

# The Isolation and Crystal Structure of [Ph(2-Pyr)NLi]·(HMPA)·[Ph(2-Pyr)NH]; a Model Monomeric Organonitrogen–Lithium Species containing Co-ordination of Lithium by both an Anchimeric Pyridyl N-Atom and by a Potentially Reactive Amine Ligand†

Donald Barr,<sup>a</sup> William Clegg,<sup>\*b</sup> Robert E. Mulvey,<sup>a</sup> and Ronald Snaith<sup>\*a</sup>

<sup>a</sup> Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

<sup>b</sup> Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D3400 Göttingen, West Germany

The compound [Ph(2-Pyr)NLi]·(HMPA)·[Ph(2-Pyr)NH], (**1**), isolated from reactions of 2-anilinopyridine with Bu<sup>n</sup>Li–HMPA, has been shown by X-ray crystallography to be monomeric, with lithium's co-ordination sphere including the pyridyl N atoms of both the amide and protonated amine ligands, making (**1**) a model compound for the study of the mechanisms both of directed (*ortho*,  $\alpha$ ) lithiations of C–H bonds in :X-atom substituted aromatic and heterocyclic compounds (:X=O, S, N) and of lithiations of :X–H bonds themselves.

We report the isolation and crystal structure of [Ph(2-Pyr)NLi]·(HMPA)·[Ph(2-Pyr)NH] (**1**), obtained from reactions of 2-anilinopyridine with Bu<sup>n</sup>Li–HMPA.‡ As well as being the first structurally characterised monomeric organonitrogen–lithium compound, (**1**) has additional significance provided by (i), the intramolecular ('anchimeric') co-ordination of a pyridyl nitrogen, N(112) of Figure 1, of the amide ligand to the lithium, and (ii), the presence, as a ligand, of a non-lithiated secondary amine molecule. These observations are relevant to proposed mechanisms for (i), lithiations commonly selectively directed *ortho* and  $\alpha$  to potential donor atoms :X (*e.g.*, :X = O, S, N) in substituted aromatic and heterocyclic compounds respectively, 1–3 and for (ii), the act of lithiation of :X–H bonds. Such reactions have been thought to proceed *via* initial complexation of :X to the organolithium reagent, (RLi)<sub>n</sub> [*n* commonly 4,6], 4,5 thereby bringing the Li and H in close proximity, and possibly enhancing its lithiating power by reducing the state of association (*e.g.*, to *n* = 1). Compound (**1**) represents the first isolated and structurally characterised 'model' compound for such mechanistic proposals.

Amidolithiums, (RR'NLi)<sub>n</sub>, are being increasingly used *in situ* for selective lithiations.<sup>6</sup> Those so far isolated and structurally characterised have (NLi)<sub>n</sub> ring systems (with *n* = 3,4); when *n* = 4, RR'N = Me<sub>2</sub>C·(CH<sub>2</sub>)<sub>3</sub>·Me<sub>2</sub>C·N,<sup>7</sup> and with *n* = 3, R = R' = Me<sub>3</sub>Si,<sup>8</sup> PhCH<sub>2</sub>.<sup>9</sup> The complexes (RR'NLi·donor)<sub>n</sub> are dimeric if the donor is monodentate, *e.g.*, R = R' = PhCH<sub>2</sub>, donor = OEt<sub>2</sub> or HMPA,<sup>9</sup> but seemingly monomeric with multidentate donors, *e.g.*, R = Ph, R' = Me, donor = PMDETA.† In this study, lithium was provided with only a monodentate donor (HMPA), but had the added opportunity of using a donor site within the R group of the amide residue. Thus, reaction of equimolar amounts of 2-anilinopyridine, HMPA, and Bu<sup>n</sup>Li in ether–hexane afforded pale yellow crystals (m.p. 115–117°C). The product was thought to be [Ph(2-Pyr)NLi·HMPA]<sub>n</sub> (**2**); however, the particular crystal selected and examined by X-ray diffraction

† Abbreviations: Pyr = pyridyl; HMPA = hexamethylphosphoramide, O=P(NMe<sub>2</sub>)<sub>3</sub>; PMDETA = pentamethyldiethylenetriamine; TMEDA = tetramethylethylenediamine; THF = tetrahydrofuran.

‡ Crystal Data for (**1**): C<sub>28</sub>H<sub>37</sub>N<sub>7</sub>POLi, Space group *P2<sub>1</sub>/n*, *a* = 11.058(1), *b* = 11.773(1), *c* = 23.249(3) Å,  $\beta$  = 103.67(1)°, *Z* = 4, *R* = 0.059 for 2797 reflections with *I* > 3 $\sigma$ (*I*). Anisotropic thermal parameters for all non-H atoms; H(21) freely refined with isotropic thermal parameters; other H atoms in calculated positions. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

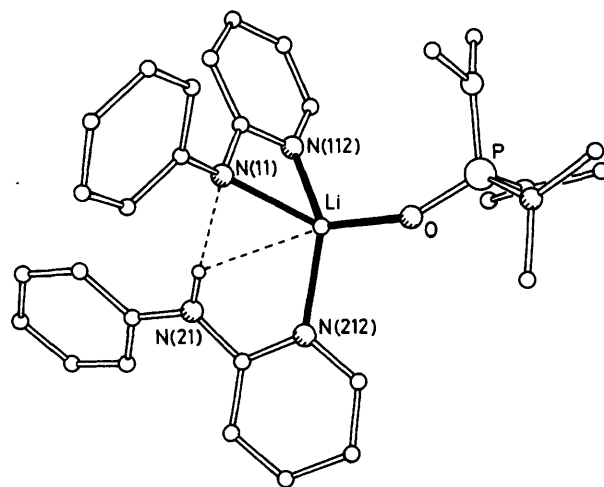


(**2**)

was of its amine complex (**1**). Nonetheless, the bulk material was mainly (**2**), as shown by its analytical data, by its i.r. spectrum which showed no N–H bands (*cf.* two in the parent amine's i.r. spectrum<sup>10</sup>) though these were apparent after brief air-exposure, and by its 360 MHz <sup>1</sup>H n.m.r. spectrum *e.g.* no N-attached proton was detected, and integration corresponded to 1 Ph : 1 Pyridyl : 1 HMPA.

The clear implication that the amine complex (**1**) was a minor product arising from the addition of a slight deficiency of Bu<sup>n</sup>Li to the amine–HMPA mixture has subsequently been confirmed by its isolation (yield 80%; pale yellow crystals, m.p. 104–106°C) from a deliberate 2 amine : 1 HMPA : 1 Bu<sup>n</sup>Li reaction.

Compound (**1**) is monomeric (see Figure 1), with the Li atom bonded to the O atom of the HMPA, to the central amido N(11), and pyridyl N(112) of the amide ligand, and to the pyridyl N(212) of the second, protonated N-ligand. [*cf.* the few known C–Li monomers, *viz* MeC·B<sub>10</sub>H<sub>10</sub>·CLi·(PMDETA),<sup>11</sup> (Me<sub>3</sub>Si)<sub>2</sub>CHLi·(PMDETA),<sup>12</sup> and S(CH<sub>2</sub>)<sub>3</sub>SC(Ph)·Li·(THF)·(TMEDA)<sup>13†</sup> also with 4-co-ordinate Li, and the recently reported<sup>14</sup> 3-co-ordinate Li monomer, {Li[C(SiMe<sub>2</sub>Ph)<sub>3</sub>]·(THF)}, where lack of association seems to be due to the bulkiness of the neutral donor(s) and/or the



**Figure 1.** Molecular structure of [Ph(2-Pyr)NLi]·(HMPA)·[Ph(2-Pyr)NH], (**1**). Bonds to lithium filled, others open. Lithium co-ordination geometry: Li–O 1.815(6), Li–N(11) 2.091(7), Li–N(112) 2.111(6), Li–N(212) 2.078(6) Å. O–Li–N(11) 129.3(3), O–Li–N(112) 117.0(3), O–Li–N(212) 106.0(3), N(11)–Li–N(112) 65.5(2), N(11)–Li–N(212) 109.7(3), N(112)–Li–N(212) 126.4(3)°.

C-attached groups.] To our knowledge, the observation of such donation from the pyridyl N(112) is the first specific structural corroboration that intramolecular, anchimeric co-ordination can occur, and hence may well be involved in directing lithiation *ortho* and  $\alpha$  to a heteroatom in substituted aromatic and heterocyclic organic compounds.<sup>1-3</sup>

The amine's presence is particularly significant. Compound (1) is, we believe, the first example of a lithium species containing a reactive yet unreacted Lewis base, *cf.* 'activating' tertiary amine bases (*e.g.*, TMEDA, PMDETA) commonly used to lower the association of, and to increase the carbanionic nature of,  $(RLi)_n$  compounds.<sup>5</sup> In this co-ordination, the N(21)-H $\cdots$ N(11) interaction [H $\cdots$ N(11), 2.11(6) Å] seems especially crucial in that the fairly short Li $\cdots$ H contact (2.516 Å) cannot then be avoided. The strength of the N-H $\cdots$ N interaction is implied by the distinct non-planarity of bonds to N(11), which lies 0.353 Å out of the plane of its three bonded atoms [sum of angles around N(11) 343.6°; *cf.* 359.8° around N(21)]; further, potentially free rotations about the two N(21)-C bonds, and about the N(212)-Li bond, mean that a great variety of alternative conformations are available. The rigidly fixed co-ordination implies that complex (1) is a model system for the lithiation of the parent amine itself, and, indeed, that lithiation of R-H bonds in general (particularly where R contains a basic group) may well proceed through similar, but transient, complexes.

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

Reed and I. H. Sadler of the S.E.R.C.-Edinburgh University n.m.r. facility for recording spectra.

Received, 13th January 1984; Com. 048

### References

- 1 J. J. Eisch, *J. Organomet. Chem.*, 1980, **200**, 101.
- 2 K. Smith, *Chem. Br.*, 1982, **18**, 29.
- 3 J. T. B. H. Jastrzebski, G. van Koten, M. Konijn, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 5490.
- 4 M. E. O'Neill and K. Wade, 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 1, p. 1.
- 5 J. L. Wardell, in ref. 4, p. 43.
- 6 M. Fieser, 'Reagents for Organic Synthesis,' Wiley, London, 1982, vol. 10, and earlier vols.
- 7 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.
- 8 R. D. Rogers, J. L. Atwood, and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229.
- 9 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 285.
- 10 T. Mizuno, M. Hirota, Y. Hamada, and Y. Ito, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1583.
- 11 W. Clegg, D. A. Brown, S. J. Bryan, and K. Wade, *Polyhedron*, in the press.
- 12 M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323.
- 13 R. Amstutz, J. D. Dunitz, and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 465.
- 14 C. Eaborn, P. B. Hitchcock, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1983, 1390.