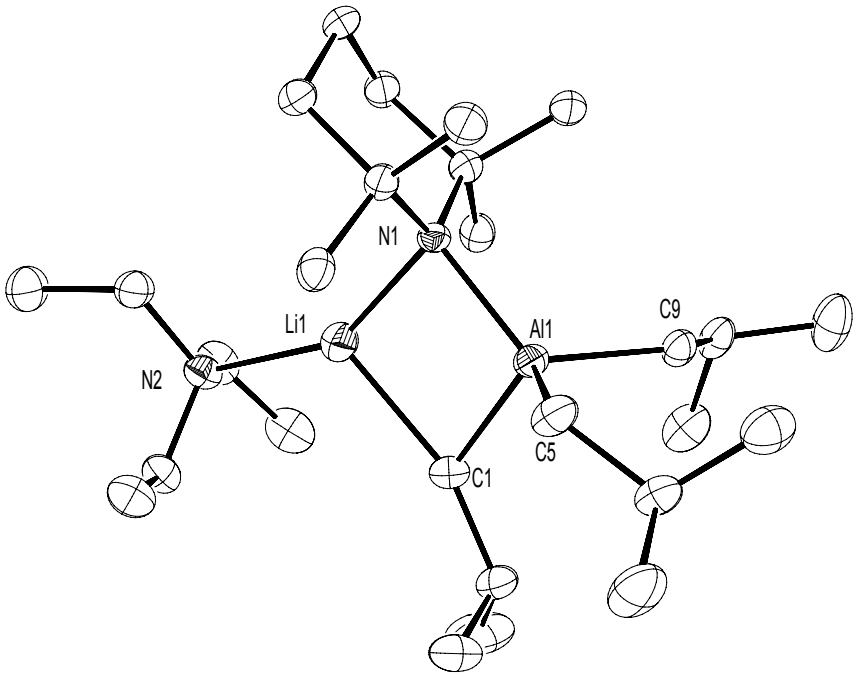

Figure 2. Molecular structure of **2** with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

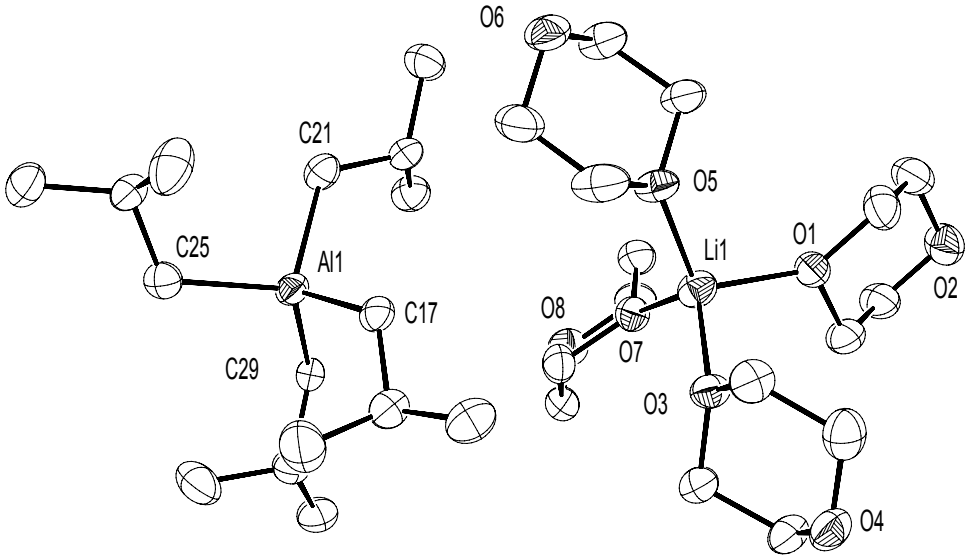

Figure 2. Molecular structure of **5** with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.