Synthesis, X-ray crystal structure and solution NMR spectroscopic studies of $[Li\{N(H)C(Me){=}C(H)(CN)\}(py)_2]_2$ (py = NC_5H_5)†

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The ω-cyano-eneamidolithium compound $[Li\{N(H)C(Me){=}C(H)CN\}]_n$ obtained from $Li[N(SiMe_3)Bu^t]$ and an excess of MeCN, yields the crystalline dinuclear complex $[Li\{N(H)C(Me]{=}C(H)CN)\}(py)_2]_2$ 2a, containing a 12-membered macrocycle having four-coordinate lithium and a *cis*-arrangement of Me and H about the C=C bond; in $[^2H_5]$pyridine solution compound 2a is fluxional, a *trans*-isomer 2b being implicated.

Nitriles containing α-hydrogen are, in principle, trifunctional. Thus, they may (*i*) be deprotonated, (*ii*) act as nitrogen-centred donors, and (*iii*) respond to nucleophilic attack at C_{sp}. In the vast majority of nitrile reactions, only one of these modes is manifested. We now describe a system in which *each* of (*i*)–(*iii*) is operative.

We report that (*a*) treatment of $Li[N(SiMe_3)Bu^t]$ with an excess of MeCN yields the ω-cyanoeneamidolithium compound $[Li\{N(H)C(Me){=}C(H)CN\}]_n$ **1**;‡ (*b*) **1** forms a crystalline pyridine (py) adduct $[Li\{N(H)C(Me){=}C(H)CN\}(py)_2]_2$ **2**; (*c*) the X-ray molecular structure of crystalline **2** (Fig. 1) shows it to be a single stereoisomer **2a**;§ and (*d*) a pyridine solution of **1**, which probably contains the tight ion pair $[Li(py)_4][N(H)C(Me){=}C(H)CN]$, undergoes fluxional behaviour (NMR spectroscopy) involving exchange between **2a** and its geometrical isomer **2b**, Scheme 1 [which also illustrates the probable pathway to **2** from the reagents in (*a*)].

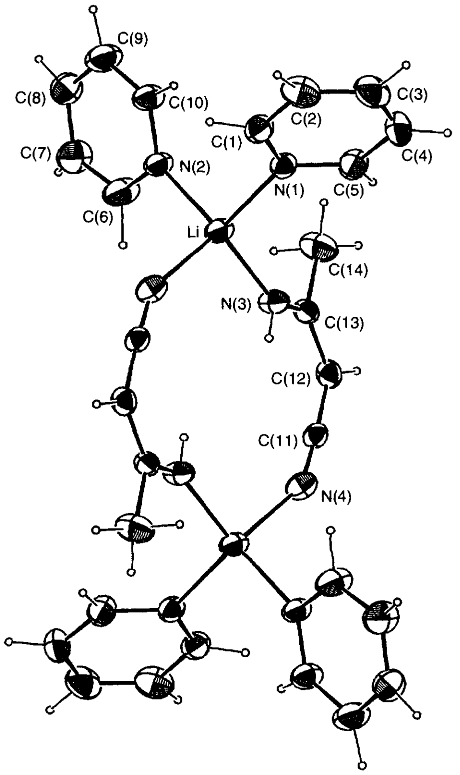


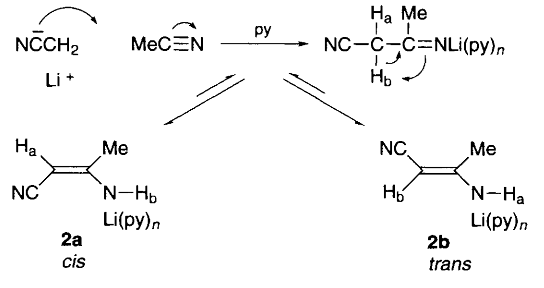
Fig. 1 The molecular structure, with atom numbering, of compound **2** and selected bond lengths (Å) and angles (°) (see also text): Li–N(1) 2.105(7), Li–N(2) 2.070(7), N(3)–C(13) 1.294(5), C(12)–C(13) 1.394(3), C(11)–C(12) 1.364(3), C(11)–N(4) 1.161(5); N(3)–C(13)–C(12) 127.8(4), C(11)–C(12)–C(13) 120.8(4), C(12)–C(11)–N(4) 176.4(4)

Compounds **1** and **2** gave satisfactory microanalyses. The IR spectra (in Nujol) showed single sharp C≡N stretching bands at 2131 cm^{-1} (**1**) and 2164 cm^{-1} (**2**). The N–H stretching mode for **1** appeared as a sharp band at 3175 cm^{-1}, while for **2** there was a broad absorption centred at 3431 cm^{-1}. The ^{13}C, ^{15}N and ^7Li CP MAS NMR spectra of solid **1** showed signals at chemical shifts very similar to those of **2** in $[^2H_5]$pyridine;¶ **1** and **2** were insoluble in non-polar solvents. From an NOE ^1H NMR spectroscopic experiment on **1** in $[^2H_5]$pyridine at 239 K, separate signals were identified for the *cis* (similar to **2a**, *ca.* 60%) and *trans* (similar to **2b**, *ca.* 40%) isomers. In this region of low temperature and relatively viscous solvent, all NOEs were negative. Irradiating the methyl signals in turn showed that those at δ 1.94 (Me) and 3.57 (CH) were due to the *cis* isomer (an NOE of −41%) and those at δ 2.32 (Me) and 3.96 (CH) to the *trans* isomer (an NOE of −9%). Interestingly, both methyl signals showed an NOE to the NH signal; in the *cis* isomer it was −3% and in the *trans* −22%. At 239 K the signals due to the *trans* isomer became significantly broadened while those of the *cis* isomer were unaffected. At 228 K splitting of both the *trans* methyl and the *trans* NH signal was observed; this is attributed to restricted rotation about the N(H)–C(Me) bond.

A variable-temperature study by both ^6Li and ^7Li NMR spectroscopy of **1** in $[^2H_5]$pyridine showed only one lithium environment down to 228 K. This failure to observe splitting may be due to the insensitivity of the lithium chemical shift or to rapid intermolecular exchange at the lithium centres even at the lowest accessible temperatures.

A $^6Li\{^1H\}$ NOE study performed in the same solvent at 298 K showed significant enhancements of the ^6Li signal on irradiation of both the *ortho* pyridine (22%) and the amide NH (30%) protons. This demonstrates that the lithium is close (≤3 Å) to both types of proton and thus rules out the possibility of fully dissociated ions in solution.

The X-ray structure of crystalline **2** (Fig. 1) shows it to comprise a central twelve-membered macrocycle, with a pair of pendant pyridine ligands at each of the four-coordinate, approximately tetrahedral lithium atoms, angles at lithium



Scheme 1 Proposed reaction pathway to the ω-cyanoeneamido compound **2a** and a mechanism for the *cis* (**2a**)/*trans* (**2b**) fluxionality

ranging from 102.4(3) to 116.6(3)°. The molecule is centrosymmetric with the Me and H substituents on the alkenic double bond *cis* to one another. The terminal N-bonded nitrile groups, unusually, are arranged in a non-linear fashion, the Li–N(4)–C bond angle being 151.5(3), a consequence of its being endocyclic. The presence in this molecule of a nitrile coordinated to a lithium imide or amide appears to have only a single structurally authenticated precedent, $[Li\{\mu\text{-}N(SiMe_3)_2\}(N{\equiv}CBu^t)]_2$,[1] having C≡N bond lengths of 1.142(6) and 1.136(5) Å compared with 1.161(5) Å in **2** or 1.137(4) Å in PhCN,[2] and Li–N(CBu^t) bond lengths of 2.046(7) and 2.051(8) Å compared with Li–N(H) 1.973(5) and Li–N(C) 2.041(9) Å in **2**. The other geometric parameters are unexceptional with respect to known lithium–nitrogen compounds.[3] However, cyanoalkyllithium compounds have received attention, an example being [1-cyano-2,2-dimethylcyclopropyllithium-(THF)]$_\infty$(3THF)$_\infty$.[4] The α-lithiated benzonitrile–tmen complex is a dimer $[\{Li(\mu\text{-}N{=}CCHPh)(Me_2NCH_2CH_2NMe_2)\}]$,[5a] while the complex formed from $PhCH_2CN + 2LiNPr^i_2 + 2$ tmen is $[Li(N{=}CCHPh)(tmen)(\mu\text{-}NPr^i_2)Li(tmen)]$.[5b] MNDO calculations on $LiCH_2CN$ support an eight-membered ring, while the solvated L complex is predicted to be $[\{Li(\mu\text{-}N{=}CCH_2)L_2\}_2]$.[6] Li–C–heteroatom macrocycles are unusual; another is $[\{LiC(SiMe_2OMe)_3\}_2]$.[7]

Relevant to the above data are Krüger's observations that treatment of acetonitrile with $Na[N(SiMe_3)_2]$ gave either a 1 : 1 or a 2 : 1 complex.[8] From IR (see also ref. 9) and ^1H NMR spectroscopic data in $[^2H_5]$pyridine, the latter was believed to be a mixture of *cis*- (3 parts) and *trans*- (4 parts) cyanoeneamidosodium complexes, which upon hydrolysis gave the *cis*- and *trans*-enamines $MeC(NH_2){=}CHCN$.

In a full paper we shall report on the CP MAS NMR spectra of **1** and **2** and on sodium and potassium analogues of **1** and their role as precursors to ω-cyanoeneamido complexes of other metals.

We thank FMC Ltd. (and Dr F. Reed) for their continued interest and support.

Footnotes

† No reprints available.

‡ Typically MeCN (10 cm^3, 0.19 mol) was added dropwise to a stirred solution of $Li[N(SiMe_3)Bu^t]$ (0.76 g, 5 mmol) in diethyl ether (100 cm^3); the mixture was stirred for 2 h. Removal of solvent *in vacuo*, followed by heating to 80 °C at 10^{-3} Torr yielded $[Li\{N(H)C(Me){=}C(H)(CN)\}]_n$ **1** (0.43 g, 98%). Compound **1** (0.10 g) was dissolved in pyridine (1.0 cm^3), the solution was kept at −30 °C for 2 weeks during which single crystals of **2** were deposited.

§ *Crystal data* for **2** [T = 293 K, Enraf-Nonius CAD-4 diffractometer, Mo-Kα radiation (λ = 0.71073 Å)], no crystal decay, full-matrix least-squares refinement on F with non-hydrogen atoms anisotropic. $C_{28}H_{30}Li_2N_8$, $M = 485.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.681(2)$, $b = 10.061(2)$, $c = 10.262(2)$ Å, $\alpha = 116.09(2)$, $\beta = 105.84(3)$, $\gamma = 100.58(2)°$; $U = 725.0(4)$ Å^3, $Z = 1$, $D_c = 1.11$ g cm^{-3}, $F(000) = 257$, μ(Mo-Kα) = 0.6 cm^{-1}, specimen 0.3 × 0.2 × 0.1 mm. 2543 Unique reflections for $2 < \theta < 23$, of which 1250 with $|F^2| > 2\sigma(F^2)$ were used in the refinement; $R = 0.063$, $R' = 0.064$, $S = 1.7$. The molecule lies across a crystallographic inversion centre. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/229.

¶ NMR chemical shifts (δ) (at 298 K in NC_5D_5 for ^1H and NC_5H_5–NC_5D_5 for ^{13}C. ^1H at 360.14 MHz and ^{13}C at 62.90 MHz). ^1H: **1** 1.94 and 2.32 (Me), 3.57 and 3.96 (CH), 6.51 (br, NH); ^{13}C: **1** 24.5 and 25.9 [q, ^1J(CH) 124.8 Hz], 46.3 and 48.8 [d, ^1J(CH) 160.7 Hz], 131.2 and 133.1 (s, C≡N), 175.2 and 175.5 (s, NCMe).

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Received, 5th July 1996; Com. 6/04739D