

# Supporting Information

## Unprecedented participation of a four-coordinate hydrogen atom in the cubane core of lithium and sodium phenolates

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## 1. General Experimental Details.

The ligand (**1**, 2,2',2''-[Nitrilotris(methylene)]tris[4,6-di(methyl)phenol] was prepared by the method of Kol and co-workers.<sup>1</sup> Lithium and Sodium hexamethyldisilazide salt (MHMDS), *n*-Butyllithium (1.6 M solution in hexane) and pentachlorophenol were bought from Aldrich and used without further purification.

All experimental manipulations were performed under an atmosphere of dry, oxygen-free argon, using standard Schlenk or glovebox techniques. All solvents were degassed, eluted over activated alumina columns and stored under argon prior to use.

<sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature and referenced to residual protio solvent peaks, unless otherwise stated. <sup>7</sup>Li{<sup>1</sup>H} NMR spectra were recorded on a Bruker 400 MHz and referenced to an external 1M LiCl solution in D<sub>2</sub>O. THF-*d*<sub>8</sub> and toluene-*d*<sub>8</sub> (Aldrich) were degassed and stored over sodium. Coupling constants *J* are given in Hertz.

## 2. Preparation and Characterisation of **2**.

To a stirred solution of **1** (0.500 g, 1.193 mmol) in 30 mL of acetonitrile pentachlorophenol (0.318 g, 1.194 mmol) was added slowly. A white solid was formed almost immediately, and the resulting suspension was stirred for 1 h. Then the solid was collected by filtration, washed with hexane (2 x 20 mL) and dried under vacuum for at least three hours (0.694 g, 85%). Anal. Calcd. for C<sub>33</sub>H<sub>34</sub>Cl<sub>5</sub>NO<sub>4</sub>: C, 57.97; H, 5.01; N 2.04. Found C, 57.40; H, 4.87; N, 2.04. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 6.69, 6.54 (2 x s, 2 x 3H, 2 x Ar-H), 5.37 (bs, 3H, O-H), 3.44 (s, 6H, NCH<sub>2</sub>), 2.12, 2.11 (2 x s, 2 x 9H, 2 x Ar-Me) ppm. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):

9.32 (bs, 1H, N-H), 6.80 (s, 2 x 3H, 2 x Ar-H), 3.66 (s, 6H, NCH<sub>2</sub>), 3.89 (bs, 3H, O-H), 2.16, 2.11 (2 x s, 2 x 9H, Ar-Me) ppm.

### 3. Preparation and Characterisation of 3.

#### 3.1 Preparation and spectroscopic data.

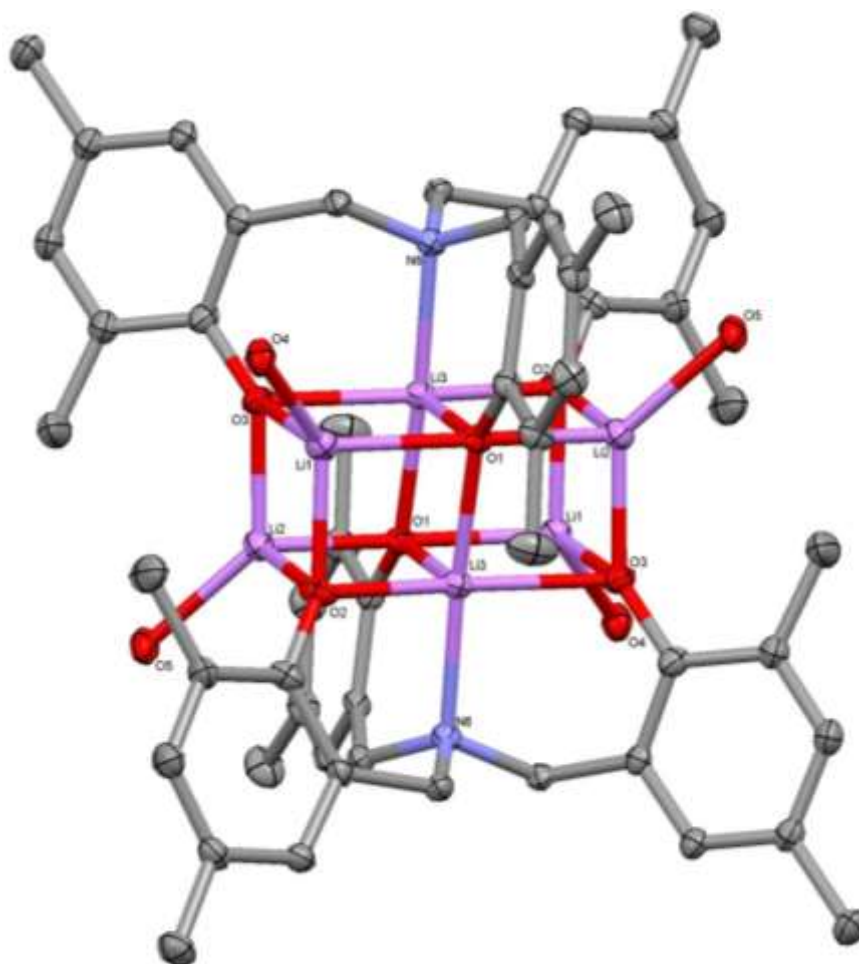
To a stirred solution of **1** (0.420 g, 1.00 mmol) in 10 mL of THF, 1.95 mL of a 1.6M BuLi solution in hexane (3.12 mmol) were slowly added. The resulting solution was stirred for one hour, and then solvent was partially removed under vacuum. Some fine precipitate formed was re-dissolved by heating and the resulting solution was cooled to 253 K. X-ray quality crystals were grown overnight, decanted from solution, washed with hexane (2 x 10 mL) and dried under vacuum (unoptimised yield: 0.345 g, 53%). Found C, 71.80; H, 7.68; N, 2.25. C<sub>74</sub>H<sub>108</sub>N<sub>2</sub>Li<sub>6</sub>O<sub>11</sub> requires C, 71.49; H, 8.75; N 2.25. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 298 K): 6.63 (s, 3H, Ar-H), 6.52 (s, 3H, Ar-H), 3.62 [m, 8H, OCH<sub>2</sub>(THF)], 3.26 (bs, 6H, NCH<sub>2</sub>), 2.08 (s, 9H, Ar-Me), 2.06 (s, 9H, Ar-Me), 1.77 [m, 8H, CH<sub>2</sub>(THF)] ppm. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 216 K): 6.62 (s, 3H, Ar-H), 6.52 (s, 3H, Ar-H), 3.98 (d, *J*<sub>HH</sub> = 12, 3H, NCH<sub>2</sub>), 3.62 [m, 8H, OCH<sub>2</sub>(THF)], 2.45 (d, *J*<sub>HH</sub> = 12, 3H, NCH<sub>2</sub>), 2.08 (s, 9H, Ar-Me), 2.06 (s, 9H, Ar-Me), 1.79 [m, CH<sub>2</sub>(THF)] ppm. <sup>7</sup>Li{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 298 K): -1.25 (s) ppm. <sup>7</sup>Li{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 216 K): 0.37 (bs, N-Li), -2.03 (s, O-Li) ppm.

#### 3.2 Crystallographic data for 3.

Data were collected at 100 K on a Nonius KappaCCD area detector diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), and the structure were solved by direct methods and refined on all  $F^2$  data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined

using the riding model.<sup>2</sup> Some of the THF rings and the tripodal ligand were found to be disordered over two positions which were modelled satisfactorily using restraints.

*X-Ray data for 3:* C<sub>78</sub>H<sub>108</sub>Li<sub>6</sub>N<sub>2</sub>O<sub>12</sub>, *M* = 1307.3, colourless prism, 0.44 x 0.20 x 0.16 mm<sup>3</sup>, monoclinic, space group P2<sub>1</sub>/n, *a* = 12.8870(2), *b* = 13.0390(2), *c* = 21.4410(3) Å,  $\alpha = \gamma = 90$ ,  $\beta = 89.79^\circ$ , *V* = 3602.78(9) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.205 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1408, Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), *T* = 100(2)K,  $2\theta_{max} = 55^\circ$ , 63006 reflections collected, 8233 unique [*R*(int) = 0.0599]. *Final GooF* = 1.104, *R*1 = 0.0980, *wR*2 = 0.2525, *R* indices based on 7010 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 589 parameters.



**Figure S1.** Ortep diagram of compound **3** with H atoms and THF molecules (except O atoms) omitted.

## 4. Preparation and Characterisation of 4.

### 4.1 Preparation and spectroscopic data.

Solid NaHMDS (0.550 g, 3.0 mmol) was added to a stirred solution of ligand **1** (0.420 g, 1.00 mmol) in Et<sub>2</sub>O (10 mL). The resulting solution was stirred for one hour, and then solvent was partially removed under vacuum. Some fine precipitate formed was re-dissolved by heating and the resulting solution cooled to 253 K. X-ray quality crystals were grown overnight, decanted from solution, washed with hexane (2 x 10 mL) and dried under vacuum (unoptimised yield: 0.452 g, 71%). <sup>1</sup>H NMR (tol-*d*<sub>8</sub>, 298 K): 6.99 (s, 3H, Ar-H), 6.94 (s, 3H, Ar-H), 4.14 (bs, 3H, NCH<sub>2</sub>), 3.15 [q, 8H, OCH<sub>2</sub>(Et<sub>2</sub>O)], 2.88 (bs, 3H, NCH<sub>2</sub>), 2.34 (s, 9H, Ar-Me), 1.67 (bs, 9H, Ar-Me), 1.01 [t, 12H, Me(Et<sub>2</sub>O)] ppm.

### 4.2 Crystallographic data for 4.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), and the structure were solved by direct methods and refined on all  $F^2$  data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model.<sup>2</sup> Some of the Et<sub>2</sub>O molecules are disordered over two positions which were modelled satisfactorily.

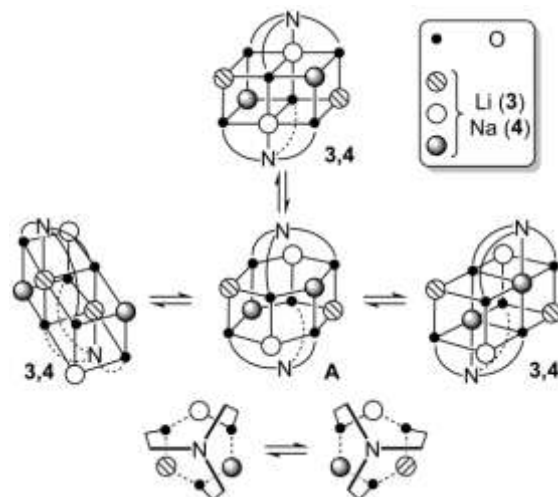
*X-Ray data for 4:* C<sub>70</sub>H<sub>100</sub>Na<sub>6</sub>N<sub>2</sub>O<sub>10</sub>,  $M = 1267.5$ , colourless prism, 0.16 x 0.11 x 0.10 mm<sup>3</sup>, orthorhombic, space group  $P b c a$ ,  $a = 20.0070(2)$ ,  $b = 21.3360(3)$ ,  $c = 32.6610(2) \text{ \AA}$ ,  $\alpha = \gamma = \beta = 90^\circ$ ,  $V = 13942.0(3) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 1.208 \text{ g/cm}^3$ ,  $F_{000} = 5440$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ),  $T = 150(2)\text{K}$ ,  $2\theta_{max} = 45.08^\circ$ , 102918 reflections collected, 9025 unique [R(int) = 0.0773]. *Final GooF* =

1.034,  $R1 = 0.0576$ ,  $wR2 = 0.1528$ ,  $R$  indices based on 7060 reflections with  $I > 2 \sigma(I)$  (refinement on  $F^2$ ), 813 parameters.

## 5. Solution Structure of Compounds 3-4

The available NMR data for complexes **3-4** are essentially consistent with the solid-state structures, but supports the occurrence of fluxional processes in solution. Thus, although in these molecules there are two chemically different environments for the metal centers (tetrahedral and square pyramidal) and hydrocarbon chains, the  ${}^7\text{Li}\{\text{}^1\text{H}\}$  NMR spectra of **3** exhibits just a single resonance, which eventually splits into the expected separate resonances (with 1:2 intensity ratio) at low temperature (216 K). Besides this, its room temperature  ${}^1\text{H}$  NMR spectrum displays just one set of resonances for the three aromatic rings of the tripodal ligand and just one averaged signal for the six protons of the three methylenic groups ( $\text{NCH}_2$ ). On lowering the temperature, the aromatic resonances broaden (but are not resolved into the expected two sets), and the methylenic resonance transforms into an  $AB$  multiplet ( $J_{\text{HH}} = 12$  Hz). The expected further splitting of this multiplet into separated multiplets with 1:2 relative intensity (as observed for the Li resonance) was not observed even at 216 K. We should note that these changes were essentially independent of the sample concentration, thus disfavouring the occurrence of deaggregation equilibria. Altogether these observations can be explained by assuming the occurrence of two fluxional processes: (a) a conformational exchange of the methylenic protons within each hydrocarbon chain, as usually observed in the metal complexes of this tripodal ligand (Figure S2, bottom),<sup>3</sup> and (b) a rearrangement of the  $\text{M}_6\text{O}_6\text{N}_2$  cores, which would exchange the environments of the metal atoms and hydrocarbon chains through an open structure (**A** in Figure S2) following the reversible cleavage of the  $\text{N-M-O}(\mu_4)$  bonds, thus effectively rendering a pseudo  $C_3$ -axis. Although we have not studied the VT NMR spectra

of the sodium compound **4** so far, the fact that the room temperature  $^1\text{H}$  NMR spectrum displays just one set of aromatic resonances and just one *AB* multiplet for all methylenic protons suggest the occurrence of dynamic processes similar, although somewhat slower, to those proposed for the lithium complex **3**.



**Figure S2.** Proposed fluxional processes of compounds **3** and **4** in solution.

## 6. Preparation and Characterisation of **5**.

### 6.1 Preparation and spectroscopic data.

A Schlenk tube was charged with **2** (0.100 g, 0.146 mmol) and dissolved in 10 mL of THF. Three molar equivalents of  $\text{LiN}(\text{SiMe}_3)_2$  (0.075 g, 0.438 mmol) were added to the colourless solution. The reaction mixture was stirred for one hour, and then approximately 70% of the solution was removed *in-vacuo*. The precipitate was re-dissolved by heating, and the vessel was left to cool down slowly by immersion in a bath of hot (80 °C) water. The resulting crystalline material was collected by filtration, washed with hexane (2 x 5 mL) and dried under vacuum (0.097 g, 72%). Anal. Calcd. for  $\text{C}_{45}\text{H}_{55}\text{Cl}_5\text{Li}_3\text{NO}_7$  requires C, 58.75; H, 6.03; N 1.52. Found: C, 58.91; H, 6.81; N 1.61.  $^1\text{H}$  NMR ( $\text{THF-}d_8$ ): 12.68 (bd,  $^3J_{\text{HH}} = 8$ , 1H, N-H), 6.73, 6.50 (2 x s, 2 x 3H, 2 x Ar-H), 4.41 (d,  $^2J_{\text{HH}}$

= 12, 3H, NCH<sub>2</sub>), 3.54 [m, 12H, OCH<sub>2</sub>(THF)], 3.15 (ft, <sup>2</sup>J<sub>HH</sub>=12, <sup>3</sup>J<sub>HH</sub> = 8, 3H, NCH<sub>2</sub>), 2.05 (s, 2 x 9H, 2 x Ar-Me), 1.69 [m, 12H, CH<sub>2</sub>(THF)] ppm. <sup>7</sup>Li{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): -0.89 (s) ppm.

## 6.2 Crystallographic data for 5.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), and the structure were solved by direct methods and refined on all  $F^2$  data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model,<sup>2</sup> excepting the central N bound H atom which was localized in the Fourier maps and refined independently. One of the coordinated THF molecules is disordered over two positions which were modelled satisfactorily applying isotropic restraints.

*X-Ray data for 5:* C<sub>45</sub>H<sub>55</sub>Cl<sub>5</sub>Li<sub>3</sub>NO<sub>7</sub>,  $M = 919.97$ , colourless prism, 0.65 x 0.60 x 0.25 mm<sup>3</sup>, triclinic, space group P -1,  $a = 9.8010(2)$ ,  $b = 13.9220(3)$ ,  $c = 18.4310(3) \text{ \AA}$ ,  $\alpha = 89.201(2)$ ,  $\beta = 87.934(2)$ ,  $\gamma = 70.553(1)^\circ$ ,  $V = 2369.88(8) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.289 \text{ g/cm}^3$ ,  $F_{000} = 964$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ),  $T = 150(2)\text{K}$ ,  $2\theta_{max} = 45.08^\circ$ , 31166 reflections collected, 10697 unique [R(int) = 0.0372]. *Final GooF* = 1.036, R1 = 0.0488, wR2 = 0.1178,  $R$  indices based on 8035 reflections with  $I > 2 \text{ sigma}(I)$  (refinement on  $F^2$ ), 570 parameters.

## 7. Preparation and Characterisation of 6.

### 7.1 Preparation and spectroscopic data.

A Schlenk tube was charged with **2** (0.200 g, 0.292 mmol) and dissolved in 10 mL of Et<sub>2</sub>O. Three molar equivalents of NaN(SiMe<sub>3</sub>)<sub>2</sub> (0.161 g, 0.876 mmol)



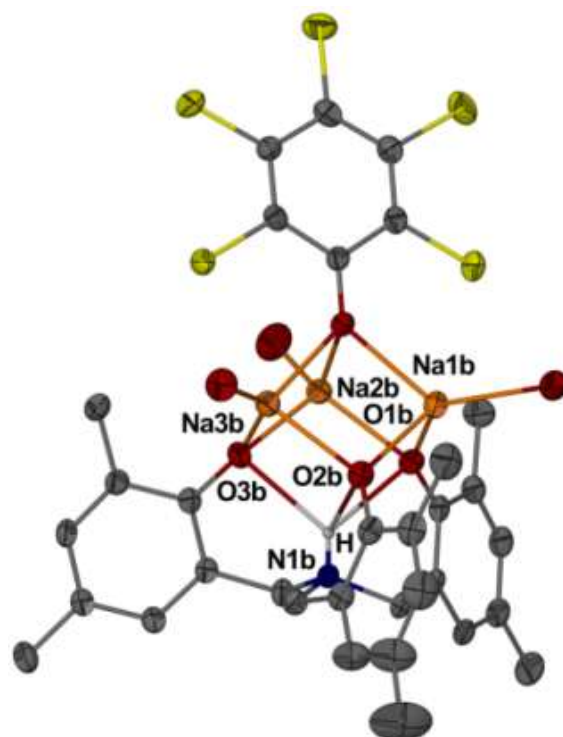
were added to the colourless solution, and the reaction mixture was stirred for one hour at room temperature. Then approximately 70% of the solution was removed in-vacuo, the precipitate formed was re-dissolved by heating, and the reaction vessel was left at 253 K overnight. The resulting solid was collected by filtration, washed with hexane (2 x 5 mL) and dried under vacuum (0.135 g, 46%). No satisfactory elemental analysis could be obtained for this complex due to its fast decomposition during the sample preparation process.  $^1\text{H}$  NMR (THF- $d_8$ ): 11.66 (b, 1H, N-H), 6.73, 6.53 (2 x s, 2 x 3H, 2 x Ar-H), 4.37 (bs, 3H, NCH<sub>2</sub>), 3.39 [q,  $J_{\text{HH}} = 7$ , 12H, OCH<sub>2</sub>(Et<sub>2</sub>O)], 3.05 (bs, 3H, NCH<sub>2</sub>), 2.08, 2.05 (2 x s, 2 x 9H, 2 x Ar-Me), 1.12 [t,  $J_{\text{HH}} = 7$ , 18H, Me(Et<sub>2</sub>O)] ppm.

## 7.2 Crystallographic data for 6.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), and the structure were solved by direct methods and refined on all  $F^2$  data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model.<sup>2</sup> One of the coordinated Et<sub>2</sub>O molecules is disordered over two positions which were modelled satisfactorily, other minor incipient disorder processes were observed (as high C anisotropic factors) for other solvent molecules, but no attempts to model these were done due to the low quality of the diffraction data.

*X-Ray data for 6:* C<sub>94</sub>H<sub>132</sub>Cl<sub>10</sub>N<sub>2</sub>Na<sub>6</sub>O<sub>15</sub>,  $M = 2022.46$ , colourless prism, 0.30 x 0.25 x 0.2 mm<sup>3</sup>, triclinic, space group P -1,  $a = 12.8510(3)$ ,  $b = 20.6590(5)$ ,  $c = 21.2810(5) \text{ \AA}$ ,  $\alpha = 107.1770(10)$ ,  $\beta = 90.7680(10)$ ,  $\gamma = 92.202(2)^\circ$ ,  $V = 5392.1(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.246 \text{ g/cm}^3$ ,  $F_{000} = 2132$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ),  $T = 150(2)\text{K}$ ,  $2\theta_{\text{max}} = 55.06^\circ$ , 59857 reflections collected, 23305 unique [R(int) = 0.164]. *Final GooF* = 1.468, R1 = 0.1079, wR2 = 0.2834, R

indices based on 12240 reflections with  $I > 2 \sigma(I)$  (refinement on  $F^2$ ), 1177 parameters.



**Figure S3.** Diagram of compound **6** with most H atoms and Et<sub>2</sub>O molecules (except O atoms) omitted. The central N–H atom was located in the difference Fourier map and refined isotropically. Only one of the two independent molecules is shown.

## 8. References.

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3. Licini, G., Mba M., Zonta, C. *Dalton Trans.*, **2009**, 5265.