Metallocene Bis(Aza-crown ether) Ligands and Related Compounds. Their Syntheses, Co-ordination Chemistry, and Electrochemical Properties

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The syntheses of new ferrocene and ruthenocene bis(aza-crown ethers) (**11**)—(**14**) containing amide bond linkages between the metallocene redox centre and aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) and aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclo-octadecane) are described. Variable-temperature ^{13}C n.m.r. studies on these compounds reveal a common intramolecular dynamic process involving rotation about the N–CO bond whose energy barrier to rotation is cation (Na^+ or Li^+) dependent. The sodium cation forms 1 : 2 stoicheiometric complexes with the ferrocene bis(aza-crown ethers), whereas potassium produces a 1 : 1 intramolecular sandwich complex with the former and a 1 : 2 complex with the latter. Electrochemical investigations reveal that binding of Na^+ and K^+ guest cations at the respective aza-crown ether co-ordinating sites results in shifts of the ferrocene oxidation wave to more positive potentials. Lithium produces analogous electrochemical effects with these two compounds, however ^{13}C n.m.r. results suggest this cation exclusively co-ordinates to the respective amide carbonyl oxygen donor atoms. This rationalisation is supported by 'model' ferrocene bis(tertiary amide) derivatives which exhibit redox-responsive behaviour to Li^+ while being electrochemically insensitive to Na^+ and K^+.

Appropriately designed oxidisable[1–6] or reducible[7–9] redox-active macrocyclic receptor molecules can electrochemically recognise cationic (metal, ammonium[10]) and anionic[11] (bromide) guest species either 'through space' electrostatic perturbation and/or *via* various conjugated bond linkages connecting the heteroatoms of the ionophore to the redox centre.[12] The proximity of the host binding site and nature of the bond linkage are factors of paramount importance in determining the magnitude and type (one- or two-wave) of the shift in the respective redox couple of these host systems produced by charged guest binding.[12] We report here the syntheses, co-ordination and electrochemical properties of new redox-responsive bis(aza-crown ether) ligands in which the metallocene redox-active centre is appended to aza-crown ether cation binding units *via* amide covalent bonds. A preliminary report of this work has been published.[13]

Results and Discussion

Syntheses.—The condensation of 1,1′-bis(chlorocarbonyl)-metallocenes (**1**) and (**2**)[14] with 2 mol of an appropriate secondary amine or aza-crown ether[15] in the presence of triethylamine gave, after column chromatography, the respective bis(amide) derivatives (**3**)—(**8**) and the metallocene bis(aza-crown ethers) (**11**)—(**14**) in good yields (Scheme 1). The structures of all these new air-stable compounds were characterised by elemental analyses, mass spectrometry, and ^1H and ^{13}C n.m.r. spectroscopy (see Experimental section). A notable feature in their ^{13}C n.m.r. spectra was the temperature dependence of the NCH_2 carbon resonances, a variable-temperature ^{13}C n.m.r. study of which is described below.

With the ultimate aim of synthesising methylene-linked metallocene aza-crown ether analogues, attempts to reduce compound (**11**) to (**15**) using diborane or $LiAlH_4$ were unsuccessful. The same conversion was attempted *via* the isolation of a thioamide intermediate.[16] Thus, treatment of (**5**) with Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulphide] in refluxing toluene gave the corresponding bis(thioamide) derivative (**16**). Adding triethyloxonium tetrafluoroborate to (**16**) gave (**18**) *in situ* and finally reduction with $NaBH_4$ gave the desired product (**19**) in yields of only 25% (Scheme 2). Although ^1H n.m.r. and mass spectrometry verified the compound's structure, elemental analyses were always unsatisfactory and so application of this synthetic route to the metallocene bis(amido-crown ethers) was not undertaken.

Variable-temperature ^{13}C *N.M.R. Studies.*—Variable-temperature ^{13}C n.m.r. studies on compounds (**5**)—(**8**), (**11**)—(**14**), (**16**), and (**17**) revealed a common intramolecular dynamic process involving rotation about the N–CE (E = O or S) bond. At low temperatures there were two absorptions for the respective NCH_2 carbons of these compounds. On warming, these individual signals begin to broaden and eventually coalesce (Figure 1). These observations suggest that at the respective coalescence temperature, T_c and above, the morpholine, thiomorpholine, or aza-crown ether rings are not fixed relative to the carbonyl groups and rotation about the N–CE bond is fast on the n.m.r. time-scale (Figure 2). The $\Delta G^‡$ values for this intramolecular dynamic process common to these compounds were calculated using initially the Gutowsky equation[17] (1) where k is the first-order rate constant for the

$$k = \pi\Delta\nu/2^{\frac{1}{2}} \qquad (1)$$

process, $\Delta\nu$ the frequency separation of resolved signals at the temperature at which the amide or thioamide bond rotation was stopped on the n.m.r. time-scale. The energy barriers $\Delta G^‡$ (Table 1) were then obtained from the Eyring equation[18] (2) where $R = 8.314$ J K^{-1} mol^{-1} and T_c is the respective coalescence temperature in Kelvin.

$$\Delta G^‡ = 2.303RT_c(10.319 - \log_{10}k + \log_{10}T_c) \qquad (2)$$

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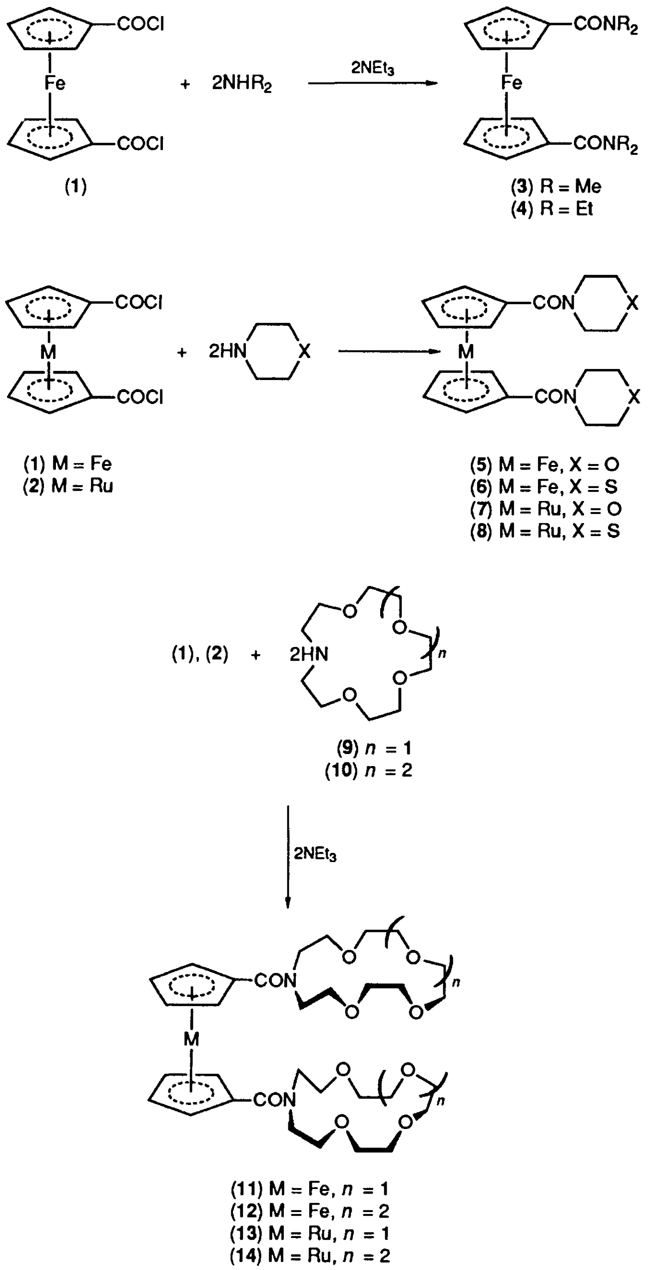
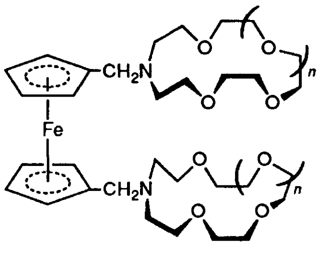


Scheme 1.



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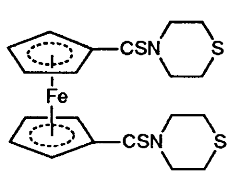
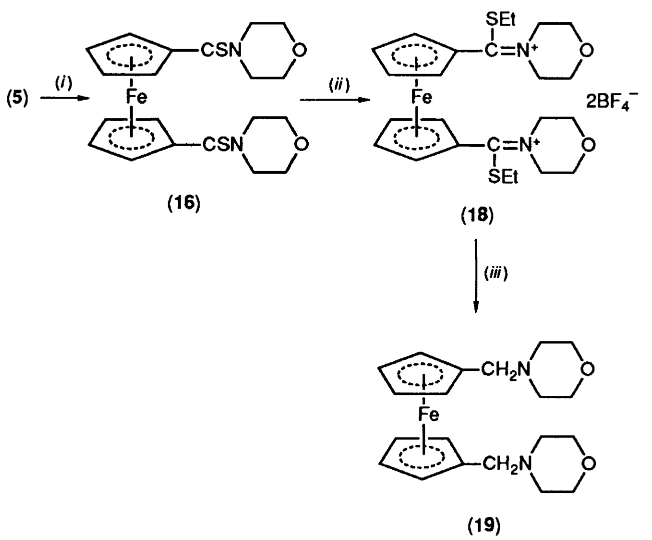


(17)

Comparison of $\Delta G^{\ddagger}$ values for compounds (**5**) and (**6**) shows, within experimental error, that the energy barrier to rotation for a given metallocene moiety is independent of the ether atom provided the amide linkage is identical. This is also the case for the pairs (**7**) and (**8**), and (**16**) and (**17**). It is also evident from Table 1 that the $\Delta G^{\ddagger}$ values are independent of the metallocene moiety for a given amide. However, converting the amide into a thioamide linkage increases the magnitude of $\Delta G^{\ddagger}$ by approximately 4 kJ mol^{-1}. This is probably a result of the larger sulphur atom hindering free rotation about the N–CS bond to a greater extent than the oxygen atom in the N–CO bond.



Scheme 2. (*i*) Lawesson's reagent, (*ii*) $[OEt_3][BF_4]$, (*iii*) $NaBH_4$.

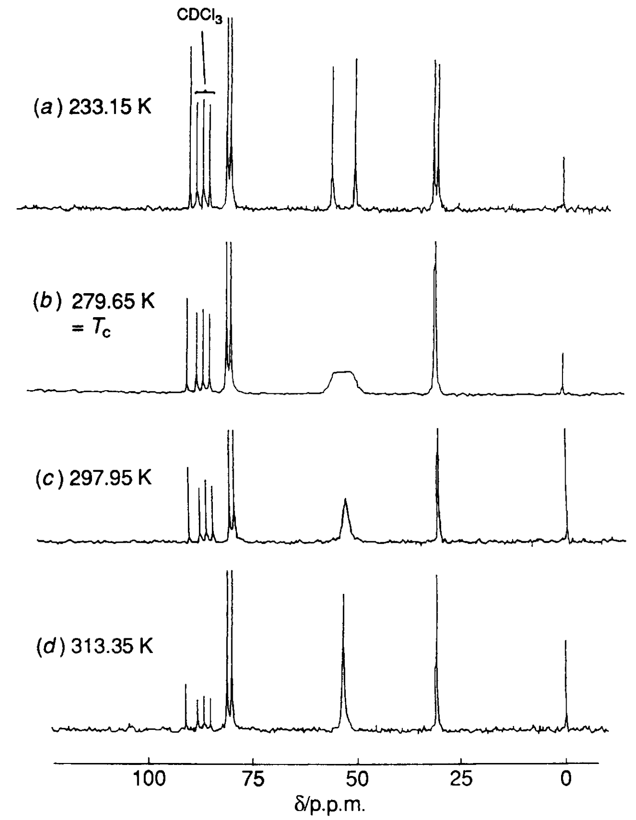


Figure 1. Variable-temperature broad-band-decoupled ^{13}C n.m.r. spectra of compound (**6**) in $CDCl_3$

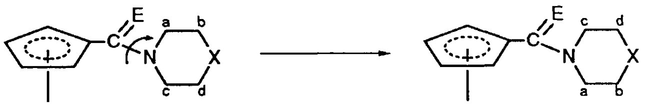


Figure 2. Rotation about the N–CE bond

Rotation about the amide bond in the presence of Na^+ *and*

Table 1. Coalescence temperatures (T_c), and energy barriers ($\Delta G^\ddagger$) for metallocene bis(amides) and aza-crown ethers in $CDCl_3$

Compound	T_c/K	$\Delta G^\ddagger$/kJ mol^{-1}
(5)	281	55.8
(6)	280	55.6
(7)	298	54.5
(8)	280	55.7
(11)	319	65.0
(12)	319	62.0
(13)	320	64.1
(14)	323	61.4
(16)	280	59.3
(17)	285	60.0

Table 2. Coalescence temperatures (T_c) and energy barriers ($\Delta G^\ddagger$) for compounds (**12**) and (**14**) in the presence/absence of Na^+ and Li^+ as guest cations in CD_3CN

Compound	T_c/K	$\Delta G^\ddagger$/kJ mol^{-1}
(14)	315	60.4
(14) + 2.5 equivalents $NaPF_6$	295	55.7
(12)	315	61.1
(12) + 2.5 equivalents $LiBF_4$	325	63.9

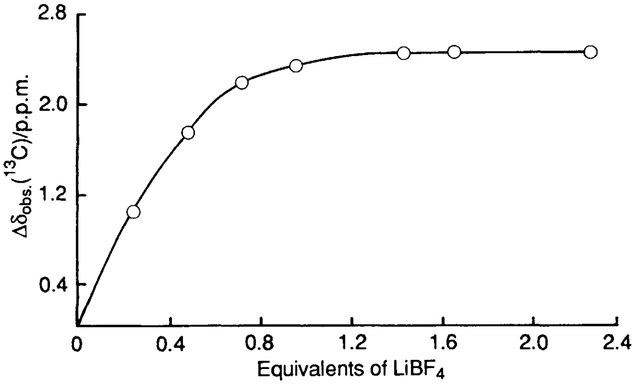
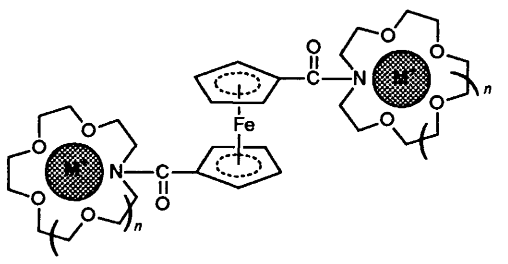
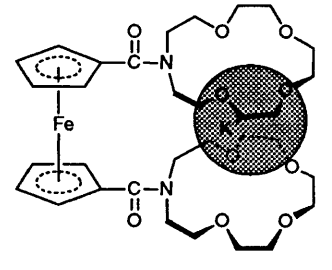


Figure 3. Carbon-13 n.m.r. titration curve of compound (**3**) with $LiBF_4$ in CD_3CN



Scheme 3. n = 1, M = Na; n = 2, M = Na or K.



Scheme 4.

Li^+. Further variable-temperature n.m.r. experiments were performed with the metallocene bis(aza-crowns) (**12**) and (**14**) in the presence of metal ions (Na^+, Li^+) in order to investigate the effect of complex formation upon the energy barrier for rotation about the amide bond. All these studies were carried out in CD_3CN to ensure solubility of both the metallocene bis(crown ether) and the added metal salt and the results are shown in Table 2.

In the case of sodium ion addition the $\Delta G^\ddagger$ value is lowered by approximately 5 kJ mol^{-1}. This is expected as the metal cation bound to the respective aza-crown ether macrocycle attracts electron density and correspondingly lowers the π-electron density associated with the amide bond. In direct contrast, the addition of lithium ions to (**12**) *raises* the $\Delta G^\ddagger$ value by approximately 2.8 kJ mol^{-1}. This can be rationalised by the suggestion that the lithium ions co-ordinate to the carbonyl oxygen donor atoms of the amide linkages and do *not* bind within the crown ether rings. This further polarises the carbonyl bond, decreasing the charge density of the carbonyl carbon and in turn increases the π-electron density associated with the nitrogen–carbonyl carbon linkage. With respect to size, the lithium cation is too small and the aza-18-crown-6 cavity too large for macrocyclic complex formation. Subsequent ^{13}C n.m.r. titration studies confirm this postulated mode of lithium co-ordination. The stepwise addition of $LiBF_4$ to acetonitrile solutions of compounds (**3**) and (**12**) led to considerable shifts of the respective carbonyl signal of up to 2 p.p.m. The stoicheiometry of Li^+ to ligand calculated from the resulting $\Delta\delta$ (p.p.m.) *versus* [$LiBF_4$] titration curves was found to be 2:1 for (**3**) (Figure 3) and 1:1 for (**12**). In the former case this suggests Li^+ is forming a four-co-ordinate complex with two molecules of (**3**) binding to the metal through the four carbonyl oxygen donor atoms. This type of co-ordination chemistry is commonly found for lithium.[19–22] Because of the size of the respective aza-crown ether rings of (**12**) only a 1:1 complex can form presumably with the Li^+ exclusively co-ordinating to the two carbonyl oxygen donors.

Co-ordination Studies.—The co-ordination chemistry of the ferrocene bis(aza-crown ether) compounds was investigated by refluxing aqueous methanolic solutions of the macrocyclic receptor molecules with excess of sodium and potassium hexafluorophosphates. Cooling of the concentrated solutions led to the isolation of orange crystalline complexes of stoicheiometry $[(\mathbf{12})\cdot 2M][PF_6]_2$ (M = Na or K). The elemental analyses suggest that compounds (**11**) and (**12**) form 1:2 ligand: sodium cation guest complexes in which each aza-crown ether macrocycle acts independently of the other (Scheme 3). In contrast, (**11**) containing the smaller aza-15-crown-5 macrocycle forms a 1:1 intramolecular sandwich complex with the K^+ guest cation (Scheme 4).

Electrochemical Studies.—The electrochemical properties of the metallocene bis(amides) and bis(aza-crown ethers) were investigated in acetonitrile using cyclic voltammetry with $NBu^n{}_4BF_4$ as the supporting electrolyte. Apart from (**7**), each compound exhibited a reversible one-electron oxidation wave in the 0.6—0.7 V region (*versus* s.c.e.) typical of a substituted ferrocene derivative (Table 3). With the ruthenocene derivative (**7**) two irreversible one-electron oxidations were observed. Ruthenocene itself is known to exhibit similar irreversible oxidation behaviour at less anodic peak potentials.[23]

Cyclic voltammograms were also recorded after progressively adding stoicheiometric equivalents of Li^+, Na^+, or K^+ to the electrochemical solutions of compounds (**3**)—(**5**), (**11**), and (**12**) and the results are summarised in Table 3. Significant one-wave anodic shifts are observed for Na^+ and K^+ *only* in the cases of (**11**) and (**12**) in which crown ether recognition sites are

Table 3. Electrochemical data and cation dependence for ferrocene bis-(aza-crown ethers) and 'model' analogues

	Compound					
	(3)	**(4)**	**(5)**	**(7)**	**(11)**	**(12)**
$E_{\frac{1}{2}}{}^{a}$/V	+0.68	+0.62	+0.60	$+1.09^{b}$ $+1.59^{b}$	+0.67	+0.67
$\Delta E(\text{Na}^+)^c$/mV	<10	<10	<10	—	40	35
$\Delta E(\text{K}^+)^c$/mV	<10	<10	<10	—	20	20
$\Delta E(\text{Li}^+)^d$/mV	360	390	320	—	70	75

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} NBu$^n{}_4$BF$_4$ as supporting electrolyte. Solutions were *ca.* 2 × 10^{-3} mol dm^{-3} in compound, and potentials were determined with reference to the s.c.e. [b] Irreversible oxidation process. [c] One-wave shift in oxidation potential produced by the presence of metal cations (4 equivalents) added as their perchlorate salts. [d] Two-wave situation; ΔE quoted is the difference between $E_{\frac{1}{2}}$ of the compound and the position of the new redox couple associated with the complex of Li$^+$.

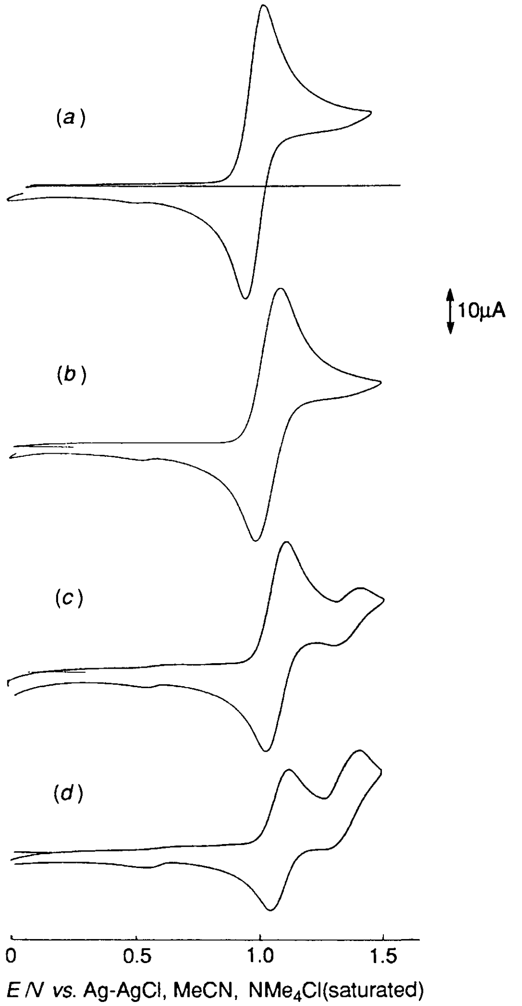
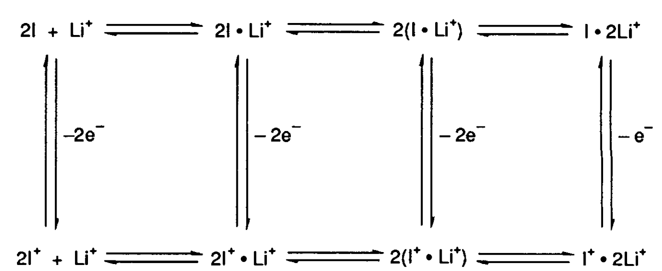


Figure 4. Cyclic voltammetry in acetonitrile solution of (*a*) compound (3) (3 mmol), (*b*) (3) +0.5 equivalents Li$^+$, (*c*) (3) + 2 equivalents Li$^+$, and (*d*) (3) + 4 equivalents Li$^+$. Sweep rate 50 mV s^{-1} scanning from 0 to +1.5 V



Scheme 5. Redox and complexation equilibria for a ferrocene 1,1′-bis-(tertiary amide) ligand, I

available for complexation of these cations. In agreement with electrochemical recognition studies of ferrocenyl benzo-crown ether ligand systems,[5,12] the magnitude of the shift (ΔE) is dependent upon the polarising power of the particular cationic guest. Similar one-wave anodic shifts are observed with Li$^+$, however ^{13}C n.m.r. titration and variable-temperature ^{13}C n.m.r. experiments discussed previously suggest this type of electrochemical recognition results from this metal cation co-ordinating to the respective amide carbonyl oxygen donor atoms only. This suggestion is further supported by the fact that although the model compounds (**3**)—(**5**) are electrochemically insensitive to the presence of Na$^+$ and K$^+$, the addition of Li$^+$ to these simple acyclic ferrocene bis(tertiary amide) derivatives results in large anodic shifts of the respective ferrocene oxidation wave and depending on the lithium concentration the appearance of the new redox couple associated with a lithium complex. For example, addition of LiBF$_4$ to an electrochemical solution of (**3**) led to a progressive shift of the redox wave towards more positive potentials. This shift was visible after the addition of 0.5 equivalent of LiBF$_4$ [Figure 4(*a*) and (*b*)]. Solutions treated with larger amounts of LiBF$_4$ ($\geqslant$2 equivalents) showed an additional effect. Thus, following an equilibration period, a new redox couple some 300 mV to more positive potential than that of the initial wave was observed [Figure 4(*c*)]. The height of the new wave increased further at the expense of the initial wave of solutions containing 4 equivalents of LiBF$_4$ [Figure 4(*d*)]. Somewhat surprisingly, in the presence of $\geqslant$6 equivalents. LiBF$_4$ the height of the new wave diminished compared with that observed at 4 equivalents. Analogous effects were observed with compounds (**4**) and (**5**).

A possible explanation for these electrochemical results is shown in Scheme 5, where I refers to a ferrocene bis(amide) ionophore [*i.e.* (**3**), (**4**), or (**5**)]. Since the shift in potential of the wave due to I is observed at low lithium concentration levels (comparable to those added in the n.m.r. experiments) we attribute this effect to the formation of a labile 2:1 complex 2I·Li$^+$. Electrochemical oxidation of this species is followed by rapid decomplexation to give the free ligand I$^+$, and therefore no new redox couple associated with 2I·Li$^+$ is detected. Larger amounts of LiBF$_4$ would be expected to displace the equilibria in favour of the 1:1 complex I·Li$^+$ and the new redox couple is attributed to this species. (Solubility problems negated ^{13}C n.m.r. titration experiments at these lithium concentrations.) This implies that the complex I$^+$·Li$^+$ is either stable or undergoes slow decomplexation on the voltammetric timescale, and indeed, the reverse wave, corresponding to the reduction of I$^+$·Li$^+$, is also observed. Since even larger amounts ($\geqslant$6 equivalents) of LiBF$_4$ did not lead to complete conversion into I·Li$^+$, the presence of a third species is likely. This could be a complex I·2Li$^+$ indistinguishable from I electrochemically because of either a similar redox and/or rapid decomplexation of I$^+$·2Li$^+$. We envisage the shift in redox potential resulting from the complexation I $\longrightarrow$ I·Li$^+$ as arising from the electrostatic effect of Li$^+$ held (co-operatively by two amide carbonyls) close to the iron redox centre. Indeed Hall *et al.*[24] have recently reported, from electrochemical and ^{13}C n.m.r.[25] investigations, a ferrocene cryptand that forms both 1:1 and 2:1 (host–guest) complexes through similar amide carbonyl co-ordination of a range of divalent cations in a ratio critically dependent upon temperature and concentrations.

Conclusion

A series of bis(aza-crown ethers) have been synthesised in which a metallocene redox centre bridges the respective aza-crown ether moieties, linked *via* amide covalent bonds. The ferrocene bis(aza-crown ether) ligands (**11**) and (**12**) electrochemically recognise Na^+ and K^+ *via* initial aza-crown ether–cation complexation and electrostatic communication of the positively charged bound guest species through the amide bond linkage. Although similar one-wave anodic shifts are observed with Li^+, ^{13}C n.m.r. titrations and variable-temperature ^{13}C n.m.r. investigations suggest this metal cation co-ordinates exclusively to the respective amide carbonyl oxygen donor atoms of (**11**) and (**12**). This rationalisation is supported by the simple 'model' ferrocene bis(tertiary amides) (**3**)—(**6**) being electrochemically insensitive to Na^+ and K^+, and uniquely redox-responsive to Li^+ resulting in the appearance of a new redox couple associated with a complex of Li^+.

Experimental

Reactions were carried out under an atmosphere of dry nitrogen and solvents were distilled prior to use from an appropriate drying agent. Proton n.m.r. spectra were recorded at 400 and 270 MHz and ^{13}C n.m.r. spectra at 100 and 67.8 MHz using tetramethylsilane as internal standard. Microanalyses were performed by the Birmingham University Chemistry Department microanalytical service. Electrochemical measurements were performed using a PAR 174A polarographic analyser. Cyclic voltammetric measurements were carried out in acetonitrile solution containing 0.2 mol dm^{-3} $NBu^n_4BF_4$ or saturated NMe_4Cl as supporting electrolyte using a platinum-bead working electrode with ferrocene as internal reference. Values are quoted relative to the saturated calomel reference electrode (s.c.e.). Positive-ion fast-atom-bombardment mass spectrometry was performed using a primary atom beam of argon (6 KeV, *ca.* 9.6×10^{-16} J) on a Kratos MS80 RF mass spectrometer coupled to a Kratos DS55 data system.

1,1′-Bis(chlorocarbonyl)ferrocene (**1**),[14] 1,1′-bis(chlorocarbonyl)ruthenocene (**2**),[14] aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) (**9**),[15] aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclo-octadecane) (**10**),[15] 1,1′-bis(dimethylcarbamoyl)- and 1,1′-bis(diethylcarbamoyl)-ferrocene (**3**) and (**4**)[26] were prepared using literature procedures. The secondary amines were obtained commercially from Aldrich Chemical Company and used without purification.

1,1′-Bis(morpholinocarbonyl)ferrocene (**5**).[26]—To a stirred solution of morpholine (0.28 g, 3.22 mmol) and triethylamine (0.33 g, 3.22 mmol) in anhydrous toluene (85 cm^3), under N_2 was added dropwise a solution of compound (**1**) (0.50 g, 1.61 mmol) in anhydrous toluene (80 cm^3) over 1 h. When the addition was complete, stirring was continued for 30 min and the solution was filtered. The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane (85 cm^3), washed with water, dried ($MgSO_4$), filtered, and rotary evaporated. The crude product was chromatographed on an alumina column eluting with 99% dichloromethane–1% methanol. The orange band was collected and, after removal of the solvents, recrystallisation from dichloromethane–n-hexane gave the product (**5**) as orange crystals, 0.66 g (83% yield), m.p. 173—175 °C, *m/z* 412; i.r. 1 610 cm^{-1} (C=O stretch). N.m.r. ($CDCl_3$): ^1H, δ 3.67 (s, 16 H, NCH_2CH_2O), 4.41 (t, *J* 2, 4 H, ferrocene H), and 4.60 (t, *J* 2 Hz, 4 H, ferrocene H); ^{13}C, δ 45.40 (br, NC), 66.90 (OC), 71.21, 72.05 (ferrocene C), 80.31 [ferrocene C (*ipso*)], and 168.80 (C=O) (Found: C, 58.5; H, 6.1; N, 6.7. Calc. for $C_{20}H_{24}FeN_2O_4$: C, 58.3; H, 6.3; N, 6.8%).

1,1′-Bis(1-thia-4-azacyclohexane-4-carbonyl)ferrocene (**6**).—This compound was prepared as for (**5**), from (**1**) (0.60 g, 1.93 mmol) and thiomorpholine (0.4 g, 3.96 mmol) in the presence of triethylamine (0.39 g, 3.86 mmol). The product was obtained as orange crystals, 0.73 g (85% yield), m.p. 199—201 °C, *m/z* 444; i.r. 1 640 cm^{-1} (C=O stretch). N.m.r. ($CDCl_3$): ^1H, δ 2.64 (br s, 8 H, SCH_2), 3.91 (t, *J* 5, NCH_2), 4.40 (t, *J* 2, 4 H, ferrocene H), and 4.58 (t, *J* 2 Hz, 4 H, ferrocene H); ^{13}C, δ 27.70 (SC), 47.50 (br, NC), 71.11, 72.12 (ferrocene C), 80.90 [ferrocene C (*ipso*)], and 168.81 (C=O) (Found: C, 55.1; H, 5.3; N, 6.2. Calc. for $C_{20}H_{24}FeN_2O_2S_2$: C, 54.1; H, 5.4; N, 6.3%).

1,1′-Bis(morpholinocarbonyl)ruthenocene (**7**).—This compound was prepared, using an analogous procedure to that employed for (**5**), in 80% yield, m.p. 180—182 °C, *m/z* 458; i.r. 1 620 cm^{-1} (C=O stretch). Proton n.m.r. ($CDCl_3$): δ 3.64 (m, 16 H), 4.69 (t, *J* 2, 4 H), and 4.89 (t, *J* 2 Hz, 4 H) (Found: C, 51.7; H, 5.3; N, 5.7. Calc. for $C_{20}H_{24}N_2O_4Ru$: C, 52.6; H, 5.3; N, 6.1%).

1,1′-Bis(1-thia-4-azacyclohexane-4-carbonyl)ruthenocene (**8**).—This compound was prepared, using a procedure analogous to that employed for (**5**), from (**2**) (0.35 g, 0.98 mmol) and thiomorpholine (0.20 g, 1.97 mmol) in the presence of triethylamine (0.22 g, 2.18 mmol). The product was obtained as pale yellow crystals, 0.34 g (70% yield), m.p. 193—195 °C, *m/z* 490. N.m.r. ($CDCl_3$): ^1H, δ 2.60 (t, *J* 10, 8 H, SCH_2), 3.90 (t, *J* 10, 8 H, NCH_2), 4.70 (t, *J* 5, 4 H, ruthenocene H), and 4.90 (t, *J* 5 Hz, 4 H, ruthenocene H). ^{13}C, δ 27.90 (SC), 47.76 (br, NC), 73.30, 74.00 (ruthenocene C), 84.11 [ruthenocene C (*ipso*)], and 167.48 (C=O) (Found: C, 48.3; H, 4.7; N, 5.6. Calc. for $C_{20}H_{24}N_2O_2S_2Ru$: C, 49.1; H, 5.0; N, 5.7%).

1,1′-Bis(1-morpholinothiocarbonyl)ferrocene (**16**).—This compound was prepared by employing the literature method.[16] Compound (**5**) (0.80 g, 1.94 mmol) and Lawesson's reagent (0.78 g, 3.88 mmol) were dissolved in anhydrous toluene (200 cm^3) and the solution was heated under reflux (nitrogen atmosphere) for 48 h. The reaction mixture was allowed to cool to room temperature then filtered and the toluene removed *in vacuo*. The crude product was dissolved in dichloromethane (75 cm^3), washed with water, dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The residue was purified by column chromatography (alumina, 99% CH_2Cl_2–1% CH_3OH as eluant). A red band was collected and, after removal of the solvents, recrystallisation from dichloromethane–n-hexane gave the product (**16**) as dark red crystals, 0.75 (87% yield), m.p. 179—181 °C, *m/z* 444; i.r. 1 160 cm^{-1} (C=S stretch). N.m.r. ($CDCl_3$): ^1H, δ 3.82 (s, br, 16 H, NCH_2CH_2O), 4.46 (t, *J* 2, 4 H, ferrocene H), and 4.72 (t, *J* 2 Hz, 4 H, ferrocene H); ^{13}C, δ 52.22 (br, NC), 66.52 (OC), 72.12, 76.3 (ferrocene C), 89.20 [ferrocene C (*ipso*)], and 198.73 (C=S) (Found: C, 54.9; H, 5.4, N, 6.9. Calc. for $C_{20}H_{24}FeN_2O_2S_2$: C, 54.1; H, 5.4; N, 6.3%).

The procedure for the preparation of compound (**17**) was similar to that described for (**16**), from (**6**) (0.77 g, 1.73 mmol) and Lawesson's reagent (0.79 g, 1.95 mmol). The product was obtained as red crystals, 0.74 g (90% yield), m.p. 135—137 °C, *m/z* 476; i.r. 1 135 cm^{-1} (C=S stretch). N.m.r. ($CDCl_3$): ^1H, δ 2.70 (t, *J* 5, 8 H, SCH_2), 4.40 (t, *J* 5, 8 H, NCH_2), 4.50 (t, *J* 2, 4 H, ferrocene H), and 4.65 (t, *J* 2 Hz, 4 H, ferrocene H); ^{13}C, δ 27.77 (br, SC), 54.30 (br, NC), 72.00, 76.22 (ferrocene C), 90.10 [ferrocene C (*ipso*)], and 199.32 (C=S) (Found: C, 50.7; H, 5.2; N, 6.1. Calc. for $C_{20}H_{24}FeN_2S_4$: C, 50.4; H, 5.0; N, 5.9%).

1,1′-Bis(morpholinomethyl)ferrocene (**19**).—The synthesis of this compound was attempted using a slightly modified literature method.[16] A stirred solution of compound (**17**) (0.20 g, 0.45 mmol) in dry dichloromethane (7 cm^3) was cooled to 0 °C under N_2. To this was addded a solution of triethyloxonium tetrafluoroborate in dichloromethane (5 cm^3 of a 1 mol dm^{-3} solution, 5.0 mmol) and the reaction mixture was stirred at 0 °C for 35 min after which the cooling bath was removed and stirring continued for 2.5 h. After removal of the solvent under pressure using an oil pump the residue was dissolved in anhydrous methanol (8 cm^3) and cooled to 0 °C. Excess of $NaBH_4$ (0.85 g, 22.4 mmol) was added in portions over 1 h. The reaction mixture was stirred at 0 °C for 35 min after which time the cooling bath was removed and stirring continued for 48 h. The solution was again cooled to 0 °C, treated with 10% HCl (15 cm^3), and then stirred at 0 °C for 10 min. The cooling bath was removed and stirring continued for 5 min, after which the solution was basified with 10% NaOH to pH 11. The mixture was extracted with diethyl ether. The ether extracts were washed with brine, dried ($MgSO_4$), filtered, and the ether removed *in vacuo*. The crude product was chromatographed on an alumina column eluting with 99% dichloromethane–1% methanol. The yellow band was collected and, after removal of the solvents, recrystallisation from boiling n-hexane gave the product (**19**) as yellow crystals, 0.043 g, (25% yield), m.p. 91—93 °C, *m/z* 384. Proton n.m.r. ($CDCl_3$): δ 2.41 (t, *J* 4, 8 H, NCH_2), 3.35 (s, sharp, 4 H, $C_5H_4CH_2N$), 3.67 (t, *J* 4, 8 H, OCH_2), 4.10 (t, *J* 2, 4 H, ferrocene H), and 4.12 (t, *J* 2 Hz, 4 H, ferrocene H). (Found: C, 59.2; H, 8.0; N, 6.2. Calc. for $C_{20}H_{28}FeN_2O_2$: C, 62.5; H, 7.3; N, 7.3%).

The ferrocene bis(aza-crown ethers) (**11**) and (**12**) were prepared as reported previously.[13]

1,1′-*Bis*(1,4,7,10,13-*pentaoxa*-16-*azacyclo-octadecane*-16-*carbonyl*)*ruthenocene* (**14**).—A solution of compound (**2**) (0.32 g, 0.9 mmol) in toluene (50 cm^3) was added dropwise over 30 min to a stirred solution of aza-18-crown-6 (0.49 g, 1.86 mmol) in toluene (70 cm^3) containing triethylamine (0.28 g, 2.77 mmol). When addition was complete stirring was continued for 1 h and the solution filtered. Removal of solvents gave the crude product which was chromatographed on an alumina column using methylene chloride–2% methanol. Recrystallisation from diethyl ether–hexane gave compound (**14**) (0.63 g, 80% yield) as light yellow crystals, m.p. 69—70 °C, *m/z* 810; i.r. 1 608 cm^{-1} (C=O stretch). Proton n.m.r. ($CDCl_3$): δ 3.64 (m, 48 H, crown H), 4.68 (t, *J* 2, 4 H), and 5.02 (t, *J* 2 Hz, 4 H) (Found: C, 53.2; H, 7.3; N, 3.8. Calc. for $C_{36}H_{56}N_2O_{12}Ru$: C, 53.4; H, 7.0; N, 3.5%).

An analogous procedure was used to prepare 1,1′-bis(1,4,7,10-tetraoxa-13-azacyclopentadecane-13-carbonyl)ruthenocene (**13**), 75% yield, as light yellow crystals, m.p. 64–66 °C, *m/z* 722; i.r. 1 620 cm^{-1} (C=O) stretch. Proton n.m.r. ($CDCl_3$): δ 3.70 (m, 40 H, crown H) (Found: C, 52.2; H, 6.9; N, 3.1. Calc. for $C_{32}H_{48}N_2O_{10}Ru$: C, 53.2; H, 6.7; N, 3.9%).

Sodium and Potassium Complexes of Compounds (**11**) *and* (**12**).—To a methanolic solution of either compounds (**11**) or (**12**) (1 mmol) was added an excess of alkali-metal hexafluorophosphate salt (5 mmol). The resulting solution was refluxed for 30 min and upon cooling an orange precipitate was collected and dried *in vacuo*. Recrystallisation from ethanol gave the respective complexes in quantitative yields: [(**11**)·2Na][PF_6]$_2$ (Found: C, 37.2; H, 5.1; N, 3.2. Calc. for $C_{32}H_{48}F_{12}Fe_2N_2Na_2O_{10}P_2$: C, 37.9; H, 4.7; N, 2.8%); [(**11**)·K]PF_6 (Found: C, 44.6; H, 6.2; N, 3.2. Calc. for $C_{32}H_{48}F_6FeKN_2O_{10}P$: C, 44.6; H, 5.6; N, 3.3%); [(**12**)·2Na][PF_6]$_2$ (Found: C, 37.9; H, 5.1; N, 2.4. Calc. for $C_{36}H_{56}F_{12}FeNa_2N_2O_{12}P_2$: C, 39.3; H, 5.1; N, 2.5%); [(**12**)·2K][PF_6]$_2$ (Found: C, 37.5; H, 4.6; N, 2.6. Calc. for $C_{36}H_{56}F_{12}FeK_2N_2O_{12}P_2$: C, 38.2; H, 5.0; N, 2.5%).

Acknowledgements

We thank the S.E.R.C. for an 'earmarked' studentship (to A. D. K.), the British Council for a studentship (to H. S.), MediSense Research Corporation Trust, L. and D. Blond for additional financial support, and the S.E.R.C. for use of the high-field n.m.r. service at the University of Warwick.

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Received 4*th April* 1990; *Paper* 0/01493A