

Synthesis of 2,5-bis{(diethyl-3'-indolyl)methyl}furan and its *N,N'*-dimetallated complexes (lithium, sodium and potassium): X-ray crystal structures of 2,5-bis{(diethyl-3'-indolyl)methyl}furan and the polymeric tetrahydrofuran adduct of the dilithiated complex

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Abstract

The synthesis of 2,5-bis{(diethyl-3'-indolyl)methyl}furan by the acid catalysed condensation of 2,5-bis(diethylhydroxymethyl)furan with indole is presented. Dilithium, disodium and dipotassium derivatives are prepared by the reaction of the bis(indole) with *n*-BuLi, NaH and K, respectively, in the presence of various Lewis bases. The X-ray structures of 2,5-bis{(diethyl-3'-indolyl)methyl}furan and the dilithiated derivative (as a polymeric tetrahydrofuran adduct) are reported.

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1. Introduction

Pyrrolide-based anionic ligands commonly bind to most metals through σ -N and μ -N bonding modes. In some circumstances π -bonding modes have been observed, which holds promise for pyrrolide-containing anions to function as feasible alternatives to traditionally used cyclopentadienyl-based ligand systems [1,2]. Applications have already been demonstrated in this area for η^5 -bound pyrrolide systems [3]. Multi-hapto binding modes are generally less frequently observed in simple complexes containing pyrrolide, $C_4H_4N^-$, itself, unless indirect factors lead to particular stability of the metal if such a binding mode is adopted (e.g., con-

formity with the 18-electron rule in $[Fe(\eta^5-C_5H_5)(\eta^5-C_4H_4N)]$ [4]. Two approaches have been utilised recently to modify the bonding mode of pyrrolide anions, (i) 2,5-disubstitution of the pyrrolide ring [5] and, (ii) more than one pyrrolide ring being present in the molecule [2]. Metallo-porphyrinogen complexes represent important examples of the latter approach, where macrocyclic ring strain is influential in forcing η^5 -binding modes on large radii metal centres bound within the macrocyclic cavity [6,7]. Simpler systems, such as bis(2-dipyrrolide)methane complexes, also have been studied in which η^5 -binding modes are frequently obtained for some metals [8].

Indolide complexes, the related benzannulated *N*-heterocyclic anion bearing the five-membered pyrrolide ring as a substructure, have coordinating abilities similar to the simpler pyrrolide systems. Indolide coordination chemistry is poorly documented and π -bond-

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ing modes appear to be difficult to obtain [9]. Thus, indolide based systems currently lack feasibility as competitive substitutes for the corresponding bicyclic aromatic (hydrocarbyl) indenyl-based anions without further study. Relatively few studies have been reported where an attempt has been made to alter the binding mode of indolide anions using ring substitution [10] approaches and even fewer have exploited chelate ring strain or macrocyclic ring strain to influence the coordination modes. Recent studies of Group 1 metal 18-crown-6 complexes featuring pendant 3-indole substituents have shown η^5 -bonding to be obtainable, which is of biological relevance [11]. Further bonding possibilities are conceivable for indolides by way of the extended aromatic system, though participation of the six-membered ring has been noted as rarely being involved in binding to metal centres [12].

In this report, we outline initial studies into Lewis base substitution of the indole skeleton as a means to favour multihapto-binding in the derived indolide complexes. The synthesis of an acyclic bis(3'-indole)-furan is presented, together with its Group 1 metal complexes (dilithium, sodium and potassium) formed through double deprotonation, targeted specifically owing to the potential for the dianionic ligand system to yield *ansa*-metallocene complexes, particularly when transferred to early transition metals. Crystal structures have been obtained for the parent heterocycle and the tetrahydrofuran (THF) adduct of its dilithium complex.

2. Experimental section

2.1. General

Unless stated all manipulations of complexes were carried out under an argon atmosphere by the use of standard Schlenk techniques. 2,5-bis(diethylhydroxymethyl)furan (**1**) was prepared according to a modified literature procedure [13]. Methanol and ethanol were degassed prior to use and other solvents were dried over Na or Na/K and distilled. All other chemicals were obtained from Aldrich and used as received. ^1H and ^{13}C NMR spectra were recorded using a 400 MHz Varian-Inova spectrometer at 399.694 (^1H) and 100.512 MHz (^{13}C) at 298 K, internally referenced to the residual ^1H resonances of the solvents (CDCl_3 or appropriately dried C_6D_6 or OC_4D_8). IR spectra were recorded as Nujol mulls on NaCl plates. Melting points were determined in glass capillaries and are uncorrected. GC/MS spectra were obtained on a HP 5890 instrument. The CSL, University of Tasmania, or the Chemical and Analytical Services Pty. Ltd., Melbourne performed elemental analyses.

2.2. Synthesis of 2,5-bis{(diethyl-3'-indolyl)methyl}furan (**2**)

To a flask containing 2,5-bis(diethylhydroxymethyl)furan (**1**) (4.8 g, 20.0 mmol) and indole (4.8 g, 41.0 mmol) in degassed absolute ethanol (80 mL), trifluoroacetic acid (0.32 mL, 0.47 g, 4.2 mmol) was added dropwise with stirring and the mixture refluxed overnight. The precipitated product was collected by filtration and washed with methanol (3×10 mL) three times to leave a colourless solid (6.2 g, 71%), m.p. 173–176 °C. ^1H NMR (CDCl_3): δ 0.63 (t, 12H, CH_3), 2.00 (m, 8H, CH_2), 6.12 (s, 2H, =CH, fur), 6.59 (t, 2H, =CH, ind_{5/6}), 6.86 (t, 2H, =CH, ind_{5/6}), 7.06 (s, 2H, =CH, ind₂), 7.16 (d, 2H, =CH, ind_{4/7}), 7.27 (d, 2H, =CH, ind_{4/7}), 7.57 (s, broad, 2H, NH). ^{13}C NMR: δ 8.4 (CH_3), 28.2 (CH_2), 43.8 (CET_2), 106.1, 110.8, 118.6, 120.1, 121.0, 121.1, 122.3, 126.2, 136.5, 158.4 (=CH and =CR, fur and ind). MS *m/z* (% and assignment): 438 ($[\text{M}]^+$, 8%), 409 ($[\text{M-Et}]^+$, 100%), 380 ($[\text{M-2Et}]^+$, 20%), 365 ($[\text{M-2Et-Me}]^+$, 18%). IR (KBr disc): ν 485 (s), 584 (m), 737 (s), 963 (m), 1107 (m), 1242 (w), 1333 (m), 1422 (m), 1457 (s), 1545 (w), 1618 (w), 2873 (m), 2963 (s), 3430 (s). Anal. Calc. for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}$: C, 82.15; H, 7.81; N, 6.39. Found: C, 81.97; H, 8.01; N, 6.30%.

2.3. Synthesis of the THF adduct of *N,N'*-dilithiated 2,5-bis{(diethyl-3'-indolyl)methyl}furan (**3**)

To a solution of the bis(indole) **2** (1.32 g, 3.01 mmol) in toluene (40 mL), was added *n*-butyllithium (4.5 mL, 1.6 M in hexane, 7.2 mmol) with stirring at ambient temperature and the solution was left to stir overnight. THF (20 mL) was added and the product precipitated as a crystalline colourless product which was collected by filtration (2.00 g, 90%). ^1H NMR (OC_4D_8): δ 0.82 (t, 12H, CH_3), 1.90 (m, 16H, CH_2 , THF), 2.25 (m, 8H, CH_2), 3.77 (m, 16H, OCH_2 , THF), 5.93 (s, 2H, =CH, fur), 6.59 (t, 2H, =CH, ind_{5/6}), 6.71 (t, 2H, =CH, ind_{5/6}), 7.31 (s, 2H, =CH, ind₂), 7.34 (d, 2H, =CH, ind_{4/7}), 7.39 (d, 2H, =CH, ind_{4/7}). ^{13}C NMR (OC_4D_8): δ 10.4 (CH_3), 27.0 (CH_2 , THF), 31.7 (CH_2), 46.5 (CET_2), 68.8 (OCH_2 , THF), 107.2, 114.4, 115.5, 116.3, 120.8, 130.5, 137.6, 150.0, 150.2, 161.2 (=CH and =CR, fur and ind). IR (Nujol mull): ν 736 (s), 892 (s), 1012 (s), 1048 (s), 1104 (w), 1138 (s), 1162 (s), 1200 (m), 1230 (m), 1300 (s), 1334 (s), 1596 (w). Anal. Calc. for $\text{C}_{46}\text{H}_{64}\text{Li}_2\text{N}_2\text{O}_5$: C, 74.77; H, 8.73; N, 3.79. Found: C, 74.65; H, 8.48; N, 3.64%.

2.4. Synthesis of the TMEDA adduct of *N,N'*-disodiated 2,5-bis{(diethyl-3'-indolyl)methyl}furan (**4**)

To a solution of the bis(indole) **2** (1.32 g, 3.01 mmol) in THF (40 mL), sodium hydride (0.17 g, 7.1 mmol) was added at ambient temperature with stirring. The mixture

was allowed to stir overnight and the solution was filtered from any remaining solids. The volume of the solution was reduced (20 mL) and TMEDA (2.79 g, 3.62 mL, 24.0 mmol) was added, followed by toluene (10 mL). A colourless crystalline product appeared after storage for two weeks at ambient temperature, which was collected (1.57 g, 65%). ^1H NMR (OC_4D_8): δ 0.89 (t, 12H, CH_3), 2.31 (s, 24H, NCH_3 , TMEDA), 2.38 (m, 8H, CH_2), 2.48 (s, 8H, NCH_2 , TMEDA), 2.49 (s, 3H, CH_3Ph , toluene), 6.15 (s, 2H, $=\text{CH}$, fur), 6.68 (t, 2H, $=\text{CH}$, ind_{5/6}), 6.86 (t, 2H, $=\text{CH}$, ind_{5/6}), 7.32 (s, 2H, $=\text{CH}$, ind₂), 7.26–7.38 (m, 5H, C_6H_5 , toluene), 7.48 (d, 2H, $=\text{CH}$, ind_{4/7}), 7.55 (d, 2H, $=\text{CH}$, ind_{4/7}). ^{13}C NMR (OC_4D_8): δ 10.2 (CH_3), 22.1 (CH_3Ph , toluene), 31.0 (CH_2), 46.3 (CET_2), 46.8 (NCH_3 , TMEDA), 59.5 (NCH_2 , TMEDA), 106.6, 115.5, 116.4, 117.0, 117.1, 120.9, 126.6, 129.5, 130.3, 137.8, 138.7, 149.8, 161.2 ($=\text{CH}$ and $=\text{CR}$, fur, ind and toluene). IR (Nujol mull): ν 734 (s), 942 (m), 1020 (m), 1170 (m), 1290 (s), 1334 (m). Anal. Calc. for $\text{C}_{49}\text{H}_{72}\text{N}_6\text{Na}_2\text{O}$: C, 72.92; H, 8.99; N, 10.41. Found: C, 72.68; H, 8.80; N, 9.61%.

2.5. Synthesis of the PMDETA adduct of *N,N'*-disodiated 2,5-bis{(diethyl-3'-indolyl)methyl}furan (**5**)

To a solution of bis(indole) **2** (1.32 g, 3.01 mmol) in THF (40 mL), sodium hydride (0.17 g, 7.20 mmol) was added at ambient temperature with stirring. The mixture was let stir overnight and the solution was filtered from any remaining solids. The solution was concentrated to 10 mL and PMDETA (4.16 g, 5.01 mL, 24.0 mmol) was added. Recrystallisation from THF gave a colourless crystalline product (2.26 g, 91%). ^1H NMR (OC_4D_8): δ 0.92 (t, 12H, CH_3), 2.21 (d, 6H, NCH_3 , PMDETA), 2.33 (d, 24H, NCH_3 , PMDETA), 2.38 (m, 8H, CH_2), 2.41–2.60 (m, 16H, NCH_2 , PMDETA), 6.11 (s, 2H, $=\text{CH}$, fur), 6.68 (t, 2H, $=\text{CH}$, ind_{5/6}), 6.86 (t, 2H, $=\text{CH}$, ind_{5/6}), 7.35 (s, 2H, $=\text{CH}$, ind₂), 7.48 (d, 2H, $=\text{CH}$, ind_{4/7}), 7.56 (d, 2H, $=\text{CH}$, ind_{4/7}). Anal. Calc. for $\text{C}_{48}\text{H}_{78}\text{N}_8\text{Na}_2\text{O}$: C, 69.53; H, 9.48; N, 13.51. Found: C, 69.44; H, 9.55; N, 13.68%.

2.6. Synthesis of *N,N'*-dipotassiated 2,5-bis{(diethyl-3'-indolyl)methyl}furan (**6**)

To the solution of bis(indole) **2** (1.32 g, 3.01 mmol) in THF (40 mL), potassium (0.28 g, 7.2 mmol) was added with stirring and the mixture refluxed for 2 h and let cool to room temperature. The solution was filtered from any remaining solids and concentrated to 20 mL. Recrystallisation from THF led to a white product which was isolated by filtration (1.43 g, 92%). ^1H NMR (OC_4D_8): δ 0.83 (t, 12H, CH_3), 2.10 (m, 4H, CH_2), 2.26 (m, 4H, CH_2), 6.46 (s, 2H, $=\text{CH}$, fur), 6.56 (t, 2H, $=\text{CH}$, ind_{5/6}), 6.72 (t, 2H, $=\text{CH}$, ind_{5/6}), 7.02 (s, 2H, $=\text{CH}$, ind₂), 7.05 (d, 2H, $=\text{CH}$, ind_{4/7}), 7.10 (d, 2H, $=\text{CH}$, ind_{4/7}).

^{13}C NMR (OC_4D_8): δ 9.3 (CH_3), 28.9 (CH_2), 45.1 (CET_2), 106.4, 116.1, 116.4, 117.1, 117.8, 120.1, 128.9, 136.4, 148.2, 161.8 ($=\text{CH}$ and $=\text{CR}$, fur and ind). IR (Nujol mull): ν 734 (s), 962 (m), 1028 (m), 1116 (w), 1144 (m), 1266 (s), 1278 (m), 1342 (m). Anal. Calc. for $\text{C}_{30}\text{H}_{32}\text{K}_2\text{N}_2\text{O}$: C, 69.99; H, 6.27; N, 5.44. Found: C, 67.92; H, 6.41; N, 4.86%.

2.7. X-ray structure determinations for compounds **2** and **3**

Data for the crystal structure determinations were collected on Bruker SMART (**2**) and KappaCCD (**3**) diffractometers, using crystals coated with a layer of hydrocarbon oil, attached to glass fibers, and cooled to 150 (**2**) and 123 K (**3**) using ($\text{Mo K}\alpha$ (0.71073 Å)) radiation. The structures were solved by direct methods and refined using XTAL 3.7 [14] (**2**) and SHELX programs systems [15] within XSEED 1.5 (**3**) [16]. All non-H atom displacement parameter forms were refined anisotropically for **2** and **3**. All H atoms were located and refined in (x , y , z , U_{iso}) for **2**, except for those of a disordered ethyl group (50:50% fixed occupancy) that were included and constrained at estimated values. All H atoms were calculated and constrained to ride with the attached carbon atoms for **3**, except for those of the methyl groups of a partial occupancy toluene solvent molecule that were not included. Disorder in the structure of **3** included a refined occupancy coordinated THF molecule (conformational disorder), a refined occupancy (orientational disorder) toluene molecule and a refined occupancy toluene/THF molecule population disorder (some restraints were applied to model the solvent disorder). Results are presents in Figs. 1, 2 and Tables 1 and 3.

3. Results and discussion

3.1. Synthesis

2,5-Bis{(diethyl-3'-indolyl)methyl}furan (**2**) was prepared according to Scheme 1. Treatment of furan with *n*-butyllithium (2.5 equiv.), followed by the addition of 3-pentanone (2.5 equiv.) gave the diol precursor 2,5-bis(diethylhydroxymethyl)furan (**1**) in moderate yield [13]. Attempts to improve the synthesis of **1** were unsuccessful, but led to an understanding of the reduced yield being due to the competing proton exchange between the dilithiated furan and α -protons of the enolisable ketone (based on acetone- d_6 reactions with the 2,5-dilithiofuran affording 2-(d_6 -dimethylhydroxymethyl)-5-deutero-furan in $\approx 50\%$ yield). The crude diol **1** was reacted with indole (2 equiv.) in the presence of trifluoroacetic acid in absolute ethanol leading to the formation of 2,5-bis{(diethyl-3'-indolyl)methyl} furanin 71% yield. The formation of the bis(3-indolyl) isomer **2** was selective, with no bis(2-indolyl) isomers isolable.

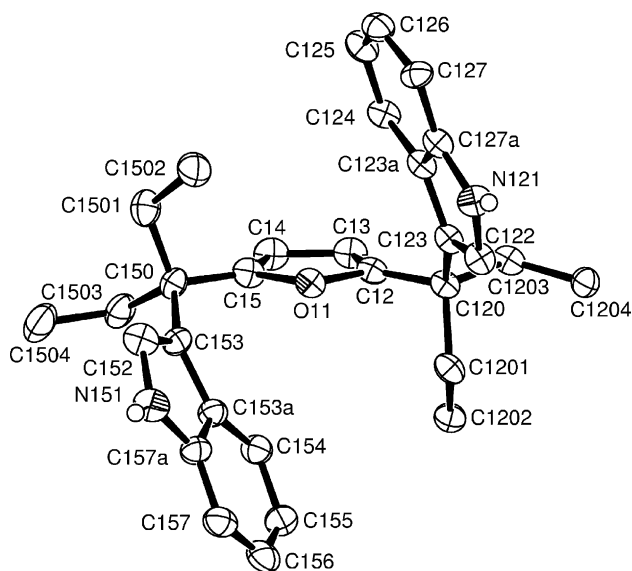


Fig. 1. Molecular structure and atom numbering scheme for 2,5-bis-bis(diethyl-3'-indolyl)methylfuran **2**. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms. N–H hydrogen atoms are shown with arbitrary radii of 0.1 Å.

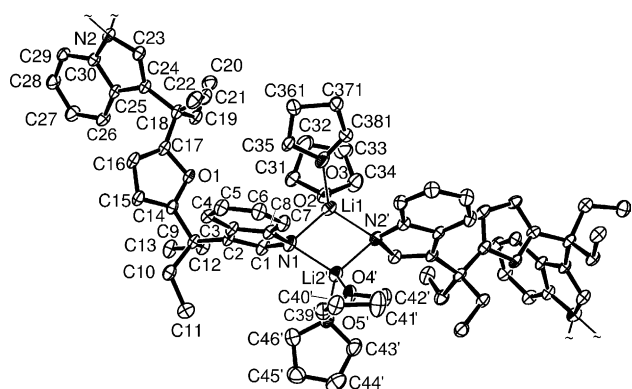


Fig. 2. Molecular structure and atom numbering scheme for the polymeric THF adduct of *N,N'*-dilithiated 2,5-bis-bis(diethyl-3'-indolyl)methylfuran **3**. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms.

The bis(2-indolyl) isomer of **2** is a desirable species for our aims of preparing π -complexes of indolides in relation to the successes of 2,5-disubstituted pyrrolide anions in this endeavour. Deliberate attempts to prepare bis(2-indolyl) analogues by the reaction of 3-methylindole with the diol (**1**) were unsuccessful, affording only traces of the desired bis(2-indolyl) product (3%, GC/MS).

The bis(indole) **2** was characterised by ^1H and ^{13}C NMR spectroscopy, and infrared spectroscopy, mass spectrometry, satisfactory microanalysis and X-ray crystal structure determination. The bis(indole) **2** is a colourless crystalline solid, soluble in diethyl ether, THF, benzene, less soluble in hexane, and is insoluble in methanol and ethanol.

The ^1H and ^{13}C NMR spectra of the bis(indole) **2** confirm the formulation, in particular the 3-indole substitution, Table 2. Of note, the two ethyl groups which are borne on the quaternary carbons bridging the furan and indole rings appear chemically equivalent in solution by both ^1H and ^{13}C NMR spectroscopy. This is an indication of non-restricted conformational freedom in solution at room temperature. Variable temperature NMR spectroscopy studies were not conducted to further study this phenomenon.

Mass spectrometric studies of the bis(indole) **2** shows the molecular ion peak at 438 (M^+ , 8%). Other ions include 409 ($M\text{-Et}$, 100%) and 380 ($M\text{-2Et}$, 20%). The IR spectrum of **2** features the NH stretching band at 3430 cm^{-1} .

Dimetallation of the bis(indole) **2** was achieved according to Scheme 2, by which four complexes were isolated in pure form with reproducible formulations. The dilithium complex was isolated as the THF adduct **3**, the disodium complex isolated as both TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) and PMDETA (PMDETA = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine) adducts **4** and **5**, while the dipotassium complex **6** was isolated in solvent free form in 90%, 65%, 91% and 92% yields, respectively. The colourless complexes were characterised by ^1H , ^{13}C NMR and infrared spectroscopies. A crystal X-ray structure determination was performed in the case of the dilithium complex **3**. All complexes gave satisfactory microanalyses, except **6**, which gave low carbon content (3% lower carbon percentage than the postulated solvent free formulation).

The dilithium complex **3** is slightly soluble in THF and insoluble in toluene. The disodium and dipotassium complexes **4–6** are moderately soluble in THF. The THF adduct of the disodium complex (isolated but not fully characterised) loses coordinated THF during repeated recrystallisation from toluene or evaporation under vacuum, resulting in a white powder which is no longer soluble in THF, while the solubility of the corresponding unsolvated dipotassium complex remained unaffected by the same process. The dipotassium complex is considered to initially exist as THF adduct of undetermined stoichiometry when isolated from a THF solution, but completely loses the coordinated THF in vacuo (298 K, 10^{-2} mbar, 1 h). The TMEDA adduct of the dipotassium complex was obtained as a pure white powder, but could not be crystallised.

The ^1H NMR spectra of complexes **3–6** are summarised in Table 2. Significant differences are found between the spectra of the dilithium or disodium complexes and the dipotassium complex for the proton resonances of the furanyl ring and the 2, 4 and 7 positions of the indolide rings. The dilithium complex **3** and disodium complexes **4** and **5** display their singlet (protons at indolide position 2) and two doublet

Table 1
Crystal data and refinement details for **2** and **3**

Compound	2	3
Empirical formula	C ₃₀ H ₃₄ N ₂ O	C ₄₆ H ₆₄ N ₂ O ₅ Li ₂ · 1.5(C ₇ H ₈) · 0.5(C ₄ H ₈ O)
Formula weight	438.62	913.13
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	9.986(1)	15.0093(3)
<i>b</i> (Å)	14.118(2)	23.2614(6)
<i>c</i> (Å)	19.207(2)	16.6626(4)
α (°)	104.949(2)	90
β (°)	96.480(2)	111.661(2)
γ (°)	105.403(2)	90
<i>V</i> (Å ³)	2474.0(5)	5406.7(2)
<i>Z</i>	4	4
Crystal size (mm ³)	0.38 × 0.35 × 0.16	0.3 × 0.3 × 0.3
Reflections collected	24,389	42,247
Independent reflections	12,034	5023
<i>R</i> _{int}	0.019	0.083
Reflections with <i>I</i> > 2σ(<i>I</i>)	7986	3273
Parameters	856	723
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.024	<i>R</i> ₁ = 0.065
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.050	<i>wR</i> ₂ = 0.183

Table 2
¹H NMR spectroscopic data for compounds **3–6** (399.694 MHz, OC₄D₈, 298 K; resonances for contained solvent are not given)

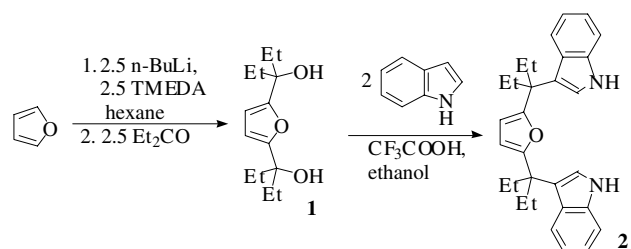
Compound	2	3	4	5	6
CH ₃ (t)	0.63	0.82	0.89	0.92	0.83
CH ₂ (m)	2.00	2.25	2.38	2.38	2.10, 2.26
=CH, fur (s)	6.12	5.93	6.15	6.11	6.46
=CH, ind _{5/6} (pseudo t)	6.59, 6.86	6.59, 6.71	6.68, 6.86	6.68, 6.86	6.56, 6.72
=CH, ind ₂ (s)	7.06	7.31	7.32	7.35	7.02
=CH, ind _{4/7} (d)	7.16, 7.27	7.34, 7.39	7.48, 7.55	7.48, 7.56	7.05, 7.10
NH (broad, s)	7.57	–	–	–	–

Data for compound **2** are included for comparison (399.694 MHz, CDCl₃, 298 K).

Table 3
Selected bond lengths (Å) and angles (°) for **3**

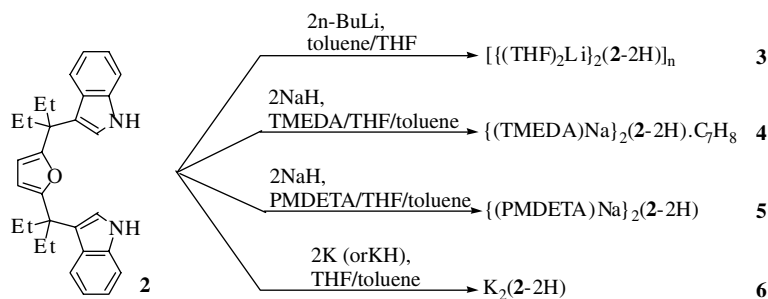
Bond lengths			
Li(1)–O(3)	1.960(9)	Li(1)–O(2)	1.978(8)
Li(1)–N(2)′	2.062(9)	Li(1)–N(1)	2.072(9)
Li(2)–O(4)	1.922(8)	Li(2)–O(5)	1.971(9)
Li(2)–N(1)′	2.030(9)	Li(2)–N(2)	2.078(9)
Li(1) ··· Li(2)′	2.572(11)		
Bond angles			
O(3)–Li(1)–O(2)	98.8(4)	O(3)–Li(1)–N(2)′	123.3(4)
O(2)–Li(1)–N(2)′	108.3(4)	O(3)–Li(1)–N(1)	109.2(4)
O(2)–Li(1)–N(1)	115.9(4)	N(2)′–Li(1)–N(1)	102.3(4)
O(4)′–Li(2)′–O(5)′	100.6(4)	O(4)′–Li(2)′–N(1)	118.1(4)
O(5)′–Li(2)′–N(1)	107.6(4)	O(4)′–Li(2)′–N(2)′	108.6(4)
O(5)′–Li(2)′–N(2)′	119.8(4)	N(1)–Li(2)′–N(2)′	103.1(4)
Li(2)′–N(1)–Li(1)	77.7(3)	Li(1)–N(2)′–Li(2)′	76.8(3)
C(1)–N(1)–Li(2)′	125.0(4)	C(8)–N(1)–Li(2)′	123.3(4)
C(1)–N(1)–Li(1)	107.9(4)	C(8)–N(1)–Li(1)	117.4(4)
C(30)′–N(2)′–Li(1)	117.2(4)	C(30)′–N(2)′–Li(2)′	126.3(4)

′ denotes symmetry operator 1–*x*, *y*–1/2, 1/2–*z*.



Scheme 1.

resonances (protons at indole positions 4 and 7) shifted downfield relative to the bis(indole) **2** (0.2–0.3 ppm), but for the dipotassium complex **6** an upfield shift relative to **2** (0–0.2 ppm) for the same proton resonances is noted. The dipotassium complex **6** experiences a downfield chemical shift (0.34 ppm) for the singlet resonance of the protons of the furan ring relative to the bi-



Scheme 2.

s(indole) **2**, while the other dilithium and disodium complexes show slight changes for the same proton resonance relative to **2** (0.09, 0.03, 0.01 ppm for **3**, **4** and **5** respectively). The significant differences noted in the ^1H NMR chemical shifts among complexes **3–6** suggest that the different sized metals very likely have different bonding modes with the tricyclic unit in the solution. The proton resonances of the furanyl ring have been affected noticeably by potassium incorporation, but only slightly in the cases of the other small sized metals, which indicates that potassium might coordinate to both indolyl and furanyl rings, while the other small sized metals most likely coordinate with indolide rings only, as in the solid state structure of the dilithium complex **3** in which lithium cations are σ -bound only to indolyl rings through the nitrogen centres, vide infra. This proposal is supported further by the appearance of the methylene protons of the ethyl groups for the dipotassium complex **6**, which indicate a conformational restriction resulting from the coordination of potassium with both indolide and furanyl rings that would be expected for such a chelate ring structure. In addition, differences in the mode of interaction of the various metals with the indolide functionalities is likely, perhaps with potassium forming multihapto-interactions, as evident from the different chemical shifts of the indolide protons in the dipotassium complex **6** compared to the dilithium and disodium complexes **3–5** (particularly for the protons in positions 2, 4 and 7).

The ^{13}C NMR spectra of complexes **3–6** display all of the resonances expected at typical chemical shifts and have not been assigned to individual aromatic carbons of the indolide or furan units. IR spectroscopy of complexes **3–6** confirmed the dimetallation of the bis(indole) **2** with removal of both NH protons in all cases.

3.2. X-ray crystal structures of **2** and **3**

Crystals of the bis(indole) **2** suitable for single crystal X-ray structure determination were grown from a saturated diethyl ether/hexane solvent mixture (1:1; v/v), which was stored at -30°C for three days. The asymmetric unit contains two molecules with nearly identical

geometries; they pack in the lattice with most indolyl planes lying parallel to inversion-related neighbours. Fig. 1 shows the disposition of molecule 1.

The conformation of the bis(indole) **2** in the solid state features each of the indole units extending on either side of the plane of the furan unit in *anti*-dispositions. The oxygen centre of the furan functionality is directed inwards towards the void created by the two indole units. The conformation of the diindole is preorganised for an unusual C_2 symmetric internally coordinated *ansa*-metallocene that could be envisaged upon dimetallation of the indole functionalities. Interplanar dihedral angles between the pairs of indolyl skeletons are $43.16(5)^\circ$, $38.07(5)^\circ$ (molecules 1 and 2, respectively) and from the indolyl planes to the central furan plane are $73.94(6)^\circ$, $62.53(6)^\circ$ (molecule 1), and $69.61(7)^\circ$ and $67.39(7)^\circ$ (molecule 2).

Colourless prismatic crystals of the dilithium complex **3** suitable for single crystal X-ray structure determination were grown by the dropwise addition of a toluene solution of the lithium complex into THF and left to stand for 3 h. The asymmetric unit consists of one monomeric unit of **3** and disordered solvent molecules modeled as THF and toluene molecules (1.5 toluene and 0.5 THF in asymmetric unit) with some geometry restraints. The crystal structure reveals **3** to be a polymeric species in the solid state, Fig. 2 shows a portion of the polymeric structure of **3**. Each bis(indolide) dianion coordinates with four lithium cations by μ_2 -bridging through indolide units, two per indolide. Each lithium cation σ -binds to two indolide units of adjacent bis(indolide) dianions through the bridging nitrogen centres and also with two coordinated THF molecules. Two bridging lithium cations and two σ -bound indolide nitrogen centres comprise four-membered Li_2N_2 ring cores. Thus each diindolide unit participates in a Li_2N_2 core with two other bis(indolide) units and, in this way, the molecule extends to a polymeric form.

The Li_2N_2 ring in complex **3** is quite planar, which is similar to that seen in $[\{N\text{-lithioindole}(\text{THF})_2\}_2]$ [17], but different from that of $[\text{N-lithioindole}(\text{TMEDA})_2]$ [18] in which the shape of the Li_2N_2 ring is obviously affected by the chelating TMEDA molecules or desire for

the lithium centres to attain a higher coordination number through interaction with the 2-position of the indolide. The tetracoordinated lithium cations in **3** are similar to dimeric [*N*-lithioindole(THF)₂]₂, but different from [*N*-lithioindole(TMEDA)₂] in which the lithium cations are five coordinate as a result of the η²-indolide binding. For this reason, the Li–N bonds in **3** are of similar lengths (2.062(9), 2.072(9), 2.030(9), 2.078(9) Å) to those in [*N*-lithioindole(THF)₂]₂ (2.067(6), 2.092(7) Å) rather than two short and two long bonds in [*N*-lithioindole(TMEDA)₂] (2.004(7), 2.231(10) Å) arising from the distorted nature of the μ₂-N bridging indolide units which imply lesser and greater amounts of involvement of the aromatic sp² orbitals on the nitrogen centres of the indolide units. The N–Li–N (102.3(4)° and 103.1(4)°) and Li–N–Li (77.7(3)° and 76.8(3)°) angles related to Li₂N₂ ring for **3** are also similar to those of [*N*-lithioindole(THF)₂]₂ (103.6(3)° and 76.4(2)°) but different from those of [*N*-lithioindole(TMEDA)₂] (96.6(3)° and 82.5(3)°) further indicating the different bonding nature.

The indolide rings in complex **3** are orientated in a *syn*-disposition relative to the Li₂N₂ ring. This is different from [*N*-lithioindole(THF)₂]₂ in which the rings are arranged *anti*-despite also being solvated by THF. A *syn*-arrangement is also noted for [*N*-lithioindole(TMEDA)₂]. The indolide units involved in the Li₂N₂ ring cores are not parallel with each other, nor are they perpendicular to the plane of the Li₂N₂ ring, which differs from the closest reported analogous structure based on indolide itself, [*N*-lithioindole(THF)₂]₂.

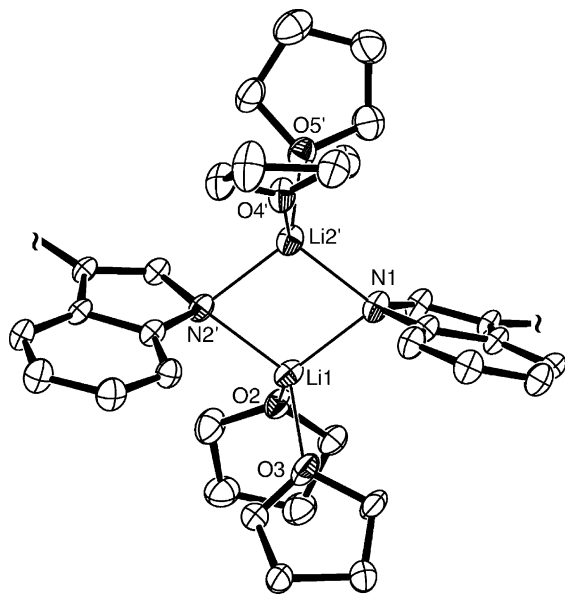


Fig. 3. View of the Li₂N₂ core for the polymeric THF adduct of *N,N'*-dilithiated 2,5-bis{(diethyl-3'-indolyl)methyl}furan **3**. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms.

The twisting in complex **3** is clearly the result of the substitution of bis(indolide) and the geometric restraints that this imposes on the formation of the polymeric complex and perhaps interactions between the six-membered rings of the indolide units.

In contrast to the polymeric structure of complex **3** featuring μ₂-bridging indolide anions, bulky 2-substituents have been shown to result in monomeric lithium indolides such as [*N*-Li-2-{SiMe₂(*t*-Bu)}C₈NH₅(THF)₃] [10]. Clearly, the substitution of the indolide in the 3-position of complex **3** does not have such a drastic effect in bringing about this structural change (see Fig. 3).

4. Conclusion

We have reported a new bis(indole) with donor atom functionality that offers interesting structural possibilities for its *N,N'*-deprotonated complexes, together with a series of such Group 1 metal complexes. We are continuing to pursue a range of possibilities to control the binding modes of anionic nitrogen heterocycles in order to structurally mimic their hydrocarbyl analogues that feature π-bound multihapto-interactions and investigate the reactivity of such complexes.

5. Supplementary material

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 242531 for compound **2**, CCDC no. 242532 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax. (int code) +44(1223)336-033 or e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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