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FULL PAPER

A solid state and theoretical study of the solvent effects controlling the mono- and di-lithiation of aromatic primary amines†

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Reaction of 1-naphthylamine, 4-tritylaniline or 4-methylaniline with two equivalents of Bu^nLi in Et_2O or thf affords rare geminal N,N-dilithiates of general formula $(L)_n{\cdot}(Li_2NAr)_{10}$ (L = Et_2O, $n = 6$, Ar = 1-$C_{10}H_7$ **1**, C_6H_4-4-CPh_3 **2**; L = thf, $n = 10$, Ar = C_6H_4-4-Me **3**). X-Ray crystal structure analyses reveal that the core $(Li_{14}N_{10})^{6-}$ frameworks consist of two fused rhombic dodecahedra. *Ab initio* M.O. calculations on the mono- and di-lithiation of 1-naphthylamine and 4-methylaniline suggest that the selectivity with which polymetallation occurs is solvent dependent and so help to rationalise the experimentally observed structures.

Introduction

Lithiated amines (lithium amides) are frequently employed in organic syntheses[1] and this has led to significant interest being expressed in their structural properties. In this context a large number of N-monolithiated species have been characterised.[2] These have generally been metallated secondary amines and Lewis base complexes thereof and their structural chemistry has been dominated by cyclic $(LiN)_n$ ($n = 2, 3$) rings and ladder-shaped oligomers formed by the lateral fusion of dimeric examples of these arrays.[3] More recently, however, the structural chemistry of monolithiated *primary* amines has been considered in greater detail in both the solid state[4–6] and in solution[6,7] and this has led to the observation of infinite ladders[8] akin to those previously postulated for lithiated monofunctional amines.[2] These results have, in turn, led to a better understanding of the dynamic (dis-)assembly processes undergone by lithium amides on treatment with Lewis bases.[5,9] Of course, primary amines are capable of being doubly N-deprotonated to afford (Li_2NR)-type species (R = organic). Nevertheless, in spite of the intense interest in N-monolithiated primary amines, such dilithiated analogues remain relatively obscure — and poorly understood — species. We report here the isolation and structural characterisation of three such geminally dilithiated primary amines, the solid-state structures of which are isostructural and reveal complex cores based on fused rhombic dodecahedra. Furthermore, geometry optimisation by *ab initio* techniques proves useful in highlighting the solvent dependence with which dimetallation occurs.

Results and discussion

Solid-state structures

Four dilithiates featuring geminally dimetallated fragments have been reported in which deprotonation has occurred at a carbon centre: the dilithiosulfone $(thf)_{10}{\cdot}[Li_2C(SiMe_3)SO_2Ph]_6{\cdot}Li_2O$,[10] the P–C–P methanide salt $Li_2C[P({=}NSiMe_3)Ph_2]_2$,[11] the α,α-dilithiated phosphane oxide co-complex $[(TMEDA)_2{\cdot}Li]^+(\{Li_2C[P({=}O)(OMe)_2]SiMe_3\}_3{\cdot}NMe_2)^-$ [12] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) and, most recently, the α,α-dilithiated sulfoximine $(thf)_6{\cdot}Li_2C(Ph)S({=}O)(Ph){=}NMe{\cdot}Li_2O$.[13] Moreover, the dimetallation of phosphorus and arsenic centres has been noted in the oxide-encapsulation complexes $Li_{16}(PR_3)_8{\cdot}Li_2O$ and $Li_{24}(AsR_3)_{12}{\cdot}Li_2O$ [R = $Si(Mes)Pr^i_2$ (Mes = mesityl)], respectively.[14] However, there exist very few literature precedents for the geminal dilithiation of nitrogen. Although a Li_{12} aggregate which reveals both N,N- and N,C-dimetallation has been found to result from the sequential 1 : 2 : 1 reaction of 2-methylpyridine with $LiNPr^i_2$ and PhCN,[15] to date only one example has been communicated wherein a geminally N,N-dilithiated primary amine has been structurally characterised: the treatment of 1-naphthylamine in Et_2O with 2 eq. Bu^nLi (Scheme 1) affords the Li_{20}-aggregate $(Et_2O)_6{\cdot}(1\text{-}Li_2NC_{10}H_7)_{10}$ **1** for which formulation a further molecule of uncoordinated Et_2O resides in the lattice (though NMR spectroscopy suggests that solvent is readily lost when the crystalline material is separated from the mother liquor).[16]

$$10\ H_2NAr + 20\ Bu^nLi \xrightarrow{L} (L)_n{\cdot}(Li_2NAr)_{10} + 20\ Bu^nH$$

L = Et_2O, $n = 6$, Ar = 1-$C_{10}H_7$ **1**;
L = Et_2O, $n = 6$, Ar = C_6H_4-4-CPh_3 **2**;
L = thf, $n = 10$, Ar = C_6H_4-4-Me **3**.

Scheme 1

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† Electronic supplementary information (ESI) available: modelled geometries for **4a**–**18f** and tables of absolute and relative energies. See http://www.rsc.org/suppdata/dt/b1/b107970k/

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X-Ray diffraction reveals a *N*,*N*-dilithio-1-naphthylamide complex. In spite of considerable disorder in both naphthyl and diethyl ether groups the nature of the supramolecular core of **1** can be unambiguously resolved, with the naphthylamide dianions falling into three categories as has been described previously.[16] However, a recent re-refinement of the data now allows a more precise consideration of the structure than was previously possible. The molecular structure of **1** is shown in Fig. 1a. At its core is a $(Li_{14}N_{10})^{6-}$ arrangement which describes two fused dodecahedra, with a further six peripheral, mono-OEt_2 solvated metal centres (Fig. 1b). Li8 and its symmetry equivalent bridge the face-sharing rhombohedra while the remaining four Li^+ ions are each terminally bonded to a single N-centre at the cluster extrema. In spite of its apparent complexity, therefore, the solid-state structure of **1** reveals a surprisingly straightforward pattern of metal coordination in which the Li–N bond distances observed, at 1.971(15)–2.213(15) Å (Table 1), are in the normal range for such interactions.[2] The two rhombic dodecahedra share approximately planar N1 [Li2–N1–Li4 = 110.3(5)°, Li3–N1–Li4 = 70.2(5)°, Li2–N1–Li5 = 73.8(5)°, Li3–N1–Li5 = 105.5(5)°] and approximately tetrahedral Li1 [N1–Li1–N2 = 108.3(5)°, N1–Li1–N3 109.2(5)°, N1A–Li1–N2 = 107.9(5)°, N1A–Li1–N3 112.1(5)°] centres. Moreover, this metal cation combines with two N-centres (N2, N3) that chelate *exo*-oriented Li8. This yields the four-membered Li1–N2–Li8–N3 metallocycle [mean Li–N = 2.062 Å, mean N–Li–N = 110.1°, mean Li–N–Li = 69.9°] which bridges between core rhombohedra (see above). Just as Li8 resides *exo* to the cluster core, so too do Li9, Li10 and their symmetry equivalents. However, unlike trigonal Li8, the latter four cations each bond to just one nitrogen centre [N5A–Li9 = 2.022(13) Å, N4–Li10 = 1.995(19) Å]. The remaining alkali metal ions in the cluster core (Li2–7 and their symmetry equivalents) adopt trigonal pyramidal geometries (Table 1).

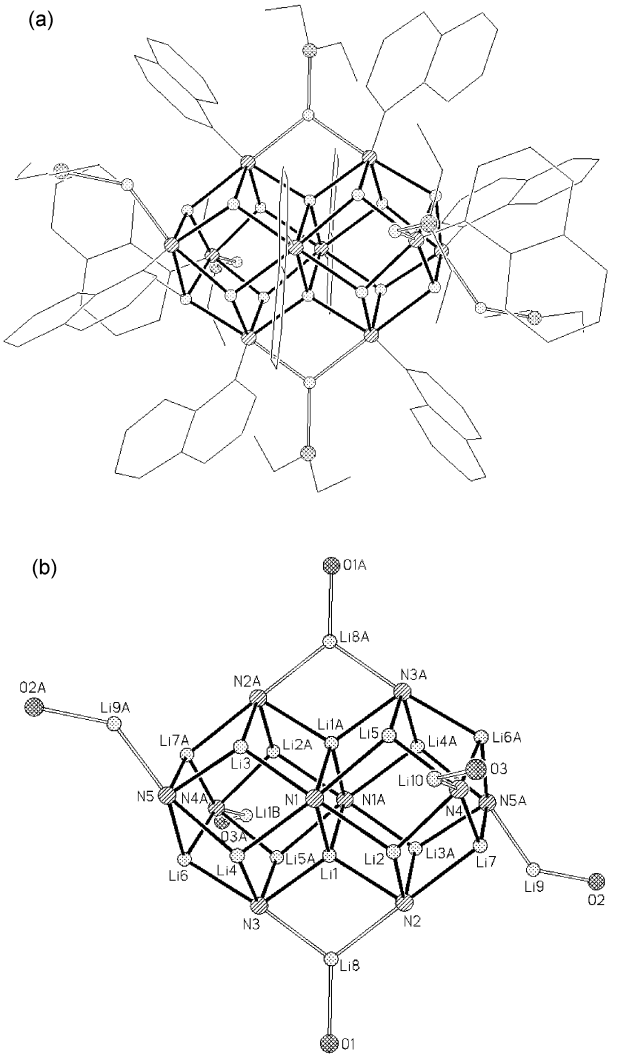

Fig. 1 (a) Molecular structure of **1**. Hydrogen atoms, lattice solvent molecule and disorder omitted for clarity. (b) The $(Li_{14}N_{10})^{6-}$ nucleus of **1**, also showing the six *exo* $Li\cdot OEt_2$ groups (oxygen centres only of diethyl ether molecules shown).

Table 1 Selected bond lengths (Å) and angles (°) in **1**

Li1–N1	2.071(12)	Li5–N3A	2.011(15)
Li1–N1A	2.196(12)	Li5–N4	1.990(13)
Li1–N2	2.035(11)	Li6–N3	2.107(12)
Li1–N3	2.006(12)	Li6–N4A	2.213(15)
Li2–N1	2.110(11)	Li6–N5	2.110(14)
Li2–N2	1.999(12)	Li7–N2	2.166(13)
Li2–N4	1.989(13)	Li7–N4	2.072(13)
Li3–N1	2.077(11)	Li7–N5A	1.971(15)
Li3–N2A	2.027(13)	Li8–N2	2.114(14)
Li3–N5	2.017(13)	Li8–N3	2.091(12)
Li4–N1	2.148(13)	Li8–O1	1.944(16)
Li4–N3	2.001(14)	Li9–N5A	2.022(13)
Li4–N5	2.169(12)	Li10–N4	1.995(19)
Li5–N1	2.140(13)		
N1–Li1–N1A	105.6(5)	Li1A–N1–Li5	63.8(5)
N1–Li1–N2	108.3(5)	Li2–N1–Li4	110.3(5)
N1A–Li1–N2	107.9(5)	Li2–N1–Li5	73.8(5)
N1A–Li1–N3	112.1(5)	Li3–N1–Li4	70.2(5)
N1–Li1–N3	109.2(5)	Li3–N1–Li5	105.5(5)
N2–Li1–N3	113.4(6)	Li1–N2–Li2	73.2(4)
N1–Li2–N2	108.2(5)	Li1–N2–Li3A	71.6(5)
N1–Li2–N4	103.2(5)	Li2–N2–Li7	66.8(5)
N2–Li2–N4	117.1(5)	Li3A–N2–Li7	71.5(5)
N3A–Li6A–N4	102.9(5)	Li2–N4–Li7	68.8(5)
N3–Li6–N5	106.7(6)	Li5–N4–Li6A	69.9(5)
N4–Li6A–N5A	102.5(6)	Li7–N4–Li6A	69.7(6)
N2–Li7–N4	106.8(5)	Li2–N4–Li10	91.7(8)
N2–Li7–N5A	104.3(6)	Li6A–N4–Li10	141.8(9)
N4–Li7–N5A	113.0(7)	Li3–N5–Li7A	75.9(5)
N2–Li8–N3	106.8(6)	Li4–N5–Li6	70.1(5)
Li1–N1–Li1A	74.4(5)	Li7A–N5–Li6	73.7(6)
Li1–N1–Li2	70.2(4)	Li3–N5–Li9A	89.7(6)
Li1–N1–Li4	70.0(5)	Li4–N5–Li9A	145.8(6)
Li1A–N1–Li3	67.5(4)		

In a similar vein to the synthesis and characterisation of **1**, 4-tritylaniline has been treated with 2 eq. Bu^nLi in toluene–Et_2O to afford $(Et_2O)_6\cdot[Li_2N(C_6H_4\text{-}4\text{-}CPh_3)]_{10}$ **2** (Scheme 1), for which formulation there are nine molecules of disordered lattice toluene. X-Ray crystallography reveals that this cluster is unambiguously analogous to that observed for **1** with two rhombic dodecahedra being fused *via* a central $(LiN)_2$ face. However, extensive disorder in the diethyl ether solvent and, more particularly, in the lattice toluene molecules means that the structure of **2** has a significantly higher *R*1 value than that of **1** and this precludes a detailed discussion of bonding parameters.

Having synthesised and isolated the two comparable N,N-dilithiates discussed, attention was directed towards the related complex of 4-methylaniline. This organic residue offers the chance to probe the behaviour of an anion smaller than 1-naphthylamide and flatter than 4-tritylanilide. Of particular note is the possibility that the product dilithiate would be of a different solid-state geometry to that observed for **1** and **2** by virtue either of the inclusion of more monodentate or else of polydentate Lewis base. In this context the attempted synthesis of $(TMEDA)_n\cdot[Li_2N(C_6H_4\text{-}4\text{-}Me)]_m$ afforded only microcrystalline material. However, reaction of 2 eq. Bu^nLi with this primary amine in toluene/thf afforded $(thf)_{10}\cdot[Li_2N(C_6H_4\text{-}4\text{-}Me)]_{10}$ **3** (Scheme 1), for which decameric formulation two one-quarter occupancy thf molecules reside in the lattice. X-Ray crystallography reveals the core of **3** to be isostructural with those of **1**

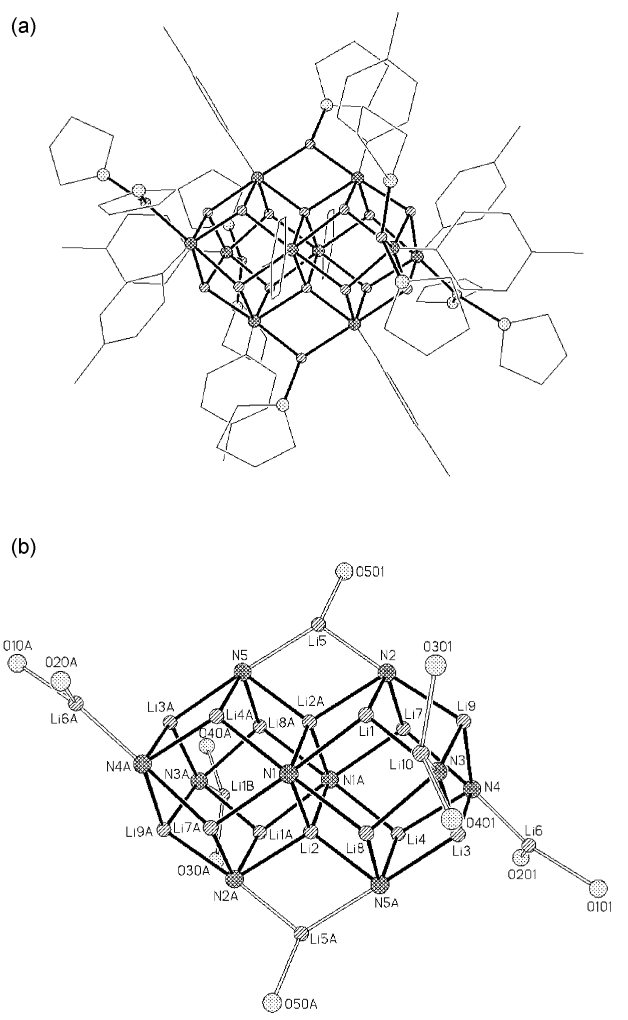

Fig. 2 (a) Molecular structure of **3**. Hydrogen atoms, lattice thf molecule and disorder omitted for clarity. (b) The $(Li_{14}N_{10})^{6-}$ nucleus of **3** showing also the *exo* Li·2thf groups (only the oxygen centres of the thf molecules are shown).

Table 2 Selected bond lengths (Å) and angles (°) in **3**

Li1–N1	2.088(13)	Li5–N2	2.072(13)
Li1–N2	2.015(13)	Li5–N5	2.026(14)
Li1–N3	1.992(13)	Li6–N4	2.00(2)
Li2–N1	2.058(11)	Li7–N1A	2.111(13)
Li2–N1A	2.058(11)	Li7–N2	1.926(12)
Li2–N2A	2.060(12)	Li7–N4	2.114(14)
Li2–N5A	1.978(12)	Li8–N1	2.136(13)
Li3–N3	2.134(13)	Li8–N3	1.988(13)
Li3–N4	2.015(14)	Li8–N5A	2.017(12)
Li3–N5A	2.068(14)	Li9–N2	2.063(13)
Li4–N1A	2.068(13)	Li9–N3	2.119(13)
Li4–N4	1.996(14)	Li9–N4	2.191(12)
Li4–N5A	2.042(13)	Li10–N3	2.020(13)
N1–Li2–N1A	108.4(5)	Li2A–N1–Li4A	110.0(5)
N1–Li2–N2A	104.5(5)	Li2–N1–Li7A	70.7(5)
N1–Li2–N5A	108.2(5)	Li2–N1–Li8	112.1(5)
N1–Li2A–N2	109.9(5)	Li7A–N1–Li8	110.3(5)
N1–Li2A–N5	113.3(5)	Li4–N1A–Li7	70.9(5)
N2A–Li2–N5A	112.0(5)	Li1–N3–Li9	71.0(5)
N3–Li3–N5A	107.2(6)	Li3–N3–Li8	68.1(5)
N4–Li3–N5A	104.9(6)	Li3–N3–Li9	70.7(5)
N3–Li3–N4	111.6(6)	Li8–N3–Li10	98.5(6)
N2–Li5–N5	109.6(6)	Li9–N3–Li10	137.6(6)
N1–Li8–N5A	105.6(6)	Li3–N4–Li4	75.3(5)
N1–Li8–N3	103.8(5)	Li3–N4–Li9	71.4(5)
N3–Li8–N5A	115.2(6)	Li4–N4–Li6	99.2(7)
N2–Li9–N3	105.1(6)	Li6–N4–Li7	148.0(7)
N2–Li9–N4	104.9(5)	Li7–N4–Li9	67.6(5)
N3–Li9–N4	105.6(5)	Li2–N5A–Li4	69.2(5)
Li1–N1–Li8	72.7(5)	Li2–N5A–Li8	75.6(5)
Li1–N1–Li2A	68.8(5)	Li3–N5A–Li4	73.2(5)
Li1–N1–Li4A	106.1(5)	Li3–N5A–Li8	68.9(5)
Li2–N1–Li2A	71.6(5)		

and **2**. Fig. 2a shows the molecular structure of **3**, while the core [comprising the $(Li_{14}N_{10})^{6-}$ nucleus and six thf-solvated *exo* metal centres] is represented in Fig. 2b and selected bond lengths and angles are given in Table 2. Whereas the $(Li_{14}N_{10})^{6-}$ nucleus of **3** is, therefore, unchanged from those of **1** and **2**, it is apparent that the choice of 4-methylaniline as substrate has had two significant effects. Firstly, the coordination of more Lewis base to the complex core has been enabled (each of these thf molecules revealed positional disorder for some or all of their atoms and were modelled over two sites with individual occupancies summing to unity). Secondly, in spite of a low temperature phase change preventing data-collection on **3** below 230 K, this complex reveals a superior *R*1 value to those noted for either **1** or **2**, allowing a more confident analysis of bonding parameters.

The two Li^+ ions which bridge the fused dodecahedra (Li5 and its symmetry equivalent) are mono-thf solvated (*cf.* mono-OEt_2 solvation of the bridging Li centres in both **1** and **2**). However, the more extensive thf solvation revealed by each of Li6 and Li10 and their symmetry equivalents Li6A and Li1B contrasts with mono-OEt_2 coordination of the analogous metal ions in **1** and **2**, suggesting that a combination of the employment of a flat organic dianion (*cf.* 4-tritylanilide in **2**) and a more strongly coordinating solvent (*cf.* Et_2O in **1** and **2**) facilitates the inclusion of 10 eq. Lewis base at the periphery of the cluster (*cf.* 6 eq. in **1** and **2**). The lithium–nitrogen superstructure of crystalline **3** reveals bond distances which [at 1.926(12)–2.191(12) Å] are normal for Li–N bonds.[2] Akin to **1**, the two dodecahedra in **3** are fused by an essentially planar N^{2-} ion [Li1–N1–Li8 = 72.7(5)°, Li1–N1–Li4A = 106.1(5)°, Li4–N1A–Li7 = 70.9(5)°, Li7A–N1–Li8 = 110.3(5)°] and a nearly tetrahedral Li^+ ion [N1–Li2A–N2 = 109.9(5)°, N1–Li2–N2A = 104.5(5)°, N1–Li2–N5A = 108.2(5)°, N1–Li2A–N5 = 113.3 (5)°]. The two remaining N-centres (N2, N5) to which Li2A is bonded are incorporated in a four-membered Li2A–N2–Li5–N5 ring. The other four *exo* Group 1 metal centres (Li6, Li10 and their symmetry equivalents) each bond to just one N-centre [Li6–N4 = 2.00(2) Å, Li10–N3 = 2.020(13) Å]. The remaining Li-centres in the cluster core are trigonal pyramidal (*cf.* **1**).

Theoretical calculations

In light of the solid-state characterisation of **1**, geometry optimisation by *ab initio* methods[17] (6-31G* basis set[18] at the RHF level) was employed in an attempt to rationalise the structural parameters noted. The most stable monolithiated 1-naphthylamine model was that of the straightforward N-metallate **4a** (Fig. E1 and Table E1; see ESI) in which *ortho*-stabilisation of the metal centre affords a four-membered C_2NLi chelate ring (Li–N = 1.841 Å, Li–C_{ortho} = 2.243 Å), with extremely weak *ipso*-coordination yielding a long (> 2.9 Å) cross-ring contact. An alternative N-lithiated geometry, **4b**, incorporates a metal centre which, while formally bonding to nitrogen, bridges between C_{ipso} and C_{peri} (Li–N = 1.834 Å, Li–C_{ipso} = 2.490 Å, Li–C_{peri} = 2.373 Å). However, the energy of **4b** is only nominally higher — by 0.4 kcal mol^{-1} (1 kcal = 4.184 kJ) — than that of **4a** (all relative energies quoted are for SCF + ZP values). The remaining models are all formally C-metallates and are appreciably less stable than either **4a** or **4b**.

Four dilithiated isomers reveal a significant theoretical predilection for N,C_{peri}-dilithiation such that both metals bridge symmetrically between anionic centres (Fig. E2) with **5a** being formally N,C_{peri}-dimetallated. The next most preferable isomer — N,C_{ortho}-dilithiated **5b** — showed a similar symmetrical bridging motif but was 11.9 kcal mol^{-1} less stable than **5a**. The remaining modelled complexes each incorporated one terminal Li centre with **5c** and **5d** revealing N,C$_{ipso}$,C$_{ortho}$- and N,C$_{ipso}$,C$_{peri}$-bridging of the second metal ion, respectively. Both of these structures were, accordingly, high in energy (Table E2).

Fig. E3 and Table E3 summarise modelled mono-, bis- and tris-OMe$_2$ solvated dilithium analogues of computed structures **5a** and **5c**, respectively. The preferred monosolvated structure, **6a**, retains symmetric bridging of N- and C$_{peri}$-positions by the alkali metal centres (*cf.* **5a**) but reveals extended Li–X interactions (Li–N = 1.954 Å, Li–C = 2.130 Å; *cf.* 1.928 Å and 2.092 Å, respectively, in **5a**) and shows an energetic preference of 20.1 kcal mol^{-1} over the corresponding geminal dilithiate, **6b**. This complex, too, reveals the extension of Li–N bonds (to 1.741 Å and 1.891 Å, *cf.* **5c**). The latter distance involves a lithium centre which, like its analogue in **5c**, interacts with both C$_{ipso}$ (2.116 Å, *cf.* 2.079 Å in **5c**) and C$_{ortho}$ (2.233 Å, *cf.* 2.160 Å in **5c**). The bis-solvation of each metal ion yields structures which differ less significantly in energy with the geminal dilithium salt (**6d**) being 15.2 kcal mol^{-1} less favourable than the N,C$_{peri}$ complex (**6c**). In the most stable of these two isomers, Li–X bond lengths suggest — when compared with those noted for the corresponding monosolvated analogue — that the alkali metal centres are migrating to the C$_{peri}$ position (Li–N = 2.007 Å, Li–C = 2.040 Å). Just as the Li–N bond lengths are extended in **6c**, so too are they lengthened in **6d** to 1.821 Å and 1.919 Å — the latter distance involving the metal centre which was stabilised by both C$_{ipso}$ and C$_{ortho}$ in **6b** but which now interacts with just the former C-centre (Li–C$_{ipso}$ = 2.206 Å). Significantly, tris-solvation of each metal centre results in a re-ordering of the different dilithiated isomers. The N,C$_{peri}$ salt **6f** (for which Li–N = 1.972 Å and Li–C = 2.135 Å) is significantly altered relative to its mono- and bis-solvated congeners. Tris-solvation of each Li$^+$ ion has made it unnecessary for the metal centres to bridge between deprotonated sites and, in consequence, the lithium amide moiety has rotated to minimise steric interaction between the two bulky Li·(OMe$_2$)$_3$ fragments. This complex is now 4.5 kcal mol^{-1} *less stable* than geminal N,N-dimetallate **6e** by virtue of the significantly larger enthalpy of solvation (ΔH_{solv}) per molecule of dimethyl ether for the latter compound (−10.6 kcal mol^{-1} for **6e** *versus* −6.1 kcal mol^{-1} for **6f**). Unlike in **6d**, bond distances between lithium and nitrogen centres in **6e** are nearly equivalent (1.900 Å and 1.917 Å) by virtue of the loss not just of C$_{ortho}$ stabilisation but also of C$_{ipso}$ bonding.

Complex formation between 1-naphthylamine and LiH (used here as a simple model of a lithiating agent) logically represents the first stage precursor to monolithiation of the substrate and has been studied in the context both of a σ-complex between the reactive N-centre and the alkali metal (**7a**) and also as an η^6 π-complex involving either aromatic system (**7b/c**) with the result that the first of these models represents the preferred precursor to deprotonation (Fig. E4 and Table E4). Relative to the optimised structures of 1-naphthylamine and LiH, **7a** reveals an enthalpy of complexation (ΔH_{comp}) which, at −19.8 kcal mol^{-1}, is 4.8 kcal mol^{-1} and 6.4 kcal mol^{-1} more favourable than those associated with **7b** and **7c**, respectively. The preferred initial complex (**7a**) is, in fact, 1.8 kcal mol^{-1} more stable than even the most stable unsolvated, monomeric monolithiated *product* (**4a**) plus one molecule of H$_2$ (for which SCF energy = −1.126827 Hartrees and SCF + ZP energy = −1.116243 Hartrees). The conversion of intermediate **7a** to two different transition states has been probed, with structures **8a** and **8b** differing only in the mechanisms by which the H$_2$ leaving group forms. Hence, **8a** represents the transition state (TS) which leads to **4a**. It is 26.4 kcal mol^{-1} higher in energy than initial complex **7a** and is 1.2 kcal mol^{-1} less stable than **8b** (precursor to **4b**).

In a similar vein, the initial complexes and transition states *en route* to various *di*lithio-1-naphthylamide isomers have been probed (Fig. E5 and Table E5). The most stable initial complex (**4b·**LiH) is a slightly rearranged variant on the second most stable monolithiated species (**4b**) whereby all C-stabilisation of the N-bonded metal centre has been removed. The result is that **4b·**LiH incorporates only Li–N and Li–H coordination and reveals a ΔH_{comp} value of −48.7 kcal mol^{-1} relative to optimised **4b** + LiH. Only nominally less stable (with an enthalpy of complexation of −47.7 kcal mol^{-1} relative to optimised **4a** + LiH) was **4a·**LiH. Higher in energy than **4b·**LiH by 3.6 kcal mol^{-1} and 4.2 kcal mol^{-1}, respectively, were **9a** and **9b**. Neither of these incorporated any interaction between the newly introduced Li centre and the amide group.

Computed transition state precursors to the dilithium salts of 1-naphthylamine systems are detailed in Fig. E6 and Table E6. It transpires, however, that in the absence of aggregation and external solvation the preferred transition state (**10a**) is that which leads to a N,C$_{peri}$-dilithiate. This species reveals symmetrical interaction of both metal ions not only with the nitrogen centre (Li–N = 1.933 Å) but also weakly with the C$_{peri}$ position (Li–C = 2.238 Å). The C$_{peri}$–H bond has lengthened to 1.574 Å with concomitant formation of an H–H bond (of 0.952 Å) in the leaving group. The TS for geminal N,N-dimetallation (**10b**) reveals similar lengthening of the bond between the monolithiated N-centre and the leaving proton (N–H = 1.456 Å) with both metals bridging this interaction. While one of these Li$^+$ ions is extensively stabilised (by both leaving H-centres as well as N,C$_{ipso}$, C$_{ortho}$ and H$_{ortho}$) the remaining metal interacts only with nitrogen and the leaving proton. Logically, the presence of this low coordinate Li centre in TS **10b** is responsible, at least in part, for the 18.4 kcal mol^{-1} energetic preference for TS **10a**.

The observation of a polyhedral array for **3** comparable to those noted for **1** and **2** reinforces the view of an extremely stable arrangement wherein an essentially ionic cluster core retains a high charge density and is encapsulated within a shell of lipophilic organic residues. Accordingly, the complex stability of the best of these experimental structures, that of *N*,*N*-dilithio-4-methylanilide **3**, was probed by *ab initio* methods with a view to interpreting the positional selectivity of both mono- and di-lithiation and also to consider the effect on this issue of solvent interaction with the metal centres. Calculations[17] (6-31G* basis set[18] at the RHF level) were done initially on the various isomers of monomeric, monolithiated 4-methylaniline, the most theoretically favourable model of a monomeric *N*-lithio-4-methylanilide being employed thereafter to investigate the stability of various dilithiated monomers. Finally, the effect on selected *N*,*N*-dilithio-4-methylanilides of complexation of each Li-centre by external Lewis base was examined.

Akin to the results noted for monolithiated 1-naphthylamine, *ab initio* calculations on the monolithiated, monomeric isomers of 4-methylaniline point to the favourability of N-metallation (Table E7). The various isomers modelled are shown in Fig. E7. For the monolithiate with the most stable configuration, **11a**, extensive *ipso*- and *ortho*-stabilisation of the metal centre is revealed to incur the formation of contiguous three-membered CNLi rings [Li–N = 1.829 Å, Li–C$_{ipso}$ = 2.213 Å, Li–C$_{ortho}$ = 2.303 Å]. Calculations reveal a 1.0 kcal mol^{-1} preference for this structure type over the analogous N-lithiate (**11b**) which lacks any such aryl ring stabilisation (Li–N = 1.795 Å). Models based on C-metallation of either the ring or 4-methyl substituent prove to be significantly less stable.

Initial theoretical probes of unsolvated dilithio-4-methylanilide monomers reveal results which, like those for dilithio-1-naphthylamide, contrast with experiment. Calculated energies and optimised geometries are given in Table E8 and Fig. E8, respectively. In the first instance, the most stable calculational configuration differs significantly from the observed solid-state structure of **3** inasmuch as the second lithiation site is the *ortho*-carbon centre, affording vicinal N,C$_{ortho}$- rather than geminal N,N-dilithiation. This model (**12a**) reveals alkali metal cations disposed symmetrically above and below the aromatic plane, both showing N- and C_{ortho}-stabilisation (Li–N = 1.912 Å, Li–C_{ortho} = 2.064 Å). Moreover, in the absence of aggregation and/or external solvation, **12a** shows more effective charge distribution — a feature consistent with the preponderance of vicinal dilithiates which have been achieved by polymetallating biphenyls[19] and other mono-[15,20] and di-substituted[21] benzenoids, salenH_2 [= *N*,*N′*-ethylenebis(salicylideneimine)],[22] diarylthioureas,[23] diamines[24] and also conjugated diketones[25] and diynes.[26] However, loss of symmetry in the vicinal dimetallate **12c** results in the inability of nitrogen to stabilise both Li^+ ions and a concomitant destabilisation (28.1 kcal mol^{-1} relative to **12a**). Intermediate between the two and 14.0 kcal mol^{-1} less stable than **12a** is the calculated N,N-dilithiate **12b**. This latter monomer, instead of incorporating a symmetrical NLi_2 arrangement with C-stabilisation of both metal centres, reveals a surprising structural motif with a single, otherwise unstabilised N-bonded Li^+ ion (Li–N = 1.720 Å), and a second extensively stabilised metal ion (Li–N = 1.848 Å) which interacts with both C_{ipso} and C_{ortho} (Li–C = 2.045 Å and 2.204 Å, respectively). The remaining models, all of which are N,C-dimetallated, are (by 29.7–30.0 kcal mol^{-1}) significantly disfavoured relative to **12a**.

The results of extending calculations on the most stable unsolvated, monomeric N,C_{ortho}- and N,N-dilithium structures (**12a/b**) to monomeric complexes (Fig. E9) in which the metal centres are externally Me_2O-solvated and also to dimeric complexes (Fig. E10) are summarised in Table E9. Just as for dilithio-1-naphthylamide, mono-, bis- and tris-solvates have been modelled and the results bear out the same important trend as was observed (in Table E3) for this former set of isomers. The most stable of the first of these types (**13a**) reveals extended N- and C_{ortho}-bonds to the (symmetrically disposed) metal centres (Li–N = 1.938 Å, Li–C_{ortho} = 2.098 Å) in what is otherwise an analogue of **12a** and shows an enthalpy of solvation of −34.2 kcal mol^{-1} relative to **12a** + $2Me_2O$ (that is, $\Delta H_{\mathrm{solv}} = -17.1$ kcal mol^{-1} for each molecule of solvent). Less stable by 12.5 kcal mol^{-1} is **13b** wherein the metal centre, which is N- and C_{ipso}-bonded (Li–N = 1.867 Å, Li–C = 2.133 Å), reveals only a weak C_{ortho} interaction (Li–C_{ortho} = 2.290 Å). This energy difference is noted in spite of the nominally greater value of ΔH_{solv} associated with this species (−17.8 kcal mol^{-1} for each solvent molecule). A similar trend is noted for solvates **13c/d**. Whereas **13c** is structurally analogous to **13a**, the more numerous metal–solvent interactions in **13d** make Li–C interactions of the type noted in **13b** largely rendundant (Li–C_{ipso} = 2.257 Å, Li ··· C_{ortho} = 2.526 Å). **13c** is preferred to **13d** by 8.1 kcal mol^{-1}. The process of Li–C bond cleavage is completed in the optimised structure of heavily solvated **13e**. Here, the tris-solvation of each metal centre has the effect of rendering both Li–N interactions similar (Li–N = 1.866 and 1.904 Å). Just as for the calculated naphthylamide complexes, and in the context of experimental structures **1**–**3**, it is particularly interesting to note that extensive coordination of the Li centres by an etherate solvent again favours N,N- over N,C_{ortho}-deprotonation (*cf.* **12a/b**), with geminally dilithiated **13e** being preferred to vicinally dimetallated **13f** by 5.5 kcal mol^{-1}.

An examination (Fig. E10) of whether dimerisation would allow a formally N,N-dilithiated complex to become more stable than a vicinally dimetalled analogue (in the absence of an etherate solvent) revealed enthalpies of aggregation of −44.6 and −62.8 kcal mol^{-1} for **14a** [incorporating a flexible, central eight-membered $(LiNC_2)_2$ ring] and **14b** [based on a four-membered $(LiN)_2$ core], respectively, relative to 2 eq. of the corresponding monomers (**12a** and **12b**). However, despite a more favourable dimerisation energy for the geminal dilithiate (**14b**), this species is still 9.8 kcal mol^{-1} less stable than a dimer with the lithium centres formally residing at the N- and C_{ortho}-positions (**14a**).

The noted theoretical preference for vicinal dilithiation (notwithstanding the presence of excess etherate solvent) has been probed in the context of transition states prior to both mono- and di-metallation of the substrate. Calculations on the initial complex between LiH and 4-methylaniline at nitrogen, **15a** (leading to N-lithio TS **15b**), and η^6 to the aromatic ring, **16a** (leading to C_{ortho}-lithio TS **16b**), reveal a straightforward preference for N-metallation on the basis of TS energy relative to the reactants (Table E10 and Fig. E11). A more complicated story emerges, however, for metallation of the N-monolithioanilide. The initial complexes for both N- and C_{ortho}-dilithiation are coincident (**11b**·LiH, Table E11 and Fig. E12), with the subsequent TS for C_{ortho}-metallation (**17a**) being preferred to that for geminal deprotonation (**17b**) by 8.1 kcal mol^{-1}. Thus, the theoretical preference for N,C_{ortho}-dilithiation is reflected not only in the product dilithiates themselves (see above, **12a**–**f**) but is also suggested by the structure of the preferred TS. However, just as the optimisation of dilithiated solvates revealed that external coordination by Me_2O markedly decreased not only the effects of C-stabilisation of the metal centres but also the energetic preference for C_{ortho}-lithiation in the polymetallated species, so solvent effects also play a crucial role in directing complex formation between *N*-lithio-4-methylanilide and the organolithium substrate and, thus, in TS formation.

Optimisation of either the N- or C_{ortho}-complex between $(H_2O)_n$·**11b** (n = 2, 3) and LiH yields, in each case, N-centred complexes of the type **18a** (n = 2) and **18b** (n = 3). These reveal similar ΔH_{comp} values with respect to $(H_2O)_n$·**11b** (for which SCF + ZP = −483.534147 Hartrees for n = 2 and −559.544054 Hartrees for n = 3; Table E12 and Fig. E13). Analysis of the subsequent reaction of **18a** suggests a 4.6 kcal mol^{-1} preference for the TS (**18c**) preceding N,C_{ortho}-dilithiation over that (**18d**) which gives the N,N-dilithiate. Meanwhile, **18e/f** suggest a negligible (0.8 kcal mol^{-1}) preference for the N,C_{ortho}-deprotonation of **18b** (*cf.* the 8.1 kcal mol^{-1} preference for **17b** over **17a** — that is, in the absence of external solvation). Plainly, therefore, increasing the extent to which the first alkali metal is solvated diminishes the preference for the second Li^+ ion to bond formally to C_{ortho} and, therefore, increases the energetic likelihood of geminal reaction.

Conclusions

The synthesis, isolation and structural characterisation of **1**–**3** points to a preference for the geminal N,N-dimetallation of aromatic primary amines and to the stability of solvated and aggregated fused rhombohedral motifs in such systems. These data are borne out by patterns observed in the theoretical likelihood of N,N-dilithiation for both 1-naphthylamine and 4-methylaniline substrates under a variety of conditions. Hence, whereas **6a/b** and **6c/d** point to a predilection for N,C_{peri}-dimetallation, the presence of sufficient Lewis base in **6e/f** leads to an energetic preference of 4.5 kcal mol^{-1} for the geminal N,N-process. In the same way, the 4-methylaniline analogues (**13a**–**f**) reveal a tendency for N,C_{ortho}-dilithiation in the absence of extensive solvation, with the energetic preference diminishing in the presence of incremental Me_2O (**13a**–**d**). Moreover, the tris-solvation of each Li^+ ion (**13e/f**) once more results in a predilection (by 5.5 kcal mol^{-1}) for geminal N,N-reaction. The isolation and structural characterisation of the complexes discussed here appears to be critically dependent on the existence of mechanisms to offset the charge density at nitrogen in the dilithiated compounds. The result is that clusters **1**–**3** are enabled by both extensive association and the inclusion of etherate solvent molecules. Of interest is the differing extent of solvation in the complexes isolated and characterised thus far. Spectroscopic studies into the lability with which external solvent molecules coordinate and the viability of extensive (charge-delocalising) clusters in solution are ongoing and will be reported subsequently.

Experimental

Methods and materials

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard double manifold and glove-box techniques. Chemical reagents were used as received from Aldrich without further purification. Toluene, Et_2O and thf were distilled off sodium or sodium–potassium amalgam immediately prior to use.

NMR data were collected on either a Bruker DRX 400 (400.12 MHz for ^1H) or a DRX 500 (500.05 MHz for ^1H) FT NMR spectrometer at 27 °C. Chemical shifts are quoted relative to TMS.

All crystals were mounted directly into the cold stream of a Cryostream crystal cooling apparatus, installed on a Stoe-Siemens four-circle or a Rigaku AFC7 diffractometer, using perfluoropolyether oil.

Synthesis and characterisation

Synthesis of $(Et_2O)_6\cdot(Li_2NC_{10}H_7)_{10}\cdot OEt_2$, 1·OEt$_2$. A solution of 1-aminonaphthalene (0.72 ml, 5.0 mmol) in diethyl ether (7.5 ml) was treated with Bu^{n}Li (6.3 ml, 1.6 M in hexanes, 10.0 mmol) at −40 °C under nitrogen. The resultant fluorescent green mixture was stirred until it turned orange. At *ca.* −20 °C a yellow precipitate formed which dissolved at *ca.* 0 °C to give a yellow solution, refrigeration of which afforded yellow cubic crystals of **1**·OEt$_2$, mp decomp. from 230 °C, yield 68%. Found: C 73.36, H 6.83, N 7.14. Calc. for $C_{128}H_{140}Li_{20}N_{10}O_7$: C 74.29, H 6.82, N 6.77%. ^1H NMR spectroscopy (400 MHz, dmso), δ 8.04 (s, br, 1H, Ar), 7.18 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar), 6.99 (dt, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 6.79 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar), 6.64 (t, br, 1H, Ar), 5.86 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar), 3.38 (q, $^3J_{HH}$ = 7.00 Hz, 2H, Et_2O), 1.09 (t, $^3J_{HH}$ = 7.0 Hz, 3H, Et_2O).

Synthesis of $(Et_2O)_6\cdot[Li_2N(C_6H_4\text{-}4\text{-}CPh_3)]_{10}\cdot 9PhMe$, 2·9PhMe. A solution of 4-tritylaniline (0.67 g, 2.0 mmol) in 2 : 1 toluene–diethyl ether (4 : 2 ml) was reacted with Bu^{n}Li (2.5 ml, 1.6 M in hexanes, 4.0 mmol) at −78 °C under nitrogen and the mixture was allowed to reach room temperature. Storage of the resultant yellow solution in an oil bath (35 °C) gave yellow crystals of **2**·9PhMe, mp 320–321 °C, yield 42%. Found: C 85.72, H 6.57, N 2.42, Li 2.86. Calc. for $C_{337}H_{321}Li_{20}N_{10}O_6$: C 85.27, H 6.82, N 2.96, Li 2.92%. ^1H NMR spectroscopy (400 MHz, dmso), δ 7.20–7.06 (m, 19H, Ph), 6.17 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C_6H_4), 5.7 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C_6H_4), 3.36 (q, $^3J_{HH}$ = 7.0 Hz, 1.5H, Et_2O), 2.27 (s, 2H, Ph*Me*), 1.07 (t, $^3J_{HH}$ = 7.0 Hz, 2.3H, Et_2O).

Synthesis of $(thf)_{10}\cdot[Li_2N(C_6H_4\text{-}4\text{-}Me)]_{10}\cdot 0.5thf$, 3·0.5thf. Bu^{n}Li (3.2 ml, 1.6 M in hexanes, 5.0 mmol) was added to a solution of 4-methylaniline (0.27 g, 2.5 mmol) in 4 : 3 thf–toluene (4 : 3 ml) at −78 °C under nitrogen. The yellow precipitate obtained by stirring at room temperature was dissolved by gentle heating. Slow cooling of the resultant solution afforded yellow crystals of **3**·0.5thf, mp 233–235 °C, yield 67%. Found: C 69.32, H 8.13, N 7.28, Li 6.14. Calc. for $C_{112}H_{154}Li_{20}N_{10}O_{10.5}$: C 69.08, H 7.97, N 7.19, Li 7.20%. ^1H NMR spectroscopy (500 MHz, dmso), δ 6.26 (d, $^3J_{HH}$ = 7.9 Hz, 2H, C_6H_4), 5.82 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4), 3.9 (m, 3.5H, thf), 1.91 (s, 3H, CH_3), 1.74 (m, 3.5H, thf).

X-Ray crystallography

The structures of **1**·OEt$_2$ and **3**·0.5thf were solved by direct methods[27] and refined against F^2 values[28] of all data. For **1**·OEt$_2$, non-H atoms were refined with anisotropic displacement parameters, which were subject to similarity and rigid-bond restraints within each ligand; H atoms were made to ride on the relevant carbon atoms with idealized geometries (but were not included on the uncoordinated ether molecule). Geometrical similarity restraints were also applied to all naphthylamine groups and to all ether molecules to assist in the refinement of the disorder, which was resolved for some of the naphthylamine ligands.

Table 3 Crystallographic data for **1**·OEt$_2$ and **3**·0.5thf

	1·OEt$_2$	**3**·0.5thf
Formula	$C_{128}H_{140}Li_{20}N_{10}O_7$	$C_{112}H_{154}Li_{20}N_{10}O_{10.5}$
M_r	2069.30	1947.28
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$ (no. 2)
a/Å	14.111(2)	14.854(9)
b/Å	14.270(3)	17.152(9)
c/Å	28.866(5)	14.186(9)
α/°	90	111.47(5)
β/°	93.84(2)	105.16(5)
γ/°	90	65.89(4)
V/Å^3	5799.5(18)	3043(3)
Z	2	1
Radiation	Cu-Kα (λ = 1.54184 Å)	Mo-Kα (λ = 0.71069 Å)
μ/mm^{-1}	0.537	0.065
T/K	150(2)	230(2)
Measured reflections	7116	9896
Unique reflections	7116	5652
R_{int}	—	0.0557
Final $R(F)$, $wR(F^2)$	0.1372, 0.4970	0.1121, 0.3913
Parameters	943	631

For **3**·0.5thf, ordered non-hydrogen atoms were refined with anisotropic displacement parameters, and H-atoms were allowed to ride on the relevant carbon atoms with idealized geometries. The disordered coordinated thf molecules were refined with common isotropic displacement parameters, with atoms in the rings disordered over two sites. The asymmetric unit revealed 0.25 thf molecules of crystallization (0.5 molecules per decamer) and these were refined with fixed bond parameters and a common isotropic displacement parameter. Crystallographic data are given in Table 3.

CCDC reference numbers 170108 and 170109.

See http://www.rsc.org/suppdata/dt/b1/b107970k/ for crystallographic data in CIF or other electronic format.

Theoretical calculations

Ab initio geometry optimisations were carried out on the various isomers of monomeric lithio-1-naphthylamide and lithio-4-methylanilide using GAUSSIAN 94[17] employing the 6-31G*[18] basis set at the RHF level. Zero point contributions were calculated and SCF + ZP terms used to derive all relative energies quoted. 6-31G* parameters[18] were then utilised to model the monomeric dilithiate using the theoretically most stable optimised monolithiate monomer. The above calculations were also repeated using the 6-311G**[29] basis set at the DFT level (B3LYP method)[30] to determine whether the inclusion of correlation energy affected the conclusions. However, results indicated no significant change (Table E13). The effects of solvation on dilithiation were considered with selected mono- and di-meric arrangements of dilithio-4-methylanilide being examined in the presence of various amounts of coordinating Lewis base, R_2O (R = H, Me). It was found that all the computed transition states have one negative frequency and that these frequencies lie in the range −1161.1 cm^{-1} to −1803.1 cm^{-1}. IRC calculations[31] were used to verify that each transition state was connected to the two appropriate energy minima. Tables detailing the results of *ab initio* and DFT calculations are available as ESI.

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