

# Synthesis of novel chiral bis(ferrocenyl) ligands and their use as voltammetric metal cation sensors

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Received 20 March 2002; accepted 8 May 2002

## Abstract

Bis(ferrocenyl) derivatives **3a**, **3c** and **3d** containing secondary chelating substituents act as efficient voltammetric sensors of  $Mg^{2+}$  and  $Zn^{2+}$  ions in acetonitrile solution in concentrations as low as 10 mol%: a new redox peak appears in the cyclic voltammogram, positively shifted by 170–225 mV for **3a**, 160–175 mV for **3c** and 160–170 mV for **3d**. Compounds **3b** and **4** are selective for  $Zn^{2+}$  (215 mV shift) and  $Mg^{2+}$  (205 mV shift) ions, respectively, whilst **3d** is also responsive to  $Ca^{2+}$  ions (165 mV shift) with no interference from a large excess of several other metal salts. The X-ray crystal structure of **3a** is also reported. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Ferrocene; Imidazoline; Chiral ligands; Electrochemistry; Crystal structures; Sensor

## 1. Introduction

There is continued interest in the study of redox-active ligands in molecular recognition processes whereby complexation of a guest species (e.g. a metal ion) in solution leads to a change in the electrochemical response of the host molecule [1–3]. Ferrocene derivatives have been widely employed in this context [4–12]. Cation binding at an adjacent receptor site induces a positive shift in the redox potential of the ferrocene–ferrocenium couple by through-bond and/or -space electrostatic interactions. By varying the applied potential the complexing ability of the ligand can be switched on and off.

In early work, macrocyclic receptors attached to ferrocene were extensively studied and cation selectivity could be achieved by tailoring the cavity size. More recently, non-macrocyclic functional groups which act as cation binding sites have provided new voltammetric sensors. For example, Beer and Wild observed that 1,2-dimethoxy-4-(iminoferrocenyl)benzene was responsive to  $Mg^{2+}$  ions by coordination at the imine linkage [7]

and we reported that certain ferrocenyl–oxazoline [11,12] and –imine derivatives [12] display remarkably high selectivities to  $Mg^{2+}$  and  $Ca^{2+}$  ions with no interference from a large excess of other metal salts. Tucker and co-workers have attached pyridine ligands to ferrocene derivatives and monitored their complexation with 'd' block metals, especially  $Cu^+$  and  $Zn^{2+}$  ions [9,10]. We now report cation recognition studies using the new bis(ferrocenyl) systems **3a–d** and **4** which contain the imidazoline unit.

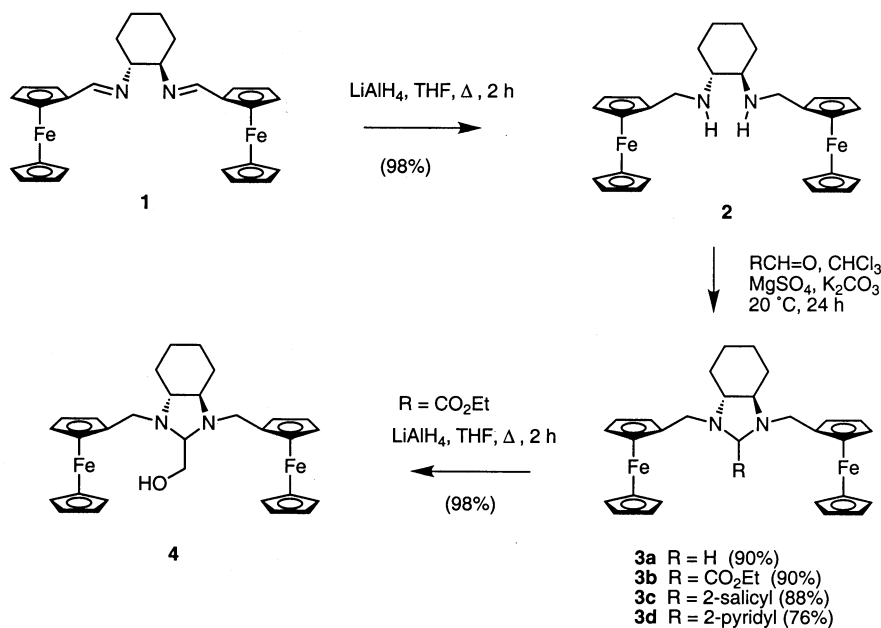
## 2. Results and discussion

### 2.1. Synthesis

Compound **1** was synthesised as described [13]. Reduction of **1** to diamine derivative **2** was achieved by reaction with lithium aluminium hydride using a method adapted from Tendero et al. [14]. Compounds **3a–3d** were synthesised by condensation of diamine **2** with the corresponding aldehyde using a modification of the method reported by Coldham et al. [15]. Ester derivative **3b** was cleanly reduced to the alcohol derivative **4** with lithium aluminium hydride (Scheme 1). All the reactions are high yielding and the structures of the new products were confirmed by standard

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Scheme 1.

spectroscopic methods and elemental analysis, and additionally for **3a** by X-ray crystallography.

## 2.2. X-ray crystal structure of **3a**

The asymmetric unit of **3a** in the crystal structure comprises two molecules (A and B) of similar conformation (Fig. 1 shows molecule A). The cyclohexane ring adopts a chair conformation and the heterocycle an envelope conformation (four atoms coplanar, C(1) deviating from their plane by 0.68–0.69 Å). The rings are fused in a *trans* fashion with both chiral centres C(1) and C(2) having *R*-configurations. Both N atoms are pyramidal, their lone pairs are nearly antiparallel (forming an angle of 160° in molecule A and 164° in B) and point to opposite sides of the octahydrobenzimidazole system's mean plane. Hence chelation of a metal ion by both N atoms of **3a** is impossible.

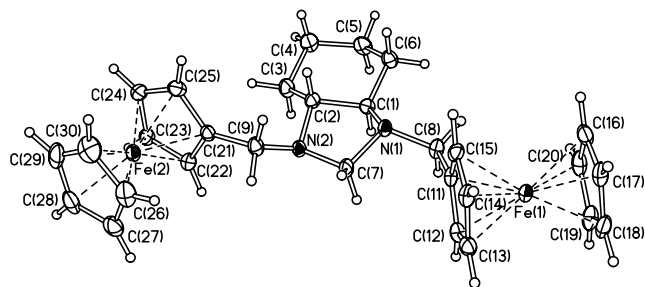


Fig. 1. Molecule A in the crystal of **3a**, showing 50% thermal ellipsoids.

## 2.3. Metal coordination studies

We reported recently that diimine **1** is a voltammetric sensor for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions [12]. It was, therefore, of interest to investigate the electrochemical properties of **2**, **3a–3d** and **4** by cyclic voltammetry (CV). Compounds **2**, **3a–3d** and **4** each exhibited a reversible two-electron redox wave typical of a bis(ferrocenyl) derivative with non-interacting ferrocene units. The criteria applied for reversibility was a ratio of  $1.0 \pm 0.1$  for the intensities of the cathodic and anodic currents, and no shifts of the half-wave potentials with varying scan rates. Diamine **2** was unresponsive to a wide range of metal cations in acetonitrile solution. In contrast, for compounds **3a–3d** and **4** titration studies with the addition of metal perchlorate salts revealed a typical two-wave response [1] with the appearance of a new wave at more positive potentials ascribed to the metal complexed species. For the series **3a–3d** it is notable that the cation selectivity changes markedly depending on the substituent attached at C(2) of the heterocycle (Table 1). For example, **3a** and **3c** are responsive to  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ , whereas **3b** is selective for  $\text{Zn}^{2+}$ . Compound **4** is selective for  $\text{Mg}^{2+}$ . Attempts to grow X-ray quality crystals of metal complexed species to shed light on the precise sites of binding were unsuccessful. The data for **3a** in the presence of 0.6 equivalents of  $\text{Zn}(\text{ClO}_4)_2$  are shown in Fig. 2. A small (ca. 30 mV) positive shift in the potential of the wave corresponding to  $E_{\text{free}}^{1/2}$  is also observed in the presence of the metal salt. Notably, the presence of a range of other metal cations in solution [ $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  (all as their perchlorate salts)]

Table 1  
Cyclic voltammetric data

Ligand ( $M^{2+}$ )	$E_{\text{free}}^{1/2}$ (mV)	$E_{\text{complex}}^{1/2}$ (mV)	$\Delta E$ (mV)	Min. eq. $M^{2+}$ <sup>a</sup>	Max. eq. $M^{2+}$ <sup>b</sup>	$K_1/K_2$ <sup>c</sup>
3a–Mg	455	615	170	0.2	0.5	$2.6 \times 10^5$
3a–Ca	455	–	0	–	–	0
3a–Zn	455	680	225	0.2	0.5	$4.1 \times 10^7$
3b–Mg	455	–	0	–	–	0
3b–Ca	455	–	0	–	–	0
3b–Zn	455	670	215	0.2	0.6	$1.9 \times 10^7$
3c–Mg	455	605	160	0.2	0.7	$1.2 \times 10^5$
3c–Ca	455	–	0	–	–	0
3c–Zn	455	620	165	0.2	0.6	$3.8 \times 10^5$
3d–Mg	455	615	160	0.1	0.7	$2.6 \times 10^5$
3d–Ca	455	610	155	0.2	0.9	$1.7 \times 10^5$
3d–Zn	455	605	150	0.1	0.6	$1.2 \times 10^5$
4–Mg	455	650	195	0.2	0.6	$3.9 \times 10^6$
4–Ca	455	–	0	–	–	–
4–Zn	455	–	0	–	–	–

<sup>a</sup> Minimum equivalents of metal perchlorate salt required to produce a detectable second redox peak

<sup>b</sup> Equivalents of metal salt required for the complete disappearance of the original ligand redox peak ( $E_{\text{free}}$ ).

<sup>c</sup> Binding enhancement for the complexation of the metal cation calculated using the equation employed in Ref. [1]. The equilibrium constants  $K_1$  and  $K_2$  correspond to complexation processes by the neutral and oxidised forms of the ligand.

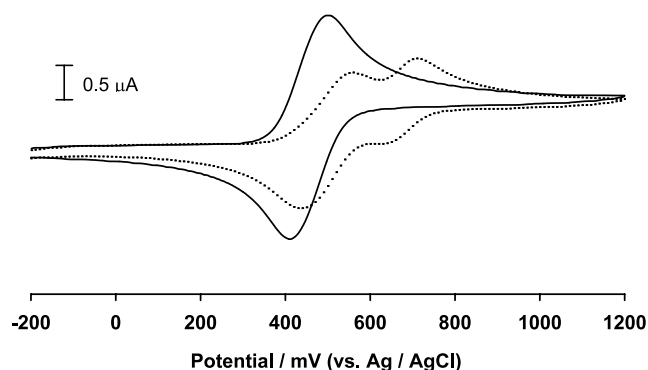


Fig. 2. Cyclic voltammograms of **3a** in MeCN (—) and after the addition of  $Zn(ClO_4)_2$  (0.6 equivalents) (---).

$Al(CF_3SO_3)_3$  and  $MnSO_4$ ] had no effect on the CVs of **3a–3d** and **4**. The selectivity is striking, suggesting that specific binding geometries are obtained with the different ligand–metal combinations. The electrochemical response was shown not to arise from adventitious protonation or hydration of the ligands: the addition of perchloric acid or water did not give new redox waves corresponding to those observed in the presence of metal cations.

<sup>1</sup>H-NMR titration studies provide further evidence for metal complexation. A typical [6,10–12] downfield shift was observed for the protons in the vicinity of the site of complexation. Fig. 3 shows the relevant data for compound **3a** upon addition of aliquots of  $Zn(ClO_4)_2$ . The chemical shifts of the hydrogen atoms on the cyclohexane and Cp rings were essentially unchanged due to the increased separation from the coordination site. The response saturates upon addition of 0.9 equivalents of  $Zn^{2+}$ . Upon addition of additional

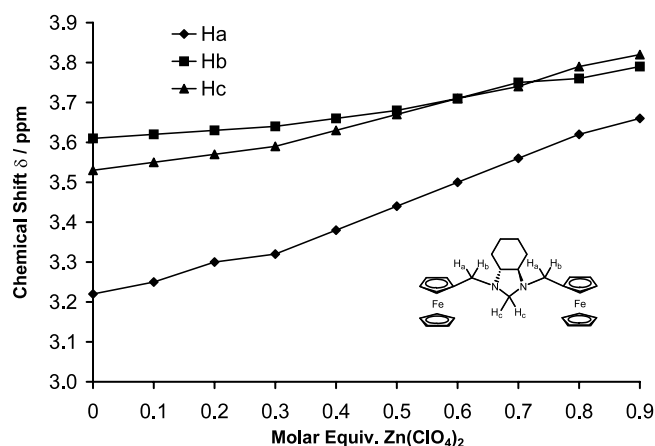


Fig. 3. <sup>1</sup>H-NMR titration curves of  $H_a$ ,  $H_b$  and  $H_c$  of **3a** with added equivalents of  $Zn(ClO_4)_2$  in  $CD_3CN$ .

$Zn^{2+}$  decomposition products were observed, the spectra of which partially overlapped the signals from the protons which were being monitored. Job plots suggested 1:1 complexation for **3a–Zn<sup>2+</sup>, **3a–Mg**<sup>2+</sup> and **3d–Ca**<sup>2+</sup>. We note that CV and NMR techniques used to monitor metal binding of **3a–3d** and **4** do not always suggest the same stoichiometry for ligand–metal combinations. This is a known feature of related systems arising from the different concentrations and timescales employed in these techniques [1].**

In summary, we have demonstrated that a series of new imidazoline ligands bearing ferrocene substituents are efficient redox sensors for metal cations, with high selectivity displayed by some derivatives. This recognition process is easily monitored by CV techniques which show a significant positive shift in the potential of the

ferrocene–ferrocenium redox couple. Complementary evidence for metal binding is provided by  $^1\text{H-NMR}$  titration studies. The chirality of these compounds is an attractive feature for synthetic applications, e.g. catalysis in metal-mediated asymmetric transformations under electrochemical control [16].

### 3. Experimental

$^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra were obtained on Oxford 200, Varian Unity 300 and Varian VXR 400 spectrometers; chemical shifts are quoted in ppm, relative to tetramethylsilane ( $\text{Me}_4\text{Si}$ ) as an internal reference (0 ppm).  $J$ -values are given in Hz. Mass spectra (EI) were recorded on a Micromass Autospec spectrometer operating at 70 eV. IR spectra were recorded using a Paragon 1000 FTIR spectrometer operated from a Grams Analyst 1600. M.p. were recorded on a Phillip Harris m.p. apparatus and are uncorrected. Elemental analyses were obtained on a Carlo–Erba Strumentazione instrument. CV experiments were performed on a BAS CV50 electrochemical analyser using the ligand ( $10^{-3}$  M) and  $^n\text{Bu}_4\text{NClO}_4$  (0.1 M) in HPLC grade MeCN, versus Ag/AgCl with a platinum working electrode at 20 °C. Sequential additions of 0.1 equivalents of solutions of the appropriate metal perchlorate salt in MeCN ( $10^{-2}$  M) were monitored by CV. All reagents were of commercial quality and solvents dried, where necessary, using standard procedures. All reactions were performed under an inert atmosphere of nitrogen which was pre-dried by passing through  $\text{P}_2\text{O}_5$ .

#### 3.1. (*R,R*)-*N,N'*-Cyclohexane-1,2-bis[(ferrocenylmethyl)amine] (**2**)

Lithium aluminium hydride (0.46 g, 12 mmol) was added to a solution of compound **1** [13] (2.0 g, 4 mmol) in anhydrous THF (50 ml). The mixture was heated at reflux for 2 h under a positive flow of dry nitrogen and then cooled to room temperature (r.t.). Methanol (10 ml) and deionised water (10 ml) were added (CARE!) and the reaction mixture filtered. The pale yellow solution was extracted with EtOAc ( $3 \times 100$  ml), dried over anhydrous  $\text{Mg}_2\text{SO}_4$  and concentrated in vacuo. Recrystallisation from MeOH gave compound **2** (1.98 g, 98%) as a yellow solid, m.p. 102–103 °C. Anal. Found: C, 65.8; H, 6.8; N, 5.5. Calc. for  $\text{C}_{28}\text{H}_{34}\text{Fe}_2\text{N}_2$  requires: C, 65.9; H, 6.7; N, 5.5%;  $[\alpha]_{\text{D}}^{20}$  ( $c = 2.0$ ,  $\text{CHCl}_3$ ) =  $-63$ ;  $\nu_{\text{max}}$  (Nujol) 3320 (NH,  $\text{cm}^{-1}$ );  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.95–1.18, 1.20–1.34 and 1.65–1.80 (bm, 6H, cyclohexyl-H), 1.91 (bs, 2H,  $2 \times \text{NH}$ ), 2.05–2.19 and 2.20–2.29 (m, 4H, cyclohexyl-H), 3.36 (d, 2H,  $J$  15, Fc- $\text{CH}_2$ -NH), 3.62 (d, 2H,  $J$  15, NH- $\text{CH}_2$ -Fc), 4.07–4.20 (m, 18H, Fc-H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 25.1 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 46.0 ( $\text{CH}_2$ ), 61.3 (CH), 67.5 (Fc-CH), 68.0 (Fc-CH), 68.1 (Fc-CH), 68.4

(Fc-CH) and 87.8;  $m/z$  510 ( $[\text{M}^+]$ , 6%), 311 (6), 199 (4) and 189 (100).

#### 3.2. General procedure for preparation of 2-substituted-(*R,R*)-*N,N'*-bis(ferrocenylmethyl)octahydrobenzimidazoles (**3a–d**)

To a solution of the appropriate aldehyde (1.5 mmol),  $\text{K}_2\text{CO}_3$  (0.5 g), and  $\text{Mg}_2\text{SO}_4$  (0.5 g) dissolved in anhydrous  $\text{CHCl}_3$  (10 ml) was added a solution of compound **2** (0.51 g, 1.0 mmol) in anhydrous  $\text{CHCl}_3$  (5 ml). The mixture was stirred overnight under a positive flow of dry nitrogen. The solid suspension was filtered off, washed with  $\text{CHCl}_3$  (10 ml) and the combined organic fractions concentrated in vacuo. Recrystallisation from MeOH gave the corresponding 2-substituted-(*R,R*)-*N,N'*-bis(ferrocenylmethyl)octahydrobenzimidazole.

##### 3.2.1. (*R,R*)-*N,N'*-Bis(ferrocenylmethyl)octahydrobenzimidazole (**3a**)

Yield: 0.47 g, 90%. Yellow–orange crystals, m.p. 156–157 °C. Anal. Found: C, 66.4; H, 6.6; N, 5.4. Calc. for  $\text{C}_{29}\text{H}_{34}\text{Fe}_2\text{N}_2$  requires: C, 66.7; H, 6.5; N, 5.4%;  $[\alpha]_{\text{D}}^{20}$  ( $c = 2.0$ ,  $\text{CHCl}_3$ ) =  $-51$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.05–1.30, 1.70–1.80, 1.80–1.90 and 2.05–2.19 (bm, 10H, cyclohexyl-H), 3.22 (d, 2H,  $J$  13, Fc- $\text{CH}_2$ -N), 3.53 (s, 2H, N- $\text{CH}_2$ -N), 3.61 (d, 2H,  $J$  13, N- $\text{CH}_2$ -Fc), 4.02–4.20 (m, 18H, Fc-H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 24.3 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 52.8 ( $\text{CH}_2$ ), 67.9 (CH), 68.0 (Fc-CH), 68.4 (Fc-CH), 68.5 (Fc-CH), 69.5 (Fc-CH), 69.6 (Fc-CH), 76.3 (N- $\text{CH}_2$ -N), 84.2;  $m/z$  522 ( $[\text{M}^+]$ , 15%), 443 (15), 336 (8), 199 (100), 189 (54) and 121 (5). Crystals for X-ray analysis were grown by slow diffusion of  $n\text{-C}_6\text{H}_{14}$  into a solution of **3a** in  $\text{CH}_2\text{Cl}_2$ .

##### 3.2.2. (*R,R*)-*N,N'*-Bis(ferrocenylmethyl)octahydrobenzimidazole-2-carboxylic acid ethyl ester (**3b**)

Yield: 0.53 g, 90%. Yellow–orange crystals, m.p. 133–135 °C. Anal. Found: C, 64.6; H, 6.3; N, 4.6. Calc. for  $\text{C}_{32}\text{H}_{38}\text{Fe}_2\text{N}_2\text{O}_2$  requires: C, 64.7; H, 6.4; N, 4.7%;  $[\alpha]_{\text{D}}^{20}$  ( $c = 2.0$ ,  $\text{CHCl}_3$ ) =  $-80$ ;  $\nu_{\text{max}}$  (Nujol) 1731 (C=O ester)  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.00–1.30 (bm, 4H, cyclohexyl-H), 1.20 (t, 3H,  $J$  7,  $\text{CO}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 1.72–1.87, 1.90–2.05 (bm, 4H, cyclohexyl-H), 2.25 (bt, 1H, ring junction-H), 2.81 (bt, 1H, ring junction-H), 3.48 (d, 1H,  $J$  7,  $\text{CO}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 3.58 (d, 2H,  $J$  14, Fc- $\text{CH}_2$ -N), 3.60 (d, 1H,  $J$  7,  $\text{CO}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 3.70 (d, 2H,  $J$  14, N- $\text{CH}_2$ -Fc), 4.02–4.15 (m, 19H, Fc-H, N- $\text{CH}(\text{R})$ -N);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 14.3 ( $\text{CH}_3$ ), 24.3 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 29.1 ( $\text{CH}_2$ ), 29.7 ( $\text{CH}_2$ ), 46.6 ( $\text{CH}_2$ ), 51.4 ( $\text{CH}_2$ ), 60.0 ( $\text{CH}_2$ ), 65.7 (CH), 66.9 (CH), 67.6 (Fc-CH), 67.8 (Fc-CH), 68.0 (Fc-CH), 68.4 ( $2 \times \text{Fc-CH}$ ), 69.7 (Fc-CH), 70.0 (Fc-CH), 70.2 (Fc-CH), 79.9 (CH), 82.9, 84.7, 172.0 (C=O ester);  $m/z$  594 ( $[\text{M}^+]$ , 13%), 521 (12), 322 (4), 199 (100), 149 (23) and 121 (30).

### 3.2.3. (*R,R*)-*N,N'*-Bis(ferrocenylmethyl)-2-(2'-hydroxyphenyl)octahydrobenzimidazole (**3c**)

Yield: 0.54 g, 88%. Yellow–orange crystals, m.p. 173–175 °C (MeOH). Anal. Found: C, 68.4; H, 6.3; N, 4.6. Calc. for C<sub>35</sub>H<sub>38</sub>Fe<sub>2</sub>N<sub>2</sub>O requires: C, 68.4; H, 6.2; N, 4.6%; [ $\alpha$ ]<sub>D</sub><sup>20</sup> (*c* = 2.0, CHCl<sub>3</sub>) = –90;  $\nu_{\max}$  (Nujol) 1583 (Ar-ring), 1601 (Ar-ring), 3190 (OH, cm<sup>–1</sup>);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.00–1.35, 1.70–1.80, 2.05–2.09 and 2.26–3.34 (bm, 8H, cyclohexyl-H), 2.61 (dt, 2H, *J* 2, 9.5, ring junction-H), 3.13 (d, 1H, *J* 14, Fc–CH<sub>2</sub>–N), 3.29 (d, 1H, *J* 14, Fc–CH<sub>2</sub>–N), 3.53 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 3.79 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 3.91–4.11 (m, 18H, Fc–H), 4.72 (s, N–CH(R)–N), 6.74–6.83 (m, 3H, Ar–H), 7.18–7.24 (m, 1H, Ar–H), 12.2 (bs, 1H, –OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 24.3 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 47.4 (CH<sub>2</sub>), 48.9 (CH<sub>2</sub>), 63.6 (CH), 67.3 (CH), 67.9 (Fc–CH), 68.1 (Fc–CH), 68.3 (Fc–CH), 68.4 (Fc–CH), 68.6 (Fc–CH), 69.5 (Fc–CH), 70.0 (Fc–CH), 70.2 (Fc–CH), 70.8 (Fc–CH), 79.7, 83.4 (CH), 86.1, 116.6 (Ar–CH), 118.8 (Ar–CH), 121.5, 129.7 (Ar–CH), 131.5 (Ar–CH), 158.4; *m/z* 614 ([M<sup>+</sup>], 18%), 507 (13), 415 (47), 199 (100) and 121 (41).

### 3.2.4. (*R,R*)-*N,N'*-Bis(ferrocenylmethyl)-2-(2'-pyridyl)octahydrobenzimidazole (**3d**)

Yield: 0.46 g, 76%. Yellow–orange crystals, m.p. 141–143 °C. Anal. Found: C, 68.3; H, 6.2; N, 7.1. Calc. for C<sub>34</sub>H<sub>37</sub>Fe<sub>2</sub>N<sub>3</sub> requires: C, 68.1; H, 6.2; N, 7.0%; [ $\alpha$ ]<sub>D</sub><sup>20</sup> (*c* = 2.0, CHCl<sub>3</sub>) = –40;  $\nu_{\max}$  (Nujol) 1570 (Ar-ring), 1588 (Ar-ring, cm<sup>–1</sup>);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.08–1.34, and 1.68–2.16 (bm, 8H, cyclohexyl–H), 2.24–2.37 (bm, 1H, ring junction-H), 2.65–2.8 (bm, 1H, ring junction-H), 3.14 (d, 1H, *J* 14, Fc–CH<sub>2</sub>–N), 3.41 (d, 1H, *J* 14, Fc–CH<sub>2</sub>–N), 3.52 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 3.63 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 3.87–4.06 (m, 18H, Fc–H), 4.61 (s, N–CH(R)–N), 7.10 (t, *J* 5, Ar–H), 7.32 (d, *J* 8, Ar–H), 7.52 (t, *J* 8, Ar–H), 8.52 (d, *J* 5, Ar–H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 24.4 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 48.9 (CH<sub>2</sub>), 65.3 (CH), 66.4 (CH), 67.0 (Fc–CH), 67.6 (Fc–CH), 67.7 (Fc–CH), 68.3 (2 × Fc–CH), 69.5 (Fc–CH), 69.9 (Fc–CH), 70.2 (Fc–CH), 70.5 (Fc–CH), 82.4, 84.8 (CH), 86.1, 122.1 (Ar–CH), 123.9 (Ar–CH), 135.6 (Ar–CH), 148.3 (Ar–CH), 162.2; *m/z* 599 ([M<sup>+</sup>], 17%), 400 (48), 334 (13), 199 (100), 121 (40) and 83 (42).

### 3.3. (*R,R*)-*N,N'*-Bis(ferrocenylmethyl)octahydrobenzimidazole-2-methanol (**4**)

Lithium aluminium hydride (0.11 g, 3.0 mmol) was added to a solution of **3b** (0.594 g, 1.0 mmol) in anhydrous THF (50 ml). The mixture was heated at reflux for 2 h under a positive flow of dry nitrogen and then cooled to r.t. Methanol (10 ml) and deionised water (10 ml) were added (CARE!) and the reaction mixture filtered. The pale yellow solution was extracted with EtOAc (3 × 100 ml), dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and

concentrated in vacuo. Recrystallisation from MeOH gave compound **4** (0.54 g, 98%) as an orange crystalline powder, m.p. 118–120 °C. Anal. Found: C, 65.2; H, 6.5; N, 5.0. Calc. for C<sub>30</sub>H<sub>36</sub>Fe<sub>2</sub>N<sub>2</sub>O requires: C, 65.2; H, 6.6; N, 5.1%; [ $\alpha$ ]<sub>D</sub><sup>20</sup> (*c* = 2.0, CHCl<sub>3</sub>) = –70;  $\nu_{\max}$  (Nujol) 3120 (OH) cm<sup>–1</sup>;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.00–1.07, 1.15–1.25, 1.29–1.35, 1.74–1.8 and 1.92–2.00 (bm, 8H, cyclohexyl–H), 2.26 (bs, 1H, –OH), 2.32 (dt, 1H, *J* 3, 11, ring junction-H), 2.52 (dt, 1H, *J* 3, 11, ring junction-H), 3.06 (dd, 1H, *J* 5.5, 11, CH–CH<sub>2</sub>–OH), 3.11 (d, 1H, *J* 13, Fc–CH<sub>2</sub>–N), 3.24 (dd, 1H, *J* 3.5, 11, CH–CH<sub>2</sub>–OH), 3.54 (d, 1H, *J* 13, Fc–CH<sub>2</sub>–N), 3.60 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 3.64 (dd, 1H, *J* 3.5, 5.5, CH–CH<sub>2</sub>–OH), 3.65 (d, 1H, *J* 14, N–CH<sub>2</sub>–Fc), 4.05–4.18 (m, 19H, Fc–H, N–CH(R)–N);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 24.3 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 48.1 (CH<sub>2</sub>), 50.6 (CH<sub>2</sub>), 62.2 (CH<sub>2</sub>), 63.8 (CH), 66.0 (CH), 67.6 (Fc–CH), 68.2 (Fc–CH), 68.3 (Fc–CH), 68.4 (Fc–CH), 68.5 (Fc–CH), 69.1 (Fc–CH), 70.1 (2 × Fc–CH), 70.2 (Fc–CH), 81.1 (N–CH–CH<sub>2</sub>–OH), 82.7, 85.7; *m/z* 552 ([M<sup>+</sup>], 9%), 534 (7), 521 (34), 334 (9), 199 (100), 149 (14) and 121 (24).

### 3.4. X-ray crystallography

A single-crystal X-ray diffraction study of **3a** was carried out on a SMART 3-circle diffractometer with a 1K CCD area detector, using graphite monochromated Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N<sub>2</sub> gas cryostat. *Crystal data*: C<sub>29</sub>H<sub>34</sub>Fe<sub>2</sub>N<sub>2</sub>, f.w. 522.28, *T* = 120 K, crystal size 0.04 × 0.36 × 0.40 mm, monoclinic, space group *P*2<sub>1</sub> (No. 4), *a* = 13.220(1), *b* = 9.712(1), *c* = 19.154(1) Å,  $\beta$  = 99.35(1)°, *U* = 2426.6(3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.43 g cm<sup>–3</sup>,  $\mu$  = 1.22 mm<sup>–1</sup>. 30 103 reflections covered full sphere of the reciprocal space to  $2\theta \leq 58^\circ$ , of them 12 188 were independent (including 5405 Friedel pairs). An absorption correction by numerical integration based on the crystal face indexing (transmission factors 0.617–0.952) reduced *R<sub>int</sub>* from 0.082 to 0.040. The structure was solved by direct methods and refined by full-matrix least-squares against *F*<sup>2</sup> of all data, using SHELXTL software [17]. Non-H atoms were refined with anisotropic displacement parameters; all H atoms were treated as ‘riding’. The absolute configuration was determined from anomalous X-ray scattering (the Flack parameter [18] of –0.018(9)), and was consistent with the *R,R*-configuration of the starting material. The refinement converged at *R* = 0.031 for 11 427 reflections with  $I \geq 2\sigma(I)$ , *wR*(*F*<sup>2</sup>) = 0.071 for all data.

### 4. Supplementary material

Structural data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 169847 for compound **3a**.



Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

### Acknowledgements

We thank EPSRC for funding this work.

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