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# The syntheses and structures of Group 1 expanded dipyrrolides: the formation of a 12-rung amidolithium circular ladder†

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*Received (in Cambridge, UK) 2nd April 2003, Accepted 20th May 2003*
*First published as an Advance Article on the web 5th June 2003*

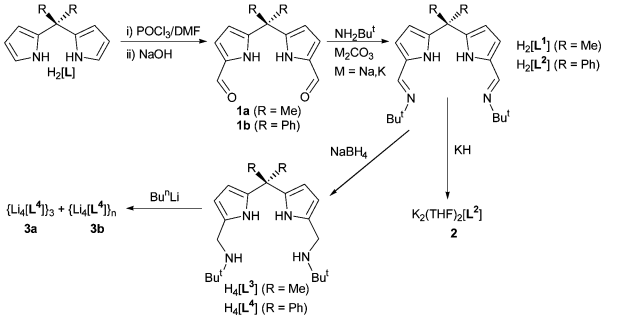
**Elaboration of *meso*-disubstituted dipyrromethanes to incorporate imino or amino donors results in ligands that adopt unique, aggregated structures with Group 1 metals.**

The dipyrrolides (**L**, R = alkyl, aryl) are proving to be versatile dianionic ligands for the electropositive metals.[1,2] While the combination of both cyclopentadienyl and amido ligand characteristics encourages the stabilisation of highly reactive metal species through aggregation,[3] the creation of reactive, multimetallic compounds is still difficult to control. In order to generate ligand sets that have well-defined donor compartments, a strategy to increase the denticity of the dipyrromethane ligand is being pursued by us. Similar methodology has been used in the preparation of expanded porphyrins.[4] Herein, we describe the first syntheses of N-donor-elaborated *meso*-disubstituted dipyrromethanes and the syntheses and structures of Group 1 complexes incorporating these ligands. Such compounds can provide insight into the structural chemistry of these ligand sets and also afford salt elimination routes to the incorporation of transition metals.[5] The binding of alkali metals to the pyrrolic framework can also moderate the redox potentials of the resulting transition metal complex.[6]

The Vilsmeier–Hack reactions between $H_2$[**L**] and $POCl_3$–DMF result in the carbonylation of the dipyrromethanes in the 5,5′-positions, so forming **1a** and **1b** (Scheme 1).† Dialdehyde **1b** was crystallographically characterised, and adopts a dimeric structure formed by hydrogen bonding between the pyrrole protons and carbonyl oxygens of discrete monomers.‡ Reaction of **1** with excess $Bu^tNH_2$ in MeOH in the presence of anhydrous carbonate yields the diiminodipyrromethanes $H_2$[**L¹**] and $H_2$[**L²**] in good yield; $H_2$[**L¹**] is volatile and is best purified by sublimation at 150 °C/$10^{-2}$ mbar. Reduction of the imines with $NaBH_4$ in methanol results in the formation of the diaminodipyrromethanes $H_4$[**L³**] and $H_4$[**L⁴**].

The reaction between $H_2$[**L²**] and KH in THF caused rapid gas evolution and the generation of the dipotassium salt $K_2(THF)_2$[**L²**] **2** in good yield. NMR data are consistent with a symmetrical ligand arrangement and confirmed the presence of two coordinated THF molecules. Slow cooling of a solution of **2** in THF resulted in the deposition of X-ray quality crystals; the solid state structure of **2** is shown in Fig. 1. Unlike the solution data, the solid state structure reveals different coordination environments for the potassium ions. Both K1 and K2 are bound to the dipyrrolide ligand in the same manner; the metal is π-bound to one pyrrolide ring and σ-bound to the adjacent pyrrolide nitrogen and the associated imine nitrogen. This bonding motif has been observed for other transition metals and *f*-element *meso*-dipyrrolide systems and promotes effective aggregate formation.[2,3] While the coordination environment of K1 is completed by two THF molecules, K2 undergoes further π-bonding to a pyrrolide group of an adjacent molecule, so forming a polymeric zigzag chain (Fig. 1a). The K2–pyrrolide–K1B interaction deviates considerably from linearity (K2–cent–K1B = 164.6°) and is asymmetric (K2–cent = 3.103, K1B–cent = 2.968 Å). Similar polymeric chain motifs have been seen in a potassium octaalkylporphyrinogen structure,[7] and in the alkali metal cyclopentadienyls $[K(THF)_n(C_5Me_5)]_\infty$, although in the latter the K–cent–K′ interactions approach linearity.[8]

The reaction between $H_4$[**L⁴**] and $Bu^nLi$ (4 equiv.) in $Et_2O$ resulted in the formation of the amidopyrrolides **3a** and **3b** in a combined, isolated yield of 75%; **3a** precipitated from $Et_2O$, while **3b** was isolated from the supernatant liquors and was crystallised from pentane.† The $^1H$ and $^7Li\{^1H\}$ NMR spectra



**Scheme 1** Synthesis of diimino- and diamidodipyrrolides.

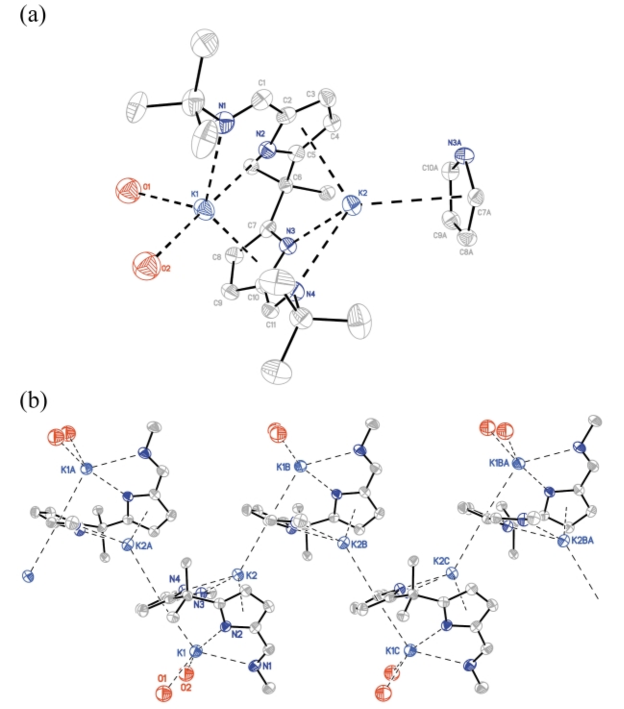


**Fig. 1** X-Ray crystal structure of **2** [50% ellipsoids, $Bu^t$ and THF carbons removed for clarity].

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† Electronic supplementary information (ESI) available: full experimental details and crystallographic data. See http://www.rsc.org/suppdata/cc/b3/b303611a/

DOI: 10.1039/b303611a

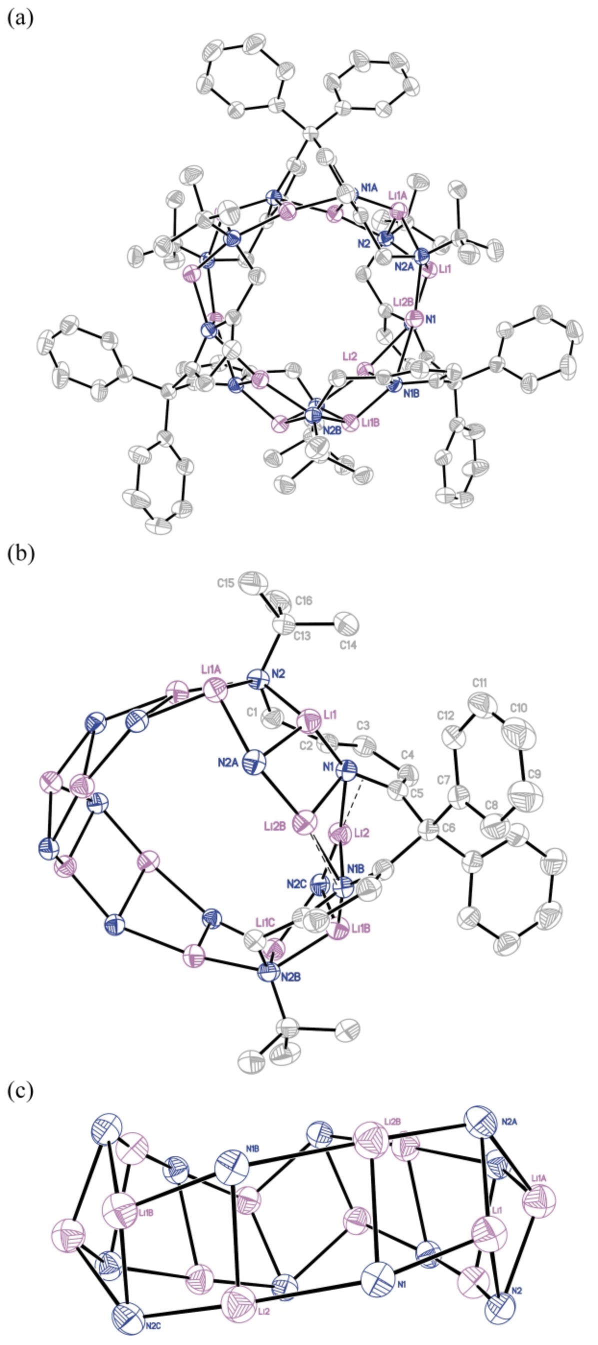

**Fig. 2** The X-ray crystal structure of **3b** [50% ellipsoids].

for **3a** and **3b** are very similar and are consistent with both complete deprotonation of the aminopyrrole ligand H$_4$[**L$^4$**] and the formation of complexes that contain two distinct lithium environments [*e.g.* **3b**: $\delta_{\rm Li}$ 0.08 (br s), $-7.65$ (br s)]. The simplicity of the NMR data for **3b** is consistent with, but not reflected by, the X-ray structure (Fig. 2), where it is immediately apparent that a remarkable structural aggregation has occurred to maximise electrostatic interactions between the Li ions and N-donors. In the solid state, **3b** exists as three interlocked Li$_4$[**L$^4$**] units, the core of which is a unique 12-rung lithium amide circular ladder (Fig. 2c) which is delimited by a helical ligand periphery (Fig. 2b). As with **2**, the dipyrrolide moiety adopts alternating σ-N/π-C$_4$H$_2$N bonding to Li2 (and Li2B); the coordination sphere of Li2 is completed by amido-N2C ligation from a second Li$_4$[**L$^4$**] unit (analogous to K–imine bonding in **2**). Unlike **2**, the structure is further complicated by the presence of the second Li environment, Li1, which coordinates to both amido-N2 and pyrrolide-N1, and to amido-N2A of a second monomer, so generating the circular ladder. This ladder has a pronounced and unusual twist,[9] (Fig. 2c) which results in distorted pyramidal Li1 ($\Sigma$ N–Li–N = 318.2, *cf.* Li2 $\Sigma$ = 349.8°) and rhombohedral Li1–N2–Li1a–N2a [internal angles = 104.9 and 69.6°, Li1–N2 2.074(4), Li–N2A 2.002(4) Å], and is a likely consequence of amido-arm geometrical constraint. Li-amide circular ladders that are derived from monodeprotonated amines, *e.g.* [LiN(H)Bu$^t$]$_8$,[10] usually form by straightforward edge-to-edge LiN ring association between dimeric units. However, with the tetradeprotonated tetraamine **3b**, the formation of simple LiN repeating units in the monomer is precluded, and results instead in a laterally-shifted LiN chain (Fig. 3). The combination of three of these chains, coupled with cyclisation would result in the observed structure. Like other LiN ladders, **3b** contains approximately alternating long–short edge bonds with an intermediate rung length.[11]

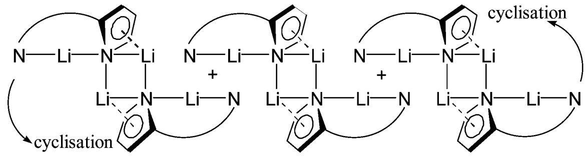

**Fig. 3** Possible mechanism for the formation of **3b**.

We thank the Royal Society (J.B.L., University Research Fellowship), the University of Nottingham, the EPSRC (S.D.R.), and the Nuffield Foundation (A.N., Undergraduate Research Bursary) for support.

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‡ CCDC 207484–207486. See http://www.rsc.org/suppdata/cc/b3/b303611a/ for crystallographic data in .cif format.

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