The First Structurally Characterised Sodium Primary Amide Complex; Synthesis and Crystal Structure of 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$

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The compound 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$ has been synthesised by a 1 : 1 reaction of sodium hydride with 2-phenoxyaniline in toluene in the presence of *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien); X-ray crystallography revealed a solid-state structure comprising a near-symmetrical Na_2N_2 ring dimer with each sodium cation chelated by a tridentate pmdien ligand in an unprecedented near-planar conformation.

Alkali-metal amides are of considerable importance as reagents in organic synthesis.[1] Solution and solid-state structural investigations of these reagents have concentrated largely on lithium amides,[2] and to a lesser extent on sodium derivatives of secondary amines.[3] As an extension to these investigations we report here the synthesis and low-temperature X-ray crystal structure determination of the first sodium primary amide complex 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$ **1**.

We reported recently the results of the monometallation of a di(aminoaryl) ether with sodium hydride in the presence of hexamethylphosphoramide (hmpa).[4] Such metallation induced an unexpected intramolecular S_NAr reaction, known as a Smiles rearrangement, leading to a sodium aryloxide complex. Generally, Smiles rearrangements have been favoured for aromatic amines activated by *ortho* and/or *para* electron-withdrawing groups,[5] though this rearrangement has also been observed for non-activated and even deactivated organic amides on deprotonation by NaH in the presence of hmpa or dimethylformamide (dmf).[6] However, the rearrangement observed[4] was the first example involving an amine and a deactivated ring. It was suspected that the ethylmethoxy side-arms present in this amine played an important role in the reaction mechanism by 'solvating' the sodium cation and enhancing the nucleophilicity of the amine anion, which would be severely deactivated if the sodium cation was associated solely with the deprotonated nitrogen. Alternatively, the hmpa could completely solvate the sodium cation leaving a 'naked anion' which would be free to rearrange. In order to research further the requirements for this type of Smiles rearrangement, we investigated the reaction of the primary amine 2-phenoxyaniline with sodium hydride in the presence of the Lewis base *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien). Since the ligand 2-phenoxyaniline does not possess donor atom side-arms, if a Smiles rearrangement were to take place it would have to be *via* an ion-separated 'naked anion' route, with the sodium cation solvated by the pmdien Lewis base molecules.

Complex **1** was prepared by adding 1 equivalent of NaH to a hot toluene solution of 2-phenoxyaniline in the presence of two equivalents of pmdien.† After filtering, the pale orange solution was refrigerated at −20 °C for 24 h after which time colourless, highly air-sensitive, cubic crystals of **1** were isolated and characterised by X-ray diffraction‡ and spectroscopic techniques.

The solid-state structure of complex **1** (Fig. 1) reveals that the ligand has not undergone a Smiles rearrangement. Nonetheless the structure contains a number of unusual features. To our knowledge,§ complex **1** is the first structurally characterised sodium derivative of a primary amine. The structure is that of a ring dimer with each sodium five-co-ordinate and approximately trigonal bipyramidal. The core unit is an essentially symmetrical, planar Na_2N_2 ring typical of known sodium and lithium amide structures.[2,3] Each sodium cation is then chelated by a tridentate pmdien ligand, the conformation of which is unprecedented. Previous examples of pmdien-containing lithiated or sodiated organic complexes[9–11] possess pmdien chelating the alkali-metal cation in a 'tripod' fashion so that the three nitrogen atoms and the metal are not in the same plane. However, in **1** the nitrogen atoms [N(1), N(2) and N(3)] and the sodium cation [Na(1)] all lie approximately in the same plane

† Experimental data for **1**. Dry pmdien (2.1 cm^3, 10 mmol) was added to a stirred suspension of NaH (dry, 95%, 0.12 g, 5 mmol) and 2-phenoxyaniline (Aldrich, sublimed 45 °C, 0.926 g, 5 mmol) in dry toluene (14 cm^3). After a slight effervescence had subsided, the solution was stirred at 100 °C under dry N_2 for 1.5 h. The resulting pale orange solution was filtered; refrigeration at −20 °C for 24 h then yielded a crop of colourless, highly air-sensitive, cubic crystals of **1** (1.39 g, 73%, m.p. 117–119 °C, satisfactory C, H and N analyses); ^1H NMR (360 MHz, C_6D_6, 283 K): δ 1.83–1.97 {broad s, 11 H, $NMe[(CH_2)_2NMe_2]_2$}, 2.03 {s, 12 H, $NMe[(CH_2)_2NMe_2]_2$}, 3.08 (s, 1 H, $PhOC_6H_4NH$), 6.29 (t), 6.66 (dd), 6.82 (tt), 7.05–7.12 (m), 7.13 (t), 7.18(s), 7.21 (s, 9 H, all aryl H).

‡ Crystal data for **1**. 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$, $C_{21}H_{33}N_4ONa$, M = 380.5, monoclinic, space group $P2_1/n$, a = 10.858(2), b = 16.140(3), c = 12.739(3) Å, β = 98.04(3)°, U = 2210.5(8) $Å^3$, $F(000)$ = 824, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 0.088 mm^{-1}, T = 153(2) K, Z = 4, D_c = 1.143 Mg m^{-3}. Data were collected on a Stoe-Siemens diffractometer in the range 3.66 ≤ θ ≤ 22.5° (3030 reflections collected, 2884 independent reflections). The structure was solved by direct methods[7] and refinement, based on F^2, was by full-matrix least-squares techniques[8] (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions) to R_1 = 0.0540, wR_2 = 0.1140 for 1844 unique reflections [$I > 2\sigma(I)$], $w^{-1} = [\sigma^2F^2 + 0.0811P]$ where $P = [0 \text{ or } F_o^2 + 2F_c^2]/3$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

§ Search of the Cambridge Crystallographic Database.

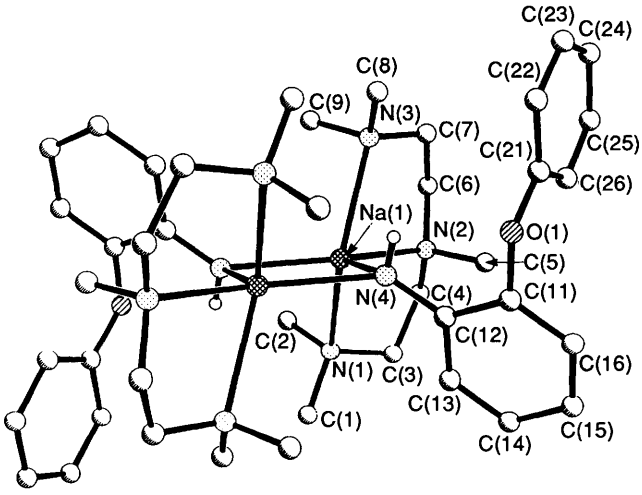

Fig. 1 Molecular structure of 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$ **1** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Na(1)–N(4) 2.419(3), Na(1)–N(4′) 2.428(3), Na(1)–N(2) 2.528(3), Na(1)–N(3) 2.574(3), Na(1)–N(1) 2.725(3), Na(1)–C(5) 3.114(4), Na(1)–Na(1′) 3.208(2), N(4)–Na(1)–N(4′) 97.12(9), Na(1)–N(4)–Na(1′) 82.88(9), C(5)–N(2)–Na(1) 99.0(2)

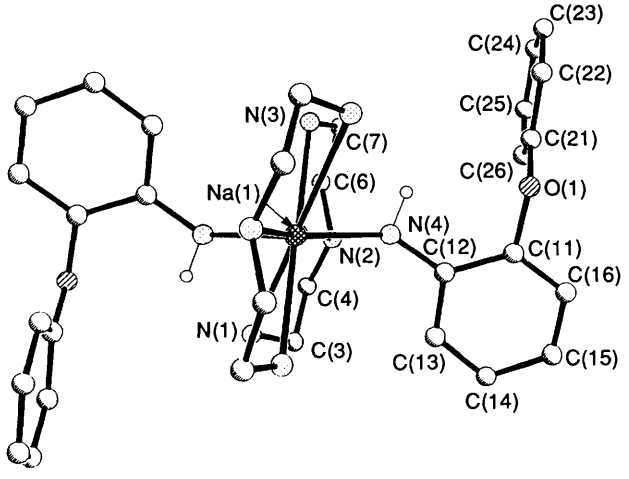

Fig. 2 Molecular structure of 2-$PhOC_6H_4NHNa{\cdot}NMe[(CH_2)_2NMe_2]_2$ **1** showing the planar nature of the pmdien ligands (hydrogen atoms and pmdien methyl groups omitted for clarity)

(Fig. 2) [angle between the two planes defined by Na(1), N(2), C(4), C(3) and N(1), and Na(1), N(2), C(6), C(7) and N(3) 156.4°]. Thus, complex **1** is the first example of an alkali-metal complex containing a 'planar' pmdien ligand. Although one of the sodium to pmdien bond lengths is significantly longer [Na(1)–N(1) 2.725(3) Å] than the other two [mean Na–N 2.551(3) Å], interactions of this distance are not unknown for sodium pmdien complexes.[10] The interactions between the sodium cation and the pmdien nitrogen centres are largely electrostatic, so the pmdien conformation is dictated largely by the steric and/or electronic requirements of the other constituents of the complex. This written, it is not clear what such requirements there might be. There are no obvious hydrogen bonds [*e.g.* between C(5)–H and O(1)] influencing the pmdien molecules to adopt their unusual geometry (Fig. 1). There is a short contact between Na^+ and C(5) of the pmdien; the distance [3.114(4) Å] is similar to others taken previously to reflect C · · · Na interactions of some significance.[11] This contact is accompanied by a small C(5)–N(2)–Na(1) angle of 99.0(2)°. However, it is not possible to determine whether such an interaction is a consequence of the planar conformation of the pmdien ligand, or is itself the cause of such planarity.

Returning to the subject of the Smiles rearrangement, it seems unlikely, given these latest results, that the rearrangement we described recently progresses *via* the 'naked anion' route.[4] It is far more probable that reactions of this type occur because of the nature of the ligand (in particular the presence of side-arm donors), rather than as a result of the reagents and conditions employed. We are currently investigating the reactions of similar ligands to 2-phenoxyaniline, in particular those with aryl rings activated by halogen substituents.

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