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The arched four-rung ladder structure of the unsolvated dilithium salt of *N*,*N′*-bis(trimethylsilyl)-2-aminobenzylamine, and its structural deformation on THF complexation

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The X-ray crystal structures of 2-Li(SiMe$_3$)NC$_6$H$_4$CH$_2$N(SiMe$_3$)Li 1 and 2-Li(SiMe$_3$)NC$_6$H$_4$CH$_2$N(SiMe$_3$)Li·THF 2 show that both compounds exist in the solid state as discrete dimers that display an analogous four-rung ladder core, allowing us to analyse the effect of THF coordination.

The aggregation of lithium amides *via* so-called ring-laddering processes is now well documented, and a wide variety of architectures has been described in the literature.[1] In the absence of coordinating Lewis bases, these compounds generally adopt polymeric infinite ladder structure, but examples of shorter arrangements have been reported. On exposure to solvating ligands, these structures are often broken down to smaller entities which can however still be assembled into oligomeric ladders of limited length if only partial solvation has taken place.[1] Here, we present the first structural characterization of a heteroditopic dilithium diamide, both in its unsolvated and THF monoadduct forms. The unsolvated compound 2-Li(SiMe$_3$)NC$_6$H$_4$CH$_2$N(SiMe$_3$)Li **1** is dimeric and exhibits an arched four-rung ladder structure which had not been observed previously for an uncomplexed amidolithium compound. Coordination of THF to give 2-Li(SiMe$_3$)NC$_6$H$_4$CH$_2$N(SiMe$_3$)Li·THF **2** changes the structural parameters of this edifice, but alters neither its dimeric nature nor its conformation, providing the opportunity to analyse the fundamental bond modifications upon lithium complexation in such ladder frameworks.

Compound **1**† was obtained as colourless crystals through double deprotonation of the diamine 2-NH(SiMe$_3$)C$_6$H$_4$CH$_2$NH(SiMe$_3$)[2] by Bu^{n}Li in pentane, followed by concentrating the reaction mixture under reduced pressure and cooling the resulting solution to −20 °C. Its high solubility in hydrocarbons restricted the isolated yield to 58%. Its molecular structure was established by X-ray diffraction analysis‡ (Fig. 1). The three fused (NLi)$_2$ rings that build the four-rung ladder are strictly planar and significantly twisted with respect to each other, as shown by the average value of the two N–Li–N–Li edge dihedral angles (51.1°). The chelating 2-benzyl linkages bridge the nitrogen atoms along each edge and are located on the same face of the ladder, which imposes the arch-like folding, the nearly parallel orientation of the two aromatic rings (which is not the result of π-stacking, the two ring planes being staggered and distant by *ca.* 4 Å), and the cisoid configuration of the four SiMe$_3$ substituents.

The four-coordinate anilinic nitrogens are located in the outer rungs, while the five-coordinate benzylic nitrogens occupy the inner positions, leading to a 'head-to-tail' arrangement. Although the molecule shows only approximate and not crystallographic C_2 symmetry, the discussion of its dimensional parameters can be restricted to one half of the dimer.

Interestingly, the two outer lithium atoms are only two-coordinate with respect to nitrogen ligation and hence highly electron-deficient, which results in short outer rungs [Li(1)–N(4) 1.964(4) Å] and close contacts with carbons of the neighbouring aromatic rings [Li(1)–C(5) 2.350(5) Å, Li(1)–C(10) 2.627(5) Å]. These relatively strong lithium–carbon interactions are certainly at the origin of the limited length of this unsolvated ladder (together with the steric hindrance of the SiMe$_3$ substituents at the ladder ends), and of its folding down into an arch. On the other hand, the inner lithium atoms are three-coordinate with respect to nitrogen ligation and pyramidal. Although less unsaturated, they interact similarly with the benzylic carbons [Li(2)–C(4) 2.484(4) Å], tying the 2-benzyl framework even closer to the (NLi)$_4$ core, accounting further for the severely folded structure of the ladder [Li(1)–N(1)–Li(2) 106.00(2)°, N(1)–Li(2)–N(2) 108.8(2)°], and leading to inner Li–N edges that are relatively shorter than the inner rungs [Li(2)–N(1) 2.025(4) Å, Li(4)–N(1) 2.113(4) Å]. ^{1}H NMR spectra† suggest that this dimeric structure is maintained in benzene solution, and show that the molecule is fluxional.

It should be pointed out that lithium amides exhibiting a four-rung ladder structure have been described previously, but are either solvated at the terminal lithium centers[3] (as **2**, *vide infra*) or folded into stairs.[4] Both of these characteristics are found together in a few compounds.[5] The example of unsolvated dimeric [Li(Dipp)NCH$_2$CH$_2$N(Dipp)Li]$_2$[4] (Dipp = 2,6-diisopropylphenyl) is of particular interest owing to its close analogy with **1**. It similarly contains strong lithium–carbon interactions, but exists as a stepped four-rung ladder.[4] We presume this different geometry arises from the fact that the Li–C inter-

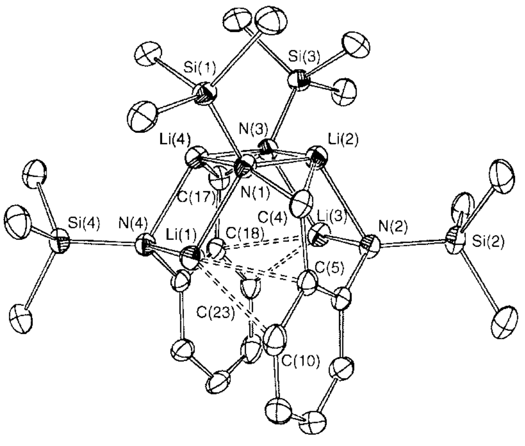

Fig. 1 Molecular structure of **1** showing the atom numbering scheme. The H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Li(1)–N(1) 2.038(4), Li(2)–N(1) 2.025(4), Li(2)–N(2) 2.035(4), Li(1)–N(4) 1.964(4), Li(4)–N(1) 2.113(4), Li(1)–C(5) 2.350(5), Li(1)–C(10) 2.627(5), Li(2)–C(4) 2.484(4), Li(1)–Li(4) 2.427(5), Li(2)–Li(4) 2.389(6); Li(1)–N(1)–Li(4) 71.52(2), Li(2)–N(1)–Li(4) 70.47(2), Li(1)–N(1)–Li(2) 106.00(2), Li(1)–N(4)–Li(4) 74.99(2), N(1)–Li(1)–N(4) 109.2(2), N(1)–Li(2)–N(2) 108.8(2), N(1)–Li(4)–N(3) 108.4(2), N(1)–Li(4)–N(4) 104.1(2), N(3)–Li(4)–N(4) 110.9(2).

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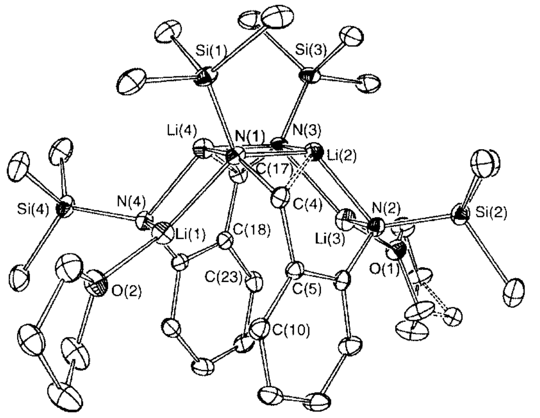

Fig. 2 Molecular structure of **2** showing the atom numbering scheme. The H atoms have been removed for clarity. Selected interatomic distances (Å) and angles (°): Li(1)–N(1) 2.116(6), Li(2)–N(1) 2.051(5), Li(2)–N(2) 1.974(6), Li(1)–N(4) 2.030(5), Li(4)–N(1) 2.063(5), Li(1)–O(2) 1.979(5), Li(1)–C(5) 2.762(6), Li(1)–C(10) 2.906(5), Li(2)–C(4) 2.546(5), Li(1)–Li(4) 2.467(7), Li(2)–Li(4) 2.318(7); Li(1)–N(1)–Li(4) 72.3(2), Li(2)–N(1)–Li(4) 68.6(2), Li(1)–N(1)–Li(2) 116.7(2), Li(1)–N(4)–Li(4) 75.9(2), N(1)–Li(1)–N(4) 103.8(2), N(1)–Li(2)–N(2) 114.3(2), N(1)–Li(4)–N(3) 110.8(2), N(1)–Li(4)–N(4) 107.7(2), N(3)–Li(4)–N(4) 113.9(2).

actions in this latter compound do not involve the edge-hugging chelating bridges as in **1**, but the other nitrogen substituent of the secondary amides (Dipp in that case).

Compound **2**† was obtained serendipitously by the reaction of **1** with 0.5 equiv. $ZrCl_4(THF)_2$ in toluene.[6] A single-crystal X-ray structure determination‡ showed that its molecular structure is in all respects similar to that of **1**, and the same numbering scheme was thus used for the sake of clarity (Fig. 2). Coordination of THF occurs at the outer lithium atoms which become three-coordinate, but the four-rung ladder core of **1** is not broken down in **2** and its peculiar geometry is furthermore retained. However, the $(NLi)_4$ arch is significantly flattened, as shown by the increased distance between the two outer rungs [from 3.653 Å in **1** to 4.337 Å in **2** for Li(1)–N(2) for instance], the more obtuse edge angles Li(1)–N(1)–Li(2) and N(1)–Li(2)–N(2) (+10.7 and +5.5°, respectively), and the less pyramidal inner lithium atoms, whose average summed angles vary from 323.3° in **1** to 333.6° in **2**. Moreover, the ladder framework is more severely twisted in **2**, the N–Li–N–Li edge dihedral angles increasing to 67° (average value), and, most importantly, the 2-benzyl aromatic rings are considerably withdrawn from the outer lithium atoms [Li(1)–C(5) 2.762 Å, Li(1)–C(10) 2.906 Å]. Undoubtedly, the outer lithium atoms have become less electron deficient on complexation by THF, and the above structural modifications are the consequence of subsequent weakening of their interactions with the aromatic ring of the 2-benzyl bridges.

The Li–N bond distances within the ladder core are also modified accordingly, both edges and rungs involving the outer lithiums being lengthened by an average value of 0.078 Å. The electrons of the four nitrogen atoms become thereby more available for the inner lithium atoms, leading to the strengthening of the corresponding Li–N bonds and to their average shortening by *ca.* 0.045 Å, with the notable exception of the two inner edges Li(2)–N(1) and Li(4)–N(3). These indeed are slightly longer in **2** than in **1**, [+0.026 Å for Li(2)–N(1) for instance], as are the lithium–carbon distances between the inner lithium atoms and the benzylic carbons [+0.062 Å for Li(2)–C(4)]. THF complexation of the outer lithium atoms hence also results in higher electron density on the inner ones. This weakens the lithium–methylene interactions that squeezed the inner Li–N edges in **1**, to such an extent that also these latter bonds are lengthened in **2**.

We dedicate this paper to the memory of Professor John A. Osborn. We thank the CNRS and the Ministère de l'Education Nationale, de la Recherche et de la Technologie for funding this work.

Notes and references

† **1**: satisfactory C, H, N analysis; δ_H(25 °C, 300 MHz, C_6D_6): 6.94 (dt, 1H, C^5H), 6.84 (dd, 1H, C^3H), 6.58 (dt, 1H, C^4H), 6.27 (d, br, 1H, C^6H), 4.39 and 3.68 (d, ^2J 10.3 Hz, br, 1H, ArC*H*H′ and ArCH*H*′), 0.22 (s, 9H, ArNSi*Me*$_3$), 0.05 (s, 9H, CH_2NSi*Me*$_3$); δ_C(25 °C, 75 MHz, C_6D_6): 157.26 (C^2), 136.53 (C^1), 131.60, 129.62, 125.83 and 119.11 (C^3, C^4, C^5 and C^6), 48.78 (CH_2), 2.96 and 0.60 (ArNSi*Me*$_3$ and CH_2NSi*Me*$_3$). **2**: δ_H(25 °C, 300 MHz, C_6D_6); 7.04 (m, 2H, C^3H or C^6H and C^4H or C^5H), 6.70 (m, br, 1H, C^3H or C^6H), 6.59 (t, 1H, C^4H or C^5H), 4.10 (s, br, 2H, ArC*H*$_2$) 3.37 (m, 4H, OCH_2), 1.21 (m, 4H, OCH_2CH_2), 0.26 (s, br, 18H, ArNSi*Me*$_3$ and CH_2NSi*Me*$_3$).

‡ *Crystal data* for $C_{26}H_{48}N_4Li_4Si_4$ **1**: $M = 556.81$, monoclinic, space group $P2_1/n$, $a = 9.7590(2)$, $b = 21.3540(4)$, $c = 16.7940(6)$ Å, $\beta = 98.073(5)$°, $U = 3465.1(3)$ Å^3, $Z = 4$, $D_c = 1.07$ g cm^{-3}, $\mu = 0.186$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 173$ K, 25648 data measured, 4455 data with $I > 3\sigma(I)$, $R = 0.038$, $R_w = 0.058$.

For $C_{34}H_{64}Li_4N_4O_2Si_4$ **2**: $M = 701.02$, monoclinic, space group $P2_1/c$, $a = 19.9167(9)$, $b = 9.8818(2)$, $c = 22.1151(9)$ Å, $\beta = 99.750(2)$°, $U = 4289.7(5)$ Å^3, $Z = 4$, $D_c = 1.09$ g cm^{-3}, $\mu = 0.170$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 173$ K, 29787 data measured, 4972 data with $I > 3\sigma(I)$, $R = 0.043$, $R_w = 0.064$. One β carbon atom of one THF molecule occupies two distinct positions (Fig. 2).

The structures were solved using direct methods and refined by full-matrix least squares on *F*.

CCDC 182/1609. See http://www.rsc.org/suppdata/cc/b0/b002004o/ for crystallographic files in .cif format.

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6 Adding an excess of THF to **1** or **2** leads to the monomeric tetra-THF adduct.