

Synthesis of Unsymmetrical 4,4'-Disubstituted 2,2'-Bipyridines containing Benzo Crown Ether and Ferrocene Moieties

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A simple one-pot synthesis of unsymmetrical 4,4'-disubstituted 2,2'-bipyridine ligands containing benzo crown ether and redox-active ferrocene moieties is described.

Ruthenium,^{1,2} osmium,³ and rhenium^{4,5} polypyridyl complexes exhibit properties of importance to redox electrocatalysis and solar energy conversion.^{6,7} With respect to the latter, although simple transition metal 2,2'-bipyridyl (bpy) co-ordination compounds are known to be effective photosensitisers⁶ Gratzel and co-workers⁸ have shown that unsymmetric 4,4'-dialkyl-2,2'-bipyridineruthenium(II) complexes can substantially improve the efficiency of visible light photocatalytic cleavage of water. Surprisingly, very few reports⁹⁻¹¹ have subsequently described the syntheses of these desired unsymmetrical bipyridyl ligands. We present here a simple one-pot synthesis of unsymmetrical 4,4'-disubstituted 2,2'-bipyridine compounds using step-by-step lithiation of the commercially available 4,4'-dimethyl-2,2'-bipyridine **1**.

Monolithiation of **1** using 1 equiv. of lithium diisopropylamide (LDA) in tetrahydrofuran is known to produce **2**.¹¹ Reaction of **2** with the appropriate aldehyde (R¹CHO) gave the intermediate **3a-e** (X = Li) [the corresponding alcohol **3a-e** (X = H) can be isolated in excellent yield (Table 1)], and *in situ* this lithium salt can be further lithiated with 1 equiv. of LDA to give **4**. Subsequent addition of a different aldehyde (R²CHO) followed by quenching of the reaction mixture with water gave the crude product which after purification by flash chromatography produced the respective unsymmetrical diol **5a-e** (Scheme 1, Table 1).

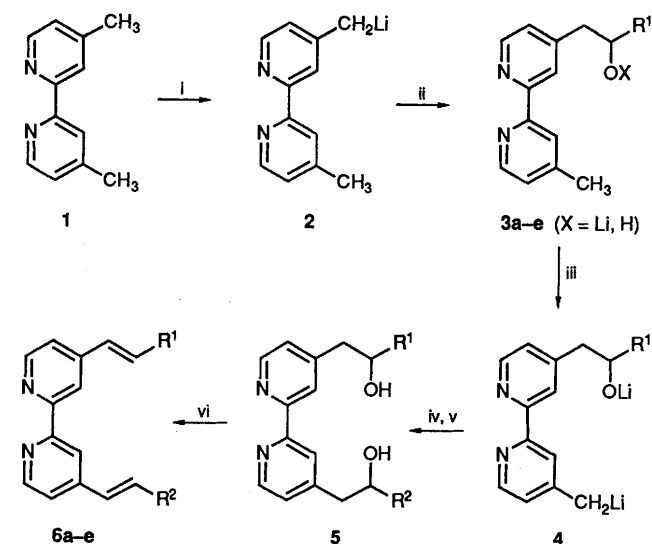
Dehydration of the diols **5a-e** with pyridinium toluene-*p*-sulphonate (PTPS) in boiling toluene afforded the respective *E,E*-dienes **6a,b,d,e** in very good yields (Table 1). The structures

of all these new compounds were characterised on the basis of spectroscopic and analytical evidence.† Interestingly with **5c** complete dehydration could not be achieved and only the mixed vinyl-alcohol compound **7** was isolated.

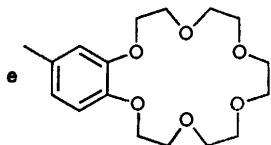
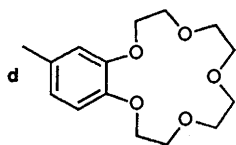
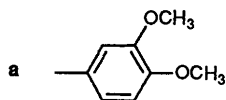
The new unsymmetrical bipyridyl ligands are all polytopic in design and contain recognition sites for binding transition metal and Group 1A/IIA metal guest cations. For example, preliminary

† All new compounds gave spectroscopic and analytical data in accordance with assigned structures. Data are quoted for compounds **5b** and **6b**. For **5b** m.p. 71–72 °C (Found: C, 62.3; H, 6.3; N, 4.0. C₃₈H₄₂FeN₂O₇·2H₂O requires C, 62.46; H, 6.34; N, 3.83%); δ_H (270 MHz, CDCl₃) 2.37 (1 H, b s, OH), 2.77 (1 H, b s, OH), 2.98–3.10 (4 H, m, CH₂), 3.74 (8 H, s, OCH₂), 3.85–3.90 (4 H, m, OCH₂), 4.09–4.14 (4 H, m, ArOCH₂), 4.17–4.26 (9 H, m, Fc-H), 4.69 (1 H, t, *J* 6.4 Hz, CH-Fc), 4.93 (1 H, t, 6.7 Hz, CH-Ar), 6.78–6.88 (3 H, m, ArH), 7.05 (1 H, d, *J* 4.9 Hz, 5-PyH), 7.12 (1 H, d, *J* 4.8 Hz, 5'-PyH), 8.25 (1 H, s, 3-PyH), 8.26 (1 H, s, 3'-PyH), 8.49 (1 H, d, *J* 4.9 Hz, 6-PyH), 8.50 (1 H, d, *J* 4.9 Hz, 6'-PyH); *m/z* (FAB) 695 (*M* + H⁺, 75%).

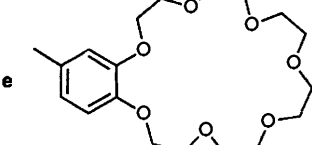
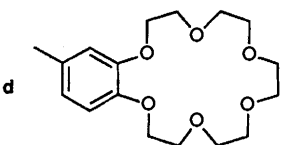
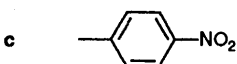
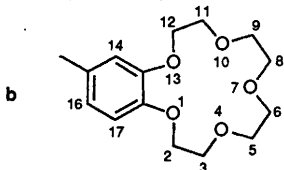
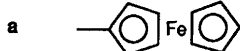
For **6b**, m.p. 83–85 °C (decomp.) (Found: C, 65.6; H, 5.8; N, 4.0. C₃₈H₃₈FeN₂O₅·2H₂O requires C, 65.71; H, 6.09; N, 4.03); δ_H (270 MHz, CDCl₃) 3.77 (8 H, s, OCH₂), 3.94–3.97 (4 H, m, OCH₂), 4.16 (5 H, s, unsubst. Fc ring), 4.16–4.21 (4 H, m, OCH₂), 4.36 (2 H, t, *J* 1.8 Hz, β,β'-FcH), 4.52 (2 H, t, *J* 1.8 Hz, α,α'-FcH), 6.72 (1 H, d, *J* 16.1 Hz, =CH-Fc), 6.86–6.89 (1 H, m, ArH), 6.98 (1 H, d, *J* 16.3 Hz, =CH-Ar), 7.10–7.12 (2 H, m, ArH), 7.25–7.38 (3 H, m, 5,5'-PyH and =CH-Fc), 7.39 (1 H, d, *J* 16.3 Hz, =CH-Ar), 8.47 (1 H, s, 3'-PyH), 8.52 (1 H, s, 3-PyH), 8.62 (1 H, d, *J* 5.1 Hz, 6'-PyH) and 8.66 (1 H, d, 6.1 Hz, 6-PyH); *m/z* (FAB) 659 (*M* + H⁺, 100%).



For 3, 5 and 6

R¹

For 5 and 6

R²

Scheme 1. Reagents and conditions: i, LDA (1 equiv.), -78°C in THF; ii, R^1CHO , -78 to 0°C ; iii, $\text{X} = \text{Li}$ LDA (1 equiv.), -78 to 0°C in THF; iv, R^2CHO , 0°C to room temp; H_2O , PTPS/toluene, reflux.

co-ordination studies reveal ligand **5b** to form the heteropolymetallic ruthenium(II)-ferrocene-sodium cation complex **8**.*

* Characterised by elemental analysis of the isolated heteropolymetallic hexafluorophosphate complex. (Found: C, 45.1; H, 3.7; N, 5.2. $\text{8}\cdot 3\text{PF}_6$ requires C, 45.5; H, 3.5; N, 5.5%).

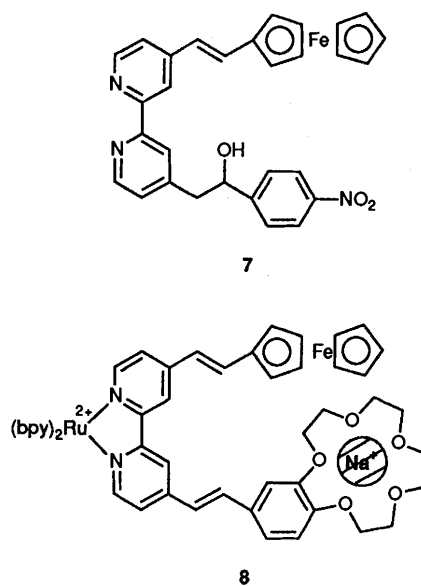


Table 1. Yields (%) of **3** ($\text{X} = \text{H}$), **5** and **6**

Compd.	3 ($\text{X} = \text{H}$)	5	6
a	95	52	88
b	77	59	86
c	77	30	—*
d	76	58	90
e	73	54	85

* Identified as **7**, 46% yield.

The photo- and electro-chemical properties of **8** and other heteropolymetallic transition metal complexes of ligands **5** and **6** are under current investigation.

Experimental

Typical Procedure using the Preparation of 4-[2-Hydroxy-2-(2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxapentadecin-15-yl)ethyl]-4'-[2-hydroxy-2-(ferrocenyl)ethyl]-2,2'-bipyridine 5b.—A solution of compound **1** (2.5 g, 13.6 mmol) in anhydrous THF (75 ml) was added under a nitrogen atmosphere to a stirred solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (2.0 ml, 14.3 mmol) and butyllithium (1.6M solution in hexane; 8.8 ml, 14.1 mmol) at -78°C . The resulting dark orange-red mixture was allowed to warm to 0°C and stirred for 1 h at this temperature. A solution of ferrocenecarbaldehyde (3.0 g, 14.0 mmol) in anhydrous THF (20 ml) was added dropwise during 5 min and stirring was continued at 0°C until the reaction was completed (2 h, monitored by TLC). The reaction mixture was then cooled to -78°C and treated successively with diisopropylamine (2.0 ml, 14.3 mmol) and butyllithium (1.6M solution in hexane; 8.8 ml, 14.1 mmol). After being stirred at -78°C for 20 min and at 0°C for 1 h, 2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxapentadecine-15-carbaldehyde (4.15 g, 14.0 mmol) in THF (50 ml) was added dropwise and the resulting mixture stirred at 0°C for 2 h and then at room temperature overnight. The reaction mixture was poured into ice-water and extracted with dichloromethane and the extracts were dried (MgSO_4) and evaporated. The crude product was then purified by flash chromatography on silica gel with dichloromethane-methanol-ammonium hydroxide (100:5:1) as the eluant to afford the diol **5b** (5.57 g, 59%).

Typical Dehydration Procedure using Preparation of 6b.—A solution of **5b** (1 g, 1.44 mmol) and PTPS (0.25 g) in dry toluene (150 ml) was refluxed overnight using a Dean–Stark trap. The cooled solution was washed with water and dried (MgSO_4). The solvent was removed under reduced pressure and the resulting crude product purified by flash chromatography on silica gel with dichloromethane–methanol–ammonium hydroxide (100:5:1) as the eluant to afford **6b** (0.82 g, 86%).

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