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Modulation of the metal recognition properties of a new type of azaferrocenophane-based chemosensors: co-ordination chemistry towards Mg²⁺, Ca²⁺, Zn²⁺ and Ni²⁺

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The structure–redox chemistry relationship of a new type of azaferrocenophane-based chemosensors, **3** and **4**, in the presence of protons and several kinds of metal ions, has been studied. Electrochemical studies, carried out in CH_2Cl_2 , in the presence of increasing amounts of Mg^{2+} , Ca^{2+} , Zn^{2+} and Ni^{2+} showed that the wave corresponding to the Fc/ Fc⁺ couple of the uncomplexed ligands is gradually replaced by a new reversible wave at more positive potentials corresponding to the Fc/Fc⁺ couple of the complexed ligands. The maximum shift of the ferrocene oxidation wave was found for **4b** in the presence of Mg^{2+} , whereas for **3f** a selective sensing response for Mg^{2+} in the presence of hydrated Ca^{2+} cations was observed, with a concomitant highly visual output response consisting of a deep purple colour.

Introduction

One of the most attractive ways of achieving sensor design is to functionalise a receptor capable of both selective substrate binding with a metal centre and reporting on the recognition event through a variety of physical responses. In this context, the design of redox-active receptors in which a change in electrochemical behaviour can be used to monitor complexation of guest species is an increasingly important area of molecular recognition.¹⁻¹⁰ Thus, from a synthetic standpoint, ferrocene is a very convenient building block for redox-active ligands as it can be relatively easily functionalized and incorporated in many structures. These facts, coupled with its electrochemical and UV-vis spectroscopic properties, which can be perturbed by the proximity of bound guests, demonstrate that ferrocene is a particularly attractive functional antenna in this research area.

Most of the receptors containing a neutral ferrocenyl moiety are substituted with macrocyclic ligands which exhibit interesting electrochemical ion recognition effects because the complexing ability of the receptors can be switched on and off by varying the applied electrochemical potential. In general, cation binding at an adjacent receptor site of a ferrocene-based host, includes a positive shift in the redox potential of the ferrocene/ ferrocenium (Fc/Fc⁺) couple either by through-bond and/or through-space electrostatic interactions, interference or conformational change.¹¹ In addition, it has been suggested that an added degree of recognition is conferred by appearance of a new set of redox waves (two-wave behaviour) associated with the oxidation of the ferrocenyl subunits in the host–guest complex, compared with a single gradual shift in the potential of the original ferrocene redox couple.⁵

Most of the reported ferrocene-based redox-responsive ionophores feature crown ethers or polyaza-macrocycles as receptor units, due to the great possibility of modulation of host co-ordination environments that they can offer by tailoring the cavity size. However, no selectivity towards magnesium or calcium ions has been reported for these systems.¹²⁻²⁴ In this context, a number of redox-active ferrocene based receptors such as imine-,²⁵ oxazoline-,²⁶⁻²⁷ imidazoline-,²⁸ and pyridinefunctionalized²⁹ ferrocene ligands have been described, which, in organic solvents, selectively respond to, but do not clearly differentiate between, Mg²⁺ and Ca²⁺ ions with no interference from a large excess of Li⁺, Na⁺ and K⁺. As a continuation of our studies on the synthesis of azaheteroaryl-substituted ferrocene derivatives displaying redoxswitchable character and electrochemical sensing behaviour³⁰⁻³² (Scheme 1) we present here the synthesis and binding properties of a new range of 1,1'-[(3,4-dihydro-2,4-quinolinediyl)-(2-hydroxy-1,2-ethanediyl)]ferrocenes, substituted at the 1 position, with aryl, heteroaryl or alkynyl groups. Additionally, the correlation between electrochemical and optical properties of these ferrocene derivatives has also been studied.



Results and discussion

Synthesis

The 1,5-difunctionalized [5]ferrocenophane derivatives **3** were prepared from [5]ferrocenophane **1**, readily available in 39% overall yield from 1,1'-diacetylferrocene by sequential treatment with *o*-azidobenzaldehyde and tri-*n*-butylphosphane,³³ and the corresponding organolithium derivative **2**, in THF at -30 °C. Purification by column chromatography afforded compounds **3** in 55–80% yield as orange solids (Scheme 2).

Electrochemical studies

Firstly, the electrochemical behaviour of ferrocene ligands 3 on their own, as well as in the presence of variable concentrations of HBF₄, was investigated. Thus, upon protonation by addition of stoichiometric amounts of HBF₄ in CH₂Cl₂ to a solution of ligands in CH₂Cl₂ all the alcohols **3a–3f** exhibited similar behaviour displaying in their corresponding voltammograms (CVs) the characteristic two-wave behaviour associated with the high difference between the half-wave potentials of the free ligand and the protonated species redox couples ($\Delta E_{1/2} = E_{1/2 \text{ protonated}} - E_{1/2 \text{ free}}$). The magnitude of the electrochemical shift ($\Delta E_{1/2}$) on protonation provides important thermo-

Table 1 Electrochemical proton-dependence of 3 and 4

beneficial proton dependence of 5 and 4							
	Ligand L	$E_{1/2L}/V^a$	$E_{1/2LH^+}/V^a$	$\Delta E_{1/2}/\mathrm{mV}$	BEF	RCE	
	3a	0.120	0.510	390	2.6×10^{-7}	3.9×10^{6}	
	3b	0.160	0.550	390	2.6×10^{-7}	3.9×10^{6}	
	3c	0.180	0.570	390	2.6×10^{-7}	3.9×10^{6}	
	3d	0.070	0.110	40^{b}	2.6×10^{-1}	4.7	
		0.190	0.610	420	$8.0 imes 10^{-8}$	1.3×10^{7}	
	3e	0.190	0.610	420	$8.0 imes 10^{-8}$	1.3×10^{7}	
	3f	0.190	0.580	390	2.6×10^{-7}	3.9×10^{6}	
	4a	0.100	0.490	390	2.6×10^{-7}	3.9×10^{6}	
	4b	0.110	0.510	400	1.7×10^{-7}	5.8×10^{6}	
	4c	0.510 ^c	0.540	30 ^{<i>b</i>}	3.1×10^{-1}	3.2	
		0.740 ^c	1.080	340	$1.8 imes 10^{-6}$	5.6×10^{5}	

^a E_{1/2} are given in CH₂Cl₂ versus Fc⁺/Fc as internal standard. ^b E_{1/2} for the monosubstituted ferrocene unit. ^c E_{1/2} are given in CH₂Cl₂ versus DMFc⁺/ DMFc as internal standard (DMFc = decamethylferrocene). When the experiment was carried out in CH₃CN/CH₂Cl₂ (3:2), the values obtained were: $E_{1/2 \text{ (monosubstituted Fc)}} = 0.540 \text{ V}$ and $E_{1/2 \text{ (disubstituted Fc)}} = 0.760 \text{ V}$, vs DMFc.



dynamic information. The shift in redox potential on protonation is related to the ratio of protonation constant for the equation: $\Delta E_{1/2} = (RT/nF)\ln(K_{red}/K_{ox})$, where K_{red} is the proton binding constant for neutral unoxidised redox responsive ligand and K_{ox} is the proton binding constant for its oxidised form. The quantity K_{red}/K_{ox} has been defined by Beer *et al.*⁷⁻⁹ as reaction coupling efficiency (RCE), whereas the quantity K_{ox}/K_{red} has been defined as binding enhancement factor (BEF), and represents a quantitative measure of the perturbation of the redox centre induced by protonation to the receptor unit. The results obtained are reported in Table 1. Although these alcohols exhibit large binding constants and consequently large RCE values, ranging from 3.9×10^6 to 1.3×10^7 , they present some differences which deserve some comment.

The CVs of **3a** and **3b** ($\mathbf{R} = \mathbf{Ph}$ and Thy), and their corresponding protonated derivatives, show a reversible one-electron redox couple giving rise to a $\Delta E_{1/2} = 390$ mV. This value is almost the same as those obtained by using the already described derivatives 4a ($\Delta E_{1/2} = 390$ mV) or 4b ($\Delta E_{1/2} = 400$ mV), respectively³⁴ (Scheme³). As a consequence, similar RCE values are also observed in these cases. However, it is noteworthy that when the same comparison is performed with compound $4c^{35}$ the $\Delta E_{1/2}$ corresponding to the disubstituted ferrocenyl moiety is smaller and the corresponding RCE value decreases by a factor of ~10. These observed differences can be explained bearing in mind that in the latter system the steric interaction between the C=N moiety and the monosubstituted



ferrocenyl unit induces some thermodynamic instability to the protonated species with reference to those in which the substituent R has a small steric volume.

When the same voltamperometric study was performed with compounds 3c-3f, in which the presence of an acetylenic moiety moves away the bulky group R from the C=N unit, it was observed that the $\Delta E_{1/2} = E_{1/2 \text{ protonated}} - E_{1/2 \text{ free}}$ for 3d (420 mV) is larger than those observed for 3c and 3f, although the steric hindrance of the monosubstituted ferrocenvl unit present in 3d is larger than that of the substituents present in 3c-3f. Therefore, the value of the redox shifts observed would depend not only on the steric effect of the substituent at the 1 position of the ferrocenophane bridge but also on some other electronic factors.

Thus, to gain a better understanding into the factors which determine the extent of the redox shifts in these type of ferrocene derivatives upon protonation, and with the aim of establishing a correlation between the distances C=N-monosubstituted ferrocene and the positive shifts of these redox potentials, we have investigated more closely the effect of the protonation of the nitrogen atom in the C=N group on the redox potentials of the structurally related homobimetallic derivatives 4c (R = Fc) and 3d. While the CV of 4c shows two reversible one-electron oxidations for the two ferrocenyl groups $(\Delta E_{1/2} = 230 \text{ mV})$ ³⁵ compound **3d** also exhibits two reversible ferrocene couples but more closely spaced ($\Delta E_{1/2} = 120$ mV), which indicates a less intermetallic interaction between the two ferrocene moieties.³⁶⁻³⁸ Remarkably, upon protonation, the anodic electrochemical shift for both compounds was larger than for the free ligands: 540 mV, for 4c, and 500 mV, for 3d, respectively (Fig. 1, Table 1).

In compounds 3d and 4c, bearing two ferrocene units, the small electrochemical shifts of the monosubstituted ferrocene (40 and 30 mV, respectively) and the large values obtained for the disubstituted ferrocenyl moiety (420 and 340 mV) clearly indicate that while the protonation process does not affect the $E_{1/2}$ of the monosubstituted ferrocenyl unit, it strongly affects the $E_{1/2}$ of the disubstituted ferrocene. Moreover, it is possible to conclude that the $E_{1/2}$ of the latter is influenced by interaction of such a disubstituted unit with the electrogenerated monosubstituted ferrocenium cation as well as with the C=N \cdots H⁺, after protonation. In addition, the difference in the RCE values for both compounds could be explained on the basis of the bigger steric hindrance existing in 4c in comparison to 3d.

The behaviour of the receptors 3e and 3f in the presence of HBF₄ was also investigated, the effect of this strong acid being protonation of the C=N as well as the pyridine nitrogen atom. In each case, the anodic redox potential shifts of the ferrocene nucleus were 420 and 390 mV, respectively (Table 1). This difference could probably be attributed to the higher electrostatic influence of the positive pyridinium cation, formed after protonation of 3e, on the ferrocene redox potential, in com-



Fig. 1 (a) Cyclic voltammogram of compound **3d** before (black) and after addition (red) of 1 equiv. of HBF₄. Conditions: 0.5 mM of **3d** and 0.1 M ["Bu₄NClO₄] in CH₂Cl₂, using a Pt disk electrode and a scan rate = 0.2 V s⁻¹. (b) DPV of compound **3d** Conditions: 0.5 mM of **3d** and 0.1 M ["Bu₄NClO₄] in CH₂Cl₂, using a Pt disk electrode, a $E_{pulse} = 10$ mV and a scan rate = 0.004 V s⁻¹.

parison with the same situation in **3f**. The isolation as a solid of the protonated form of **3e** confirms this assumption. The CV is identical to those obtained in the electrochemical cell and in the ¹H-NMR spectrum the pyridine ring protons are downfield shifted ($\delta = +0.41$ and +0.20 ppm) appearing in the region 8.10–8.63 ppm characteristic of the pyridinium ring protons.

All these data indicate that the prepared new ferrocenophanes behave as excellent electrochemical sensors for protons not only due to the basic character of their C=N bond but also due to the existence of an efficient communication between the binding site and the ferrocene nucleus as a result of a combination of through-space electrostatic and through-conjugated bond interactions. The RCE values shown in Table 1 indicate a measure of the difficulty to protonate the oxidized form of the ligand with reference to its reduced form.

It is worth noting that all the protonated ligands exhibited an irreversible reduction wave at $E_{1/2} = -0.43$ V, which is absent in the free ligand and is attributed to the reduction of the polarized C=N, because of the stabilization of the LUMO, localized on the imine group, which makes its reduction easier with respect to the neutral form.

The effect of several metal ions (Li⁺, Mg²⁺, Ca²⁺, Ni²⁺ and Zn^{2+}) on the receptor redox chemistry has also been investigated, by using different types of anhydrous and hydrated inorganic salts such as: [Ca(ClO₄)₂]·4H₂O, [Zn(ClO₄)₂]·6H₂O, $[Ni(ClO_4)_2]$ ·4H₂O, LiClO₄, Mg(ClO₄)₂, Zn(CF₃SO₃)₂ and $Ca(CF_3SO_3)_2$. It is very well established that the metal ions under study could exhibit two relevant properties in nonaqueous solution: co-ordination of the metal ions by the ligand and protonation of the ligand due to the use of hydrated metal salts, bearing ionisable protons.³⁹ It is therefore of great importance to establish in each case whether co-ordination or protonation effects are being observed and as a consequence it is necessary to adopt some criteria that allow us to differentiate experimentally between the co-ordination and protonation processes. The criteria which we have used are based on the different behaviour exhibited by the electrogenerated species after the addition of water to that media. Therefore, in the case that a co-ordination process is taking place, the CVs obtained after the addition of water should be the same as those corresponding to the free ligand, because in such a case the excess water in the media can displace the ligand from the metal co-ordination sphere. However, when a protonation process occurs, the addition of water promotes a slightly cathodic shift of the redox wave which does not agree with that of the free ligand. Although similar criteria have been used previously to differentiate both types of processes, in some cases its application is incorrect in the sense that the protonation process is ruled out when the UV-vis spectra and the CVs obtained for the ligand in organic solvents do not change after addition of water to the media, suggesting that the protonation process is only due to the added water²⁶⁻²⁷ and not to the presence of the ionisable protons in the hydrated metal salts.

The results obtained by using the ligands 3b-d and 4b-c revealed the following facts: (i) the appearance of a second wave together with that corresponding to the free ligand on stepwise addition of substoichiometric amounts of the appropriate ion, which reflects the two-wave behaviour in all the cases studied and additionally indicates large values of the corresponding complexation constants; (ii) in all cases, a reduction wave was observed as a consequence of the generation of a polarized C=N \cdots H⁺(M^{*n*+}) due to the interaction of the C=N group with the proton or the metal ion; (iii) only protonation processes were observed when $[Ca(ClO_4)_2] \cdot 4H_2O$ was used; (iv) by using [Zn(ClO₄)₂]·6H₂O and [Ni(ClO₄)₂]·4H₂O, the general effect observed is protonation except for ligand 3b, bearing a S atom, which gives rise to a co-ordination behaviour and which shows selectivity between Zn²⁺ and Ni²⁺ to some extent (Table 2); (v) the results obtained by using anhydrous salts of Ca²⁺ and Mg²⁺ are quite similar; (vi) addition of Li⁺ induces no significant variation in the corresponding CVs of the free ligands studied.

From the receptors considered, the potential shifts obtained on co-ordination or protonation are very similar, which indicates not only that the interaction of the binding site with the proton or the metal cations is almost of the same intensity but also that co-ordination or protonation is being performed on the same donor atoms. Otherwise, lower potential shifts promoted by the co-ordination processes, with respect to those of protonation, should be expected.

On the other hand, ligand 3b (R = Thy), possessing a second donor atom in the structure, gives rise to metal-ion-coordination processes when either anhydrous or hydrated salts of the cations studied are added. Only in the case of hydrated Ca²⁺ salts, is a slow protonation response observed. These facts indicate that the presence of a second donor atom in the molecule should increase the binding strength of metal ions to this receptor and, as a consequence, their corresponding complexation constants. However, and in order to favour the effective and simultaneous co-ordination of two different donor atoms to one metal centre, it would be necessary for the cation to be located far away from the redox centre and therefore the electrostatic interactions of the cation-redox centre and those through the C=N would be less effective. In other words: the bigger the stability of the complex formed, the smaller the efficiency of communication with the redox centre. Consequently, the potential shifts of the ferrocene nucleus on co-ordination are smaller than on protonation, because in the latter case the proton should be preferentially bound to the more basic C=N group. These data also suggest that although in the quinolinophane framework, present in all the derivatives studied, there are two different types of donor atoms (N and O), the complexation processess should take place through the C=N fragment.

It is worth noting that this data obtained from the voltammetric studies completely agreed with that obtained from the X-ray crystallographic data of compound $4c^{35}$ which demonstrates that the orientation of the –OH and C=N groups is not

Table 2 Electrochemical cation-dependence of 3b-d and 4b-c

	Ligand L	$E_{1/2L}/V^a$	$E_{1/2 \text{ complex}}/\mathrm{V}^a$	$\Delta E_{1/2}/\mathrm{mV}$	RCE	Effect	
	3 b •Ca ²⁺	0.160	0.510	350	8.2×10^{5}	Co-ordination	
	3b·Mg ²⁺	0.160	0.530	370	1.8×10^{6}	Co-ordination	
	3b·Zn ^{2+ b}	0.160	0.550	390	3.9×10^{6}	Co-ordination	
	3b·Ni ^{2+ b}	0.160	0.510	350	7.0×10^{5}	Co-ordination	
	3c·Ca ²⁺	0.180	0.560	380	8.2×10^{6}	Co-ordination	
	3c·Mg ²⁺	0.180	0.560	380 ^c	2.7×10^{6}	Co-ordination	
	3c·Zn ^{2+b}	0.180	0.570	390 °	2.7×10^{6}	Protonation	
	3d·Ca ²⁺	0.070	0.080	10 ^c	1.5	Co-ordination	
		0.190	0.570	380 ^c	3.0×10^{6}		
	3d·Mg ²⁺	0.080	0.080	0 ^c		Co-ordination	
	8	0.190	0.570	380 ^c	2.7×10^{6}		
	4b·Ca ²⁺	0.110	0.500	390	3.9×10^{6}	Co-ordination	
	4b·Mg ²⁺	0.110	0.510	400	5.8×10^{6}	Co-ordination	
	4 b ·Zn ^{2+ b}	0.110	0.510	400	5.8×10^{6}	Protonation	
	4b·Ni ^{2+ b}	0.107	0.500	390	3.9×10^{6}	Protonation	
	$4c \cdot Mg^{2+d}$	0.540 ^e	0.570	30	3.2	Co-ordination	
	8	0.760^{e}	1.100	340	5.6×10^{5}		
	4c·Zn ²⁺	0.540 ^e	0.570	30	3.22	Protonation	
		0.760^{e}	1.100	340	5.6×10^{5}		

^{*a*} $E_{1/2}$ are given in CH₃CN/CH₂Cl₂ (3/2) *versus* Fc⁺/Fc as internal standard. ^{*b*} Hydrated M²⁺. ^{*c*} In CH₂Cl₂. ^{*d*} In the presence of [Ni(ClO₄)₂]·4H₂O the electrogenerated species are unstable in the timescale of the technique. ^{*e*} $E_{1/2}$ are given in CH₃CN/CH₂Cl₂ (3/2) *versus* DMFc⁺/DMFc as internal standard.

Table 3	Electrochemical	cation-dependence	of 3e and 3f
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Ligand L	$E_{1/2L}/V^a$	$E_{1/2 \text{ complex}}/\mathrm{V}^a$	$\Delta E_{1/2}/\mathrm{mV}$	RCE	Effect
$\begin{array}{c} {\bf 3e}{\cdot}{\rm Ca}^{2+b}\\ {\bf 3e}{\cdot}{\rm Ca}^{2+d}\\ {\bf 3e}{\cdot}{\rm Mg}^{2+}\\ {\bf 3e}{\cdot}{\rm Zn}^{2+b}\\ {\bf 3e}{\cdot}{\rm Zn}^{2+d}\\ {\bf 3f}{\cdot}{\rm Ca}^{2+b} \end{array}$	0.190 0.190 0.190 0.190 0.190 0.190	0.490 0.480 0.540 0.510	300 290 290 350 320	$\begin{array}{c} 1.2 \times 10^{5} \\ 8.0 \times 10^{4} \\ 8.0 \times 10^{4} \\ 8.2 \times 10^{5} \\ 2.3 \times 10^{5} \end{array}$	Co-ordination ^c Co-ordination Co-ordination Co-ordination ^c Co-ordination No response
$3\mathbf{f} \cdot \mathbf{Ca}^{2+d}$ $3\mathbf{f} \cdot \mathbf{Mg}^{2+}$ $3\mathbf{f} \cdot \mathbf{Zn}^{2+b}$ $3\mathbf{f} \cdot \mathbf{Zn}^{2+d}$	0.190 0.190 0.190 0,190	0.450 0.450 0.550 0.475	260 260 360 285	$\begin{array}{c} 2.5 \times 10^{4} \\ 2.5 \times 10^{4} \\ 1.2 \times 10^{6} \\ 6.6 \times 10^{4} \end{array}$	Co-ordination Co-ordination Protonation ^c Co-ordination

^{*a*} $E_{1/2}$ are given in CH₂Cl₂ versus Fc⁺/Fc as internal standard. ^{*b*} [Ca(ClO₄)₂]·4H₂O and [Zn(ClO₄)₂]·6H₂O are the hydrated salts used. ^{*c*} This is a slow process which needs the presence of a larger amount of M²⁺ to respond, in comparison with the case of using Mg²⁺. ^{*d*} Anhydrous Ca(CF₃SO₃)₂ or Zn(CF₃SO₃)₂

appropriate for the simultaneous co-ordination of the metal, and therefore the C=N is the centre mainly involved in the binding processes.

At this point, and taking into account the above results, it seemed interesting to us to test the complexation properties of ligands **3e** and **3f**, with the characteristic feature of having a pyridine unit linked to the ferrocenophane framework through an acetylenic bond. In these cases, the nitrogen atom within the heterocyclic ring is located far away from the nitrogen in the C=N bond, allowing the influence of the presence of the pyridine nitrogen atom on the redox potential shift of the ferrocene nucleus and on the corresponding complexation constants to be studied.

The cyclic voltammetric studies performed on addition of $Mg(ClO_4)_2$, $[Ca(ClO_4)_2]\cdot 4H_2O$, $[Zn(ClO_4)_2]\cdot 6H_2O$, $Zn(CF_3SO_3)_2$ and $Ca(CF_3SO_3)_2$, are summarized in Table 3. Firstly, these data indicate that the presence of the pyridine donor nitrogen atom promotes a notable differentiation between the anodic potential shifts of the ferrocene nucleus induced by the co-ordination processes in comparison with those induced by protonation (Fig. 2). Moreover, the magnitude of such electrochemical shifts on protonation is larger than those induced by co-ordination, which is in agreement with the above mentioned results.

For the molecule **3e**, containing the 2-pyridyl unit, the potential redox shift observed on addition of either anhydrous or hydrated Ca^{2+} salts are the same. Nevertheless, in the latter case, the response in CV depends greatly on the concentration of added cation probably indicating a slower complexation

process (Fig. 3). These results provide clear evidence of the greater stability of the complex formed, overcoming the hydration energy of the Ca^{2+} , in the case of using $[Ca(ClO_4)_2]$.



Fig. 2 Cyclic voltammogram of compound **3f**, before (red) and after addition of 0.5 equiv. of $Mg(ClO)_4$ (green); after addition of 1 equiv. of HBF_4 (blue). Conditions: 0.5 mM of **3f** and 0.1 M [ⁿBu₄NClO₄] in CH_2Cl_2 , using a Pt disk electrode and a scan rate = 0.2 V s⁻¹.



Fig. 3 DPV of **3e** after addition of 3 equiv. of $Ca(ClO_4)_2 \cdot 4(H_2O)$ (black); after addition of 3 equiv. of anhydrous $Ca(CF_3SO_3)_2$ (blue); after addition of 1 equiv. of HBF₄ to the resulting solution (red). Conditions: 0.5 mM of **3e** and 0.1 M ["Bu₄NClO₄] in CH₂Cl₂, using a Pt disk electrode, a $E_{pulse} = 10$ mV, a scan rate = 0.004 V s⁻¹, and Fc⁺/Fc as internal standard.

 $4H_2O$; and which was not observed in the previously studied derivatives.

A similar behaviour to the above mentioned for Ca^{2+} is observed when Mg(ClO₄)₂, or [Zn(ClO₄)₂]·6H₂O was added to an electrochemical solution of **3e** (Table 3) but in the latter case, together with the usual positive shift in the redox potential, a new binding response is observed, which is associated to a protonation process. This fact has been experimentally proven by the addition of 1 equiv. of HBF₄ to the electrochemical solution which resulted in the appearance of the redox wave, corresponding to that assigned to the protonated species, with concomitant disappearance of the redox wave due to coordination. Futhermore, in this case the redox wave of the ferrocene is shifted to the same potential value as that obtained by a direct protonation process ($\Delta E_{1/2} = 420$ mV) (Table 1). However, when anhydrous Zn(CF₃SO₃)₂ is added only the co-ordination process is observed (Table 3).

For comparison, we have also studied the electrochemical response to the same set of metal cations of **3f**, in order to determine not only the effect of these cations on the ligand but also the effect of the host–guest interaction on the oxidation potential of the ferrocene moiety upon replacing a 2-pyridyl by a 3-pyridyl unit. It is noteworthy that in contrast to the ligand **3e**, different behaviour was observed when hydrated or anhydrous salts of Ca^{2+} were added to a solution of **3f** (Table 3), because while no response was obtained with the former, a co-ordination effect was observed with the latter. Furthermore, upon addition of $[Zn(ClO_4)_2] \cdot 6H_2O$ a protonation effect was observed, whilst under the same conditions ligand **3e** gives rise to a co-ordination effect. However, addition of either anhydrous Mg(ClO₄)₂ or Zn(CF₃SO₃)₂ results in characteristic co-ordination behaviour.

Moreover, from the voltammetric behaviour of these derivatives it is clear that the binding events are strongly affected by the distance between the two binding sites as was previously suggested for the case of **3b**. This argument can also be supported by the analysis of the evolution of the reduction potential of the C=N unit after complexation, present in the structure of these derivatives, because its magnitude should be related to the distance C=N ··· M⁺ⁿ: the bigger the C=N ··· M⁺ⁿ interaction, the easier the reduction of the C=N. In this context, the reduction potentials of the C=N group in **4c** and **3f** upon addition of Mg²⁺, demonstrate that **3f** $(E_p = -0.670 \text{ V})$ exhibits a more negative value than **4c** $(E_p =$ -0.430 V), which is in agreement with a small C=N ··· Mg²⁺ interaction in **3f**.

On the other hand, the voltamperometric data also reveal that the stability of the complex formed is dependent on the relative position of the pyridine nitrogen atom, because in the case of **3f**, where the pyridine nitrogen atom is located at a bigger distance from the C=N than in **3e**, no variation of the CV was observed upon addition of hydrated Ca^{2+} , and only a protonation effect is observed when hydrated Zn^{2+} salts were added.

Spectrophotometric studies

Previous studies on ferrocene^{40–43} ligands have shown that a characteristic band between 400 and 500 nm ascribed to the lowest energy metal–ligand transition is perturbed by complexation.⁴⁴

Therefore, UV-vis spectroscopy was used for further complexation experiments with **3f**, because as has already been mentioned this ligand exhibits a different electrochemical response upon addition of Ca²⁺ and Mg²⁺. Typically, upon addition of Mg²⁺, as the chelating metal ion, into a CH₂Cl₂ solution of **3f** ($c = 6.3 \times 10^{-4}$ M), the MLCT band at $\lambda_{max} = 462$ nm ($\varepsilon = 1148.10 \text{ 1 mol}^{-1} \text{ cm}^{-1}$), entirely disappeared and was replaced by a new band at $\lambda_{max} = 525$ nm ($\varepsilon = 3475.16 \text{ 1 mol}^{-1}$ cm⁻¹), accompanied by an increase in absorbance (Fig. 4). Furthermore, its colour in the CH₂Cl₂ solution changed from orange to purple, which can be used for "naked eye" detection of Mg²⁺. In the presence of Ca²⁺ cation the colour change was less striking and only a modest darkening of the solution was observed visually.



Fig. 4 UV-vis spectra of the titration of alcohol neutral **3f** with $Mg(ClO_4)_2$ in CH_2Cl_2 ($c = 6.3 \ 10^{-4}$ mol. dm⁻³). The initial spectrum is that of starting alcohol **3f** and the final spectrum corresponds to the complexed form. Arrows indicate the absorptions that increased (up) and decreased (down) during the experiment.

The association constant of the $3f \cdot Mg^{2+}$ complex ($K_a = 1.5 \times 10^{10} \text{ M}^{-2}$) could be evaluated by means of UV-vis spectrophotometric titrimetry.⁴⁵ An isosbestic point was found, strongly indicating the presence of a unique complex in solution. A Job plot experiment between 3f and Mg(ClO₄)₂ in CH₂Cl₂ at 25 °C revealed a 1:2 (LM₂) stoichiometry.

Conclusion

In summary, we have developed new azaferrocenophane derivatives **3** and **4**, which are efficient redox sensors for protons and several kinds of metal cations. This recognition process is easily monitored by CV, which displays a large positive shift in the value of the Fc/Fc⁺ redox couple (400 mV for **4b** in the presence of Mg²⁺ cations). To the best of our knowledge the ferrocenebased ligand **3f** is the first example of a dual electrochemical– optical Mg²⁺ ion sensor in which the Fc/Fc⁺ redox couple is shifted ($\Delta E_{1/2} = 260$ mV) by cation recognition with concomitant naked eye detectable colour change from orange to purple. Interestingly, the electrochemical response of this ligand towards Ca²⁺ cation depends strongly on the nature of the salt employed: no response in the presence of hydrated salts and a two-wave behaviour when anhydrous salts are used.

Experimental

All reactions were carried out under N_2 using solvents which were dried by routine procedures. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AC200, 300 or 400 MHz, and chemical shifts refer to signals of tetramethylsilane. The EI and FAB⁺ mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer, using 3-nitrobenzyl alcohol as matrix. The UV-vis spectra were run on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Microanalyses were performed on a Perkin-Elmer 240C instrument. Electrochemical measurements were taken with a QUICELT-RON potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Electrochemical experiments were conducted in a conventional three-electrode cell under a N₂ atmosphere at 25 °C. The working electrode was a Pt disk (1 mm in diameter) polished before each recording. The auxiliary electrode was a platinum wire. The reference electrode was SCE. The experiments were in acetonitrile or dichloromethane solutions containing 0.1 M [NBuⁿ₄]ClO₄ (warning: caution) as supporting electrolyte and under these experimental conditions, the ferrocenium/ferrocene couple was observed at +0.405 V vs. SCE in acetonitrile and +0.535 V vs. SCE in dichloromethane. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. Cyclic voltammetry (CV) curves were recorded at scan rates from 0.050 to 1 V $\ensuremath{s^{-1}}$ and the scan potential was obtained in both positive and negative directions. The differential pulse voltammetry (DPV) curves were recorded at a 0.004 V s⁻¹ scan rate with a pulse height of 10 mV and a step time of 50 ms.

General procedure for the preparation of 1,1'-[(3,4-dihydro-2,4quinolinediyl)(2-alkynyl/aryl or heteroaryl-2-hydroxy-1,2ethanediyl)]ferrocene 3

To a cooled (-30 °C) solution of 1,1'-[(3,4-dihydro-2,4-quinolinediyl)(2-oxo-1,2-ethanediyl)] ferrocene **1** (0.1 g, 0.28 mmol) in dry Et₂O (30 mL), the appropriate organolithium derivative (1.5 equiv.) was added, under nitrogen. The stirred solution was then allowed to reach room temperature (3 h) and then H₂O (30 mL) was added. The reaction mixture was extracted with CH₂Cl₂ (3 × 50 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered off and evaporated under reduced pressure. The crude product was then chromatographed on a deactivated silica gel column using EtOAc/*n*-hexane (1:1) as eluent to yield the final product.

(3a): (80%) mp 223–226 °C (from EtOAc/*n*-hexane) (Found: C, 74.58; H, 5.50; N, 3.18. C₂₇H₂₃FeNO requires C, 74.84; H, 5.35; N, 3.23). v_{max}/cm⁻¹: 3390, 1580, 1565, 1440, 1120, 1095, 740 (Nujol); $\delta_{\rm H}$ (CDCl₃) 2.04 (1H, s, OH), 2.26 (1H, dd, J_{gem} = 14.4 Hz, ${}^{3}J = 11.7$ Hz), 2.42 (1H, dd, $J_{gem} = 14.4$ Hz, ${}^{3}J = 4.8$ Hz), 2.53 (1H, dd, $J_{gem} = 14.1$ Hz, ${}^{3}J = 5.1$ Hz), 3.34–3.36 (1H, m), 3.77 (1H, d, J_{gem} = 13.8 Hz), 4.10 (1H, m, Cp), 4.15 (1H, m, Cp), 4.20 (1H, m, Cp), 4.35 (1H, m, Cp), 4.50 (1H, m, Cp), 4.56 (1H, m, Cp), 4.75 (1H, m, Cp), 5.10 (1H, m, Cp), 7.10-7.40 (4H, m), 7.40 (1H, d, J = 8.1 Hz); $\delta_{\rm C}$ (CDCl₃) 31.35 (CH₂), 32.36 (CH), 42.62 (CH₂), 64.84 (CH, Cp), 66.39 (CH, Cp), 67.33 (CH, Cp), 67.97 (CH, Cp), 69.38 (CH, Cp), 70.78 (CH, Cp), 71.37 (CH, Cp), 71.73 (q), 72.88 (CH, Cp), 86.16 (q_{ipso} Fc), 98.08 (q_{ipso} Fc), 124.46 (2 × CH), 125.51 (CH), 126.31 (CH), 126.82 (CH), 127.83 (CH), 128.28 (2 × CH), 129.20 (q), 132.40 (q), 153.10 (q), 168.23 (C=N); EIMS m/z 433 (M⁺, 100%), 415 (30), 248 (56), 222 (11), 191 (21).

(3b): (70%) mp 224–227 °C (from EtOAc) (Found: C, 68.59; H, 4.70; N, 3.31. $C_{25}H_{21}FeNOS$ requires C, 68.34; H, 4.82; N, 3.19); v_{max}/cm^{-1} : 3380, 1585, 1561, 1450, 1123, 1040, 737 (Nujol; δ_{H} (CDCl₃) 2.04 (1H, t, J_{gem} = 14.1 Hz, ³J = 14.1 Hz), 2.34 (1H, s, OH), 2.46–2.55 (2H, m), 3.4–3.49 (1H, m), 3.68 (1H, d, J_{gem} = 14.1 Hz), 4.03 (1H, m, Cp), 4.22 (1H, m, Cp), 4.24 (1H, m, Cp), 4.56 (1H, m, Cp), 4.73 (1H, m, Cp), 5.1 (1H, m, Cp), 6.61 (1H, d, J = 2.7 Hz), 6.74 (1H, t, J = 5.1 Hz), 7.06–7.08 (1H, m), 7.12 (1H, d, J = 7.2Hz), 7.18 (1H, d, J = 7.8 Hz), 7.27 (1H, m), 7.38 (1H, d, J = 8.1Hz); $\delta_{\rm c}$ (CDCl₃) 31.17 (CH₂), 32.04 (CH), 43.03 (CH₂), 64.97 (CH, Cp), 65.91 (q), 66.58 (CH, Cp), 67.37 (CH, Cp), 67.93 (CH, Cp), 69.43 (CH, Cp), 70.65 (CH, Cp), 71.25 (CH, Cp), 72.88 (CH, Cp), 86.57 (q_{ipso} Fc), 97.54 (q_{ipso} Fc), 122.90 (CH), 124.64 (CH), 125.56 (CH), 125.96 (CH), 125.96 (CH), 126.41 (CH), 126.46 (CH), 127.86 (CH), 132.10 (q), 145.40 (q), 158.50 (q), 168.50 (C=N); EIMS *m*/*z* 439 (M⁺, 100%), 421 (21), 248 (55), 222 (10), 191 (22).

(3c): (70%) mp >300 °C (from CH₂Cl₂/Et₂O) (Found: C, 74.85; H, 5.10; N, 3.22. C₂₉H₂₃FeNO requires C, 76.16; H, 5.07; N, 3.06); v_{max}/cm^{-1} : 3389, 2200, 1582, 1562, 1472, 1450, 1240, 1090, 936, 822 (Nujol); $\delta_{\rm H}$ (CDCl₃) 2.15 (1H, t, $J_{gem} = 12.35$ Hz, ³J = 12.35 Hz), 2.36 (1H, s), 2.47 (1H, dd, $J_{gem} = 14.4$ Hz, ³J = 5.71 Hz) 2.58 (1H, dd, $J_{gem} = 14.8$ Hz, ³J = 5.00 Hz), 3.40– 3.42 (1H, m), 3.49 (1H, d, $J_{gem} = 13.32$ Hz) 4.14 (1H, m, Cp), 4.25 (2H, m, Cp), 4.41 (1H, m, Cp), 4.48 (1H, m, Cp), 4.57 (1H, m, Cp), 4.68 (1H, m, Cp), 5.06 (1H, m, Cp), 7.14–7.43 (9H, m); $\delta_{\rm c}$ (CDCl₃) 31.19 (CH₂), 32.2 (CH), 44.03 (CH₂), 62.79 (q), 65.36 (CH, Cp), 65.52 (CH, Cp), 66.75 (CH, Cp), 67.43 (CH, Cp), 69.11 (CH, Cp), 70.12 (CH, Cp), 70.70 (CH, Cp), 72.60 (CH, Cp), 80.40(q_{ipso}, Fc), 86.52 (q), 96.97 (q_{ipso}, Fc), 96.58 (q), 122.27 (CH), 125.23 (CH), 126.38 (CH), 128.36 (CH), 128.58 (2 × CH), 128.72 (q), 131.02 (2 CH), 131.93 (q), 145.06 (q), 167.55 (C=N); EIMS *m*/z 457 (M⁺, 26%), 439 (100), 355 (28), 248 (41), 222 (7), 191 (8).

(3d): (62%) mp 205–208 °C (from CH₂Cl₂/Et₂O) (Found: C, 70.31; H, 4.70; N, 2.39. C₃₃H₂₇Fe₂NO requires C, 70.12; H, 4.81; N, 2.48); ν_{max} /cm⁻¹: 3300, 2200, 2222, 1582, 1558, 1462, 1454, 1240, 1106, 866, 820 (Nujol); $\delta_{\rm H}$ (CDCl₃) 1.94 (1H, t, J_{gem} = 13.8 Hz, ³J = 13.8 Hz), 2.26 (dd, J_{gem} = 13.5 Hz, ³J = 5.1 Hz), 2.32 (1H, dd, J_{gem} = 14.1 Hz, ³J = 4.5 Hz), 3.45–3.52 (2H, m), 4.12 (5H, s, Cp), 4.20 (3H, m, Cp), 4.31 (4H, m, Cp), 4.47 (1H, m, Cp), 4.55 (1H, m, Cp), 4.67 (1H, m, Cp), 4.75 (1H, m, Cp), 4.88 (1H, m, Cp), 6.44 (1H, s, OH), 7.10–7.27 (4H, m); $\delta_{\rm C}$ (CDCl₃) 30.20 (CH), 30.38 (CH₂), 43.17 (CH₂), 62.77 (q), 65.27 (CH, Cp), 65.57 (CH, Cp), 66.57 (CH, Cp), 67.21 (CH, Cp), 68.39 (2 × CH, Cp), 68.77 (CH, Cp), 69.42 (5 CH, Cp), 69.89 (CH, Cp), 77.45 (CH, Cp), 77.62 (CH, Cp), 70.66 (CH, Cp), 72.36 (CH, Cp), 79.12 (q_{ipso}, Fc), 86.50 (q_{ipso}, Fc), 93.46 (q), 97.22 (q), 125.08 (2 × CH), 126.29 (CH), 127.20 (CH), 131.94 (q), 145.01 (q), 167.34 (C=N); FABMS *m*/*z* 566 (M⁺ + 1, 13%), 565 (M⁺, 17%).

(3e): (55%) mp >320 °C (from CH_2Cl_2/Et_2O) (Found: C, 73.55; H, 4.60; N, 6.23. C₂₈H₂₂FeN₂O requires C, 73.37; H, 4.84; N, 6.11); v_{max}/cm⁻¹: 3349, 2205, 1582, 1558, 1464, 1270, 1094, 1072, 906, 822 (Nujol); $\delta_{\rm H}$ (CDCl₃) 1.91 (1H, t, J_{gem} = 13.8 Hz, ${}^{3}J = 13.8$ Hz), 2.23 (1H, dd, $J_{gem} = 14.1$ Hz, ${}^{3}J = 4.8$ Hz), 2.34 (1H, dd, $J_{gem} = 13.8$ Hz, ${}^{3}J = 5.4$ Hz), 3.26–3.5 (2H, m), 4.13 (1H, m, Cp), 4.3 (2H, m, Cp), 4.45 (1H, m, Cp), 4.52 (1H, m, Cp), 4.63 (1H, m, Cp), 4.73 (1H, m, Cp), 4.84 (1H, m, Cp), 6.35 (1H, s, OH), 7.1–7.31 (5H, m), 7.7 (1H, td, J = 7.8 Hz, J = 1.8 Hz), 8.43 (1H, d, J = 5.4 Hz); $\delta_{\rm C}$ (CDCl₃) 35.42 (CH), 35.56 (CH₂), 47.71 (CH₂), 67.89 (q), 70.48 (CH), 70.65 (CH), 71.89 (CH), 72.63 (CH), 74.30 (CH), 75.22 (CH), 75.82 (CH), 77.68 (CH), 85.17 (q), 85.39 (q), 91.68 (q), 101.58 (q), 128.28 (CH), 130.35 (2 × CH), 131.44 (CH), 132.02 (CH), 132.50 (CH), 136.96 (q), 141.69 (CH), 147.38 (q), 150.21 (q), 154.97 (CH), 172.52 (C=N); EIMS m/z 458 (M⁺, 18%), 442 (13), 355 (100), 312 (56), 248 (90), 191(42), 121 (12), 103 (51).

(3f): (60%) mp >320 °C (from CH₂Cl₂/Et₂O) (Found: C, 73.20; H, 4.65; N, 6.30. C₂₈H₂₂FeN₂O requires C, 73.37; H, 4.84; N, 6.11); v_{max}/cm^{-1} : 3359, 2225, 1582, 1562, 1464, 1248, 1094, 1058, 970, 822 (Nujol); $\delta_{\rm H}$ (CDCl₃) 1.95 (1H, t, $J_{gem} = 13.0$ Hz, ³J = 13.0 Hz), 2.26 (1H, dd, $J_{gem} = 14$. Hz, ³J = 5 Hz), 2.38 (1H, dd, $J_{gem} = 13.8$ Hz, ³J = 5.4 Hz), 3.28–3.52 (2H, m), 4.17 (1H, m, Cp), 4.3 (2H, m, Cp), 4.48 (1H, m, Cp), 4.55 (1H, m, Cp), 4.66 (1H, m, Cp), 4.76 (1H, m, Cp), 4.87 (1H, m, Cp), 6.35 (1H, s, OH), 7.15–7.38 (5H, m), 7.7 (1H, d, J = 7.8 Hz), 8.43 (1H, m); $\delta_{\rm C}$ (CDCl₃) 30.23 (CH), 30.42 (CH₂), 42.71 (CH₂), 62.84 (q), 65.29 (CH, Cp), 65.50 (CH, Cp), 66.70 (CH, Cp), 67.43 (CH, Cp), 69.08 (CH, Cp), 70.01 (CH, Cp), 70.62 (CH, Cp), 72.51 (CH, Cp), 77.28 (q_{ipso}, Fc), 86.53 (q_{ipso}, Fc), 96.55 (q), 100.52 (q), 119.25 (q), 123.41 (CH), 125.15 (2 CH), 126.30 (CH), 127.31 (CH), 131.79 (q), 138.16 (CH), 145.04 (q), 148.60 (CH), 151.15 (CH), 167.34 (C=N); EIMS *m*/*z* 458 (M⁺, 18%), 442 (13), 355 (100), 312 (56), 248 (90), 191(42), 121 (12), 103 (51).

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References

- 1 G. W. Gokel, Chem Soc. Rev., 1992, 21, 39.
- 2 P. D. Beer, Adv. Inorg. Chem., 1992, 39, 79.
- 3 T. Jorgensen, T. K. Hansen and J. Becher, *Chem. Soc. Rev.*, 1994, 23, 41.
- 4 L. Fabrizzi and A. Poggi, Chem. Soc. Rev., 1995, 197.
- 5 A. E. Kaifer, S. Mendoza, in *Comprehensive Supramolecular Chemistry*, ed. G. W. Gokel, Pergamon, Oxford, 1996, vol. 1, p. 701.
- 6 P. L. Boulas, M. Gomez-Kaifer and L. Echegoyen, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 216.
- 7 P. D. Beer and P. A. Gale, Adv. Phys. Org. Chem., 1998, 31, 1.
- 8 P. D. Beer, Acc. Chem. Res., 1998, 31, 71.
- 9 P. D. Beer, P. A. Gale and G. Z. Chen, *Coord. Chem. Rev.*, 1999, 185–186, 3.
- 10 P. D. Beer and P. A. Gale, Angew. Chem., Int. Ed. Engl., 2001, 40, 485.
- 11 P. D. Beer, P. A. Gale and G. Z. Chen, J. Chem. Soc., Dalton Trans., 1999, 1897.
- 12 M. P. Andrews, C. Blackburn, J. F. McAleer and V. D. Patel, J. Chem. Soc., Chem. Commun., 1987, 1122.
- 13 P. D. Beer, C. Blackburn, J. F. McAleer and V. D. Patel, *Inorg. Chem.*, 1990, **29**, 378.
- 14 P. D. Beer, H. Sikanyika, C. Blackburn and J. F. McAleer, J. Chem. Soc., Chem. Commun., 1989, 1831.
- 15 H. Plenio and R. Diodone, Inorg. Chem., 1995, 34, 3964.
- 16 J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer and G. W. Gokel, *J. Am. Chem. Soc.*, 1992, **114**, 10583.
- 17 M. C. Grossel, D. G. Hamilton, J. I. Fuller and E. Millan-Barios, J. Chem. Soc., Dalton Trans., 1997, 3471.
- 18 M. C. Grossel, M. R. Goldspink, J. A. Hriljac and S. C. Weston, Organometallics, 1991, 10, 851.
- 19 J. M. Lloris, R. Martínez-Máñez, M. E. Padilla-Tosta, T. Pardo,

- J. Soto, P. D. Beer, J. Cadman and D. K. Smith, J. Chem. Soc., Dalton Trans., 1999, 2359.
- P. D. Beer, Z. Chen, M. G. B. Drew and A. J. Pilgrim, *Inorg. Chim. Acta*, 1994, **225**, 137.
 P. D. Beer and P. V. Bernhardt, *J. Chem. Soc., Dalton Trans.*, 2001,
- 1428. 22 J. M. Llogin, P. Martín and M.C. T. D. L. J. C. (1997)
- M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto and M. E. Padilla-Tosta, *J. Chem. Soc., Dalton Trans.*, 1998, 1635.
 P. D. Beer, J. Cadman, J. M. Lloris, R. Martínez-Máñez, J. Soto,
- T. Pardo and D. Marcos, J. Chem. Soc., Dalton Trans., 2000, 1805. 24 C. Caltagirone, A. Bencini, F. Demartin, F. A. Devillanova,
- A. Garau, F. Isaia, V. Lippolis, P. Mariani, U. Paple, L. Tei and G. Verani, *J. Chem. Soc., Dalton Trans.*, 2003, 901.
- 25 P. D. Beer and K. Y. Wild, Polyhedron, 1996, 15, 775.
- 26 A. Chesney, M. R. Bryce, A. S. Batsanov, J. A. K. Howard and L. M. Goldenberg, J. Chem. Soc., Chem. Commun., 1998, 677.
- 27 O. B. Sutcliffe, A. Chesney and M. R. Bryce, J. Organomet. Chem., 2001, 637–639, 134.
- 28 O. B. Sutcliffe, M. R. Bryce and A. S. Batsanov, J. Organomet. Chem., 2002, 656, 211.
- 29 V. Siemeling, B. Neumann, H-G. Stammler and A. Salmon, Z. Anorg. Allg. Chem., 2002, 628, 2315.
- 30 A. Tárraga, P. Molina, D. Curiel and M. D. Velasco, Organometallics, 2001, 20, 2145.
- 31 A. Tárraga, P. Molina, D. Curiel and M. D. Velasco, *Tetrahedron*, 2001, **57**, 6765.
- 32 A. Tárraga, P. Molina, D. Curiel and M. D. Velasco, *Tetrahedron Lett.*, 2002, **43**, 8453.
- 33 A. Tárraga, P. Molina and J. L. López, *Tetrahedron Lett.*, 2000, **41**, 2479.
- 34 A. Tárraga, P. Molina, J. L. López, M. D. Velasco, D. Bautista and P. G. Jones, *Organometallics*, 2002, **21**, 2055.
- 35 J. L. López, A. Tárraga, A. Espinosa, M. D. Velasco, P. Molina, V. Lloveras, J. Vidal-Gancedo, C. Rovira, J. Veciana, D. J. Evans and K. Wurts, *Chem. Eur. J.*, 2004, **10**, 1815.
- 36 D. P. Rillema, M. B. Callahan and K. B. Mack, *Inorg. Chem.*, 1982, 2589.
- 37 D. Astruc, M. H. Desbois, M. Lacoste, N. Ardoin, L. Toupet and F. Varrtet, in *Mixed Valence Systems: Applications in Chemistry*, *Physics, Biology*, ed. K. Prassides, Kluwer, Amsterdam, 1991, pp. 107–118.
- 38 L. O. Spreer, A. Li, D. B. MacQueen, C. B. Allan, J. Otvos, M. Calvin, R. B. Frankel and G. C. Papaefthymiou, *Inorg. Chem.*, 1994, 33, 1753.
- 39 P. D. Beer and D. K. Smith, J. Chem. Soc., Dalton Trans., 1998, 417.
- 40 S. R. Marder, J. W. Perry and B. G. Tiemann, *Organometallics*, 1991, **10**, 1896.
- 41 B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor and G. J. Cross, J. Organomet. Chem., 1994, 464, 225C.
- 42 Lambert, W. Gaschler, M. Zabel, R. Matschiner and R. Wortmann, J. Organomet. Chem., 1999, 592, 109.
- 43 T. J. Müller, A. Netz and M. Ansorge, *Organometallics*, 1999, 18, 5066.
- 44 J. D. Carr, S. J. Coles, M. B. Asan, M. B. Hurthouse, K. M. A. Malik and J. H. R. Tucker, J. Chem. Soc., Dalton Trans., 1999, 57.
- 45 K. A. Connors, Binding Constants: The Measurements of Molecular Complex Stability, John Wiley & Sons Ltd., New York, 1987, ch. 4.