The Structural Isomers of $\{[Ph(2\text{-}pyridyl)NLi]\cdot[O{=}P(NMe_2)_3]\}_2$: Dimeric Species with Alternative Central $(LiN)_2$ and $(LiO)_2$ Rings, the Latter involving Unprecedented Neutral Bridging Oxygen Ligands

Donald Barr,[a] William Clegg,*[b] Robert E. Mulvey,[a] and Ronald Snaith*[a]

[a] *Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.*
[b] *Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D3400 Göttingen, West Germany*

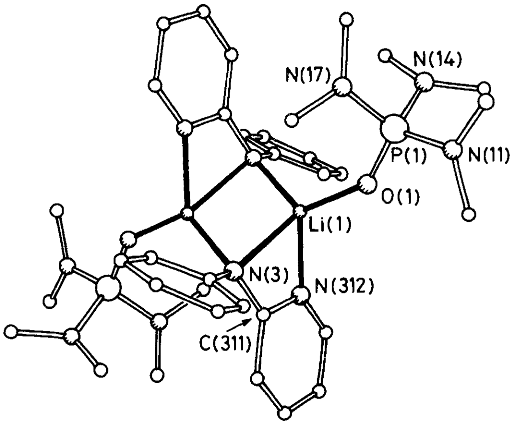
An *X*-ray crystallographic study of the title compound, (**1**), shows it to consist of two structural isomers, one, (**1A**), with a planar $(LiN)_2$ ring structure provided by μ_2-amido ligands, but the other, (**1B**), with an $(LiO)_2$ ring due to previously unobserved bridging by the oxygen of a formally neutral ligand.

We report the isolation, from a 1 : 1 : 1 reaction of 2-anilinopyridine, Ph(2-Pyr)NH : Bu^{n}Li : $O{=}P(NMe_2)_3$ (hexamethylphosphoramide, HMPA), and *X*-ray structural characterisation of the amidolithium complex, $[Ph(2\text{-}Pyr)NLi\cdot HMPA]_2$, (**1**) (Pyr = pyridyl). While the initial aim of this study was to compare the structure, particularly the state of association, of (**1**) with that of its recently reported[1] monomeric amine complex, [Ph(2-Pyr)NLi]·(HMPA)·[Ph(2-Pyr)NH], (**2**), obtained from a 2 : 1 : 1 mixture of the same reagents, the principal point of interest ensuing is that (**1**) in fact exists as two structural isomers, one of which contains hitherto-unobserved bridging of metal atoms by a formally neutral oxygen ligand (HMPA).

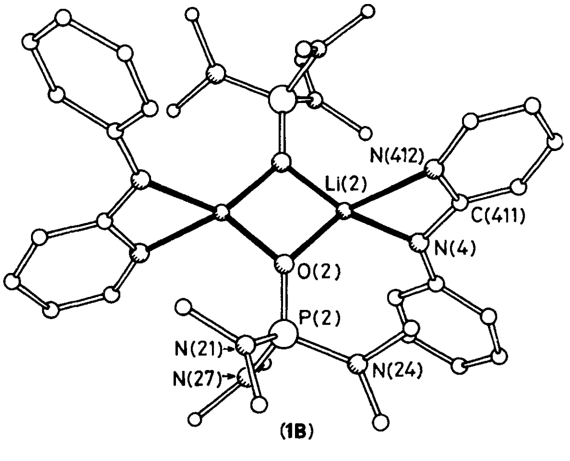
$\{[Ph(2\text{-}Pyr)NLi]\cdot[O{=}P(NMe_2)_3]\}_2$
(**1**)

$[Ph(2\text{-}Pyr)NLi]\cdot[O{=}P(NMe_2)_3]\cdot[Ph(2\text{-}Pyr)NH]$
(**2**)

The dimeric title compound, (**1**), surprisingly exists as two entirely different structural isomers, (**1A**) and (**1B**), (Figure 1), in one and the same crystal structure.† Both have planar 4-membered rings (as is required by crystallographic inversion symmetry for both molecules), and both exhibit 'anchimeric' co-ordination[2] of the pyridyl-N atoms [N(312) and N(412) respectively]. However, in isomer (**1A**) the ring is of the form $(amido\text{-}N\text{-}Li)_2$ with the expected terminally O-attached HMPA ligands, whereas the other isomer, (**1B**), employs μ_2-HMPA ligands in an $(OLi)_2$ ring, now with terminal amido-ligands. This latter feature seems unprecedented in organometallic chemistry [though neutral ketonic ligands are known to provide the means of association for certain polymeric, ionic lithium salts, *e.g.* $LiI(urea)_2$,[3a] $Li_2SO_4(urea)_3$,[3b] and $(LiClO_4)_2\cdot(MeCONH_2)_3(MeCONHCOMe)$[3c]], as it represents a formally *neutral* $(R_3P{=}O)$ oxygen ligand bridging two metal atoms, *cf.* the usual terminal, monodentate nature of neutral oxygen donors such as Et_2O, tetrahydrofuran, and HMPA itself, and the well-known bridging nature of isoelectronic *anionic* ligands such as alkoxide, $R_3C\text{–}O^-$ {*e.g.*, tri-t-butylmethoxide in $[Li(OCBu^t_3)(THF)]_2$[4]}, and germyloxide, $R_3Ge\text{–}O^-$ [*e.g.* in $(Me_2MOGeMe_3)_2$ species, where M = Al, Ga, In[5]], and of enolate anions (*e.g.* the phospha-dionate which bridges two Li atoms in $\{[(PhCO)_2P]\cdot Li\cdot(MeOCH_2CH_2OMe)\}_2$,[6a] and the butenolate ion which bridges three Li atoms in $[Bu^tC({=}CH_2)O\cdot Li\cdot(THF)]_4$[6b]).



(**1A**)



(**1B**)

Figure 1. Molecular structure of the μ_2-N-isomer (**1A**) and the μ_2-O-isomer (**1B**) of $[Ph(2\text{-}Pyr)NLi\cdot HMPA]_2$. *Crystal data* for (**1**): $C_{34}H_{54}Li_2N_{10}O_2P_2$, M = 710.7, monoclinic, space group $P2_1/n$, a = 16.137(4), b = 14.291(2), c = 17.796(4) Å, β = 99.75(3)°, U = 4044.7 Å^3, Z = 4, D_c = 1.167 g cm^{-3}, $F(000)$ = 1520, absorption coefficient μ = 1.44 cm^{-1}, R = 0.085 for 2151 reflections with $F > 4\sigma(F)$ using Mo-K_α radiation (λ = 0.71069 Å).

Some key dimensions for these structural isomers of (**1**), whose very co-existence in the same crystal structure implies that they are of similar energy, are given in Table 1. For (**1A**), the μ_2-NLi bridge bonds to the 4 co-ordinate Li atoms are, as expected, longer (2.142 Å) than those in normal 3 co-ordinate $(NLi)_2$ dimers {*e.g.*, in $[(PhCH_2)_2NLi\cdot HMPA]_2$, 2.007 Å[7]}, though the ring angles are similar {thus, in (**1A**), angle at Li, 104.4°, and at the amido-N, 75.6°; *cf.* in $[(PhCH_2)_2NLi\cdot OEt_2]_2$, 104.1 and 75.9°, respectively[7]}. In contrast, (**1B**) has shorter bridge bonds than (**1A**), (Li–O, 1.924 Å), though

---

† The atomic co-ordinates for this work are available on request from the Director of 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.

Table 1. Comparative key dimensions in the geometrical isomers of (**1**).

	(**1A**)		(**1B**)	
Bond lengths[a]/Å				
Li–amido-N	μ, Li(1)–N(3), –N(3′)	av. 2.142	t, Li(2)–N(4)	1.983
Li–O(HMPA)	t, Li(1)–O(1)	1.870	μ, Li(2)–O(2), –O(2′)	av. 1.924
$O\overset{\cdots}{-}P$	t, O(1)–P(1)	1.469	μ, O(2)–P(2)	1.488
P–N	P(1)–N(11), –N(14), –N(17)	av. 1.633	P(2)–N(21), –N(24), –N(27)	av. 1.630
Li–pyridyl-N	Li(1)–N(312)	2.055	Li(2)–N(412)	2.172
Bond angles/°				
- in $(LiX)_2$ ring				
X–Li–X	N(3)–Li(1)–N(3′)	104.4	O(2)–Li(2)–O(2′)	94.5
Li–X–Li	Li(1)–N(3)–Li(1′)	75.6	Li(2)–O(2)–Li(2′)	85.5
- in anchimeric ring				
pyridyl-N–Li–amido-N	N(312)–Li(1)–N(3)	64.3	N(412)–Li(2)–N(4)	65.3
Li–pyridyl-N–pyridyl-C	Li(1)–N(312)–C(311)	91.8	Li(2)–N(412)–C(411)	86.6
Li–amido-N–pyridyl-C	Li(1)–N(3)–C(311)	86.9	Li(2)–N(4)–C(411)	96.0
pyridyl-N–pyridyl-C–amido-N	N(312)–C(311)–N(3)	114.2	N(412)–C(411)–N(4)	111.0

[a] μ = Bridging, t = terminal.

again these are longer than the more usual 3 co-ordinate Li-bridging O links {*e.g.*, in $[Li(OCBu^t_3)(THF)]_2$, 1.841 Å[4]}, while the need for a larger ring angle at O, *cf.* N, becomes apparent (thus, angle at Li, 94.5° and at O, 85.5°). In both isomers (**1A**) and (**1B**), and indeed in the amine complex, (**2**), the dimensions of the 4-membered $\overline{Li\cdot Amido\text{-}N\cdot Pyr\text{-}C\cdot Pyr\text{-}N}$ ring formed by anchimeric co-ordination are very similar, implying that such co-ordination imposes a rather fixed geometry on this common part of the three molecules.

For the unprecedented bidentate nature of the bridging neutral HMPA donor in (**1B**), one bonding scheme would regard this ligand as the extensively-polarised $(Me_2N)_3\overset{+}{P}\text{–}\overset{-}{O}$, when the analogy with isoelectronic anionic bridge units $R_3M\text{–}O^-$ (M = C, Si, Ge) becomes more apparent. However, although there is a slight increase, the $P\overset{\cdots}{-}O$ bond lengths vary surprisingly little in going from terminal [1.469 Å in (**1A**)] to bridging [1.488 Å in (**1B**)] ligands. Further, while additional $Me_2N\colon \rightarrow P^+$ π-bonding could in theory help stabilise such a polarised form, P–N bond lengths do not evidence this [av. 1.633 Å in (**1A**), av. 1.630 Å in (**1B**)]. These results, therefore, although perplexing, show once again how lithium is peculiarly able to display unusual structural types, and, in so doing, to impose novel bonding modes on its attached ligands.

The structures of (**1**) described above can be compared with that of the amine complex, (**2**),[1] whose anchimeric co-ordination of the pyridyl-N of the amido ligand to the lithium, together with a rigidly-fixed orientation of the unreacted (yet potentially reactive) amine's N–H caused by an N–H···amido-N interaction, makes it a model compound for proposed lithiation mechanisms, *e.g.* of lithiation directed *ortho* and *alpha* to potential donor atoms (N, O, S) in substituted aromatics and heterocyclics respectively, and of the act of lithiation of element–H bonds in general.[2,8] While the monomeric nature of (**2**) may rely to some extent on electronic factors, *e.g.*, the presence of the additional amine ligand raises lithium's co-ordination number to 4, as is usually found in monomeric species such as $\overline{S\cdot[CH_2]_3S\cdot(Ph)C}Li\cdot(THF)\cdot(TMEDA)$,[9] (TMEDA = tetramethylethylenediamine) it seemed that the steric effect of the amine might be dominant. Thus, for the non-amine species (**1**), it was anticipated that dimerisation might occur, although its mode could be *via* μ_2-N–Li bridge bonding in an $(NLi)_2$ ring system [in which anchimeric co-ordination would not necessarily be retained, as, even without it, lithium would achieve three co-ordination as in other (RR′NLi·donor)$_2$ complexes, *e.g.*, R = R′ = $PhCH_2$, donor = OEt_2, HMPA[7]], or *via* pyridyl-N → Li donor bonds between [Ph(2-Pyr)NLi·HMPA] monomers, thus leading to an eight-membered ring structure, as in $[C_5H_4N\cdot(Me_3Si)_2CLi]_2$.[10] Here, the now established dimeric nature of (**1**), retaining anchimeric co-ordination of the pyridyl-N atoms and hence 4-co-ordinate lithium atoms, reinforces the view that it is the *steric* presence of the amine in (**2**) which prevents association.

We thank the S.E.R.C. (D. B., R. E. M.) and the Verband der Chemischen Industrie (W. C.) for support.

Received, 28th February 1984; Com. 268

References

1 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 469.

2 J. J. Eisch, *J. Organomet. Chem.*, 1980, **200**, 101.

3 (a) J. Verbist, R. Meulemans, P. Piret, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, 1970, **79**, 391; (b) Kh. Suleimanov, V. S. Sergienko, N. Kipkalova, and K. Sulaimankolov, *Koord. Khim.*, 1979, **5**, 1732; *Chem. Abstr.*, 1980, **92**, 50423k; (c) P. S. Gentile, J. G. White, and D. D. Cavalluzzo, *Inorg. Chim. Acta*, 1976, **20**, 37.

4 J. Hvoslef, H. Hope, B. D. Murray, and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1983, 1438.

5 H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 201.

6 (a) G. Becker, M. Birkhahn, W. Massa, and W. Uhl, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 741; (b) R. Amstutz, W. B. Schweizer, D. Seebach, and J. D. Dunitz, *Helv. Chim. Acta*, 1981, **64**, 2617.

7 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 287.

8 K. Smith, *Chem. Br.*, 1982, **18**, 29.

9 R. Amstutz, J. D. Dunitz, and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 465.

10 R. I. Papasergio, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1983, 1419.