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FULL PAPER

The effect of protonation on the spectroscopic and redox properties of a series of ferrocenoyl derivatives

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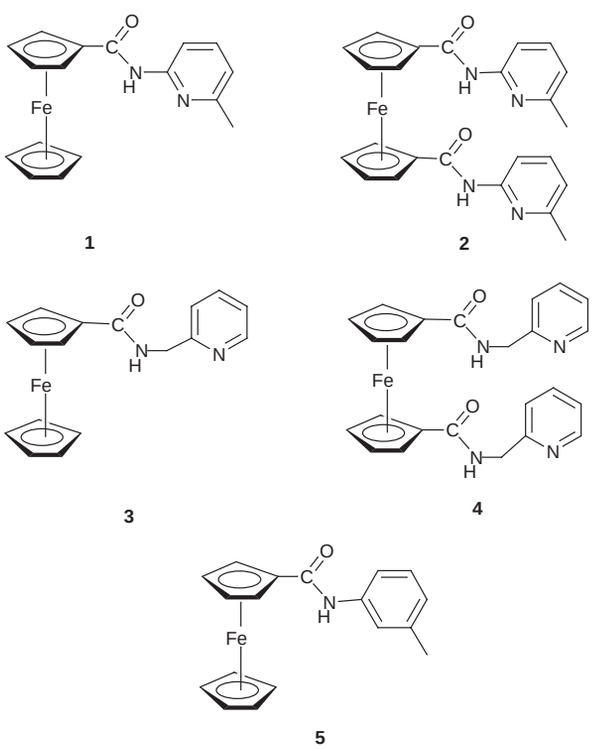
Five ferrocenoyl derivatives, containing pyridine (**1**–**4**) and benzene (**5**) moieties, were synthesised and characterised. The effect on the spectroscopic and redox properties of these compounds upon addition of H^+ was studied, with NMR studies indicating that protonation took place at the pyridine nitrogens of **1**–**4**. A crystal structure determination of the bis(amide) derivative **4** revealed the presence of two intramolecular hydrogen bonds; these remained intact in solution but were cleaved upon protonation. Protonation induced anodic shifts in the ferrocene-centred redox potential of ferrocene receptors **1**, **2** and **4** and also changes in the electronic and NMR spectra of **1**–**4**. A bathochromic shift in the lowest energy spin-allowed d–d band upon protonation was only observed for those compounds which also displayed a pronounced redox response.

Introduction

In the past few years, there have been numerous reports of metallocene receptor compounds that bind cations,[1] anions[2] and more recently, neutral molecules.[3,4] Owing to the potential application of these derivatives as electrochemical sensors and the current general interest in supramolecular electrochemistry,[5] studies have largely concentrated on the effect of complexation on the redox properties of the receptor. However, cation complexation can also affect the chromogenic properties of ferrocene ligands.[6] This is perhaps not surprising, as it is well known that the electronic spectrum of ferrocene is affected by cyclopentadienyl (Cp) substituents.[7] Accordingly, a few attempts have been made to correlate electrochemical properties with spectroscopic properties of ferrocene derivatives,[8] although no analogous systematic study has been carried out on ferrocene ligands and their complexes. In this paper, the synthesis, characterisation and proton binding properties of five simple ferrocene derivatives **1**–**5** are reported, with a view to rationalising the changes in both the redox and spectroscopic properties of the ferrocene unit upon the addition of H^+. For a comparative and systematic study with a range of receptors, H^+ has an advantage over metal cations in that H^+ provides similar steric and stoichiometric constraints for each receptor and the complexation site is very specific. Furthermore, the high charge density of H^+ should bring about large spectroscopic and redox effects. Recent work has indeed shown that H^+ induces significant changes in the redox properties of ferrocene derivatives containing basic nitrogen atoms.[6a,9]



Results and discussion

Synthesis

Compounds **1**–**5** were synthesised by addition of either chlorocarbonylferrocene[10] or 1,1′-bis(chlorocarbonyl)ferrocene[10,11] to the respective amine in dry dichloromethane, in the presence of triethylamine as base. A modified synthesis of 1,1′-bis(chlorocarbonyl)ferrocene is given in the Experimental section. Column chromatography on neutral alumina or recrystallisation was used to purify the products, which were isolated in good yield. Characterisation of these compounds was carried out using mass spectrometry, cyclic voltammetry, elemental analysis, NMR, UV/VIS and IR spectroscopy.

Crystal structure of compound 4

Suitable crystals of **4** for X-ray crystallography were grown by slow diffusion of diethyl ether into a dichloromethane solution of the ligand. A view of the molecule is presented in Fig. 1, with selected bond distances and angles listed in Table 1. The main point of interest is the presence of two intramolecular hydrogen bonds; in each case, one amide proton on one arm is bonded to one pyridine nitrogen on the other arm [N(3)–H(3)···N(2) distance 2.95 Å, N(3)–H(3)···N(2) angle 158°; N(1)–H(1)···N(4) distance 3.06 Å, N(1)–H(1)···N(4) angle 150°].

Table 1 Selected bond lengths (Å) and angles (°) for compound **4**

O(1)–C(11)	1.231(5)	O(2)–C(18)	1.231(4)
N(1)–C(11)	1.347(5)	N(3)–C(18)	1.338(5)
N(1)–C(12)	1.446(5)	N(3)–C(19)	1.454(5)
C(1)–C(11)	1.484(5)	C(6)–C(18)	1.486(6)
C(11)–N(1)–C(12)	121.2(3)	C(18)–N(3)–C(19)	119.8(3)
O(1)–C(11)–N(1)	122.1(4)	O(2)–C(18)–N(3)	122.3(4)
O(1)–C(11)–C(1)	121.2(4)	O(2)–C(18)–C(6)	121.3(4)
N(1)–C(11)–C(1)	116.7(4)	N(3)–C(18)–C(6)	116.4(3)

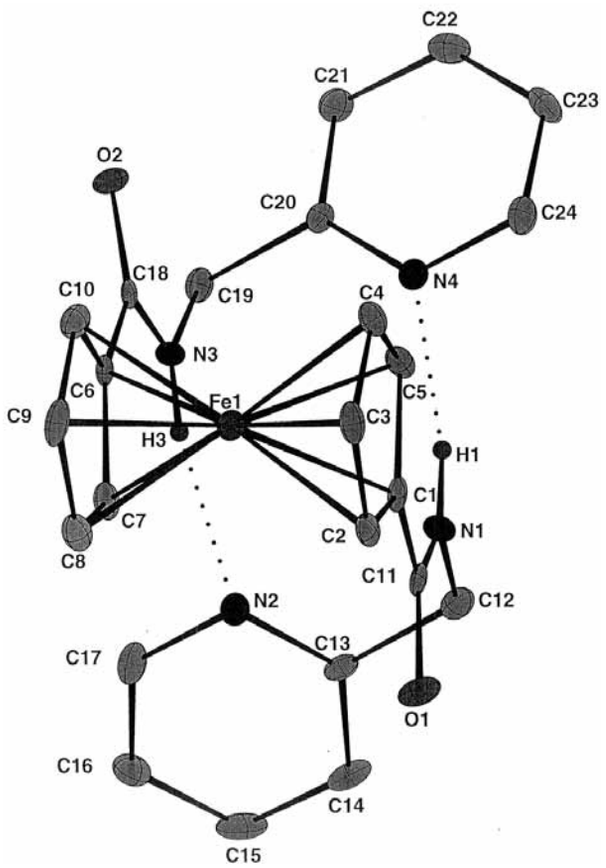


Fig. 1 Crystal structure of **4**.

The cyclopentadienyl rings are virtually coplanar and eclipsed with a rotation angle of only 2°.

^{1}H NMR studies

The resonance values of amide protons give an indication as to the extent of intra- or inter-molecular hydrogen bonding in solution. The strongly deshielded value in $CDCl_3$ for the resonance corresponding to the two amide protons of **4** (δ 9.97) indicates that hydrogen bonding is present in this compound in solution, as well as in the solid state. Support for an intramolecular, *inter*-arm interaction, similar to that observed in the crystal structure, is given by the fact that firstly, dilution from 0.04 M to 0.001 M produced no significant change in chemical shift for the amide proton resonance and secondly, the corresponding signal for the mono derivative **3** is considerably more upfield at δ 6.99. Apart from compound **4**, there is no evidence for strong hydrogen bonding in $CDCl_3$; the chemical shifts for the amide proton resonances for **1** and **2** are similar, which precludes strong *inter*-arm interactions as seen in **4**. Furthermore, dilution from 0.04 M to 0.001 M produced no significant changes in the resonance shift values for the amide protons of **1**, **2**, **3** and **5**. These values are in fact similar to those observed for related amidopyridine derivatives in $CDCl_3$.[12] The addition of H_2O (*ca.* 50-fold molar excess) to solutions of **1** and **2** (*ca.* 0.04 M) induced small downfield shifts in these resonance values (+0.12 and +0.27 ppm respectively), corresponding to weak hydrogen bonding interactions with water. However, very small changes <+0.05 ppm were observed with **3** and **4**, which indicates that increasing the polarity of the solvent does not disrupt the intramolecular hydrogen bonding in **4**.

Table 2 ^{1}H NMR spectroscopic data for compounds **1**–**4** displaying the shifts in resonance values (ppm) upon the addition of stoichiometric amounts of H^+ (298 K)

Ferrocene ligand[a]	N–H	Cp[c]	Cp[d]
1	+2.36	+0.36	+0.37
2	+2.58	+0.22	+0.25
3	+0.75	+0.04	+0.04
4[e]	—	—	—

Ferrocene ligand[b]	N–H	Cp[c]	Cp[d]
1	+2.20	+0.21	+0.22
2[e]	—	—	—
3	+0.53	+0.07	+0.10
4	−1.99	+0.12	+0.23

[a] Obtained at 300 MHz in $CDCl_3$. [b] Obtained at 300 MHz in $CDCl_3$–d_6-acetone (2:1 ratio). [c] Pair of protons adjacent to carbonyl group on derivatised Cp ring. [d] Pair of protons furthest from carbonyl group on derivatised Cp ring. [e] Precipitation occurred upon addition of two equivalents of H^+.

The addition of HBF_4 to compounds **1** and **2** (*ca.* 0.001 M) in $CDCl_3$ induced downfield shifts in the resonances corresponding to the pyridine, amide and Cp protons (Table 2). Titrations of the most downfield Cp proton against H^+ concentration revealed the expected 1:1 stoichiometry for **1** and 2:1 (acid:ligand) stoichiometry for **2**.

In comparison with **1** and **2**, addition of a slight excess of H^+ to **3** in $CDCl_3$ induced smaller downfield shifts in the amide and Cp proton resonances but similar changes were observed for those corresponding to the pyridine protons. Treatment of **4** with H^+ resulted in the immediate precipitation of an insoluble orange solid, which was presumably protonated species. Therefore, binding studies were repeated for all five compounds in $CDCl_3$–d_6-acetone (2:1 ratio). In this new solvent system, the amide proton resonance for **4** (δ 9.97) was still strongly deshielded compared to **3** (δ 7.14), which indicated that intramolecular hydrogen bonding was still intact. Once again, addition of H^+ produced changes in the NMR spectra, with smaller shifts observed in the signals for the Cp protons and amide protons of **3** compared with **1** and **4** (Table 2). Furthermore, whereas a small downfield shift in the amide proton resonance of +0.53 ppm was seen for **3**, a large upfield shift of −1.99 ppm was observed for **4**. Therefore, as expected, protonation of the two pyridine nitrogens necessitated cleavage of the intramolecular hydrogen bonds in **4**. The stoichiometry of 2:1 for the protonated complex of **4** was established by a titration of the upfield shift of the amide proton resonance against increasing H^+ concentration (Fig. 2).

The addition of H^+ produced no significant changes in the NMR spectrum of **5** in either solvent system, which confirmed that protonation was taking place at the pyridine nitrogens of **1**–**4**. However, the addition of excess of H^+ to **1**–**5** produced broadened NMR spectra if solutions were left to stand for a few hours, which indicated that any excess acid present was oxidising the ferrocene unit.[13]

IR studies

IR studies in dichloromethane gave additional evidence for intramolecular hydrogen bonding solution for the bis(amide) **4**, as evidenced by the lower stretching frequency for the amide N–H group of **4** in CH_2Cl_2 (3255 cm^{-1}), compared with **3** (3446 and 3402 cm^{-1}). These differences in wavenumber reflect the

Table 3 UV/VIS spectroscopic data[a] for compounds **1**–**5** and the chromogenic response to the addition of stoichiometric amounts of H^+ (CH_2Cl_2, 298 K)

	Ferrocene ligand		Ferrocene ligand with H^+	
	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
1	448	320	478	1280
2	450	470	472	1400
3	444	100	444	160
4	444	220	444	1880
5	444	330	444	360

[a] Data for the lowest energy spin-allowed d–d band of the ferrocene unit.

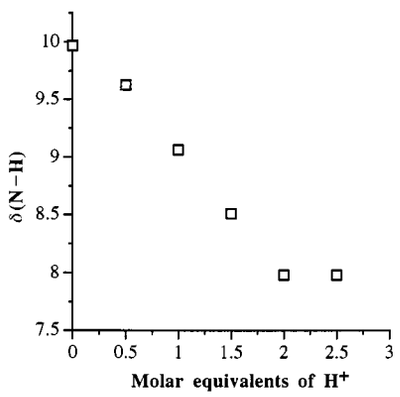


Fig. 2 ^{1}H NMR titration of the upfield shift of the amide N–H resonance of **4** as a function of molar equivalents of H^+ in $CDCl_3$–d_6-acetone (2 : 1 ratio).

fact that the amide N–H bonds in **4** are weaker as a result of hydrogen bonding with the pyridine nitrogen.[14] The addition of H^+ to CH_2Cl_2 solutions of the receptors produced very minor changes in the N–H and carbonyl stretches of all pyridine receptors apart from **4**, for which the emergence of a new N–H stretching band at higher energy (3388 cm^{-1}) was observed, in accordance with the hydrogen bonds in **4** being cleaved upon protonation.

UV/VIS studies

All receptors gave a visible band in their electronic spectrum between 400 and 500 nm of wavelength and intensity that was characteristic of the lowest energy spin-allowed d–d band of the ferrocene unit.[15] Upon the addition of a slight excess of HBF_4 to receptors **1** and **2** in dichloromethane, respective bathochromic shifts in this band of 30 nm and 22 nm occurred, accompanied by an increase in the molar absorption coefficient (Table 3). The stoichiometry of each complex was confirmed by monitoring the change in absorbance of the d–d transition in dichloromethane (*ca.* 1 mM) upon addition of aliquots of H^+ at a constant wavelength (Fig. 3).

The UV/VIS results for **1** and **2** contrast sharply with those for compounds **3**–**5**; in particular, no apparent bathochromic shift in the lowest energy d–d transition was observed upon the addition of H^+ to either **3** or **4**. In the case of **4**, interpretation was made more difficult because of strong bathochromic shifts in higher energy bands which partially obscured the lowest energy d–d band; these shifts were the main reason for the large increase in intensity in this area of the spectrum. However, in the case of **3**, it is clear that the addition of one equivalent of H^+ induced only a small increase in intensity in this band, whilst the wavelength of the transition remained constant. For compound **5**, as expected, virtually no change was observed in any region of the visible spectrum between 300 and 500 nm upon addition of approximately one equivalent of H^+. However, upon addition of excess H^+, bathochromic shifts were observed, which in all probability were due to partial oxidation of the ferrocene unit[13] (see above).

Table 4 Electrochemical data[a] for compounds **1**–**5** and the redox response (ΔE°) to the addition of stoichiometric amounts of H^+ (CH_2Cl_2, 298 K)

	E°/V	ΔE°/mV
1	+0.24	+70
2	+0.44	+180
3	+0.09	<+5
4	+0.16	+15
5	+0.35	<+5

[a] Redox potentials (E°) were referenced to ferrocene as internal standard where $E^\circ = 0.5$ ($E^\circ_{pa} - E^\circ_{pc}$). The confidence limit is ±5 mV; for conditions see Experimental section. For each voltammogram, the reversibility of the redox wave matched that of the ferrocene internal reference (ΔE°_p = 70–100 mV).

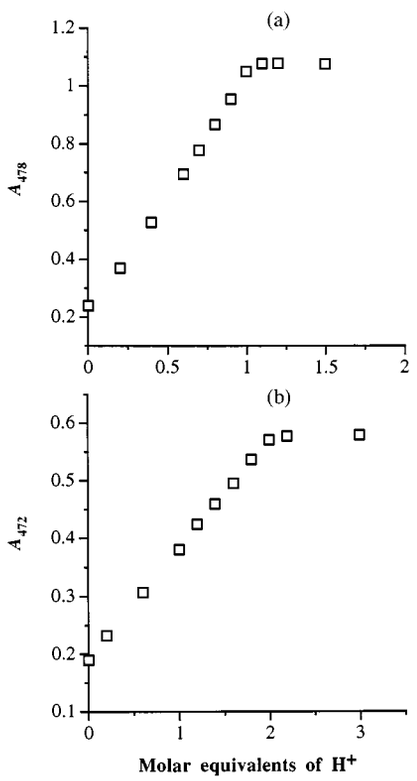
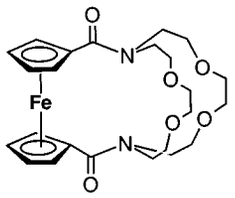


Fig. 3 UV/VIS titration of the change in absorption intensity at constant wavelength as function of molar equivalents of H^+ for compounds (a) **1** at 478 nm and (b) **2** at 472 nm in CH_2Cl_2.

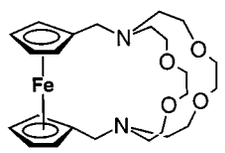
Electrochemical studies

Cyclic voltammetry experiments were carried out in dichloromethane solution at 1 mM, containing tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The redox potentials E° are displayed in Table 4, along with the change in the redox potential, ΔE°, upon addition of H^+. It is clear from this data that receptors **1** and **2** undergo the largest redox response to protonation. Titrations with aliquots of H^+ confirmed the stoichiometry of the complexes with these receptors, with full shifts in E° observed after adding exactly one equivalent of H^+ to **1** and two equivalents of H^+ to **2**. The direction of the change in the redox potentials for **1** and **2** (*i.e.* anodic shifts) is in agreement with results from other electrochemical studies on ferrocene derivatives containing basic amines.[6a,9] As expected, the magnitude of ΔE° for **2** is approximately twice that of **1**, in accordance with two positive charges being introduced in close proximity to the ferrocene unit.



larger chromogenic response
smaller redox response

6



smaller chromogenic response
larger redox response

7

Fig. 4 The effect of 1:1 complexation with Ca^{2+} on the redox and chromogenic properties of ferrocene cryptands **6** and **7** in CH_3CN.

An analysis of the spectroscopic and electrochemical results for these derivatives reveals interesting trends. Protonation of **1** and **2**, at a nitrogen site four bond lengths away from the ferrocene unit, affects the distribution of electron density at the Cp ligands, as evidenced by the downfield shifts for the NMR signals corresponding to the Cp ring proton resonances. However, the introduction of an additional methylene unit (**3** and **4**) induces smaller downfield shifts, although the effect is slightly larger for the bis(amide) **4**, probably because of conformational changes that are brought about by protonation. Furthermore, only in the case of **1** and **2** is a pronounced redox response to protonation observed, with both complexes harder to oxidise than the corresponding ligands. Beer has suggested that the origin of the redox response to complexation can either be a through-space or through-bond interaction.[1a] Clearly, a through-space interaction must dominate for those redox responsive systems in which there is little or no obvious conjugation between the complexation site and the redox centre, as is the case for **1** and **2**. Indeed, according to the work of Plenio,[9a] shifts of +70 mV for **1** and <+5 mV for **3** would be consistent with those predicted for a simple electrostatic through-space interaction for systems with a distance of four and five bond lengths respectively between the Cp ring and the protonation site. The origin of the small shift of +15 mV found with receptor **4** upon protonation is unclear. However, a positive shift of this magnitude would be consistent with a disruption of the intramolecular hydrogen bonding in this receptor upon protonation, since previous work has shown that the *formation* of hydrogen bonds *via* the amide N–H groups of **1** and **2**, induces *negative* redox shifts.[3]

There appears to be a general correlation between the redox and spectroscopic properties of these ferrocene receptors in that where protonation causes bathochromic shifts in the lowest energy spin-allowed d–d band, a pronounced redox response is also observed. In other words, protonation of either **1** or **2** must not only lower the level of the Fe centred HOMO, as evidenced by the increase in redox potential, but also decrease the energy of this d–d band. Interestingly enough, an identical trend has been observed when conjugated electron withdrawing substituents are introduced onto the Cp rings of the ferrocene unit.[7,8] This trend has been explained by firstly, the substituent making oxidation more difficult by withdrawing electron density away from the Fe centre and secondly, the low-lying Cp π* orbitals shifting to lower energy, which reduces the energy of the electronic transition. In addition, increased mixing of ligand orbitals with metal d orbitals makes such a transition more allowed by increasing the MLCT character, resulting in an increase in absorption intensity. For receptors **1** and **2**, protonation certainly induces a similar effect, as shown by the increase in the ε values in Table 3.

Bathochromic shifts in the d–d band centred at *ca.* 450 nm and an accompanying increase in absorption upon complexation have been observed with other ferrocene receptors upon addition of protons and metal cations.[6] An example of such a ligand is the bis(amide) cryptand **6**, which binds Group 2 cations through amide coordination.[16] However, upon reduction of both amide groups of **6** to form cryptand **7**,[17a] the chromogenic response to complexation of Ca^{2+}, which is now bound within the macrocyclic cavity, is reduced,† whilst the redox response is significantly enhanced (Fig. 4).‡ It follows that a large redox response to complexation does not necessarily imply a large bathochromic shift in this band. Therefore, clearly other factors must be taken into account in order to achieve a greater understanding of both redox and chromogenic effects. It has been suggested that Cp ring tilt,[18] Cp ring rotation[6b] and Fe–metal interactions[17] affect the chromogenic properties of the ferrocene centre. For example, in the case of cryptand **7**, an Fe–Ag^+ interaction has been postulated to explain the enhanced chromogenic and redox response to complexation with this cation.[17a]

Conclusion

Studies on these simple redox-active proton receptors have given further insight into the nature of the electrochemical and spectroscopic properties of ferrocene derivatives. For those compounds which give a pronounced redox response to protonation, a larger spectroscopic response, in terms of changes in the NMR spectra and bathochromic shifts in the visible spectra, is also observed. Further spectroscopic and electrochemical studies with these and other ferrocene receptors are now in progress to establish the redox and chromogenic response to the complexation of other charged species and neutral molecules.

Experimental

Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. The synthesis of all compounds was carried out under an inert gas atmosphere of nitrogen. Chlorocarbonylferrocene was prepared according to the literature procedure.[10] Column chromatography was performed on B.D.H. alumina (neutral, Brockman activity I). ^{1}H and 13C NMR spectra were recorded on either a Bruker AC 300 or a Bruker Advance DRX 400 spectrometer. IR spectra were recorded on a Nicolet Magna 550 spectrometer. UV/VIS spectra were recorded at 298 K on a Unicam UV4 spectrometer. Mass spectra (LSIMS, liquid secondary ion mass spectrometry) were obtained using a Kratos Profile HV3 instrument. The crystal stucture of **4** was determined at Cardiff University. Cyclic voltammograms were recorded at 298 K using an EG&G 273 potentiostat in dry, nitrogen-purged dichloromethane with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte, Ag as a pseudo-reference electrode and Pt wire as both counter and working electrode (scan rate 200 mV s^{-1}). Ferrocene (*ca.* 1 mM) was used as an internal reference.

Synthesis

1,1′-Bis(chlorocarbonyl)ferrocene. Oxalyl chloride (5.5 g, 43 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a suspension of 1,1′-ferrocenedicarboxylic acid (2.0 g, 7.3 mmol) in dry CH_2Cl_2 (25 mL) at 0 °C. The mixture was stirred overnight at room temperature and then refluxed for approximately 2 hours until a clear, dark red solution was obtained. This was then evaporated under reduced pressure and the crude product subjected to Soxhlet extraction with dry pentane (*ca.* 300 mL) for 24 hours. The pentane solution was then evaporated under reduced pressure to give the title compound as a red solid (1.13 g, 50%); ν_{max}/cm^{-1} (CO) 1765s (nujol); δ_H (300 MHz, $CDCl_3$) 5.04 (m, 4H, CpH), 4.76 (m, 4H, CpH).

† Chromogenic response. **6**: ε (% increase) 39%; $\Delta\lambda_{max}$ +13 nm [data taken from ref. 6(*b*)]; **7**: ε (% increase) *ca.* 10%; $\Delta\lambda_{max}$ *ca.* +5 nm [data taken from ref. 17(*a*)].

‡ Redox response. **6**: $\Delta E°$ +155 mV [data taken from ref. 16(*b*)]; **7**: $\Delta E°$ +274 mV [data taken from ref. 17(*a*)].

[{(6-Methyl-2-pyridyl)amino}carbonyl]ferrocene 1. A mixture of triethylamine (0.20 g, 2.0 mmol) and 2-amino-6-methylpyridine (0.220 g, 2.0 mmol) was added to anhydrous CH_2Cl_2 (10 mL). Chlorocarbonylferrocene (0.430 g, 1.8 mmol) in anhydrous CH_2Cl_2 (60 mL) was added dropwise at 0 °C over a period of 30 minutes. The reaction mixture was allowed to return to room temperature and stirred for 24 hours. Saturated $NaHCO_3$ (30 mL) was then added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give an orange solid. The crude product was purified by column chromatography on neutral alumina (CH_2Cl_2 with 1% methanol) to give pure **1** as an orange solid (0.437 g, 76%). The compound may be recrystallised from CH_2Cl_2–diethyl ether to give thin orange needles, mp 150–151 °C (Found: C, 61.99; H, 4.46; N, 8.36. $C_{17}H_{17}FeN_2O_{1.5}$ (0.5 equivalent of H_2O) requires C, 62.06; H, 4.86; N, 8.51%); ν_{max}/cm^{-1} (NH) 3420m, (CO) 1677s (CH_2Cl_2); δ_H (300 MHz, $CDCl_3$, standard $SiMe_4$) 8.12 (1H, d, *J* 8.3, C_5H_3N), 8.05 (1H, s, NH), 7.59 (1H, dd, *J* 8.3, 7.5 Hz, C_5H_3N), 6.88 (1H, d, *J* 7.5, C_5H_3N), 4.82 (2H, t, *J* 1.9, C_5H_4), 4.42 (2H, t, *J* 1.9, C_5H_4), 4.24 (5H, s, C_5H_5), 2.48 (3H, s, CH_3); *m*/*z* (LSIMS) 321 $(M + H)^+$.

1,1′-Bis[{(6-methyl-2-pyridyl)amino}carbonyl]ferrocene 2. The same method as for **1** was carried out, using a mixture of triethylamine (0.31 g, 3.06 mmol) and 2-amino-6-methylpyridine (0.305 g, 2.82 mmol) in anhydrous CH_2Cl_2 (10 mL) and 1,1′-bis(chlorocarbonyl)ferrocene (0.44 g, 1.41 mmol) in anhydrous CH_2Cl_2 (60 mL). After work-up, the crude product was purified by column chromatography on neutral alumina (CH_2Cl_2 with 1% methanol) to give pure **2** as an orange solid (0.46 g, 73%). The compound may be recrystallised from CH_2Cl_2–diethyl ether to give thin orange needles, mp 240 °C (decomp.) (Found: C, 62.93; H, 4.61; N, 12.17. $C_{24}H_{22}FeN_4O_2$ requires C, 63.47; H, 4.88; N, 12.33%); ν_{max}/cm^{-1} (NH) 3412m, (CO) 1678s (CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 8.31 (2H, s, NH), 8.04 (2 H, d, *J* 8.1, C_5H_3N), 7.53 (2H, dd, *J* 8.1, 7.6, C_5H_3N), 6.85 (2H, d, *J* 7.6 Hz, C_5H_3N), 4.93 (4H, m, C_5H_4), 4.52 (4H, m, C_5H_4), 2.45 (6H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 167.81 (CO), 156.50 (CR of C_5H_3N), 150.77 (CR of C_5H_3N), 138.58 (CH of C_5H_3N), 118.90 (CH of C_5H_3N), 110.88 (CH of C_5H_3N), 77.63 (CR of C_5H_4), 72.88 (CH of C_5H_4), 70.19 (CH of C_5H_4), 24.00 (CH_3); *m*/*z* (LSIMS) 455 $[M + H]^+$.

[(2-Pyridylmethylamino)carbonyl]ferrocene 3. The same method as for **1** was carried out, using a mixture of triethylamine (0.04 g, 0.4 mmol) and 2-pyridylmethylamine (0.04 g, 0.4 mmol) in anhydrous CH_2Cl_2 (10 mL) and chlorocarbonylferrocene (0.91 g, 1.0 mmol) in anhydrous CH_2Cl_2 (30 mL). A proportion of the product precipitated out overnight after the addition and this was filtered off. The remainder of the reaction mixture was worked up as before and combined with the precipitate to give an orange solid, which was then recrystallised from CH_2Cl_2–diethyl ether to give pure **3** as orange crystals (0.26 g, 82%), mp 140–141 °C; ν_{max}/cm^{-1} (NH) 3446m, 3402m, (CO) 1653s, (CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 8.58 (1H, d, *J* 7.65, C_5H_4N), 7.68 (1H, dd, *J* 7.65, 7.8, C_5H_4N), 7.35 (1H, d, *J* 7.8, C_5H_4N), 7.22 (1H, t, *J* 6.8 Hz, C_5H_4N), 6.99 (1H, s, NH), 4.74 (2H, m, C_5H_4), 4.67 (2H, d, *J* 5.2, CH_2), 4.35 (2H, m, C_5H_4), 4.17 (5H, s, C_5H_5); *m*/*z* (LSIMS) 319 $(M)^+$.

1,1′-Bis[(2-pyridylmethylamino)carbonyl]ferrocene 4. The same method as for **1** was carried out, using a mixture of triethylamine (0.21 g, 2.1 mmol) and 2-pyridylmethylamine (0.21 g, 2.1 mmol) in anhydrous CH_2Cl_2 (10 mL) and 1,1′-bis(chlorocarbonyl)ferrocene (0.30 g, 1.0 mmol) in anhydrous CH_2Cl_2 (60 mL). After work-up, the crude product was purified by column chromatography on neutral alumina (CH_2Cl_2 with 1% methanol) to give pure **4** as an orange solid (0.30 g, 65%). The compound may be recrystallised from CH_2Cl_2–diethyl ether to give orange needles, mp 230 °C (decomp.) (Found: C, 63.50; H, 4.32; N, 12.29. $C_{24}H_{22}FeN_4O_2$ requires C, 63.47; H, 4.88; N, 12.33%); ν_{max}/cm^{-1} (NH) 3255m, (CO) 1643s (CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 9.97 (2H, s, NH), 8.59 (2H, d, *J* 7.5, C_5H_4N), 7.77 (2H, dd, *J* 7.5, 7.9, C_5H_4N), 7.46 (2H, d, *J* 7.9, C_5H_4N), 7.30 (2H, t, *J* 5.1, C_5H_4N), 4.74 (4H, m, C_5H_4), 4.54 (4H, d, *J* 6.3 Hz, CH_2), 4.34 (4H, t, C_5H_4); *m*/*z* (LSIMS) 454 $(M)^+$.

[{(3-Methylphenyl)amino}carbonyl]ferrocene 5. The same method as for **1** was carried out, using a mixture of triethylamine (0.19 g, 1.9 mmol) and *m*-toluidine (0.19 g, 1.9 mmol) in anhydrous CH_2Cl_2 (10 mL), and chlorocarbonylferrocene (0.43 g, 1.8 mmol) in anhydrous CH_2Cl_2 (60 mL). A proportion of the product precipitated out overnight after the addition and this was filtered off. The remainder of the reaction mixture was worked up as before and combined with the precipitate to give an orange solid, which was then recrystallised from CH_2Cl_2–diethyl ether to give pure **5** as orange crystals (0.49 g, 85%), mp 226 °C (decomp.) (Found: C, 67.28; H, 5.24; N, 4.34. $C_{24}H_{22}FeN_4O_2$ requires C, 67.75; H, 5.37; N, 4.39); ν_{max}/cm^{-1} (NH) 3435m, (CO) 1675s (CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 7.48 (1H, s, NH), 7.36 (1H, d, *J* 6.1, C_6H_4), 7.36 (1H, s, C_6H_4) 7.23 (1H, dd, *J* 6.1, 7.5, C_6H_4), 6.94 (1H, d, *J* 7.5 Hz, C_6H_4), 4.78 (2H, m, C_5H_4), 4.42 (2H, m, C_5H_4), 4.26 (5H, s, C_5H_5), 2.37 (3H, s, CH); *m*/*z* (LSIMS) 319 $(M)^+$.

Crystallography

Crystal data for **4**. $C_{24}H_{22}N_4O_2Fe$, $M = 454.31$, triclinic, space group $P\bar{1}$, $a = 8.894(2)$, $b = 9.855(2)$, $c = 13.892(3)$ Å, $\alpha = 106.01(3)$, $\beta = 98.80(3)$, $\gamma = 113.58(3)°$, $U = 1023.6(4)$ Å^3, $T = 150(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.767 mm^{-1}, $F(000) = 472$, 4328 reflections were collected, θ range 2.36 to 25.02° (index ranges; *h* −9 to 10, *k* −11 to 11, *l* −12 to 15), which merged to give 2804 unique reflections ($R_{int} = 0.0800$) to refine against 280 parameters. Final *R* indices were $wR_2 = 0.0955$ and $R_1 = 0.0399$ ($I > 2\sigma I$) and 0.0993 and 0.0558 respectively for all data. Residual electron densities were 0.399 and −0.348 e Å^{-3}.

X-Ray crystal data were collected upon a crystal of size 0.2 × 0.16 × 0.12 mm on a Delft instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50 kV, 50 mA), using a molybdenum target [$\lambda_{(Mo\text{-}K\alpha)} = 0.71069$ Å], controlled by a MicroVax 3200 and driven by MADNES[19] software.

The structure was solved by direct methods (SHELX-S[20]) and then subjected to full-matrix least squares refinement based on F^2 (SHELX-93[21]). Non hydrogen atoms were refined anisotropically with hydrogens included in idealised positions (C–H distance = 0.97 Å) with isotropic parameters set at 1.2 times the U_{eq} of the parent atoms. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. An absorption correction (DIFABS[22]) was applied once the structure had been fully elucidated giving correction factors of 0.725 and 1.121.

CCDC reference number 186/1253.

See http://www.rsc.org/suppdata/dt/1999/57/ for crystallographic files in .cif format.

UV/VIS, NMR and CV titrations

Titrations were carried out by adding aliquots of a stock solution of HBF_4 [made up by diluting a 54% solution in diethyl ether (Aldrich) with the appropriate solvent] to a solution of the ferrocene ligand (*ca.* 10^{-3} M) in either $CDCl_3$ or $CDCl_3$–d_6-acetone (for NMR studies) or CH_2Cl_2 (for UV/VIS and CV studies). The absorbance readings from the UV/VIS spectra were adjusted to take into account the dilution of the solution during the course of each experiment.

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