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# Lithium complexes supported by tripodal diaminebis(aryloxido) ligands: Synthesis and structure<sup>†</sup>

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The diaminebis(aryloxido) ligand precursors  $H_2L^1$  and  $H_2L^2$  [ $H_2L^1 = Me_2NCH_2CH_2N(CH_2-4-CMe_2-CH_2CMe_3-C_6H_3OH)_2$ ;  $H_2L^2 = Me_2NCH_2CH_2N(CH_2-4-Me-C_6H_3OH)_2$ ] were synthesized by a straightforward single-step Mannich condensation. Their reactions with 2 molar equivalents of MeLi in thf afforded [ $Li_4(\mu-L-\kappa^4 O, N, N, O)_2(thf)_2$ ] (1a, L<sup>1</sup>; 1b, L<sup>2</sup>) and unexpectedly small amounts (~9%) of [ $Li_6(\mu-L-\kappa^4 O, N, N, O)_2(thf)_4$ ]·thf (2a·thf; L<sup>1</sup>; 2b·thf, L<sup>2</sup>). Stoichiometric reactions of LiCl, MeLi and ligand precursors  $H_2L$  led to the formation of 2a and 2b in high yield (~80%). All compounds were characterized by chemical and physical techniques including X-ray crystallography for  $H_2L^1$ ,  $H_2L^2$ , 1b, 2a and 2b.

### Introduction

Polydentate diaminebis(aryloxido) (ONNO) ligands have been used extensively in transition-metal coordination chemistry in catalyst development,<sup>1</sup> metalloenzyme mimicry,<sup>2</sup> and cytotoxicity against particular cells.<sup>3</sup> Such broad application range arises from the great modification possibilities either on the phenyl group or amine leading to convenient variation of steric factors and donor ability of this class of ligands.

One method to realize synthesis of transition-metal complexes supported by diaminebis(aryloxido) ligands is through a metathesis route that often involves lithium derivatives. To fully exploit this method, it is necessary to identify the structure of starting materials. However, only few lithium compounds of general formula [Li<sub>2</sub>(ONNO)] with diaminebis(aryloxido) ligands, being of our research interest, have been fully characterized.4,5 Kerton and co-workers showed that isomeric tripodal [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>-2,4-'Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> and linear (so-called salan)  $[MeNCH_2CH_2NMe(CH_2-2,4-^{\prime}Bu_2C_6H_2O)_2]^2$  ligands in the presence of 1,4-dioxane generated lithium complexes that exhibited a polymeric and a 1,4-dioxane bridged dimeric structure in the solid-state, respectively.5 The same tripodal  $[Me_2NCH_2CH_2N(CH_2-2,4-^tBu_2C_6H_2O)_2]^{2-}$  ligand in the absence of neutral strong bases as coligands creates the tetra-lithium complex revealing boat-like structure.<sup>4</sup> This shows that the final structure of these lithium species are strongly dependent upon the choice of solvent (Lewis basicity) used to their synthesis.

During the course of our investigation into the vanadium coordination chemistry involving diaminebis(aryloxido) ligands, new ligand precursors shown in Fig. 1, and their lithium salts were prepared and structurally characterized.



 $H_2L^2$ ,  $R = C(CH_3)_2CH_2C(CH_3)_2$  $H_2L^2$ ,  $R = CH_3$ 

Fig. 1 Tetradentate diaminebis(aryloxido) ligand precursors.

### **Results and discussion**

The synthesis of the diaminebis(aryloxido) ligand precursors  $H_2L^1$  and  $H_2L^2$  was based on a straightforward single-step Mannich condensation between N,N-dimethylethylenediamine, paraformaldehyde and 4-(1,1,3,3-tetramethylbutyl)phenol or pcresol, respectively in a 1:2:2 molar ratio according to a known procedure.<sup>6</sup> The  $H_2L^1$  and  $H_2L^2$  products precipitated as white solids with high yield, and were characterized with NMR spectra and mass spectrometry. The <sup>1</sup>H NMR spectra of H<sub>2</sub>L<sup>1</sup> and  $H_2L^2$  suggest the presence of intramolecular hydrogen bonds OH ··· N either in the solid state or in solution (Experimental section). To confirm this structural feature the crystal structures of  $H_2L^1$  and  $H_2L^2$  were obtained. However, due to the insufficient quality of the  $H_2L^1$  crystal only qualitative information could be extracted and illustrated as the DIAMOND drawing in Fig. 2a.<sup>‡</sup> These data demonstrate that compound  $H_2L^1$  contains two intramolecular hydrogen-bond interactions OH ··· N in the solid

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<sup>‡</sup> Crystal data for H<sub>2</sub>L<sup>1</sup>: C<sub>34</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>, M = 524.43, orthorhombic, space group *Pca2*<sub>1</sub>, a = 12.106(5), b = 7.740(5), c = 69.239(16) Å, Z = 8, V = 6487(16) Å<sup>3</sup>.



**Fig. 2** (a) DIAMOND drawing of the molecular structure of  $H_2L^1$ ; (b) Molecular structure of  $H_2L^2$  with thermal ellipsoids drawn at the 50% probability level. Only hydrogen atoms involved in the hydrogen bonds are shown Selected parameters (bonds, Å; angles, °): N1–C2 1.4807(17), N1–C3 1.4813(17), N1–C1 1.4862(17), N2–C6 1.4687(18), N2–C5 1.4700(18), N2–C4 1.4762(17) O11–H11A  $\cdots$  N2 2.7720(17), O21–H21A  $\cdots$  N1 2.6858(18); O11–H11A  $\cdots$  N2 153.4, O21–H21A  $\cdots$  N1 146.7.

state. Similar structural trends have been found in the tripodal  $[Me_2NCH_2CH_2N(CH_2-2,4-R_2C_6H_2OH)_2]$  (R = Me,<sup>7a</sup> 'Bu,<sup>7b</sup>) Mannich bases having alkyl substituents at *ortho* and *para* positions of the phenolate rings. Ultimately, good quality of the H<sub>2</sub>L<sup>2</sup> crystal allowed to obtain well solved X-ray data and to confirm compatibility between the model of H<sub>2</sub>L<sup>1</sup> and the structure of H<sub>2</sub>L<sup>2</sup>. The molecular structures of H<sub>2</sub>L<sup>2</sup> and selected bond lengths and angles are shown in Fig. 2b.

Reaction of the ligand precursor  $H_2L^1$  with 2 molar equivalents of MeLi in thf affords after work-up two colorless compounds  $[Li_4(\mu-L^1-\kappa^4 O,N,N,O)_2(thf)_2]$  (1a) (87.2%) and  $[Li_6(\mu-L^1-\kappa^4 O,N,N,O)_2(\mu^3-Cl)_2(thf)_4]$  thf (2a·thf) (8.5%) as shown in Scheme 1.

Compound **1a** is very well soluble in all organic solvents in contrast to **2a** which has moderate solubility in cold thf. Analytically and spectroscopically pure forms of these compounds were obtained with easy interpretable NMR spectra. Unfortunately, attempts to obtain single crystals of **1a** were unsuccessful. We have proved analytically that the chloride ions found in **2a** originated from residual LiCl (0.18%) present in the commercial MeLi



Scheme 1

(Aldrich Chemical Co.). This has been previously noticed by synthetic chemists and it is well documented that the quantity of LiCl in commercial chemical agents is important in many organolithium reactions.8 This knowledge allowed to optimize the yield of compound 2a to 84% using in its synthesis MeLi,  $H_2L^1$  and LiCl at 2:1:1 molar ratio in thf. Crystals of **2a** suitable for an X-ray determination were grown from a saturated thf solution at room temperature. However, because they displayed poor diffraction, the X-ray data for 2a allowed to extract only a model of the structure.§ Fortunately, a similar synthetic procedure as for 1a and 2a carried out using  $H_2L^2$  (see Experimental section) successfully led to the formation of  $[\text{Li}_4(\mu-\text{L}^2-\kappa^4 O,N,N,O)_2(\text{thf})_2]$ (1b) and  $[\text{Li}_6(\mu-\text{L}^2-\kappa^4 O, N, N, O)_2(\mu^3-\text{Cl})_2(\text{thf})_4]$  thf (2b thf) as crystals for which satisfactory X-ray structural data were achieved. The molecular structures of 1b and 2b thf and selected bond lengths and angles are shown in Fig. 3 and 4, respectively.

Compound **1b** contains a 'cubanoid'  $\text{Li}_4\text{O}_4$  core comprising four lithium atoms and four  $\text{O}_{aryloxide}$  atoms of the L<sup>2</sup> ligands. In the structure of **1b** two of the lithium atoms have fivecoordinate environments, and are bound to the nitrogens and the  $\mu_3$ -oxygens of the L<sup>2</sup> ligands. The angles involving the bonds coordinated to these lithium atoms are all distorted from the idealized trigonal-bipyramidal angles. Each of the other two lithium atoms is bonded by three aryloxide  $\mu_3$ -oxygen atoms, with the remainder of the coordination sphere occupied by one oxygen atom of the thf molecule, resulting in a distorted tetrahedral geometry with angles  $\mu_3$ -O-Li- $\mu_3$ -O of 92.08–98.89° and  $\mu_3$ -O-Li- $O_{thf}$  of 105.79–136.05°. The Li1–( $\mu_3$ -O) bond distances of 2.001 Å (av.) are longer than the Li2–( $\mu_3$ -O) ones of 1.972 Å (av.) as expected from the change in coordination number, and are very similar to those observed in the salen-based tetra-lithium

§ Crystal data for **2a**: C<sub>88</sub>H<sub>148</sub>Cl<sub>2</sub>Li<sub>6</sub>N<sub>4</sub>O<sub>9</sub>, M = 1518.72, triclinic, space group  $P\overline{1}$ , a = 12.829(12), b = 13.991(12), c = 15.454(12) Å,  $\alpha = 73.26$ ,  $\beta = 73.76$ ,  $\gamma = 66.78^{\circ}$ , Z = 1, V = 2385.8(2) Å<sup>3</sup>.



**Fig. 3** Molecular structure of **1b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected parameters (bonds, Å; angles, °): Li1–N1 2.257(2), Li1–N2 2.325(2), Li1–O11 1.967(2), Li1–O21 2.034(2), Li2–O11 2.059(2), Li2–O21 1.931(2), Li2–O31 1.994(2); N2–Li1–O11 141.52(10), N2–Li1–O21 123.10(10), O11–Li2–O31 136.05(10), O11–Li2–O21 94.04(9), O21–Li2–O31 105.79(9).



**Fig. 4** Molecular structure of **2b** th with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms bonded to carbon, the thf solvent species and second position of disordered thf molecule are omitted for clarity. Selected bond lengths (Å): Li1–O11 1.938(3), Li1–O41 2.013(5), Li1–Cl1 2.320(3), Li2–O11 1.945(3), Li2–O31 1.991(3), Li2–Cl1 2.299(3), Li3–O11 1.997(3), Li3–O21 2.016 (3), Li3–N1 2.158(3), Li3–N2 2.213(3), Li3–Cl1 2.761(3).

complexes.<sup>9</sup> The Li1–N bond lengths of 2.257(2) and 2.325(2) Å in **1b** are significantly longer than those found in the lithium complexes with the [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>-2,4-'Bu<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>O)<sub>2</sub>] ligand having tetrahedral lithium centers.<sup>4,5</sup> The Li–O<sub>thf</sub> distance [1.994(2) Å] is within the normal range reported in the literature

for tetrahedral lithium compounds *e.g.*  $[Li(dmp)(thf)]_4$  (dmp = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O) (av. 2.078 Å) and  $[Li_4(ONep)_4(thf)_3]$  (ONep = Me<sub>3</sub>CCH<sub>2</sub>O) (av. 1.982 Å).<sup>10</sup> Compound **1b** has a similar structural motif like those found for tetra-lithium Schiff base complexes also containing tetrahedral and trigonal-bipyramidal geometry around metal centers.<sup>9</sup> However, the structure of **1b** markedly differs from structures of lithium salts generated with the tripodal [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>-2,4-'Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH)<sub>2</sub>] ligand precursor, the *ortho* and *para* sterically demanding analogue of H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup>. As was mentioned in Introduction, polymeric and tetranuclear lithium structures created by [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>-2,4-'Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH)<sub>2</sub>] depending on reaction conditions have four-coordinate lithium atoms, but they reside in different geometries, tetrahedral and trigonal pyramidal.<sup>4,5</sup>

Compound 2b consists of two non-planar, six-membered Li<sub>3</sub>O<sub>2</sub>Cl rings, with one ring rotated 180° relative to the other, which are linked by four  $\mu_3$ -oxygens of the L<sup>2</sup> ligands and two chlorides as displayed in Fig. 4. In this structure two lithium atoms adopt a distorted trigonal-bipyramidal geometry formed by two oxygens and the tripodal nitrogen of the L<sup>2</sup> ligand occupying equatorial positions and one chloride atom and the second nitrogen of the L<sup>2</sup> ligand situated in axial sites. The remaining four lithium atoms reside in a distorted tetrahedral environment coordinated by the Cl atom and three oxygen atoms: two from the  $L^2$  ligand and one ether oxygen atom of the thf molecule. The Li1–( $\mu_3$ -O) and Li2–( $\mu_3$ -O) bond lengths of 1.947 Å (av.) are significantly shorter than the bond distances between Li3 to  $\mu_3$ -O of 2.007 Å (av.) due to the geometry around these lithium atoms in 2b. The Li-O<sub>thf</sub> distances of 2.002 Å (av.) are within statistical agreement with those in 1b and with Li-O<sub>thf</sub> bond lengths of the literature compounds.10 The Li-N distances of 2.158(3) and 2.213(3) Å exhibited by trigonal-bipyramidal Li(3) are considerably shorter than those noted for 1b probably because of the reduction in electron donation by the coordinated chloride atom, and are markedly longer comparing to those found in the lithium-diaminebis(aryloxide) compounds [2.024(6)-2.129(5) Å], containing tetrahedral lithium centers.<sup>4,5</sup> The bridging  $\mu_3$ -chloride atoms show Li–Cl bond lengths of 2.299(3), 2.320(3) and 2.761(3) Å where the highest value, longer than in a pure LiCl crystal (2.57 Å), can be a result of either the trans interaction of chloride with nitrogen atom situated in axial positions, or higher coordination number of Li3 atom than those of Li1 and Li2. Incorporation of a chloride in place of an oxygen in lithium aryloxide polynuclear structures is very rare, and so far, only four examples have been known.<sup>11</sup> In all those compounds the lithium atoms are bound in a distorted tetrahedral geometry and together with oxygen and chloride atoms are arranged in a distorted cubane.

The <sup>1</sup>H NMR spectra of **2a** and **2b** are similar and fully consistent with the solid-state structure established by crystallography for **2b**. They reveal the presence of only one set resonances of protons due to the L<sup>1</sup> and L<sup>2</sup> ligands, respectively, and consist of an AB system for the Ar–CH<sub>2</sub>–N methylene units ( $\delta$  4.68 and 2.88 ppm in **2a**, 4.62 and 2.84 ppm in **2b**). Additionally one of the two resonances assigned to the methylenic protons of the NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> unit is substantially shifted to higher field compared to the ligand precursors ( $\delta$  2.31 and 1.29 ppm in **2a**, 2.48 and 1.32 ppm in **2b**, *vs*. 2.33 and 2.05 ppm in H<sub>2</sub>L<sup>1</sup>, 2.51 and 2.48 ppm in H<sub>2</sub>L<sup>2</sup>) suggesting that the sidearm NMe<sub>2</sub> group is bound to the lithium atoms. By contrast, the

<sup>1</sup>H NMR spectra of compounds **1a** and **1b** exhibit two sets of resonances at room temperature signifying the presence of two different species in solution in a ratio  $\sim 1:1$  (Scheme 2). One set of resonances with two close triplets assigned to the methylenic protons of the NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> unit (2.63 and 2.42 ppm in 1a', 2.53 and 2.48 ppm in 1b') like in the ligand precursors suggests the dangling character of the sidearm NMe<sub>2</sub> group. The second set of resonances shows similar shifts of the corresponding protons (2.31 and 1.56 ppm in 1a, 2.28 and 1.64 ppm in 1b) to those in 2a and 2b, confirming a coordination of the sidearm NMe<sub>2</sub> to lithium, in accordance with the ground-state structure established by crystallography for 1b. These observations prove that structures of 1a and 1b do not stay intact in solution and participate in a facile equilibrium with  $[Li_4(\mu-L^1-\kappa^3O,N,O)_2(thf)_2]$  (1a') and  $[Li_4(\mu-L^1-\kappa^3O,N,O)_2(thf)_2]$  (1a')  $L^2-\kappa^3O(N,O)_2(thf)_2$  (1b') species, respectively. The sidearm NMe<sub>2</sub> unit in 1a' and 1b' is not coordinated to the lithium centers and tetrahedral geometry around all metal centers is observed. In addition, variable-temperature NMR studies (in CDCl<sub>3</sub>, from 223 to 323 K) on these systems exhibited significant differences in the equilibrium shown in Scheme 2. At lower temperatures (below 273 K) mainly species 1a and 1b exist in solution and their conversion to 1a' and 1b', respectively, increases with the temperature, leading to almost complete absence of 1a and 1b at 323 K.



It seems most likely that one of the reasons responsible for instability of the structure of **1a** and **1b** in solution might be the distinctly long Li–N distance of the sidearm NMe<sub>2</sub> detected in **1b**, longer by more than 0.1 Å than in **2b** and even more than found in the lithium-diaminebis(aryloxide) compounds containing tetrahedral lithium centers.<sup>4,5</sup> This confirms the stabilizing influence of chloride in **2a** and **2b** on the trigonal-bipyramidal geometry around lithium atoms ligated by tetradentate tripodal (ONNO) ligands.

## Conclusion

The diaminebis(aryloxido)lithium complexes 1a-2b of new tetradentate tripodal (ONNO) ligands, comprising of different substituents at position *para* to the phenolic oxygen atom,  $C(CH_3)_2CH_2C(CH_3)_3$  in  $L^1$  and  $CH_3$  in  $L^2$  have been prepared in good yields. Their structures, including also ligand precursors  $H_3L^1$  and  $H_2L^2$ , have been characterized both in solution (by NMR spectroscopy) and in the solid state (except for **1a**) by X-ray determination, allowing to conclude that these substituents do not cause a remarkable change in the lithium coordination geometry and in structures of the ligand precursors. However the

advantage of the use of  $L^2$  ligand is moderate solubility of its lithium complexes in organic solvents which results in their easy isolation and crystal growth. The molecular structures of **1b**, **2a** and **2b** revealed that the lack of a substituent at *ortho* position to the phenolic oxygen atom in the ligands  $L^1$  and  $L^2$  resulted in distinctly different coordination geometry around lithium atoms than their analogues reported in literature, containing both *ortho* and *para* substituents. The presence of chloride atoms in **2a** and **2b** results in that their structures in the solid state are consistent with solution NMR data, in contrast to the structures of **1a** and **1b**, which undergo equilibration with new species **1a'** and **1b'**, respectively.

The knowledge of the structures of the new diaminebis-(aryloxido)lithium complexes will allow us to explore the synthetic methodology for synthesis of low-valent vanadium complexes which are currently under way in our laboratory.

#### Experimental

#### General considerations

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds 4-(1,1,3,3-tetramethylbutyl)phenol, *p*-cresol, *N*,*N*-dimethylethylenediamine, paraformaldehyde and LiMe were obtained from the Aldrich Chemical Co. and used without further purification unless stated otherwise. Infrared spectra were recorded on a Bruker 113v FTIR spectrophotometer in Nujol mulls. NMR spectra were performed on a Bruker ARX 500 spectrometer. The electrospray mass spectra (ES-MS) were recorded on a Bruker MicrOTOF-Q mass spectrograph. Microanalyses were conducted with a ASA-1 (GDR, Carl-Zeiss-Jena) instrument (inhouse).

Synthesis of  $H_2L^1$ . A mixture of 4-(1,1,3,3-tetramethylbutyl)phenol (10 g, 48.5 mmol), paraformaldehyde (1.45 g, 48.5 mmol) and N,N-dimethylethylenediamine (2.7 cm<sup>3</sup>, 24.3 mmol) in EtOH (100 cm<sup>3</sup>) was stirred for 3 days at room temperature. A white precipitate formed which was filtered off, washed with ice-cold ethanol ( $3 \times 20$  cm<sup>3</sup>), and dried *in vacuo* for 4 h to yield a fine white powder (9.15 g, 72.0%). Anal. Calc. for  $C_{34}H_{56}N_2O_2$ : C, 77.80; H, 10.76; N, 5.34. Found: C, 77.60; H, 10.73; N, 5.33%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 9.61 (br s, 2H, ArOH); 7.15–7.11 (m, 6H,  $C_6H_3$ ); 3.54 (s, 4H, ArC $H_2$ N); 2.33 [t, 2H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.05 [t, 2H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 1.99 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>]; 1.72 [s, 4H, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 1.39 [s, 12H,  $C(CH_3)_2CH_2C(CH_3)_3$ ; 0.81 (s, 18H,  $C(CH_3)_2CH_2C(CH_3)_3$ ]. <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 155.2, 139.7, 127.9, 127.4, 121.7, 116.7 (C<sub>6</sub>H<sub>3</sub>); 57.2 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>], 56.0 (ArCH<sub>2</sub>N); 55.3 [C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 55.7 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 48.8  $[N(CH_3)_2];$  44.3  $[C(CH_3)_2CH_2C(CH_3)_3];$  37.6  $[C(CH_3)_2 CH_2C(CH_3)_3$ ]; 32.2 [C(CH\_3)\_2CH\_2C(CH\_3)\_3]; 31.7 [C(CH\_3)\_2- $CH_2C(CH_3)_3$ ]. ES-MS: m/z: 525.4  $[H_2L^1 + H]^+$ .

Single crystals of  $H_2L^1$  suitable for X-ray studies were grown from a saturated solution in n-hexane at room temperature after few days.

**Synthesis of H**<sub>2</sub>L<sup>2</sup>. The synthesis of the ligand precursor H<sub>2</sub>L<sup>2</sup> was carried out using a similar preparation as for compound H<sub>2</sub>L<sup>1</sup>

starting from *p*-cresol (18.88 g, 17.5 mmol), paraformaldehyde (5.25 g, 17.5 mmol) and *N*,*N*-dimethylethylenediamine (9.56 cm<sup>3</sup>, 8.8 mmol) in MeOH (100 cm<sup>3</sup>). Compound H<sub>2</sub>L<sup>2</sup> was isolated as a white powder (21.77 g, 75.9%). Anal. Calc. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.12; H, 8.60; N, 8.53. Found: C, 73.01; H, 8.58; N, 8.51%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  9.48 (br s, 2H, ArO*H*); 6.88–6.66 (m, 6 H, C<sub>6</sub>H<sub>3</sub>); 3.50 (s, 4H, ArCH<sub>2</sub>N); 2.51 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.48 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.21 (s, 6H, ArCH<sub>3</sub>); 2.14 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>]. <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  154.5, 130.6, 129.9, 128.0, 122.1, 116.6 (C<sub>6</sub>H<sub>3</sub>); 56.2, 55.7, [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 49.1 (ArCH<sub>2</sub>N) 44.8 [N(CH<sub>3</sub>)<sub>2</sub>]; 20.4 (ArCH<sub>3</sub>). ES-MS: *m*/*z*: 329.2 [H<sub>2</sub>L<sup>2</sup> + H]<sup>+</sup>.

Single crystals of  $H_2L^2$  suitable for X-ray studies were grown from a saturated solution in n-hexane at room temperature after few days.

Synthesis of  $[Li_4(\mu-L^1-\kappa^4 O, N, N, O)_2(thf)_2]$  (1a) and  $[Li_6(\mu-L^1-\kappa^4 O, N, N, O)_2(\mu^3-Cl)_2(thf)_4]$  thf (2a thf). To a solution of  $H_2L^1$  (2.0 g, 3.90 mmol) in thf (50 cm<sup>3</sup>), precooled to 273 K was slowly added MeLi (4.90 cm<sup>3</sup>, 7.80 mmol, 1.6 M in Et<sub>2</sub>O). The reaction mixture was stirred at 273 K for 1 h and then at room temperature for further 4 h. The volatile components were removed under reduced pressure. The residue was redissolved in thf (20 cm<sup>3</sup>) and allowed to stand overnight in a refrigerator. After a few days colorless crystals of **2a** were formed, which were filtered off and dried *in vacuo* (0.24 g, 8.5%). Subsequent evaporation of thf from the filtrate gave a white solid of **1a** (2.07 g, 87.2%). Anal. Calc. for  $C_{76}H_{124}Li_4N_4O_6$  (**1a**): C, 74.94; H, 10.27; N, 4.60. Found: C, 74.79; H, 10.25; N, 4. 59%.

Anal. Calc. for  $C_{ss}H_{14s}Cl_2Li_6N_4O_9$  (**2a**): C, 69.60; H, 9.83; Cl, 4.61; N, 3.69. Found: C, 69.48; H, 9.81; Cl, 4. 60; N, 3.68%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) for **2a**:  $\delta$  6.88–6.41 (m, 12 H, C<sub>6</sub>H<sub>3</sub>); 4.68 (d, 4H, NCH<sub>2</sub>Ar); 3.58 (m, 20H, thf); 2.88 (d, 4H, NCH<sub>2</sub>Ar); 2.31 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>); 1.72 (m, 20H, thf); 1.62 [s, 8H, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 1.46 [s, 24H, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 1.29 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 1.21, 1.18 [s, 12H, N(CH<sub>3</sub>)<sub>2</sub>]; 0.68 [s, 36H, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  163.7, 135.8, 128.4, 127.6, 119.2, 116.0 (C<sub>6</sub>H<sub>3</sub>); 67.9 (thf); 62.6 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 58.9 (NCH<sub>2</sub>Ar); 56.4 [C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 50.2 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 44.9 [N(CH<sub>3</sub>)<sub>2</sub>]; 37.5 [C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 32.6 [C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 32.0 [C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]; 31.9 [C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>].

Synthesis of  $[\text{Li}_6(\mu-\text{L}^1-\kappa^4O,N,N,O)_2(\mu-\text{Cl})_2(\text{thf})_4]$  thf (2a thf) by reaction of  $H_2L$ , MeLi and LiCl. A suspension of  $H_2L^1$  (1.0 g, 1.90 mmol) and LiCl (0.081 g, 1.91 mmol) in thf (50 cm<sup>3</sup>) was precooled to 273 K and slowly added MeLi (2.4 cm<sup>3</sup>, 3.84 mmol, 1.6 M in Et<sub>2</sub>O). After 20 h of stirring at room temperature, the reaction mixture was filtered to afford a white, analytically pure solid of 2a (1.21 g, 84%). Anal. Calc. for C<sub>88</sub>H<sub>148</sub>Cl<sub>2</sub>Li<sub>6</sub>N<sub>4</sub>O<sub>9</sub>: C, 69.60; H, 9.83; Cl, 4.61; N, 3.69. Found: C, 69.49; H, 9.80; Cl, 4. 60; N, 3.68%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): *δ* 6.88–6.41 (m, 12 H, C<sub>6</sub>H<sub>3</sub>); 4.68 (d, 4H, NCH<sub>2</sub>Ar); 3.58 (m, 20H, thf); 2.88 (d, 4H, NCH<sub>2</sub>Ar); 2.31 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>); 1.72 (m, 20H, thf); 1.62 [s, 8H,  $C(CH_3)_2CH_2C(CH_3)_3$ ; 1.46 [s, 24H,  $CH_2C(CH_3)_2C(CH_3)_3$ ]; 1.29 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 1.21, 1.18 [s, 12H, N(CH<sub>3</sub>)<sub>2</sub>]; 0.68 [s, 36H, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K): *δ* 163.7, 135.8, 128.4, 127.6, 119.2, 116.0

Single crystals of **2a** suitable for X-ray studies were grown from a saturated solution in thf at room temperature after a few days.

Synthesis of  $[Li_4(\mu-L^2-\kappa^4 O, N, N, O)_2(thf)_2]$  (1b). A solution of MeLi (5.4 cm<sup>3</sup>, 8.72 mmol, 1.6 M in Et<sub>2</sub>O) was added dropwise to a suspension of H<sub>2</sub>Li (1.43 g, 4.36 mmol) in thf (30 cm<sup>3</sup>) at room temperature and the mixture was stirred for 16 h. A small amount of white solid of 2b was then filtered off and the filtrate was evaporated to dryness, leading to 1b as a colorless solid (1.14 g; 63.3%). Anal. Calc. for C<sub>48</sub>H<sub>68</sub>Li<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C, 69.85; H, 8.31; N, 6.79. Found: C, 69.74; H, 8.29; N, 6.78%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  6.88–6.39 (m, 24 H, C<sub>6</sub>H<sub>3</sub>); 4.17 (d, 2H, ArCH<sub>2</sub>N); 3.75 (d, 2H, ArCH<sub>2</sub>N); 3.61 (br t, 16H, thf); 3.42 (d, 2H, ArCH<sub>2</sub>N); 3.15 (d, 2H, ArCH<sub>2</sub>N); 2.53 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.48 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.28 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.14, [s, 12H, ArCH<sub>3</sub>]; 2.10 [(s, 12H,  $N(CH_3)_2$ ; 2.09 [s, 12H, ArCH<sub>3</sub>]; 1.74 (br pnt, 16H, thf); 1.64 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>); 1.40 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 162.9, 130.4, 128.1, 127.4, 121.9, 118.6 (*C*<sub>6</sub>H<sub>3</sub>); 66.9 (thf); 61.0 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 57.7, 56.6 (NCH<sub>2</sub>Ar); 49.9 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 44.0, 43.6 [N(CH<sub>3</sub>)<sub>2</sub>]; 24.4 (thf); 19.3, 19.2  $(ArCH_3).$ 

Crystals suitable for X-ray diffraction were obtained by dissolving **1b** in warm *n*-hexane and allowing to stand at room temperature for few days.

Synthesis of [Li<sub>6</sub>(μ-L<sup>2</sup>-κ<sup>4</sup>*O*,*N*,*N*,*O*)<sub>2</sub>(μ-Cl)<sub>2</sub>(thf)<sub>4</sub>]-thf (2b-thf). The synthesis of compound **2b** was carried out using a similar preparation as for **2a** starting from H<sub>2</sub>L<sup>2</sup> (1.40 g, 4.27 mmol), MeLi (5.30 cm<sup>3</sup>, 8.54 mmol) and LiCl (0.18 g, 4.27 mmol) in thf (30 cm<sup>3</sup>) (1.64 g, 68.3%). Anal. Calc. for C<sub>60</sub>H<sub>92</sub>Cl<sub>2</sub>Li<sub>6</sub>N<sub>4</sub>O<sub>9</sub>: C, 64.02; H, 8.24; Cl, 6.22; N, 4.98. Found: C, 63.87; H, 8.23; Cl, 6.21; N, 4.97%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 6.71–6.38 (m, 12 H, C<sub>6</sub>H<sub>3</sub>); 4.62 (d, 4H, NCH<sub>2</sub>Ar); 3.52 (m, 20H, thf); 2.84 (d, 4H, NCH<sub>2</sub>Ar); 2.31 [t, 4H, NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 2.11 [s, 12H, ArCH<sub>3</sub>]; 1.67 (m, 20H, thf); 1.47 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>); 1.32 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 164.0, 131.5, 129.1, 128.3, 122.9, 119.6 (C<sub>6</sub>H<sub>3</sub>); 68.0 (thf); 62.1 [NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]; 25.5 (thf); 20.2 (ArCH<sub>3</sub>).

Single crystals of **2b**-thf suitable for X-ray studies were grown from saturated solution in thf at room temperature.

#### X-Ray crystallography

Diffraction data for complexes  $H_2L^2$  and **1a** were collected on a KM4 diffractometer with a CCD sapphire camera and for **2b**-thf with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda =$ 0.71073 Å).<sup>12</sup> All structures were solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ .<sup>13</sup> All nonhydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in geometrically calculated positions and refined by using a riding model with  $U_{iso}$  set at  $1.2U_{eq}(C)$ for aromatic and formic H atoms, and  $1.5U_{eq}(C)$  for methyl H atoms. In the structures of **1a** and **2b**. some atoms of the THF

Table 1	Crystal data and	structure refinement	details for compo	unds $H_2L^2$ , <b>1b</b> and <b>2b</b> thf
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Compound	$H_2L^2$	1b	<b>2b</b> thf
Formula	$C_{20}H_{28}N_2O_2$	$C_{48}H_{68}Li_4N_4O_6$	$C_{56}H_{84}Cl_2Li_6N_4O_8\cdot C_4H_8O_8$
$M_r$	328.44	824.82	1125.92
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Pbcn	C2/c
a/Å	14.820(3)	11.397(3)	23.417(8)
b/Å	6.049(3)	17.772(4)	12.217(4)
c/Å	21.294(5)	22.892(5)	23.689(8)
$\beta/^{\circ}$	107.48(3)	90.00	109.91(5)
$V/Å^3$	1820.8(11)	4636.7(19)	6372(4)
Ζ	4	4	4
$D_c/\mathrm{Mg}~\mathrm{m}^{-3}$	1.198	1.182	1.174
Crystal size/mm	$0.42 \times 0.18 \times 0.05$	$0.16 \times 0.15 \times 0.06$	$0.19 \times 0.18 \times 0.17$
$\mu/\mathrm{mm}^{-1}$	0.08	0.08	0.16
$\theta/^{\circ}$	3-27.5	2.9-28.0	2.9-30.0
Reflections collected	12298	33997	29932
Unique reflections	4128	5567	8667
R <sub>int</sub>	0.035	0.033	0.048
Parameters	229	303	410
Final $R_1$ , w $R_2$ $[I > \sigma(I)]$	0.040, 0.090	0.039, 0.103	0.053, 0.113
Final $R_1$ , w $R_2$ (all data)	0.070, 0.095	0.054, 0.108	0.087, 0.144
Goodness-of-fit (S)	0.983	1.064	1.018

molecules were partially disordered and they were refinement in two positions. Moreover, in **2b** some molecules of THF were refined with SAME instruction (C–C bond distances were restrained to be the same as in corresponding solvent molecules). Table 1 lists the key crystallographic parameters for  $H_2L^2$ , **1b** and **2b**-thf.

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#### Notes and references

- (a) F. Wolff, C. Lorber, R. Choukroun and B. Donnadieu, *Inorg. Chem.*, 2003, 42, 7839; (b) F. Wolff, C. Lorber, R. Choukroun and B. Donnadieu, *Eur. J. Inorg. Chem.*, 2004, 2861; (c) C. Lorber, F. Wolff, R. Choukroun and L. Vendier, *Eur. J. Inorg. Chem.*, 2005, 2850; (d) A. Yeori, S. Groysman, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, 4466; (e) S. Segal, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, 24, 200; (f) C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley and P. Mountford, *Organometallics*, 2005, 24, 309; (g) Y. Yao, M. Ma, X. Hu, Y. Hang, Q. Shen and W.-T. Wong, *Organometallics*, 2005, 24, 4014; (h) Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito and T. Katsuki, *Angew. Chem., Int. Ed.*, 2006, 45, 3478; (i) C. Lorber, *Pure Appl. Chem.*, 2009, 81, 1205; (j) X. Y. Liu, K. S. Lokare, S. K. Ganesh, J. M. Gonzales, J. Oxgaard, W. A. Goddard III and R. A. Periana, *Dalton Trans.*, 2011, 40, 301.
- 2 (a) S. Barroso, P. Adâo, F. Madeira, M. T. Duarte, J. C. Pessoa and A. M. Martins, *Inorg. Chem.*, 2010, **49**, 7452; (b) M. Velusamy, M. Palaniandavar, R. Srinivasa Gopalan and G. U. Kulkami, *Inorg. Chem.*, 2003, **42**, 8283.

- 3 (a) M. Shavit, D. Peri, C. M. Manna, J. S. Alexander and E. Y. Tshuva, J. Am. Chem. Soc., 2007, **129**, 12098; (b) C. M. Manna, M. Shavit and E. Y. Tshuva, J. Organomet. Chem., 2008, **693**, 3947.
- 4 C.-A. Huang and C.-T. Chen, Dalton Trans., 2007, 5561.
- 5 F. M. Kerton, C. M. Kozak, K. Lüttgen, C. E. Willans, R. J. Webster and A. C. Whitwood, *Inorg. Chim. Acta*, 2006, **359**, 2819.
- 6 E. Y. Tshuwa, I. Goldberg, M. Kol and Z. Goldschmidt, *Inorg. Chem.*, 2001, 40, 4263.
- 7 (a) C. Lorber, F. Wolff, R. Choukroun and L. Vendier, *Eur. J. Inorg. Chem.*, 2005, 2850; (b) D. Maity, A. Ray, W. S. Sheldrick, H. Mayer Figge, B. Bandyopadhyay and M. Ali, *Inorg. Chim. Acta*, 2006, **359**, 3197.
- 8 For the influence of traces of LiCl in commercial chemical agents on organolithium reactions, see for example: (a) A. C. Hoepker, L. Gupta, Y. Ma, M. F. Faggin and D. B. Collum, J. Am. Chem. Soc., 2011, 133, 7135; (b) Y. Ma, A. C. Hoepker, L. Gupta, M. F. Faggin and D. B. Collum, J. Am. Chem. Soc., 2010, 132, 15610; (c) L. Gupta, A. C. Hoepker, K. J. Sinh and D. B. Collum, J. Org. Chem., 2009, 74, 2231; (d) E. Hevia and R. E. Mulvey, Angew. Chem., Int. Ed., 2011, 50, 6448, and references cited therein.
- 9 (a) G. B. Deacon, T. Feng, D. C. R. Hockless, P. C. Junk, B. W. Skelton, M. K. Smith and A. H. White, *Inorg. Chim. Acta*, 2007, 360, 1364; (b) S. C. Ball, I. Cragg-Hine, M. G. Davidson, R. P. Davies, M. I. Lopez-Solera, P. R. Raithby, D. Reed, R. Snaith and E. M. Vogl, *J. Chem. Soc., Chem. Commun.*, 1995, 2147; (c) E. Solari, S. DeAngelis, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1991, 2471.
- 10 (a) T. J. Boyle, T. M. Alam, K. P. Peters and M. A. Rodrigues, *Inorg. Chem.*, 2001, **40**, 6281; (b) T. J. Boyle, D. M. Pedrotty, T. M. Alam, S. C. Vick and M. A. Rodrigues, *Inorg. Chem.*, 2000, **39**, 5133.
- 11 (a) C. D. Carmichael and M. D. Fryzuk, *Dalton Trans.*, 2008, 800; (b) J. Pauls and B. Neumuller, *Z. Anorg. Allg. Chem.*, 2000, **626**, 270; (c) K. Hyvarinen, M. Klinga and M. Laskela, *Polyhedron*, 1996, **15**, 2171.
- 12 Oxford Diffraction (2009), CrysAlis CCD and CrysAlis RED, Versions 1.171.33, Oxford Diffraction Poland, Wroclaw, Poland.
- 13 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2007, 64, 112.