

Reaction of ferrocenecarbaldehyde with *o*-phenylenediamine. Crystal structure of *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole

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Abstract

The reaction of ferrocenecarbaldehyde with *o*-phenylenediamine in the presence of *p*-toluenesulphonic acid results in the synthesis of *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole, **1**, and 2-ferrocenyl-benzimidazole, **2**. The molecular structure of **1** has been determined by single crystal X-ray analysis. It crystallises in the triclinic system, space group $P\bar{1}$, $a = 10.069(7)$, $b = 13.625(8)$, $c = 9.314(7)$ Å, $\alpha = 92.75(5)^\circ$, $\beta = 104.68(6)^\circ$, $\gamma = 95.43(6)^\circ$; $V = 1227(1)$ Å³, $Z = 2$. An electrochemical study of **1** and **2** in dichloromethane:methanol (10:1) has been carried out. **2** shows a reversible oxidation process at $E_{p_a} = 535$ mV. The addition of HCl (1 equiv.) switches the oxidation potential giving a new wave at $E_{p_a} = 800$ mV. **1** shows a reversible $2 e^-$ oxidation process at $E_{p_a} = 558$ mV which is split into two different waves when 1 equiv. of HCl is added. The switching process is reversible for **1** and **2** and addition of base (KOH) leads to the former oxidation potential.

Keywords: Iron; Ferrocene; Ferrocenecarbaldehyde; X-ray structure; Electrochemistry

1. Introduction

Molecules with the ability to exhibit several reversible oxidation or reduction processes have been of great importance as electron reservoir systems [1] and in fields such as electrocatalysis [1,2]. In recent years a large number of redox-active molecules have been synthesised, transition metal sandwiches being of special interest, mainly due to the fact that they can withstand multiple electron transfer processes without rupture. Among them ferrocene is probably the best known, and a large number of ferrocene derivatives have been obtained by suitable chemical attachment of organic groups to the cyclopentadienyl rings. Recently, there has been considerable interest in the functionalisation of metal sandwiches with molecules containing coordination sites in order to obtain ligands bearing electroactive groups [3–10]. These modified redox-active receptor molecules

can be switched by electrical energy resulting in at least two different states containing a different charge as a consequence of the oxidation or reduction of the electroactive moieties. Each state of these switched redox-active ligands is expected to have a different coordination behaviour towards substrates, taking into account that the ligand–substrate interaction could depend on the oxidation state of the electroactive moieties.

We are interested in the synthesis of electroactive ligands [8–10] and have recently reported that the reaction of ferrocenecarbaldehyde and ethylenediamine results in a Schiff-base derivative. By reduction of this compound the parent amine *N,N'*-ethylenbis((ferrocenylmethyl)amine) can be isolated which reacts with transition metal ions giving four-electron ferrocene functionalised complexes [8]. We undertook the reaction of *o*-phenylenediamine and ferrocenecarbaldehyde with the aim of obtaining the corresponding ligand *N,N'*-*o*-phenylenebis((ferrocenylmethyl)amine), but discovered that a different reaction had taken place which led to the synthesis of the complexes *N*-ferrocenylmethyl-2-ferro-

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cenyl-benzimidazole, **1**, and 2-ferrocenyl-benzimidazole, **2**.

2. Experimental details

2.1. Materials and physical techniques

IR spectra were taken on a Perkin Elmer 1750 spectrophotometer. NMR spectra were measured on a Bruker AC 200 FT spectrometer operating at 300 K. Chemical shifts for ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referred to TMS and CDCl_3 , respectively. Electrochemical experiments were performed using a programmable function generator Tacusel IMT-1 connected to a Tacusel PJT 120-1 potentiostat. The working electrode was platinum, with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent / supporting electrolyte. The auxiliary electrode was platinum wire. Ferrocenecarbaldehyde and *o*-phenylenediamine were of reagent quality. The salt tetra-*n*-butylammonium hexafluorophosphate $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ was recrystallised from ethanolic solutions and dried at 80 °C under vacuum for 24 h.

2.2. Preparation of compounds

2.2.1. Synthesis of *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole (**1**) and 2-ferrocenyl-benzimidazole, (**2**)

Ferrocenecarboxaldehyde (428 mg, 2 mmol) and *o*-phenylenediamine (108 mg, 1 mmol) were heated under reflux in chloroform in the presence of 5 mg of *p*-toluenesulphonic acid. After 3 h the reaction mixture was filtered, the solvent removed under vacuum and the crude product dissolved in dichloromethane. The solution was transferred to a chromatography column packed with silica gel in hexane. Elution with CH_2Cl_2 /ether (1:1) separated a yellow–orange band which was rotavaporated to dryness, dissolved in dichloromethane and obtained as solid by addition of hexane. *N*-ferrocenylmethyl-2-ferrocenyl-benzimidazole (**1**) (380 mg, 80%). (Found: C, 67.42; H, 5.00; N, 5.70%. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{Fe}_2$ requires C, 67.25; H, 4.80; N, 5.60%). IR spectrum (KBr disk): 1530s, 1450m, 1420m, 1310s, 1245m, 1150m, 1100s, 1025w, 1005s, 920w, 820s, 740s cm^{-1} . NMR (CDCl_3): ^1H δ 4.12 (t, 2H, C_5H_4), 4.19 (s, 5H, C_5H_5), 4.21 (s, 5H, C_5H_5), 4.24 (t, 2H, C_5H_4), 4.47 (t, 2H, C_5H_4), 4.99 (t, 2H, C_5H_4), 5.41 (s, 2H, CH_2), 7.25 (m, 2H, C_6H_4), 7.40 (m, 1H, C_6H_4), 7.75 (m, 1H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ δ 43.92 (CH_2), 68.03 (C_5H_4), 68.45 (C_5H_4), 68.87 (C_5H_5), 69.35 (C_5H_4), 69.70 (C_5H_5), 69.83 (C_5H_4), 74.24 (C_5H_4 , C_{ipso}), 83.89 (C_5H_4 , C_{ipso}), 109.51 (C_6H_4), 118.98 (C_6H_4), 121.86 (C_6H_4), 122.01 (C_6H_4), 135.87 (quaternary), 143.14

(quaternary), 152.69 (quaternary). A second orange–yellow band was separated by column chromatography using ether as eluent. The solution was rotavaporated to dryness, dissolved in dichloromethane and later precipitated as solid by addition of hexane. 2-ferrocenyl-benzimidazole (**2**) (86 mg, 18%). (Found: C, 67.45; H, 4.60; N, 9.33%. $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Fe}$ requires C, 67.59; H, 4.64; N, 9.28%). IR spectrum (KBr disk): 2921m, 1560s, 1420s, 1325w, 1272s, 1225w, 1150w, 1100m, 1005m, 970m, 825s, 748s cm^{-1} . NMR (CDCl_3): ^1H δ 4.08 (s, 5H, C_5H_5), 4.45 (t, 2H, C_5H_4), 5.01 (t, 2H, C_5H_4), 7.11 (m, 2H, C_6H_4), 7.41 (m, 1H, C_6H_4), 7.51 (m, 1H, C_6H_4), 12.35 (s, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ δ 67.26 (C_5H_4), 69.32 (C_5H_5), 69.65 (C_5H_4), 74.31 (C_5H_4 , C_{ipso}), 110.53 (C_6H_4), 117.87 (C_6H_4), 121.00 (C_6H_4), 121.43 (C_6H_4), 134.71 (quaternary), 143.97 (quaternary), 152.90 (quaternary).

2.3. Crystallographic data collection and structure determination of **1**

2.3.1. Crystal data

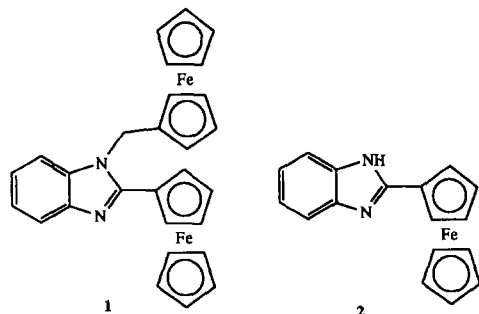
Triclinic, space group $P\bar{1}$, $a = 10.069(7)$, $b = 13.625(8)$, $c = 9.314(7)$ Å, $\alpha = 92.75(5)^\circ$, $\beta = 104.68(6)^\circ$, $\gamma = 95.43(6)^\circ$, $V = 1227(1)$ Å³, $Z = 2$, $F(000) = 575$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $T = 296$ K, $\mu(\text{Mo-K}\alpha) = 12.05$ cm^{-1} .

2.3.2. Data collection and refinement

Data were collected on a Rigaku AFC6S four circle diffractometer using a crystal of dimensions $0.25 \times 0.15 \times 0.08$ mm by the $2\theta/\omega$ method. ($4.0 < 2\theta < 50^\circ$). Psi-scan absorption corrections applied with min. / max. transmission coefficients of 0.81 / 1.00. 4600 reflections measured of which 4330 were unique and 2383 were observed with $F_o^2 > 3 \sigma(F_o^2)$, $\sigma(F_o^2)$ being estimated from counting statistics. The structure was solved by Patterson and Fourier methods followed by full-matrix least-squares refinement (TEXSAN). A very disordered solvate molecule (attributed to isooctane) was found although this could not be fully characterised. The model converged (max. shift/error = 0.40) to $R = 0.041$ and $R_w = 0.036$. Final Fourier difference functions showed peaks no higher than $+0.7 e^- \text{Å}^{-3}$.

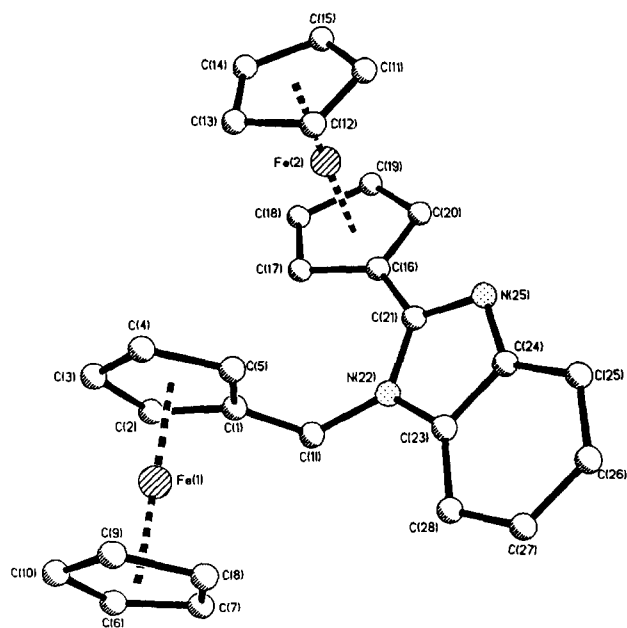
3. Results and discussion

Reaction of ferrocenecarbaldehyde with *o*-phenylenediamine in dichloromethane in the presence of small amounts of *p*-toluenesulphonic acid results in an orange–red solution. Thin layer chromatography showed the presence of two compounds which were isolated by column chromatography. A first band was separated by



Scheme 1.

elution with CH_2Cl_2 /ether (1:1) and recrystallised with CH_2Cl_2 /hexane resulting in an orange–yellow solid. ^1H NMR spectrum of this compound shows the presence of two nonequivalent ferrocenyl groups with singlets at δ 4.19 and 4.21 for the unsubstituted cyclopentadienyl rings and pseudotriplets at δ 4.12, 4.24, 4.47 and 4.99 for two different C_5H_4 moieties. An additional signal at δ 5.41 may be attributed to the presence of a CH_2 group. Four nonequivalent resonances appear in the aromatic region. $^{13}\text{C}\{^1\text{H}\}$ results are basically consistent with the ^1H NMR spectrum obtained. We have recently reported that the reaction of ferrocenecarbaldehyde with ethylenediamine under the same conditions allows isolation of the bis-imine *N,N'*-ethylenebis((ferrocenylmethylidene)amine) (ethylfc) as the sole product [8], which shows a unique environment for the ferrocenyl groups as well as a characteristic $\nu(\text{C}=\text{N})$ imine stretching absorption in its IR spectrum at 1630 cm^{-1} . However, ethylfc is unstable in solution due to hydrolysis processes and can not be chromatographed because of its decomposition to generate ferrocenecarbaldehyde.

Fig. 1. Crystal structure of **1** showing the numbering scheme adopted.

The first band obtained from the reaction between ferrocenecarbaldehyde and *o*-phenylenediamine shows in its IR spectrum a strong vibration at 1530 cm^{-1} which is quite a long way from the value expected for the stretching $\text{C}=\text{N}$ vibration. Additionally, the proton related to an imino group was not detected in the ^1H NMR spectrum. All these data indicate that the reaction of ferrocenecarbaldehyde and *o*-phenylenediamine does not result in the expected *N,N'*-*o*-phenylenebis((ferrocenylmethylidene)amine), suggesting that some kind of reorganisation has occurred.

In order to characterise the isolated compound we undertook a X-ray single crystal study. Suitable crystals for X-ray experiments were grown by slow diffusion of isooctane into dichloromethane solutions of the complex. A view of the molecule is presented in Fig. 1, whereas final atomic coordinates for nonhydrogen atoms and selected bond distances and angles are listed in Tables 1 and 2, respectively. The X-ray study indicates that the compound may be formulated as *N*-ferrocenylmethyl-2-ferrocenylbenzimidazole, **1**, (Scheme 1). The structure consists of a benzimidazole group bis-substituted in the N and 2 positions by a ferrocenylmethyl

Table 1

Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Fe(1)	0.74819(7)	0.01695(5)	0.23641(9)	3.05(3)
Fe(2)	0.81717(7)	0.36686(5)	0.74958(9)	2.98(3)
N(22)	0.9815(4)	0.2855(3)	0.3943(4)	2.5(2)
N(25)	1.1320(4)	0.3506(3)	0.6059(5)	3.3(2)
C(1L)	0.8522(5)	0.2501(4)	0.2847(5)	2.7(2)
C(1)	0.7796(5)	0.1595(4)	0.3315(5)	2.8(2)
C(2)	0.6362(5)	0.1256(4)	0.2820(6)	3.6(2)
C(3)	0.6114(6)	0.0413(4)	0.3570(7)	4.5(3)
C(4)	0.7349(7)	0.0222(4)	0.4505(7)	5.0(3)
C(5)	0.8415(5)	0.0939(4)	0.4357(6)	3.8(2)
C(6)	0.6866(6)	-0.0225(5)	0.0160(7)	4.8(3)
C(7)	0.8236(6)	0.0157(4)	0.0535(7)	4.2(3)
C(8)	0.8938(6)	-0.0428(4)	0.1568(7)	4.6(3)
C(9)	0.7992(7)	-0.1183(4)	0.1833(8)	5.4(3)
C(10)	0.6686(6)	-0.1054(5)	0.0932(8)	5.2(3)
C(11)	0.9346(7)	0.3319(7)	0.942(1)	8.5(4)
C(12)	0.894(1)	0.2498(6)	0.846(1)	9.7(4)
C(13)	0.748(1)	0.2355(5)	0.8124(8)	7.9(4)
C(14)	0.7086(7)	0.3118(6)	0.8910(8)	5.8(3)
C(15)	0.8212(8)	0.3710(6)	0.9666(8)	6.6(4)
C(16)	0.8941(5)	0.3907(3)	0.5711(5)	2.5(2)
C(17)	0.7470(5)	0.3695(4)	0.5258(6)	3.2(2)
C(18)	0.6892(5)	0.4415(4)	0.5998(6)	3.6(2)
C(19)	0.7983(6)	0.5065(4)	0.6870(6)	3.8(2)
C(20)	0.9229(5)	0.4758(4)	0.6713(6)	3.4(2)
C(21)	1.0001(5)	0.3407(4)	0.5247(5)	2.6(2)
C(23)	1.1085(5)	0.2565(3)	0.3890(6)	2.6(2)
C(24)	1.2001(5)	0.2985(4)	0.5204(6)	3.0(2)
C(25)	1.3390(5)	0.2855(4)	0.5519(6)	4.0(2)
C(26)	1.3812(5)	0.2321(4)	0.4466(7)	4.5(3)
C(27)	1.2901(6)	0.1909(4)	0.3143(7)	4.6(3)
C(28)	1.1520(5)	0.2029(4)	0.2835(6)	3.5(2)

Table 2
Selected bond lengths (Å) and angles (°) for compound 1

N(25)–C(21)	1.341(6)	C(1)–C(5)	1.418(7)
N(25)–C(24)	1.387(6)	C(24)–C(25)	1.385(7)
N(22)–C(21)	1.358(6)	C(24)–C(23)	1.391(7)
N(22)–C(23)	1.386(6)	C(25)–C(26)	1.368(7)
N(22)–C(1L)	1.459(6)	C(26)–C(27)	1.392(8)
C(1L)–C(1)	1.513(6)	C(27)–C(28)	1.373(7)
C(21)–C(16)	1.461(6)	C(6)–C(7)	1.378(8)
C(16)–C(17)	1.430(7)	C(8)–C(9)	1.408(8)
C(16)–C(20)	1.412(7)	C(11)–C(12)	1.36(1)
C(1)–C(2)	1.424(7)	C(15)–C(14)	1.34(1)
N(25)–C(24)–C(25)	128.4(5)	C(21)–C(16)–C(17)	129.8(5)
N(25)–C(21)–C(16)	122.0(5)	N(25)–C(21)–N(22)	112.4(4)
N(22)–C(21)–C(16)	125.5(4)	C(21)–N(25)–C(24)	104.3(4)
N(22)–C(23)–C(28)	133.1(5)	C(21)–N(22)–C(23)	107.5(4)
N(22)–C(1L)–C(1)	111.8(4)	C(23)–N(22)–C(1L)	123.6(4)
C(1L)–C(1)–C(5)	126.3(4)	C(1L)–C(1)–C(2)	126.4(5)
C(21)–C(16)–C(20)	123.8(4)		

and ferrocenyl group, respectively. The cyclopentadienyl groups are planar within the limits of experimental errors. The Fe(1) atom is at 1.648 and 1.650 Å from the mean planes C(1)–C(5) and C(6)–C(10), respectively, the distance of Fe(2) respect to the C(11)–C(15) and C(16)–C(20) planes being 1.652 and 1.643 Å. The Fe–C(cyclopentadienyl ring) distances range from 1.991(7) to 2.057(6) (averaging 2.027(6) Å) and intracyclopentadienyl C–C bond lengths lie in the range 1.36(1)–1.430(7) Å (averaging 1.397(8) Å).

In the reaction between the ferrocenecarbaldehyde and *o*-phenylenediamine a second compound can be isolated by elution with ether, which was characterised as 2-ferrocenyl-benzimidazole, (**2**), (see Scheme 1). Compound **2** shows in its ¹H NMR spectrum a characteristic group of signals for the ferrocenyl group with a five proton singlets for the unsubstituted cyclopentadienyl ring (δ 4.08) and two triplets corresponding to the monosubstituted ring (δ 4.45, 5.01). The remaining four nonequivalent resonances are attributed to the C₆H₄ group. The absence of a proton resonance for the HC group (expected near δ 8.4) and a ratio between ferrocenyl and phenyl protons of 2:1 support the idea that cyclisation has occurred to give a benzimidazole group substituted in the 2 position by a ferrocenyl group. In addition, a characteristic signal at 12.35 in the ¹H NMR spectrum assigned to the NH moiety in the benzimidazole group was found. IR spectrum and analytical data are also in agreement with the proposed formulation.

It is known that benzimidazoles can be synthesised by reaction of *o*-arylenediamines and carboxylic acids or carboxylic acid derivatives [11]. However, in some instances, procedures leading to 2-substituted benzimidazoles have been reported by reaction of *o*-arylenediamines with aldehydes in which the reactants are condensed in the presence of an oxidant such as cupric acetate, mercuric oxide or chloranil. The reaction of

o-phenylenediamine with benzaldehyde has been studied in some detail and several intermediates as 2-phenylbenzimidazole, 1-benzyl-2-phenylbenzimidazole and 1-benzyl-2-phenylbenzimidazoline have been proposed to explain the final compounds obtained [11]. We have monitored our reaction at different times by ¹H NMR spectroscopy and although at low reaction times some minor products could be detected we were unable to isolate or characterise them.

One important aspect is the actual role that the *p*-toluenesulphonic acid plays. We have also performed the reaction of ferrocenecarbaldehyde and *o*-phenylenediamine in chloroform without the presence of the acid. After 3 h the reaction crude was evaporated to dryness and dissolved in CDCl₃. ¹H NMR spectrum of the mixture showed the presence of two main products. One of them was clearly characterised as compound **2** whereas the other one shows a signal at δ 8.41 that may be assigned to the presence of the Schiff base derivative *N,N'*-*o*-phenylenebis((ferrocenylmethylidene)amine). Some attempts to obtain this compound as sole product have been unsuccessful until now. However, no evidence of the presence of **1** was found under these conditions, suggesting that its synthesis depends on the presence of acid in the medium.

Compound **2** shows a reversible monoelectronic oxidation process at $E_{p_a} = 535$ mV vs. S.C.E. in dichloromethane:methanol (10:1) with a ratio between cathodic and anodic intensities close to unity. It has been recently reported that there is a linear dependence of the positive shift of the redox potential in ferrocene nitrogen compounds and their protonated relatives against the inverse distance iron–nitrogen [12]. We have also studied by cyclic voltammetry the effect that the presence of H⁺ has on the redox potential of **1** and **2**. Addition of acid (HCl, 0.1 M in dichloromethane:methanol 10:1) results in the appearance of a second wave at higher anodic potential. After adding 1 equiv. of acid the first wave disappears and only the second oxidation process is observed at $E_{p_a} = 800$ mV. Fig. 2

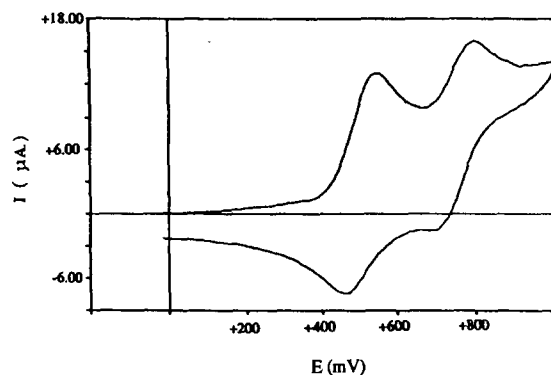
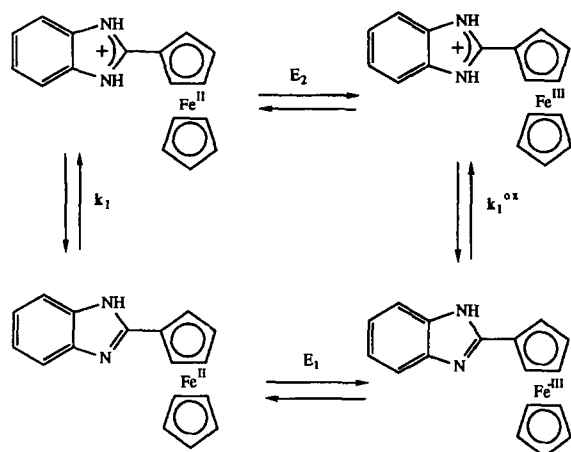


Fig. 2. Cyclic voltammogram of **2** after the addition of 0.5 equiv. HCl.



Scheme 2.

shows the cyclic voltammogram when 0.5 equiv. of HCl have been added. Scheme 2 shows the equilibrium involved in the electrode. From the equation $E_2 - E_1 = -(RT/nF)\ln(K_1/K_1^{ox})$ a ratio K_1/K_1^{ox} of $3.3 \cdot 10^{-5}$ has been found.

It is well known that redox potential of metallocene systems can be adequately changed by suitable chemical attachment of electron withdrawing or electron releasing groups. Each modified metallocene has a characteristic redox potential which is usually independent of the medium and can not usually be changed. That is a clear limitation for electron reservoir systems. It has recently been reported that functionalisation of ligands with redox-active metallocenes can result in the synthesis of electro-active receptors which can change their redox potential by binding processes with cation or anions [3–7]. Although this kind of electro-active receptor-guest association is efficient in shifting the redox potential the process is not reversible because the former receptor redox potential is generally inaccessible when the receptor-guest complex has been formed. In contrast, the switching process in **2** is reversible, and when the second wave has been obtained, addition of KOH (KOH 0.1 M in dichloromethane:methanol 1:1) regenerates the former potential E_1 .

Compound **1** shows a bielectronic oxidation process at $E_{p_a} = 558$ mV vs. S.C.E. An ΔE_p of 116 mV (ferrocene gives under the same conditions a ΔE_p of 82 mV) suggest that the two ferrocenyl groups are not totally equivalent although both oxidise near the same potential. After adding 1 equiv. of HCl a voltammogram similar to that in Fig. 2 is observed. Further addition of acid does not result in any change. This suggests that protonation of the benzimidazole group affects to the ferrocenyl group attached in the 2 position but does not

appear to induce any important shift in the redox potential of the *N*-ferrocenylmethyl framework. The addition of acid transforms $2e^-$ oxidation systems in a {1 + 1} electron molecule, with the potential of each single-electron transfer being separated by more than 250 mV. Again, the switching is reversible and the addition of KOH regenerates the $2e^-$ oxidation systems and the former voltammogram.

The functionalisation of ferrocenyl groups with pH-responsive groups led to the synthesis of versatile redox systems whose redox potential can be switched in a reversible way by adding acid or base to the medium.

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