Trimeric Dibenzylamidolithium and its Dimeric Diethyl Ether and Hexamethylphosphoramide Complexes: Structural and Theoretical Studies of Reactive Organonitrogen–Lithium Oligomers

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The coloured, crystalline title compounds have properties likely to make them synthetically useful reagents, while their isolation and structural characterisation, with the aid of *X*-ray crystallography and MO calculations, allows predictive rules to be put forward for the probable structures and reactivities of other organonitrogen–lithium species.

We describe the preparation, properties, and structures of crystalline trimeric dibenzylamidolithium, $[(PhCH_2)_2NLi]_3$, (**1**), and its dimeric diethyl ether and hexamethylphosphoramide (HMPA) complexes, $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$, (**2**), and $[(PhCH_2)_2NLi{\cdot}O{=}P(NMe_2)_3]_2$, (**3**). Such lithium derivatives of secondary amines, $(RR'NLi)_n$, are used to prepare amides of other metals[1] and, increasingly,[2] as alternatives to more common (but more nucleophilic) organolithium compounds in organic syntheses requiring proton abstraction without adverse functional group attack. As such, they are normally used *in situ*, but the isolation and structural characterisation of the above compounds allow us, with the aid of MO calculations, to predict the likely structures and reactivities of these useful N–Li reagents in general.

$[(PhCH_2)_2NLi]_3$
(**1**)

$[(PhCH_2)_2NLi{\cdot}OEt_2]_2$
(**2**)

$[(PhCH_2)_2NLi{\cdot}O{=}P(NMe_2)_3]_2$
(**3**)

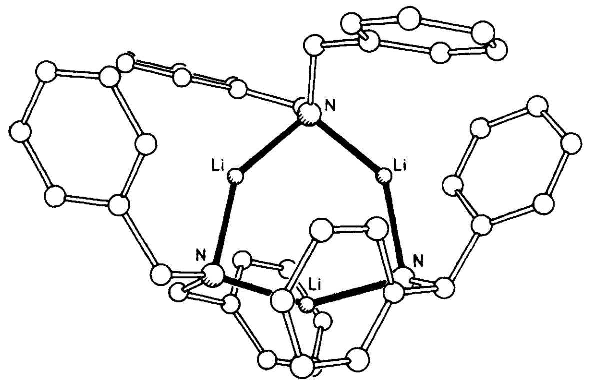

Figure 1. Molecular structure of $[(PhCH_2)_2NLi]_3$, (**1**). Bonds to lithium filled, others open. Space group $P\bar{1}$, triclinic, $a = 10.191(1)$, $b = 12.511(1)$, $c = 15.444(2)$ Å, $\alpha = 73.98(1)$, $\beta = 76.59(1)$, $\gamma = 72.22(1)°$, $Z = 2$, $R = 0.058$ for 4633 reflections with $F > 4\sigma(F)$. Key dimensions: Li–N 1.907(8)—2.038(5), $N–CH_2$ 1.452(4)—1.474(4), $H_2C–\alpha C_{Ph}$ 1.496(5)—1.521(5) Å; Li–N–Li 95.0(3)—95.3(3), N–Li–N 141.3(4)—147.0(3), $Li–N–CH_2$ 99.9(2)—125.7(2)°.

Addition of Bu^nLi in hexane over 15 min to chilled solutions of dibenzylamine in hexane (**1**), diethyl ether–hexane (**2**), or HMPA–hexane (**3**), produced coloured solids in coloured solutions. Warming [with addition of toluene for (**1**)] effected complete dissolution, and filtration and cooling (*ca.* 1 h at −10 °C) gave the products [(**1**) very pale pink, m.p. 146—148 °C, isolated yield 87%; (**2**) very pale pink, darkens 135 °C, m.p. 146—148 °C, 75%; (**3**) deep purple, 110—112 °C, 72%]. These materials meet the recently proposed criteria[3] required of useful N–Li reagents: they are simply made and isolated as high-purity, crystalline substances, thus allowing weighing-out for subsequent reaction. Although (**1**) has more limited solubility, (**2**) and (**3**) are highly soluble in the non-polar solvents desirable for further reaction and are particularly reactive, properties reflecting their lower state of aggregation *cf.* (**1**) and their increased polar character due to lithium solvation. Further valuable points are, (i) the rapidity of the high-yield synthesis and isolation from inexpensive dibenzylamine, and (ii) the colours of the solutions, a useful aid to following subsequent reactions.

The solid-state structures of trimeric (**1**) (Figure 1), and of dimeric (**2**) (Figure 2) and (**3**) (Figure 3)† add to the structural knowledge of lithiated amines {previously studied are $[Me_2\overline{C(CH_2)_3CMe_2N}Li]_4$,[3] $[(Me_3Si)_2NLi]_3$,[4] and $[(Me_3Si)_2N\text{-}Li{\cdot}OEt_2]_2$[3]}. The molecules contain planar N_3Li_3 and L_2Li_2 ring systems. In (**1**), all the benzyl units bend towards neighbouring Li atoms of the N_3Li_3 ring. In (**2**) and (**3**), two of the four benzyl units overlap the N_2Li_2 ring: in (**2**) both are on the same N atom, while in (**3**) it is one unit on each N which is so orientated.

CNDO calculations using the established self-consistent 'bond index' method[5] have been used to probe why it is that *certain* amidolithiums $(RR'NLi)_n$ [$R=R'=Me_3Si$;[4] $PhCH_2$ (**1**); cyclohexyl[6]] form such ring species, while imidolithiums adopt pseudo-cubane $[(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$[7]] or -octahedral $[(RR'C{=}NLi)_6$; $R=R'=Bu^t$; Me_2N;[8] R=Ph, $R'=Me_2N$, Bu^t[6]] clusters with μ_3 N–Li electron-deficient bonds, akin to familiar organolithium species [*e.g.*, $(EtLi)_4$,[9] (cyclohexyllithium)$_6$[10]]. For $[(Me_3Si)_2NLi]_3$, it was suggested[11] that delocalisation (possibly *via* N pπ→Si dπ) sufficiently lowers the charge density on the amido N to prevent efficient μ_3 N–Li bonding; our calculations for $(Me_3Si)_2NH$ and $(Me_3Si)_2N^-$ support such delocalisation, in that little of the additional electron charge remains on the N atom (−0.38 in the amine to −0.41 in the amide ion) and the N–Si bonds strengthen (bond indices 0.91 to 1.03). However, the isolation of (**1**), with its similar trimeric structure, shows that such delocalisation cannot be a *general* explanation, as here the methylene groups effectively block this; calculations on $(PhCH_2)_2NH$ and its amide show that the charge is largely localised on the amido N (0.77 e^- by extended Hückel), with little transfer to the CH_2 groups, and now with weakening of the $N–CH_2$ bonds (bond indices 0.97 to 0.91), reflecting their increased polarity. However, *despite* the delocalisation implied for $(Me_3Si)_2N^-$ and the lack of it for $(PhCH_2)_2N^-$, the potentially bridging N atom in the former remains considerably more negative

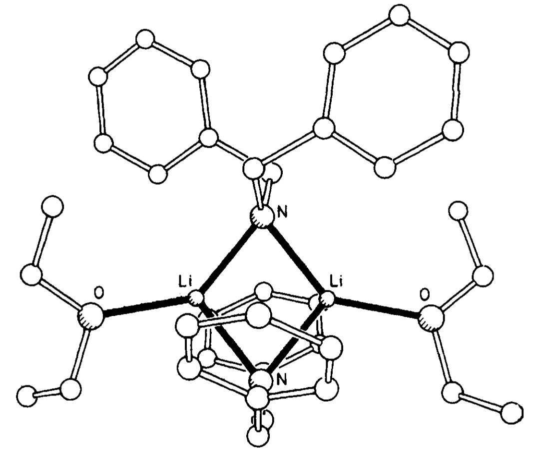

Figure 2. Molecular structure of $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$, (**2**). Space group $C2/c$, monoclinic, $a = 23.842(5)$, $b = 10.806(2)$, $c = 21.712(5)$ Å, $\beta = 142.34(1)°$, $Z = 4$, $R = 0.079$ for 2221 reflections with $F > 3\sigma(F)$. The molecule has two-fold rotation symmetry. Key dimensions: Li–N 1.982(10)—1.991(10), Li–O 2.009(12), $N–CH_2$ 1.460(5)—1.476(5), $H_2C–\alpha C_{Ph}$ 1.503(10)—1.513(6) Å; Li–N–Li 75.7(6)—76.1(6), N–Li–N 104.1(5), $Li–N–CH_2$ 113.0(2)—121.9(4)°.

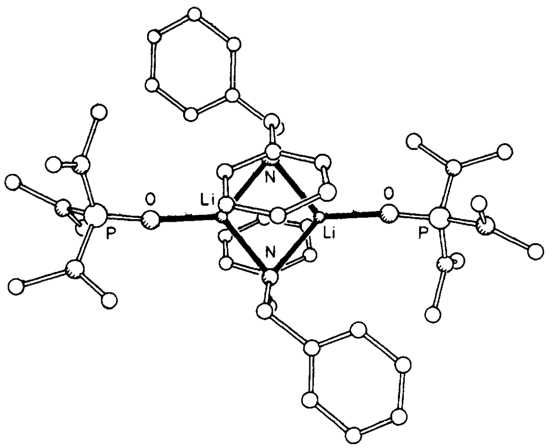

Figure 3. Molecular structure of $[(PhCH_2)_2NLi{\cdot}HMPA]_2$, (**3**). Space group $P2_1/n$, monoclinic, $a = 10.699(2)$, $b = 20.611(2)$, $c = 11.587(2)$ Å, $\beta = 115.18(1)°$, $Z = 2$, $R = 0.096$ for 1939 reflections with $F > 3\sigma(F)$. The molecule has inversion symmetry. Key dimensions: Li–N 2.001(10)—2.013(10), Li–O 1.850(9), $N–CH_2$ 1.441(8)—1.454(10), $H_2C–\alpha C_{Ph}$ 1.454(10)—1.490(12) Å; Li–N–Li 77.3(4), N–Li–N 102.7(4), $Li–N–CH_2$ 112.6(5)—116.9(5)°.

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† Atomic co-ordinates for all three compounds are available on request from the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW; any request should be accompanied by the full literature citation for this communication.

(-2.08 by extended Hückel) than in the latter (-1.40) and, indeed, is more negative than the imido N in $RR'C{=}N^-$ ions (av. -1.71). Hence, there seems no *electronic* reason why $(Me_3Si)_2N^-$ should not bridge a Li_3 face as do imide ligands; in contrast, for $(PhCH_2)_2N^-$ and, we predict, other $alkyl_2N^-$ ligands, despite localisation the N atoms are *inherently* less negative than those in either $(Me_3Si)_2N^-$ (with more polar N–Si bonds) or in imide ions (with 'unsaturated' N atoms). Thus, it seems likely that usual $alkyl_2NLi$ compounds will form crystalline, soluble N_nLi_n ring species (n = 3 or 4, depending on the steric requirements of the alkyl groups), particularly when the alkyl groups can orientate themselves close to the Li atoms [as do the benzyl groups in (**1**)], thus supplementing their low co-ordination number of 2 (see the following communication). For $(RR'NLi)_n$ compounds where R and/or R′ are aromatic, insoluble, high m.p. materials form (R = Ph; R′ = H, Me, $PhCH_2$, Ph, naphthyl, 2-pyridyl);[6] although steric effects cannot be ruled out, possibly the charge on the amide N is here yet further reduced from the value in $(PhCH_2)_2N^-$ by delocalisation into aryl groups, resulting in complex polymeric association to satisfy the valency requirements of the Li. Crystalline complexes $(RR'NLi{\cdot}L)_n$ (n = probably 2), form in the presence of L = Et_2O (for R = Ph; R′ = $PhCH_2$, Ph, naphthyl) or of the stronger donor HMPA (in all cases), as the Li valency can now be satisfied by the additional donor, while bi- and tri-dentate ligands (tetramethylethylenediamine, pentamethyldiethylenetriamine) afford exceedingly reactive, probably monomeric species (*e.g.*, R = Ph, R′ = Me).[6]

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