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A new approach to lithium–heavier alkali metal interchange reactions: synthesis of a tetralithium pentasodium mixed alkoxide–amide dome-shaped cage compound with an encapsulated hydroxide molecule †

Alan R. Kennedy, Jonathan G. MacLellan, Robert E. Mulvey * and Alan Robertson

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL.
E-mail: R.E.Mulvey@strath.ac.uk

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An investigation of metal–metal interchange reactions between alkali metal amides and alkali metal alkoxides, relevant to the area of 'superbases', has uncovered a novel adduct containing both components, which has been isolated from solution and crystallographically characterised. Formulated as $[Li_4Na_4(Bu^tO)_4\{PhN(H)\}_4(NaOH)(4\text{-Me-py})_4]$, this tetralithium pentasodium mixed alkoxide–amide can be synthesized either by reaction of lithium anilide with sodium *t*-butoxide or of sodium anilide with lithium *t*-butoxide, in the presence of the co-ordinating solvent 4-methylpyridine (4-Me-py). The single sodium hydroxide molecule in the formulation occurs adventitiously, but consistently. X-Ray crystallographic studies reveal a 17-vertex dome-shaped structure founded on a $(NaN)_4$ basal ring, above which lies a smaller $(LiO)_4$ ring then an apical Na atom: the OH^- ion occupies an internal position within the dome. Discussion focuses on the striking resemblance between this structure and that of the previously reported tetralithium pentapotassium mixed alkoxide–enolate $[Li_4K_4(Bu^tO)_4(C_6H_{11}O)_4(KOH)(THF)_5]$, and it is pointed out that the dominant factor in their common architectural design appears to be the encapsulated hydroxide molecule.

Introduction

The general equation (1) (M = Na or K) often quoted to

$$RLi + R'OM \longrightarrow RM + R'OLi \qquad (1)$$

represent the reaction of organolithium compounds with heavier alkali metal alkoxides[1] may appear trivial and unworthy of investigation in this modern era, but in reality it hides a minefield of complexity. Formally a metal–metal interchange reaction, this procedure has proved convenient in recent years as an entry to heavier alkali metal organics such as *n*-butylsodium[2] or *n*-butylpotassium[3] [eqn. (2)]. Purity is not usually a primary

$$Bu^nLi + Bu^tOM \longrightarrow Bu^nM + Bu^tOLi \qquad (2)$$

concern in such applications as often these congeners of commercially available *n*-butyllithium have been prepared unrefined for the sole purpose of providing a metallating source for generating crystalline sodium[4] or potassium amides[5] and related compounds for subsequent X-ray diffraction study. Interest in the products of reaction (1) initially revolved around their use as polymerisation catalysts;[6] but subsequently most attention has focused on their ability to function as exceptionally strong proton abstraction reagents in organic synthesis, earning them the title of 'superbases'.[7] The metal–metal interchange reaction is applicable not only to conventional carbon–lithium organics, but also to nitrogen–lithium or oxygen–lithium bonded analogues such as amides[8] or enolates.[9] Though thriving, superbase chemistry remains to a large extent a black art. This stems from the fact that the course of reaction (1) is sensitive to a combination of factors:[1] these include the natures of the R/R′ substituents; the identity of the heavier alkali metal M; the ability of reactants and/or products to form adducts with each other; the propensity of alkali metal compounds to autoaggregate; the relative solubility of each component compound; and the bulk reaction solvent. Therefore the precise composition of the superbasic mixture subsequently employed (usually *in situ*), for deprotonating the added organic substrate is generally not known with any certainty. Furthermore the recent explosion of crystal structure determinations in organolithium chemistry has not impacted at all in the superbase arena, besides a few specialised model systems with remotely relevant ligands,[10] so the structures of superbases, and linked to this their modes of reactivity, remain to be uncovered.

Our studies do not address superbases *per se*, but are more concerned with the wider context of the metal–metal interchange reaction and its potential for producing well defined, stoichiometric metallo-organic reagents. Our initial aim is to establish a greater degree of control over the nature of the products and to introduce design elements into their structures by the judicious use of templating seeds (atoms or small molecules) for promoting the orderly build up of new structural types, tempered with the use of Lewis bases for terminating growth and limiting molecular size to encourage good solubility characteristics. It is known that the addition of potassium salts (halides) can increase the efficiency of homometallic sodium amide–sodium alkoxide mixed bases,[11] so enhanced reactivity should be a realistic prospect here, but we want to take this concept a stage further by establishing a correlation between any such enhancement and the structural changes dictated by the templating seed. Herein we report on one of the early successes of this approach, albeit in this case the template (a single sodium hydroxide molecule) was not deliberately introduced, in the tetralithium pentasodium mixed alkoxide–amide $[Li_4Na_4(Bu^tO)_4\{PhN(H)\}_4(NaOH)(4\text{-Me-py})_4]$, **1**. The near isostructural relationship between the structure of **1** and that of the previously reported tetralithium pentapotassium mixed

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† Dedicated to Ron Snaith. R.E.M. remembers with affection and gratitude the many long discussions into the wee small hours on s-block chemistry with his close friend and mentor.

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alkoxide–enolate $[Li_4K_4(Bu^tO)_4(C_6H_{11}O)_4(KOH)(THF)_5]$,[12] **2** (compare Figs. 4 and 2), establishes an important link between amide chemistry and enolate chemistry and confirms that templation strategies can indeed be used to design and control molecular architectures derived from s-block metal–metal interchange reactions.

Results and discussion

Synthesis

Despite its odd looking composition, **1** is not a rogue one-off product but a genuine stoichiometric complex as reflected by its formation in different reaction mixtures. It can be produced from a lithium anilide–sodium *t*-butoxide mixture or alternatively from a sodium anilide–lithium *t*-butoxide mixture. In the former method [eqn. (3)] lithium anilide is generated *in situ*

$$LiN(H)Ph + NaOBu^t + 2(4\text{-Me-py}) \longrightarrow \mathbf{1} + 1/n\,[Li_6(Bu^tO)_4\{PhN(H)\}_2(4\text{-Me-py})_4] \quad (3)$$

by lithiation of the parent primary amine, then taken into solution by the addition of just over two molar equivalents of the Lewis base 4-methylpyridine (4-Me-py). This part of the reaction mixture has been studied separately[13] and found to deposit the crystalline solvate $[\{LiN(H)Ph(4\text{-Me-py})_2\}_2]$, which exists as a cisoid $[LiN(H)Ph]_2$ ring dimer having two donor ligands on each Li atom; in **1** the donor ligands bind to the Na atoms, thus implying that a transfer from Li to Na has taken place. Completing the reaction mixture by introducing sodium *t*-butoxide leads to the formation of a colourless crystalline product. An X-ray diffraction study of these crystals revealed co-crystallisation of two independent complexes, namely **1** and the hitherto unknown homometallic lithium compound $[Li_6(Bu^tO)_4\{PhN(H)\}_2(4\text{-Me-py})_4]$, **3**. However, unfortunately these data are not of a publishable quality, and attempts to reprepare **3** on its own by rational means have so far proved unsuccessful. No such co-crystallisation complications were encountered on preparing **1** by the latter method [eqn. (4)]. The

$$NaN(H)Ph + LiOBu^t + 2(4\text{-Me-py}) \longrightarrow \mathbf{1} \quad (4)$$

melting point of this pure sample (*ca.* 130 °C) was found to be significantly higher than that (104–106 °C) of the co-crystalline mixture. In view of the composition and structure of **1** (see below) it can be assumed that metal–metal interchange has not been reached during its formation: instead the reaction appears to stop at an intermediate stage giving a product which can be viewed as either a lithium *t*-butoxide–sodium anilide adduct or a sodium *t*-butoxide–lithium anilide adduct, depending on the preparative method employed. The key ingredient of **1** is undoubtedly the single NaOH molecule, which can be compared with the single KOH molecule residing in **2**. As was the case for the potassium system, the origin of the hydroxide ion in **1** is not known with any certainty, though adventitious moisture would seem to be the most likely culprit. Limited, sub-stoichiometric, quantities of moisture are probably needed to effect the templation; too much would almost certainly promote an alternative pathway leading to the precipitation of high lattice energy salts such as LiOH or $LiOH{\cdot}H_2O$. Hence it is perhaps understandable that, even when a standard anhydrous protocol (drying the relevant reagents and solvents over fresh molecular sieve) is followed, small yields of **1** still prevail. Though through X-ray crystallography the detection of such oxygen-based foreign ions in organometallic structures is becoming ever more prevalent (Snaith and co-workers reported a highly pertinent example in the novel cage-crossed ladder-cage architecture of $[(LiOBu^t)_{10}(LiOH)_6]$,[14] which they attributed to partial hydrolysis of the homometallic alkoxide), in general the chemistry involved in their formation is unplanned and unpredictable, and, as yet, not well understood. The complex nature of the chemistry is illustrated by the observation that two closely related mixed lithium–heavier alkali metal *t*-butoxides $[Li_6K_2(Bu^tO)_8(Li_2O)(TMEDA)_2]$[15] and $[Li_5Rb_4(Bu^tO)_9(Li_2O_2)(TMEDA)_2]$[16] each have different foreign ions (oxide and peroxide respectively) and Li : M stoichiometries (8 : 2 and 7 : 4 respectively) which, in turn, differ from those in **1** (hydroxide and 4 : 5 respectively), yet all three compounds were prepared using the same inert-atmosphere protocol.

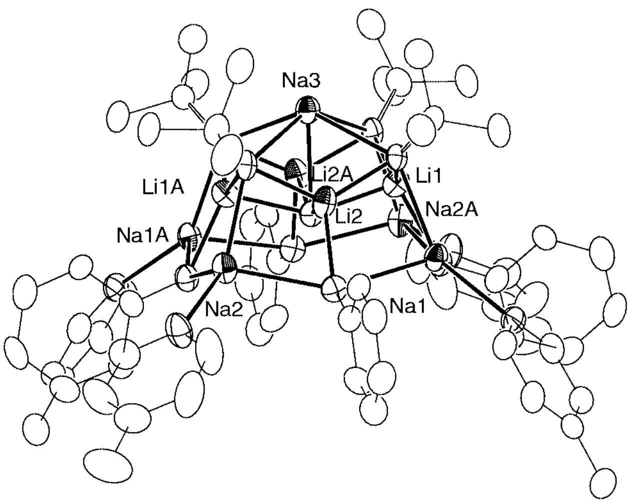

Fig. 1 Molecular structure of compound **1** showing the metal atom labelling scheme. Hydrogen atoms are omitted for clarity.

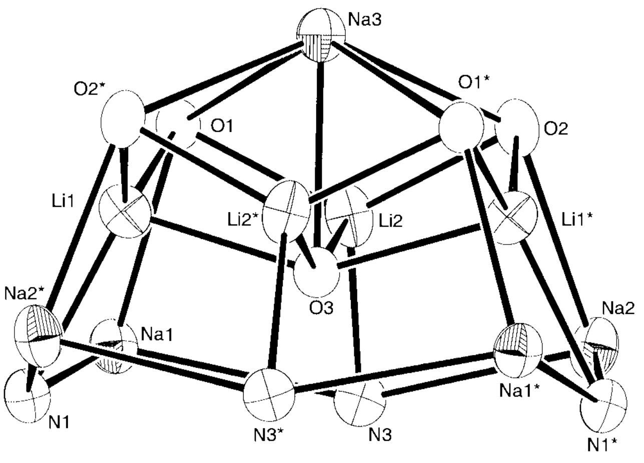

Fig. 2 The 17-vertex $Li_4Na_5N_4O_4$ dome-shaped core of compound **1** and its OH^- occupant. The hydrogen atom is omitted.

Molecular structure

X-Ray crystallographic studies have been used to elucidate the molecular structure (Fig. 1) of the pure form of **1**. Stripping away the organic scaffolding, its 17-vertex $Li_4Na_5N_4O_4$ shell (Fig. 2) clearly resembles a dome having a sodium apex and a puckered $[NaN(H)Ph]_4$ basal ring, which are separated by a smaller puckered $(LiO)_4$ ring. The unique OH^- ion occupies an internal position within the dome (below the Li_4 plane), while the 4-Me-py ligands occupy an external position (bound terminally to Na atoms in the base). Viewing from the base upwards, the dome is constructed from a series of homonuclear planes made up of four N, four Na, four Li and four O atoms (RMS deviation from planarity 0.016, 0.032, 0.003 and 0.012 Å respectively). This view is in Fig. 3, which also clearly shows the connectivities within the dome. A crystallographic twofold rotation axis runs through the Na(3)–O(3) bond of the NaOH 'molecule'. Its apical placement gives Na(3) an unusual lopsided co-ordination sphere with one side occupied by bonds to the unique OH [O(3)] and four OBu^t atoms [O(1), O(2) and

Table 1 Selected bond lengths (Å) for compound **1**

Na1–O1	2.408(3)	Li1–O1	1.929(7)
Na1–N1	2.481(4)	Li1–O2*	1.922(7)
Na1–N2	2.418(4)	Li1–O3	2.018(7)
Na1–N3	2.507(4)	Li1–N1	2.078(8)
Na2–O2	2.396(4)	Li2–O1	1.927(8)
Na2–N1*	2.516(4)	Li2–O2	1.934(8)
Na2–N3	2.481(4)	Li2–O3	2.011(6)
Na2–N4	2.395(4)	Li2–N3	2.040(9)
Na3–O1	2.553(3)		
Na3–O2	2.560(3)		
Na3–O3	2.349(5)		

* $-1 - x, y, 1.5 - z$.

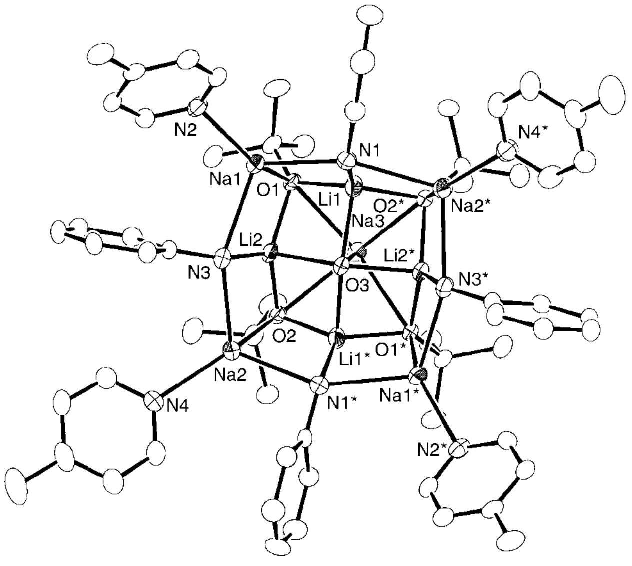

Fig. 3 Alternative view of compound **1** showing the principal atom labelling scheme. Hydrogen atoms are omitted for clarity.

their symmetry partners], while the other side has no bonding atoms. This situation can be explained by the encroachment of bulky *t*-butyl groups into the 'void' above Na(3). Table 1 lists selected bond lengths. The strength of the Na(3)–O(3)H bond is reflected by its shortness [2.349(5) Å] relative to that of the Na(3)–O(Bu^t) bonds (mean, 2.557 Å). This gives credence to the idea that the NaOH molecule acts as the templation source for the dome structure. Conversely, the Li atoms make closer contacts with the latter O atoms (mean length, 1.928 Å) than with the former one (mean length, 2.015 Å). The lithium co-ordination spheres comprise 1 *O*H, 2 *O*Bu^t and 1 *N*(Ph)H atoms, and the mean Li–N bond length is 2.059 Å. A different combination of atoms [1 *O*Bu^t, 2 *N*(Ph)H, 1 *N*C$_5$H$_4$Me] makes up the four-co-ordinate environments of the basal Na atoms. The Na–OBu^t bonds connecting the basal ring to the central ring are significantly shorter (mean length, 2.402 Å) than the corresponding ones connecting apical Na(3) to the central ring, in line with the higher co-ordination number (five) of the latter atom. The relative lengths of the Na–N bonds are strongly influenced by the mode of bonding of the ligand: those involving the μ_3-N atoms of the anilido anions are decidedly longer than those involving the terminally attached N atoms of the neutral 4-Me-py molecules (mean lengths, 2.496 and 2.407 Å respectively). Given their near orthogonal orientation to the anilide ligand plane, the long Na–N bonds appear to have considerable π (N p) character, whereas the near coplanarity of the Li–N bonds to the said plane implies substantially more σ (N sp^2) character. Note also that the orientation of the anilide ligand plane implies that the N–*H* atoms point downwards toward the more open uncapped base of the metal square antiprism. Both types of O atom adopt a high bridging mode: μ_4 for the OBu^t ligands and μ_5 for the sterically less demanding OH ligand. Turning to the bond angles, the puckered nature of the (NaN)$_4$ basal ring (RMS deviation from planarity, 0.269 Å) can be gauged from the sum of its bond angles (1020.28 *cf.* 1080° for a perfect octagon). To establish the bridge to the Na atoms the bond angle at the N atoms must open wide to a mean value of 147.0°, whereas the Na atoms do not deviate to any significant extent from a tetrahedral geometry [mean N–Na–N angle within ring, 108.1°]. Belonging to the middle section of the dome and linking the apex to the base, the (LiO)$_4$ ring shows a greater degree of puckering (sum of bond angles, 853.2°; RMS deviation from planarity, 0.443 Å). Largely as a consequence of keeping the bulky *t*-butyl groups apart, the mean bond angle within the ring at Li is large at 123.2°; the corresponding value at O is 90.2°. The geometrical strain on the Li 'linking' atoms is evident from the absence of any individual bond angles near to the perfect tetrahedral value of 109.5° (observed angles come in two ranges: 90.2–100.4 and 117.3–123.4°), though the mean value lies close to such at 106.8°. Disregarding the H atom, the co-ordination sphere around O(3) is best described as distorted square pyramidal with the distortion arising from the said atom being buried beneath the Li$_4$ plane [mean Na(3)–O(3)–Li bond angle, 73.4°]. The mean Li–O(3)–Li bond angles are 85.3 and 146.8° for *cis* and *trans* positioned Li atoms respectively. Completing the dome, the apical Na(3) atom can also be described, in approximate terms, as having a distorted square pyramidal geometry. In this case with Na(3) sitting 0.886(3) Å above the best RMS O$_4$ plane [*cf.* 0.576(7) Å for O(3) sitting below the best RMS Li$_4$ plane] the distortion is more pronounced with mean O(3)–Na(3)–O, O–Na(3)–O (*cis*) and O–Na(3)–O (*trans*) bond angles of 69.7, 83.1 and 139.4° respectively.

Comparison with the structure of compound 2 and related structures

As alluded to in the Introduction, there is a close resemblance between the structure of compound **1** and that of the tetralithium pentapotassium mixed alkoxide–enolate **2**. Adhering to the description used for **1**, the structure of **2** (Fig. 4) can be described as a dome having a potassium apex and a puckered [KO(enolate)]$_4$ basal ring, which are separated by a smaller puckered [LiO(alkoxide)]$_4$ ring (note that the metal arrangements in **1** and **2** define monocapped square antiprisms in which the basal sites are splayed out, reflecting the greater sizes of the metal atoms therein). The unique OH$^-$ ion occupies an internal position within the dome (below the Li$_4$ plane), while THF ligands occupy external positions (bound terminally to K atoms in the base). Hence the K atoms, O(enolate) atoms and THF molecules take the place of the Na atoms, N(anilido) atoms and 4-Me-py molecules, respectively, in **1**, while the Li and O(alkoxide) atoms are common to both structures. This capacity for isomorphous replacement is not unreasonable given the ionic (salt-like) nature of the dome shell. The connectivity pattern within the dome of **2** is identical to that in **1** in all but one aspect: the site above the apical K atom is occupied by a THF molecule, creating one extra K–O bond, whereas the corresponding site above the Na atom in **1** is unoccupied as previously mentioned. This distinction is purely steric in origin with K offering a wider co-ordination arc to an incoming solvent molecule than Na, even though solvation energies are generally smaller for the former alkali metal. Turning to dimensions, those in **2** which can directly be compared with those in **1** show close agreement: the mean Li–O bond length (involving 2 alkoxide and 1 enolate ligand) is 1.94 Å (*cf.* 1.928 Å for the exclusively alkoxide bonded Li in **1**); the mean Li–O(H) bond length is 2.09 Å (*cf.* 2.015 Å for **1**). The aforementioned structure of [(LiOBu^t)$_{10}$-(LiOH)$_6$][14] exhibits a rich variety of Li–O(Bu^t) and Li–O(H) bond lengths (ranges: 1.837–2.022 and 1.905–2.345 Å, respectively) reflecting the diversity of co-ordination numbers

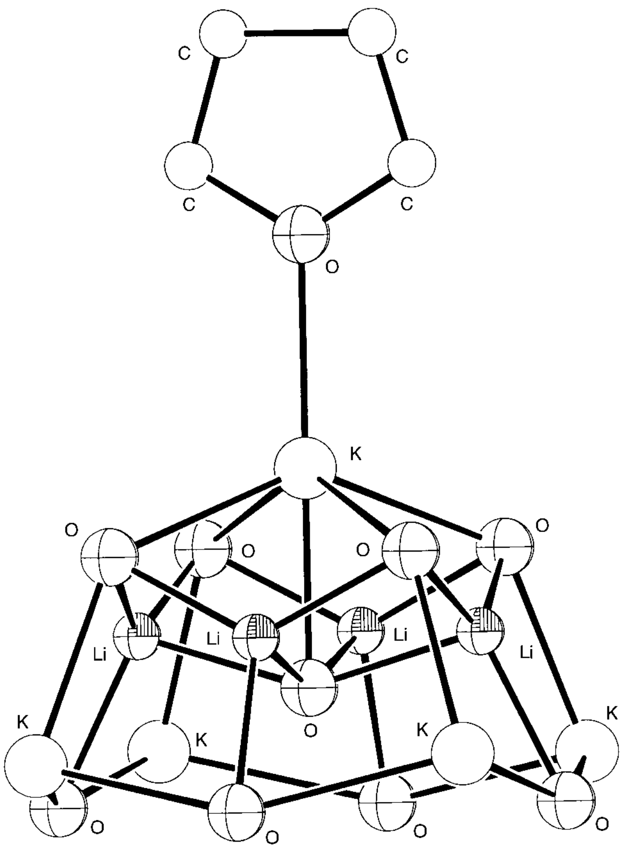

Fig. 4 Idealised depiction of the dome-shaped core arrangement of compound **2** showing the capping THF molecule.

involved: the corresponding bond lengths in **1** fall within these ranges.

The key role that the NaOH and KOH molecules play in directing the dome-shaped structure of compounds **1** and **2** respectively can be inferred indirectly from a comparison with the structure of the trimetallic complex [{LiNaK(Bu^{t}O)[PhN(H)]$_2$(TMEDA)$_2$}$_2$].[17] Despite the fact that the latter heteroalkali metal complex also contains a mixture of anilide and *t*-butoxide ligands, the absence of a molecular template leads to a fundamentally different structure: in contrast to the high aggregation observed in **1** and **2**, this structure originates from the fusing of three (metal–heteroatom)$_2$ dinuclear rings, with the central (KO)$_2$ one capped on either face by the Li atom of a mixed-metal (LiNNaN) ring, the Na atoms of which carry additional didentate TMEDA molecules. It is also significant that a tetrameric (NaN)$_4$ ring forms part of the dome of **1**, for there has been no previous example of a sodium amide structure based on a discrete (NaN)$_4$ ring system [though trimeric analogues such as (NaTMP)$_3$[18] are known (TMP = 2,2,6,6-tetramethylpiperidine)]. Made possible by the support of the adjacent (LiO)$_4$ ring, the presence of the (NaN)$_4$ ring can also be attributed to the involvement of the templating NaOH molecule. The μ_3-bonding mode of the anilide ligands here (again, indirectly occurring as a result of templation) contrasts with their μ role in the simple complexed dimer [{NaN(H)Ph(PMDETA)}$_2$] (PMDETA = *N*,*N*,*N*′,*N*″, *N*″-pentamethyldiethylenetriamine),[19] but this does not have a marked effect on Na–N bond lengths (mean value, 2.417 Å; *cf.* 2.496 Å in **1**).

Future work will be directed towards deliberately 'contaminating' metal–metal interchange reactions with small polar molecules in order to induce similar templation effects.

Experimental

Syntheses and characterisation

Anhydrous, oxygen-free argon gas was employed throughout as the inert atmosphere both for the reactions carried out in conventional Schlenk-ware and for the glove box where products were isolated and stored. Purchased from Aldrich, *n*-butyllithium was re-standardised by the diphenylacetic acid reagent-indicator method[20] immediately prior to use. Solid *n*-butylsodium was prepared in crude form by the literature method[3] from the lithium congener and sodium *t*-butoxide. This alkoxide and lithium *t*-butoxide were also purchased from Aldrich and used without further purification. The bulk solvent hexane was distilled over sodium–benzophenone and dried over molecular sieve; 4-methylpyridine was also dried over molecular sieve.

Impure 1. To a chilled solution of Bu^{n}Li (5 mmol) in hexane was delivered one molar equivalent of aniline (0.45 ml), to produce a white precipitate. This precipitate was finely divided by immersing the mixture in an ultrasonic bath for 5 minutes. Complete dissolution of the resulting slurry was achieved by adding 4-methylpyridine (1.07 ml, 11 mmol). Sodium *t*-butoxide (5 mmol) was then introduced to produce a transparent brown solution, which was subsequently cooled to *ca.* −30 °C. After one week this solution afforded a crop of small colourless crystals. An X-ray diffraction examination established these to be mixed crystals, comprising both compound **1** and [Li$_6$(Bu^{t}O)$_4${PhN(H)}$_2$(4-Me-py)$_4$] in a 1 : 1 ratio. Yield 0.45 g, 26%, mp 104-106 °C (found C, 66.9; H, 6.3; Li, 3.1; N, 9.5; Na, 6.1. $C_{116}H_{165}Li_{10}N_{14}Na_5O_9$ requires C, 66.9; H, 7.9; Li, 3.4; N, 9.4; Na, 5.5; O, 6.9%).

Pure 1. One molar equivalent of aniline (0.91 ml) was added to a suspension of Bu^{n}Na (0.96 g, 10 mmol) in hexane (5 ml). Large lumps of a pale yellow/cream precipitate formed following a quick but highly exothermic reaction involving the evolution of butane. To this mixture was added, in order, lithium *t*-butoxide (0.80 g, 10 mmol) and the donor solvent 4-methylpyridine (1.95 ml, 20 mmol), resulting in a red solution with a small amount of solid. Heating the mixture gently for a few minutes achieved complete dissolution. Allowing the solution to cool slowly to ambient temperature afforded a crop of colourless crystalline compound **1**. Yield 1.42 g, 60%, mp 130 °C (found C, 62.3; H, 7.1; Li, 2.3; N, 9.0; Na, 8.4. $C_{64}H_{89}Li_4N_8Na_5O_5$ requires C 64.4; H, 7.5; Li, 2.3; N, 9.4; Na, 9.6; O, 8.9%). ^{1}H NMR (400.13 MHz in [^{2}H$_6$]-DMSO, 300 K): δ 8.41 (d, 2 H, αH of py), 7.20 (d, 2 H, βH of py), 6.99 (t, 2H, *meta*-H of Ph), 6.54 (d, 2H, *ortho*-H of Ph), 6.47 (t, 1H, *para*-H of Ph), and 1.11 (overlapping s, 12H, Bu^t + Me-py); (in [^{2}H$_6$]benzene, 300 K) δ 8.05 (m, 2H, αH of py), 7.09 (br, Ph), 6.51 (m, 2H, βH of py), 6.41 (br, Ph), 2.69 (br s, 1H, NH), 1.69 (s, 3H, Me-py), 1.47 (s, 9H, Bu^t) and −1.20 (br s, 0.25H, OH).

Crystal structure determination

Colourless crystals of compound **1** grown from solution were mounted directly into the cold stream of a Rigaku AFC7S diffractometer using an oil drop method.

Crystal data. $C_{64}H_{89}Li_4N_8Na_5O_5$, $M = 1193.14$, monoclinic, space group $C2/c$, $a = 28.808(9)$, $b = 9.246(4)$, $c = 29.477(9)$ Å, $\beta = 115.87(2)°$, $U = 7065(4)$ Å^3, $T = 123$ K, $Z = 4$, μ(Mo-Kα) = 0.096 mm^{-1}, 5683 measured reflections, 5559 unique ($R_{int} = 0.0622$). The crystal (and others measured) were poorly diffracting. Final refinement to convergence[21] on F^2 gave $R_1 = 0.0810$ for 3608 observed reflections with $I > 2\sigma(I)$ and $wR2 = 0.2335$ for all reflections. All non-hydrogen atoms were treated anisotropically and all hydrogen atoms bonded to carbon placed in calculated positions. Hydrogen atoms bonded to oxygen or nitrogen were placed as found in difference syntheses and then allowed to ride on their parent atoms.

CCDC reference number 186/2207.

See http://www.rsc.org/suppdata/dt/b0/b006990f/ for crystallographic files in .cif format.

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