Lithiation and Dethiacarbonylation of a Heterocyclic Thioamide C6H4O-C(=S)NH by Reaction with Solid Li2S in the Presence of Hexamethylphosphoramide: Synthesis and Crystal Structure of [C6H4O-C(=S)NLi-HMPA]2-C6H4(OH)NH2

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Solid Li2S reacts with a solution of C6H4O-C(=S)NH and hexamethylphosphoramide (HMPA) in toluene to give [C6H4O-C(=S)NLi-HMPA]2-C6H4(OH)NH2, in which two equivalents of the organic acid have been lithiated while a third equivalent has been stripped of its C=S group and di-protonated; structurally, complex 1, which can also be prepared directly by reacting BuLi, C6H4O-C(=S)NH (OXSH) (7.5 mmol) and HMPA (5.0 mmol) in toluene (10 cm3). At this stage the mixture was brown and had a strong smell of H2S. Heating of the mixture at 80°C for 12 h caused gradual dissolution of the solid, giving a brown solution. Refrigeration resulted in a crop of pale golden-brown cubic crystals of [C6H4O-C(=S)NLi-HMPA]2-C6H4(OH)NH2, 1, in which two equivalents of the organic acid have been lithiated and di-protonated; structurally, complex 1, which can also be prepared directly by reacting BuLi, C6H4O-C(=S)NH (OXSH) (7.5 mmol) and HMPA (5.0 mmol) in toluene (10 cm3).

The solid-state structure of 1 (Fig. 1) was determined by X-ray diffraction. The crystal structure of 1 crystallizes in the monoclinic space group C2/c, a = 11.256(2), b = 46.214(16), c = 15.041(3) Å, β = 91.711(2)°, V = 873.89 Å3, Z = 4, Dc = 1.256 Mg m−3, F(000) = 1856, λ(Mo-Kα) = 0.71073 Å. The correct stoichiometry of the product as (OXSLi-HMPA)2-H2S, the reaction was repeated using the correct stoichiometry.

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whereas one H of the NH2 group points downwards, normally they chelate just one Li+ centre, anions are not bonded to the Li centres. However, whilst in two HMPA ligands [Li(1)-O(3), 1.937(6); Li(2)-O(4), 1.968(6)Å cf. 1.946(7) and 1.978(8) Å in the aqua complex]; such a μ2-mode is quite common for dimeric lithium-HMPA complexes. Each Li+ is bonded terminally to an N atom of an OxS- anion, coordination of a bridging bifunctional NH2C6H4OH molecule. This results in the displaced towards the (OxSLi.HMPA)2 core. Thus, in order to engage molecularly, e.g. as in the linked tetramer (MeL&-to lithiation. Usually, bifunctional donors (notably TMDA) are deliberately chosen to lack acidic protons, and moreover the ligand itself is also unusual in being one susceptible to act as a neutral ligand (which might, however, be metallated subsequently). A second point of interest concerns the actual mechanics of the synthesis of 1. We have established that OsH2 hydrolysed in toluene, with or without HMPA, does not rearrange to give NH2C6H4OH. Neither does bubbling H2S gas through a solution of OsH2 and HMPA afford this ligand. Thus, it seems that the reaction giving 1 is concerned intimately with the presence of lithium. A tempting scenario has Li2S reacting with OsH2/HMPA to give the core of 1, (OxSLi-HMPA)2, and H2S. However, instead of then acting as a ligand (as envisaged originally), the in situ generated H2S (or SH-) reacts instead with a third equivalent of OsH2, as outlined in Scheme 1. The energetics of such a process are at least feasible. Our ab initio MO calculations§ show that the summed absolute energies of the ‘products’ (NH2C6H4OH + CS2) amount to 14.4 kcal mol−1 (1 cal = 4.184 J) less than those of the ‘reactants’ (OsH2 + Li2S). Entropy changes are presumably minimal. Experimentally, it is noticeable that solid Li2S in air smells strongly of H2S (presumably owing to reaction with atmospheric moisture) and addition of Li2S under dry nitrogen to a toluene solution of the acid OsH2 and of HMPA generates this gas also (along with gaseous CS2 on heating the mixture).

The results described promise several synthetic extensions. On the organic front, we are investigating the potential of solids Li2S and Li2O to remove, under the mild conditions described, various >C=X units from various heterocycles, e.g. >C=S with Li2S to eliminate CS2 (as for 1), >C=O with Li2O to eliminate CO2, and >C=N with either to eliminate R=NH2 or >C=N-R=NR2 etc., or combinations thereof. The reactivities of such ligands ‘on site’ (including metallation) are also being explored.

§ The ab initio calculations were performed at the MP2 level† by means of the computer program GAUSSIAN 90® using the 6-31G(d) basis set. The absolute energies (in a.u.) calculated for the optimised structures were: NH2C6H4O− = −361.595538 and CS2 = −833.2078060 (sum, −1194.4013440), and NH2C6H4O− (=S)NH(OsH2) = −795.5903676 and H2S = −398.7880757 (sum, −1194.3784433).

Fig. 1 The molecular structure of [C6H4O−C(=S)H Li-HMPA]−-NH2C6H4OH. Except for those of the NH2 and OH groups, hydrogen atoms have been omitted for the sake of clarity.

![Scheme 1](image-url)
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