Monometallation of a Di(aminoaryl) Ether induces a Smiles Rearrangement leading to a Sodium Aryloxide Complex: the Synthesis and Crystal Structure of $[(MeOCH_2CH_2)(C_6H_4NHCH_2CH_2OMe)NC_6H_4O{\cdot}Na]_2$

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The title compound was synthesised by 1 : 1 reaction of sodium hydride with a di(aminoaryl) ether ligand in toluene–hexamethylphosphoramide (HMPA) solution; X-ray crystallography revealed that an *in situ* Smiles rearrangement of the ligand had taken place to give a dimeric aryloxide sodium complex, which is in stark contrast to previous results obtained by 2 : 1 reaction of Bu^nLi with the ligand in the absence of HMPA.

Some of the most common reagents utilized by organic chemists are alkali metal bases such as amides and alkoxides.[1] Until recently, however, structural knowledge of such reagents has largely been limited to simple complexes. Structural characterisations, both in the solid state and in solution, have concentrated on metallated derivatives of monobasic amines and alcohols.[2] In extending this knowledge to include alkali metal complexes of a more diverse range of organic acids, we have become interested in the lithiation of azacrowns and related ligands. We have recently reported the first lithiation of an azacrown[3] and the dilithiation (in the absence of additional Lewis base donor) of the ligand bis[2-(2-methoxyethylamino)phenyl] ether [Fig. 1(*a*)]. The dilithiation of the latter, an acyclic diamine related to 15-crown-5, provides a dimeric complex containing an unprecedented $Li_4N_4O_2$ 'adamantanoid' metal core [Fig. 1(*b*)].[4] We report here the dramatically different results obtained on monometallation of the same ligand with sodium hydride in toluene solution in the presence of a Lewis base donor [in this instance HMPA, $O{=}P(NMe_2)_3$ (hexamethylphosphoramide)]. Such a reaction affords the title complex $[(MeOCH_2CH_2)(C_6H_4NHCH_2CH_2OMe)NC_6H_4O{\cdot}Na]_2$ **1**.

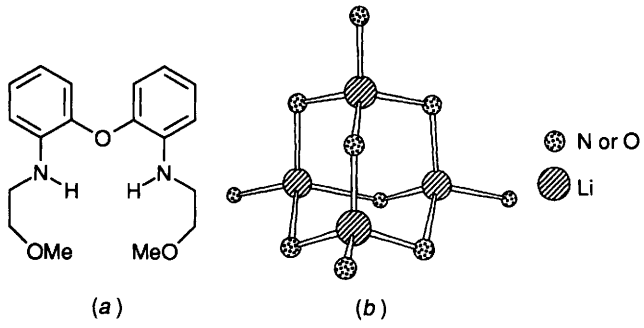


Fig. 1 (*a*) The ligand, bis[2-(2-methoxyethylamino)phenyl] ether; (*b*) the 'adamantanoid' core resulting from dilithiation of the ligand shown in (*a*)[4]

The addition of two equivalents of HMPA to a suspension of one equivalent of NaH in a hot toluene solution of the ligand caused vigorous gas evolution. After filtering off a slight excess of NaH, the brown solution yielded a crop of colourless, cubic crystals of **1** on refrigeration. Characterisation† of **1** showed that it is a monosodiated complex, not containing HMPA in spite of its presence in the reaction solution. Although unusual, such non participation of a strong Lewis base donor such as HMPA in an alkali metal complex is not unprecedented.[3]

X-Ray structure analysis‡ of **1** revealed an unpredicted twist. Instead of obtaining the expected sodium amide complex, the ligand had undergone an intramolecular rearrangement resulting in the formation of the dimeric aryloxide complex **1**, the first dimeric sodium aryloxide without external donor coordination (Fig. 2). The structure is that of a ring dimer with each Na five coordinate and approximately square pyramidal. The central Na_2O_2 ring is unsymmetrical but essentially planar [Na(1)–O(1) 227, Na(1)–O(1a) 221 pm; Na(1)–O(1)–Na(1a) 91.1 and O(1)–Na(1)–O(1a) 88.9°]. Each ligand then additionally uses the tertiary amine *ortho* to the phenoxide [N(1)] and its related ethylmethoxy side-arm [O(2)] to chelate the Na in a bidentate fashion [Na(1)–N(1) 266, Na(1)–O(2) 232 pm]. The square pyramid is rendered complete by the second methoxy group of the other ligand bridging across the dimer to Na [Na(1)–O(3a)] 236 pm] Of all the electronegative centres within the ligand only N(2)(H) (which remains protonated in the complex) is not involved in coordination to Na. Its lone pair therefore interacts with the aryl π system rendering N(2) near planar; this is in contrast to N(1), which is approximately tetrahedral owing to its coordination to Na(1). To our knowledge,[5] only three other structures of simple sodium aryloxides exist. The structures of two sodium derivatives of similar Schiffs bases are Na_4O_4 cubanes;[6] 2,4,6-tris(trifluoromethyl)phenoxy sodium is the only previously known dimeric example.[7] The central Na_2O_2 ring in the latter is, as in **1**, unsymmetrical [Na–O(1) 230, Na–O(1a) 223 pm] and the tetrahedral coordination of each Na is completed by two tetrahydrofuran (THF) ligands. In this case, further association has been prevented by the steric bulk of the phenoxide ligand used, whereas in **1** further association in order to satisfy the coordinative requirement of sodium is not necessary because of the sufficiency of internal donation sites within the ligand. The cubane structure of a metallated, multifunctional carboxylic acid in which a phenolic oxygen of one ligand coordinates another sodium in the cubane provides the closest analogue of one unusual feature observed in **1**, namely that of one arm of the ligand bridging across the dimer and coordinating to the opposite sodium.[8]

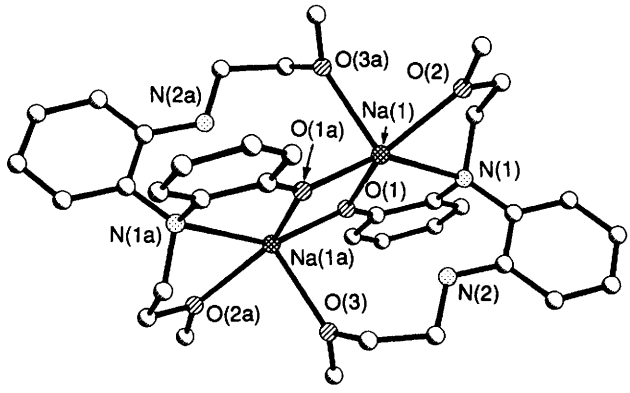
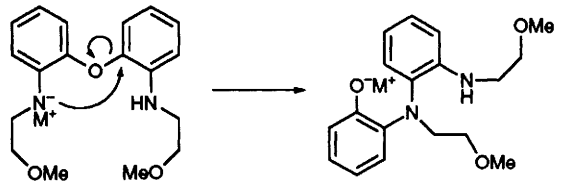


Fig. 2 Molecular structure of $[(MeOCH_2CH_2)(C_6H_4NHCH_2CH_2OMe)NC_6H_4O{\cdot}Na]_2$ **1**



Scheme 1

The rearrangement (Scheme 1) of the original ligand, once metallated, to give the anionic ligand observed in **1** is an intramolecular S_NAr reaction of the type known as a Smiles rearrangement.[9] Although displacements of aryloxide by aniline functionalities have been observed previously in diaryl ethers, such rearrangements are generally favoured when activiation of the ring is provided by electron-withdrawing *ortho* and/or *para* substituents such as nitro groups or halogen atoms. The use of NaH in the presence of HMPA or dimethylformamide (DMF), supposedly able to provide a 'naked anion', has been reported[10] to facilitate the Smiles rearrangement in non-activated and even deactivated systems, particularly when the anion is derived from an amide. The rearrangement reported here appears to be the first example of a Smiles rearrangement involving an amine and a deactivated aromatic system. More importantly, it is the first such rearrangement in which the metal–ligand complex (usually not isolated and assumed to be present only as an intermediate prior to quenching) has been isolated and characterised. As

† *Experimental data* for **1**. A suspension of NaH (dry, 95%, 51 mg, 2.0 mmol) in a dry toluene solution (4.5 ml) of bis[2-(2-methoxyethylamino)phenyl] ether (632 mg, 2.0 mmol) was stirred at 80 °C under dry nitrogen for 1 h. Addition of HMPA (0.7 ml, 4.0 mmol) caused vigorous reaction and, after stirring for a further hour at 80 °C, near complete dissolution was achieved. The red-brown solution was filtered hot; refrigeration at −5 °C for 48 h then yielded a crop of colourless, cubic crystals (0.23 g, 35%, m.p. 215–217 °C, satisfactory C, H, and N analyses); ^{1}H NMR (250 MHz, CD_3SOCD_3, 293 K, $SiMe_4$): δ 3.05 (q, 2H, $NHCH_2CH_2$), 3.18 (s, 3H, OMe), 3.22 (s, 3H, OMe), 3.3–3.5 (m, 6H, 3 × CH_2), 5.87 (t), 6.26 (d), 6.40 (d), 6.49 (t), 6.60 (d), 6.79 (t), 6.92 (t), 7.13 (d) (8 × 1H, ArH).

‡ *Crystal data* for **1**: $C_{18}H_{23}O_3Na$, M = 676.74, monoclinic, space group $C2/c$, a = 13.565(2), b = 13.907(2), c = 18.875(4) Å, β = 108.927(12)°, V = 3368.3(10) Å^3, Z = 4, D_c = 1335 mg cm^{-3}, $F(000)$ = 1440, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.113 mm^{-1}, T = 153.0(20) K. Data were collected on a Stoe-Siemens diffractometer in the range 8° ≤ 2θ ≤ 53° (4575 reflections collected, 3334 independent reflections). The structure was solved by direct methods[12] and refinement, based on F^2, was by full-matrix least-squares techniques[13] (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions) to $R1$ = 0.0422, $wR2$ = 0.0969 for 2264 unique reflections [$F > 4\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

such, it highlights the potential of utilising this and other base-promoted rearrangements in the synthesis of novel early main group metal complexes. Recent publications demonstrate that rearrangement of, and even extrusion from, acidic ligands during formation of such complexes is becoming an increasingly significant phenomenon.[11]

In our previous work,[4] reaction of the same ligand [Fig. 1(*b*)] with two equivalents of Bu^{n}Li in the absence of any Lewis base donor resulted in quite different behaviour, the ligand being dimetallated without undergoing rearrangement. We have investigated the conditions needed to promote the Smiles rearrangement. Salient findings are: (*i*) addition of two equivalents of Bu^{n}Li to the ligand, even in the presence of HMPA, does not cause rearrangement. Clearly, the dianion is not susceptible to nucleophilic substitution, presumably owing to extreme deactivation of the aromatic rings; (*ii*) monometallation with Bu^{n}Li solution or a suspension of NaH solid in toluene (as in this report), in the presence of HMPA in each case, effects complete ligand rearrangement within 24 h at 80 °C (reaction monitored by TLC); (*iii*) attempted monometallations by the same reagents as in (*ii*) but in the absence of HMPA fail. There is no reaction at all with solid NaH, and with Bu^{n}Li the low-yield product is the dimetallated 'adamantanoid' complex containing the unrearranged ligand [Fig. 1(*b*)]; (*iv*) if one equivalent of a soluble sodium reagent is used [NaN(SiMe$_3$)$_2$, sodium bis(trimethylsilyl)amide] then, even in the absence of HMPA, complete rearrangement of the ligand occurs; and (*v*) use of the corresponding soluble lithium amide reagent, also without HMPA, does not cause rearrangement, or at least no quantifiable rearrangement occurs over the same time scale. However, if HMPA is added, the rearrangement occurs rapidly.

Taken together, these observations imply that the Smiles rearrangement of this ligand can only proceed *via* monometallation and also that a strong complexant such as HMPA is always required in order for Li to effect rearrangement. In contrast to this, HMPA is only required in the case of an insoluble Na reagent (possibly to solubilise the reagent at the solid–solution interface). When a toluene-soluble reagent is used Na effects rearrangement in the absence of HMPA.

We thank Professor G. M. Sheldrick and Dr D. Stalke (University of Göttingen) for the use of X-ray facilities for the determination of the structure of **1**. This work was supported by the UK SERC (O. K., R. S. and J. F. S.) and Associated Octel Company Ltd. (CASE Studentships for M. G. D. and I. C-H.), Queens' College, Cambridge and the Associated Octel Company Ltd (Research Fellowship for F. S. M.) and St John's College, Cambridge (Research Fellowship for M. G. D.).

Received, 4th May 1993; Com. 3/02528D

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