Anion Recognition by Acyclic Redox-responsive Amide-linked Cobaltocenium Receptors

Paul D. Beer,* Clare Hazlewood, Dusan Hesek, Jana Hodacova and Sally E. Stokes
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

New acyclic tripodal mono- and 1,1'-bis-substituted amide-linked cobaltocenium ligands have been prepared. Proton NMR spectroscopic and cyclic voltammetric anion co-ordination investigations reveal that the combination of a positively charged cobaltocenium unit together with an amide N–H group are the essential components for the molecular and electrochemical recognition of anionic guest species. Correlations were found to exist between Hammett σ_p values of electron-donating and -withdrawing substituents of monosubstituted aryl amide cobaltocenium derivatives and relative magnitudes of halide-anion induced perturbations of the amide proton NMR chemical shift and cathodic shift of the respective cobaltocenium–cobaltocene reduction redox couple.

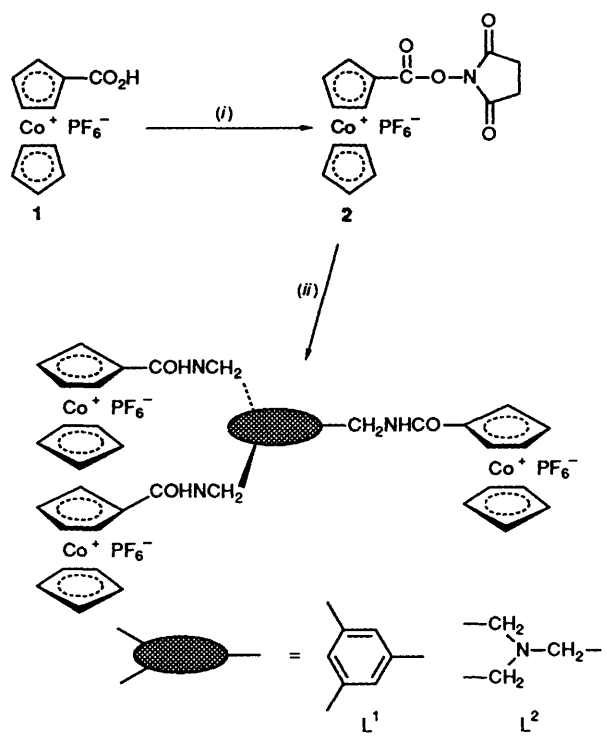
Anions are known to play ubiquitous roles in chemical and biochemical processes and their recognition by abiotic receptors is an area of intense current interest.[1] Examples of synthetic anion receptors reported to date include Lewis-acid-containing ligands,[2] ammonium quaternary salts,[3] protonated polyammonium macrocycles[4] and guanidinium.[5]

During the last few years we have successfully incorporated transition-metal redox-active centres into a variety of crown ether, aza crown ether, cryptand and polyphenolic macrocyclic structural frameworks and shown some of these host compounds to be selective and electrochemically responsive to the binding of cationic inorganic (Group 1, 2 metals, ammonium) and organic (bipyridinium) guest species.[6] As a further extension of this work we report here the first redox-responsive class of anion receptor based on the redox-active, pH-independent, positively charged cobaltocenium moiety and demonstrate that the simple combination of a cobaltocenium unit together with an amide N–H group are the essential components for anion recognition. A preliminary report of this work has recently appeared.[7]

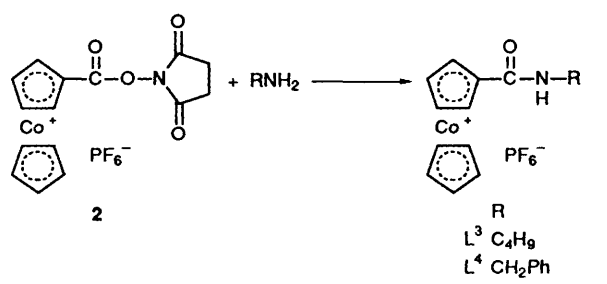
Results and Discussion

Ligand Syntheses.—We have previously reported[8] that an ester-linked polycobaltocenium macrocyclic ligand can bind and electrochemically detect the bromide guest anion, whereas simple acyclic cobaltocenium ester derivatives do not complex anions. However, the poor solubility of these types of macrocyclic ligands coupled with their arduous syntheses and lability to ester hydrolysis has led us to a new synthetic strategy which utilises the amide linkage to construct novel potential acyclic anion receptors.

Two general synthetic methods were used for the preparation of various amide derivatives of carboxycobaltocenium hexafluorophosphate **1**, the choice of method was found to be dependent upon the nature of the amine. With alkyl and benzyl amines the isolated activated ester **2**, prepared *via* the reaction of **1**[9] with *N*-hydroxysuccinimide, was the preferable synthon. The reaction of 3 moles of **2** with 1,3,5-tris(aminomethyl)benzene[10] or tris(2-aminoethyl)amine in the presence of triethylamine gave respectively the new acyclic tripodal receptors L^1 and L^2 in 71 and 61% yields (Scheme 1). The butyl- and benzyl-amide derivatives L^3 and L^4 were simply prepared from **2** and butyl- and benzyl-amine respectively (Scheme 2). By contrast the reaction of **2** with aromatic amines containing electron-donating or -withdrawing substituents failed. The desired ligands were

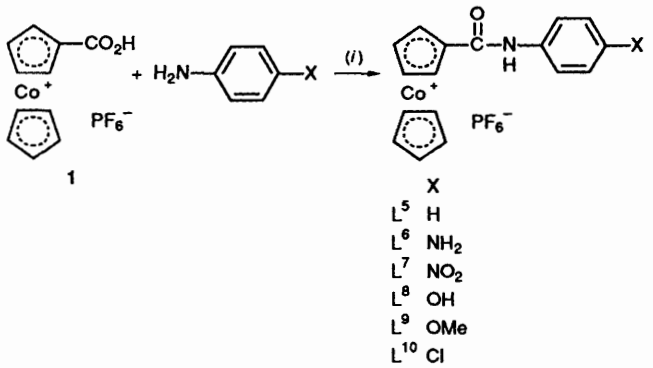


Scheme 1 (*i*) 1,3-Dicyclohexylcarbodiimide, *N*-hydroxysuccinimide, MeCN; (*ii*) NEt_3; 1,3,5-tris(aminomethyl)benzene or tris(2-aminoethyl)amine

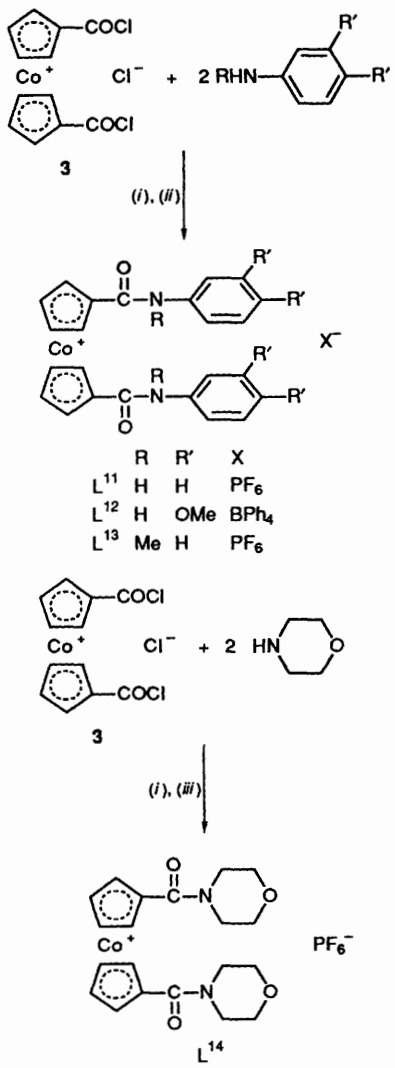


Scheme 2

prepared however by stirring a mixture of **1**, 1,3-dicyclohexylcarbodiimide and aromatic amine in dry acetonitrile at room



Scheme 3 (*i*) 1,3-Dicyclohexylcarbodiimide



Scheme 4 (*i*) NEt_3, MeCN; (*ii*) NH_4X; (*iii*) NH_4PF_6

temperature for several hours. After filtration, the solvent was removed *in vacuo* and the crude products purified by Sephadex LH20 chromatography to give ligands L^5–L^{10} in yields of up to 80% (Scheme 3).

The new 1,1′-disubstituted cobaltocenium derivatives L^{11}–L^{14} were prepared in very good yields *via* the condensation reaction of 1,1′-bis(chlorocarbonyl)cobaltocenium chloride **3**[9] and two moles of the appropriate arylamine or morpholine (Scheme 4). All these new compounds gave spectroscopic and

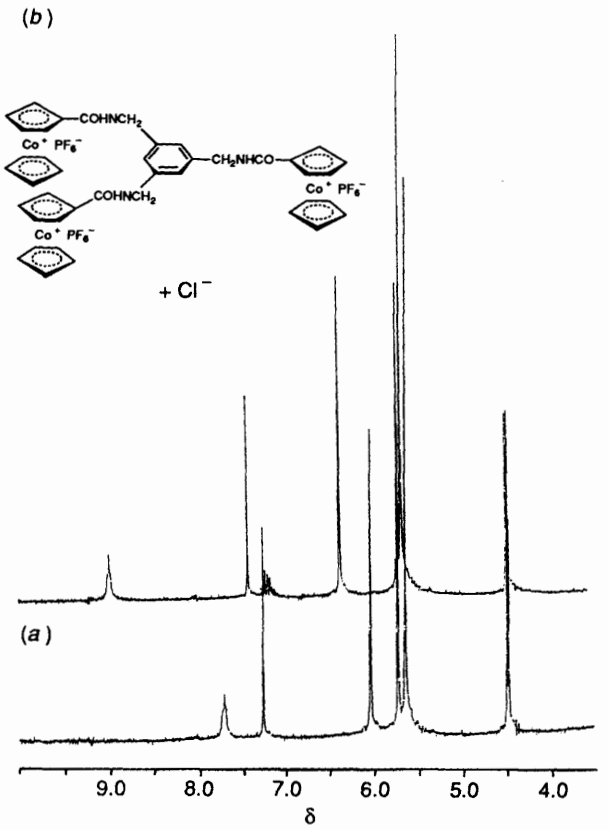
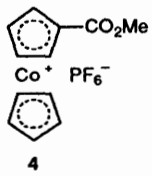


Fig. 1 Comparison of the ^1H NMR spectra in CD_3CN of (*a*) L^1 and (*b*) L^1 + 1 equivalent of NBu^n_4Cl

analytical data in accordance with assigned structures (see Experimental section).

Anion Co-ordination Studies.—Proton NMR titrations. NMR spectroscopy has been widely used to investigate receptor–substrate interactions.[11] Indeed the first reported example of anion binding by an abiotic host came from proton NMR evidence.[4a]

The addition of tetrabutylammonium chloride to deuteriated acetonitrile ^1H NMR solutions of L^1 or L^2 resulted in remarkable shifts of the respective protons of both receptors (Fig. 1). Of particular note are the substantial downfield shifts of the amide protons, $\Delta\delta$ = 1.28 ppm for L^1, 1.52 ppm for L^2, on addition of 1 equivalent of chloride. These results suggest a significant –CO–NH · · · Cl^- hydrogen-bonding interaction is contributing to the overall anion complexation process. Subsequent ^1H NMR titration studies in CD_3CN and [$^2H_6$]dimethyl sulfoxide ([$^2H_6$]dmso) with Cl^-, Br^- or NO_3^- produced titration curves suggesting 1:1 L:anion stoichiometry in all cases. Negligible shifts were observed under identical experimental conditions with cobaltocenium hexafluorophosphate itself or the ester derivative **4**. However, the simple monoamide-



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substituted cobaltocenium derivatives L^3 and L^4 did exhibit significant solution interactions with halide anions. Fig. 2 displays a comparison of ^1H NMR titration curves of L^1, L^2, L^3 and $PhCONHC_4H_9$ **5** with Cl^- guest anion in [$^2H_6$]dmso solution and Fig. 3 the titration curves of L^4 with Cl^- and Br^-

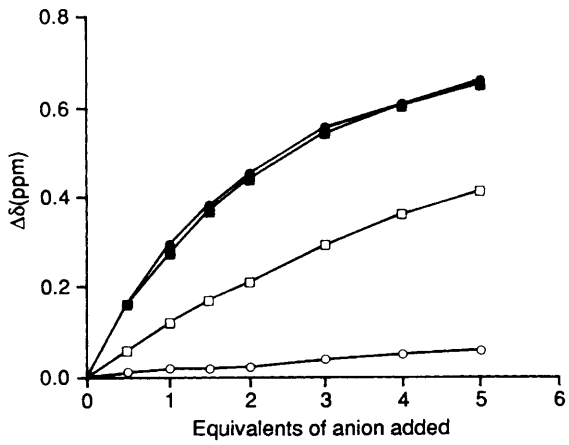

Fig. 2 Comparison of ^{1}H NMR titration curves of L^1 (■), L^2 (●), L^3 (□) and **5** (○) with Cl^- in [$^2H_6$]dmso solution, Δδ is the shift difference in ppm of the amide proton

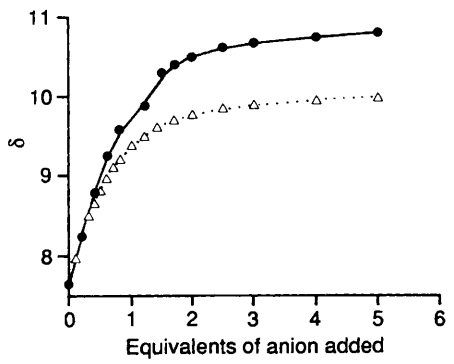

Fig. 3 Proton NMR titration curves of L^4 and Cl^- (●) or Br^- (△) in CD_3CN, δ is the shift of the amide proton

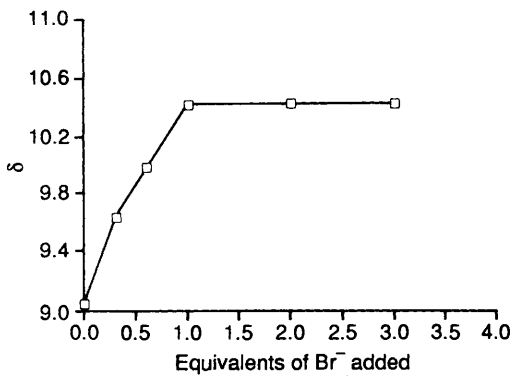

Fig. 4 Proton NMR titration curves of L^{12} and Br^- in $CDCl_3$ solution, δ is the shift of the amide proton

in CD_3CN. These results imply that it is the unique combination of the positively charged cobaltocenium moiety *and* the appending amide N–H unit which can form a favourable hydrogen bond with a co-ordinated anion guest, which are the essential components for successful anion complexation.

To test this hypothesis further the ligands L^5–L^{14} were prepared as described in the previous section in order to investigate the electronic effects of substituents on anion binding (L^5–L^{10}) and to elucidate, in the case of L^{11}–L^{14}, whether anion recognition still takes place in the absence of the NH amide group. Solution ^{1}H NMR complexation studies with Cl^- and Br^- anions revealed that remarkable shifts of the amide N–H and respective host protons were observed with ligands L^5–L^{12}. Fig. 4 for example shows the titration curve of L^{12} with Br^- which implies a 1 : 1 complex is formed in solution. Interestingly introducing a 20-fold excess of NH_4BPh_4 and repeating this ^{1}H NMR titration experiment gave the same result, negating the possibility for a simple anion exchange process. It is noteworthy that if the amide proton is replaced by a methyl or methylene group, as in the case of compounds L^{13} and L^{14}, no solution shifts of the respective host are observed under analogous experimental conditions, highlighting the importance of favourable NH–anion hydrogen bonding for anion complexation.

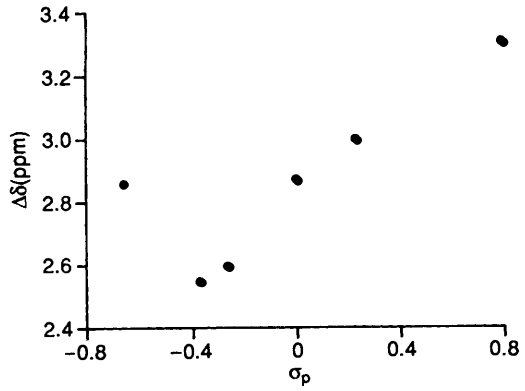

Fig. 5 Correlation of shifts of amide proton resonances upon addition of excess Cl^- in CD_3CN with Hammett substituent σ_p values for the series of ligands L^5–L^{10}

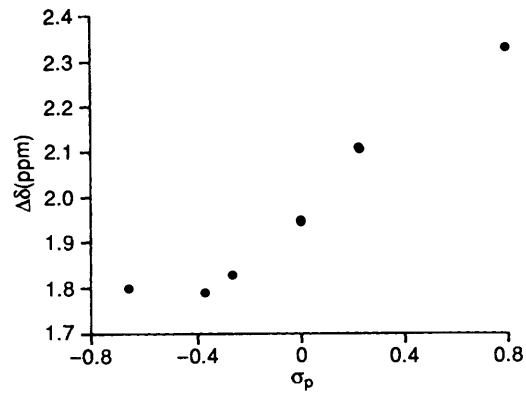

Fig. 6 Correlation of shifts of amide proton resonances upon addition of excess Br^- in CD_3CN with Hammett substituent σ_p values for the series of ligands L^5–L^{10}

In light of this finding, ligands L^5–L^{10} were prepared in an attempt to investigate and correlate the effects of electron-withdrawing and -donating substituents with the efficacy of amide N–H proton interaction with Cl^- and Br^- anion guests using ^{1}H NMR spectroscopy. Graphical representations of proton amide maximum shifts in ppm *versus* Hammett σ_p values[12] are shown in Fig. 5 for Cl^- and Fig. 6 for Br^-. With the exception of the *p*-NH_2 substituent of compound L^6 the correlations are very good, electron-withdrawing substituents such as *p*-NO_2 producing the largest magnitudes of amide shifts of up to 3.3 ppm. Clearly these results suggest that electron-withdrawing and -donating substituents which can increase or decrease the relative acidity of the arylamide N–H proton do indeed influence the relative strength of anion binding. This supports the hypothesis that a vital component to the anion-recognition process is favourable amide proton–anion hydrogen bonding. As the amide proton, through electron withdrawal, becomes more acidic in character, the strength of binding to anions would be expected to increase.

Electrochemical Anion-recognition Studies.—Although polyammonium macrocycles have been shown from electrochemical measurements to stabilise hexacyanoferrate(II) and hexacyanocobaltate(III) anions[13,14] to our knowledge these novel cobaltocenium ligands represent the first redox-responsive class of anion receptor.

Table 1 Electrochemical data

Ligand	$E_{\frac{1}{2}}$/V[a]	$\Delta E(Cl^-)$[b]/mV	$\Delta E(Br^-)$[b]/mV
L^1	−0.74[c]	30	15
L^2	−0.75[c]	30	15
L^3	−0.74[c]	30	45
L^4	−0.71	40	25
4	−0.45	< 5	< 5
L^5	−0.695	35	< 10
L^6	−0.718	35	< 10
L^7	−0.66	65	10
L^8	−0.72	30	< 10
L^9	−0.708	15	< 10
L^{10}	−0.685	—	—
L^{11}	−0.55	35	60
L^{12}	−0.52	30	55
L^{13}	−0.50	< 5	< 5
L^{14}	−0.60	< 5	< 5

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} $NBu^n_4BF_4$ as supporting electrolyte. Solutions were *ca.* 2×10^{-3} mol dm^{-3} in ligand and potentials were determined with reference to the SCE. [b] Cathodic shift in reduction potential produced by the presence of anions (up to 10 equivalents) added as their tetrabutylammonium salts. [c] Three-electron reduction process as determined by coulometric experiments.

The electrochemical properties of all these new acyclic cobaltocenium derivatives were investigated in acetonitrile using cyclic voltammetry with $NBu^n_4BF_4$ as the supporting electrolyte. Each compound exhibited a reversible redox reduction wave in the −0.5 to −0.7 V region [*vs.* saturated calomel electrode (SCE)] (Table 1). Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions, and the results are also summarised in Table 1. Only in the case where the cobaltocenium receptor contains at least one amide N–H linkage are significant one-wave *cathodic* shifts produced with the anionic guest species, in agreement with the results obtained from ^1H NMR anion-complexation experiments. Interestingly L^3 and the disubstituted arylamide ligands L^{11} and L^{12} exhibit relatively larger redox-couple perturbations for Br^- than Cl^- which is contrary to expectations based on these anions respective charge : radius ratio polarisabilities.

The $E_{\frac{1}{2}}$ reduction potentials of the series of ligands L^5–L^{10} display a correlation with the Hammett σ_p values of X (Fig. 7), the electron-withdrawing substituents exhibiting more anodic values as compared to the electron-donating substituent containing compounds.

Although, disappointingly, very small cathodic shifts of only $\leqslant 10$ mV were observed on addition of Br^- to L^5–L^{10} much larger cathodic perturbations were noted in the presence of excess amounts of Cl^-. Fig. 8 suggests that the magnitude of the shift of the respective ligand half-wave potential upon addition of chloride is dependent upon the nature of the aryl substituent. The largest shift of 65 mV was observed with L^7 containing the electron-withdrawing *p*-NO_2 group. This electrochemical finding is in agreement with the results obtained in the ^1H NMR titrations where L^7 also exhibited the largest magnitude of amide proton shift.

Conclusion

A variety of new acyclic tripodal, mono- and bis-substituted amide-linked cobaltocenium ligands have been synthesised. Preliminary anion co-ordination studies have revealed that acyclic cobaltocenium derivatives containing amide N–H groups can co-ordinate and electrochemically recognise halide anionic guest species *via* the cooperative binding forces of mutual electrostatic attraction between the positively charged host and anionic guest, and favourable amide N–H • • • anion hydrogen-bonding interactions. Such interactions have been found in an abiotic host containing three amide N–H groups which co-ordinates fluoride.[15] The importance of the latter contribution to the anion-recognition process can be highlighted when considering that those cobaltocenium derivatives L^{13} or L^{14} that contain tertiary amide linkages, *i.e.* absence of the amide N–H proton, do *not* complex anions.

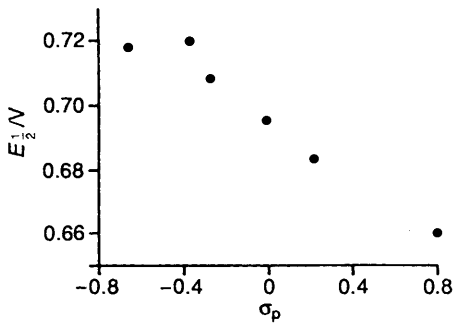

Fig. 7 Correlation of half-wave reduction potentials of L^5–L^{10} with Hammett σ_p values

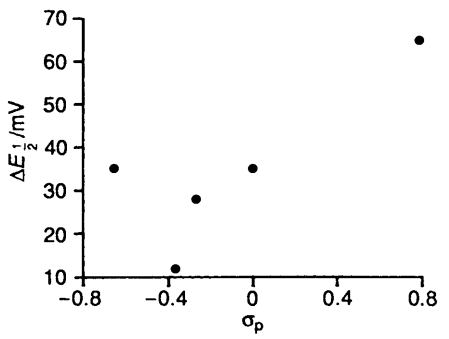

Fig. 8 Correlation of Cl^- anion-induced cathodic shifts of the half-wave reduction potentials of L^5–L^{10} upon addition of 10 equivalents of Cl^- with Hammett σ_p values

Arylamide cobaltocenium compounds L^5–L^{10} incorporating disparate electronic substituents reveal that as the acidity of the amide proton is increased by the presence of electron-withdrawing groups, the relative magnitudes of anion-induced perturbation of the amide proton in the ^1H NMR spectrum and cathodic shift of the respective cobaltocenium–cobaltocene reduction redox couple, increase. Moreover, correlations were found to exist between the Hammett σ_p values of substituents and the relative sizes of the respective amide proton and cathodic halide-anion induced perturbations. These results further support the proposition that the anion hydrogen-bonding interaction with the amide proton of a cobaltocenium derivative is an essential component for the molecular recognition of anionic guest species by these organometallic ligand systems.

Experimental

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 1710 FT IR instrument (4000–400 cm^{-1}) as KBr discs. Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using tetramethylsilane as an internal standard. Fast atom bombardment mass spectra were obtained from the SERC mass spectrometry service at University College, Swansea. Electrochemical measurements were carried out using an E.G. and G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

Solvent and Reagent Pretreatment.—Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was predried over class 4A molecular sieves (4–8 mesh) and then distilled from calcium hydride. Thionyl chloride

was distilled under nitrogen from triphenyl phosphite, triethylamine from potassium hydroxide pellets.

Unless stated to the contrary, commercial grade chemicals were used without further purification. The following compounds were prepared according to literature procedures: carboxycobaltocenium hexafluorophosphate **1**,[9] 1,1′-bis(chlorocarbonyl)cobaltocenium chloride **3**,[9] and 1,3,5-tris(aminomethyl)benzene.[10]

Syntheses.—Cobaltocenium hexafluorophosphate activated ester **2**. Carboxycobaltocenium hexafluorophosphate **1** (2.00 g, 5.3 mmol) was dissolved in dry acetonitrile (140 cm^3). *N*-Hydroxysuccinimide (0.72 g, 6.1 mmol) and 1,3-dicyclohexylcarbodiimide (1.20 g, 5.4 mmol) were added and the resulting mixture was stirred under nitrogen for 18 h at room temperature. After filtering off the 1,3-dicyclohexylcarbodiimide urea by-product the solvent was removed *in vacuo* to give a yellow powder (2.66 g, 70% yield), m.p. >260 °C (decomp.). ^1H NMR (CD_3CN): δ 2.69 (4 H, s, CH_2), 5.91 (5 H, s, cp H), 5.95 (2 H, t, J = 2.1, cp H) and 6.33 (2 H, t, J = 2.1 Hz, cp H) (Found: C, 37.3; H, 3.3; N, 3.4. Calc. for $C_{15}H_{13}CoF_6NO_4$: C, 37.9; H, 2.7; N, 3.0%).

$[C_6H_3\{CH_2NHCOC_5H_4Co(C_5H_5)\}$-1,3,5$][PF_6]_3$ (L^1). The cobaltocenium hexafluorophosphate activated ester **2** (2 g, 5.29 mmol) was dissolved in dry acetonitrile (150 cm^3) and a solution of 1,3,5-tris(aminomethyl)benzene (0.49 g, 1.74 mmol) and triethylamine (0.6 g, 5.93 mmol) in dry acetonitrile (60 cm^3) was added dropwise at room temperature under a nitrogen atmosphere. The resulting homogeneous solution was stirred at room temperature for 18 h and the solvent removed *in vacuo*. The crude product was purified using Sephadex LH-20 column chromatography with acetonitrile as eluent to give a yellow solid (1.53 g, 71% yield). Mass spectrum (FAB): m/z 1100 $[M - PF_6]^+$. NMR (CD_3CN): ^1H, δ 4.50 (6 H, d, J = 5.9), 5.66 (15 H, s, cp H), 5.75 (6 H, t, J = 2.1, cp H), 6.05 (6 H, t, J = 2.1, cp H), 7.28 (3 H, s, aryl H) and 7.71 (3 H, br t, J = 2.1 Hz, NHCO); ^{13}C, δ 44.22, 84.95, 87.08, 87.21, 95.14, 126.90, 140.43 and 162.56 (Found: C, 40.2; H, 3.4; N, 3.3. Calc. for $C_{42}H_{39}Co_3F_{18}N_3O_3P_3$: C, 40.5; H, 3.2; N, 3.4%).

$[N\{CH_2CH_2NHCOC_5H_4Co(C_5H_5)\}_3][PF_6]_3$ (L^2). This compound was prepared following the method for L^1 using activated ester **2**, (1 g, 2.65 mmol), tris(2-aminoethyl)amine (0.13 g, 0.88 mmol) and triethylamine (0.27 g, 2.67 mmol) in dry acetonitrile. Sephadex LH-20 column chromatography gave L^2 as a yellow solid (0.66 g, 61% yield). Mass spectrum (FAB): m/z 1081 $[M - PF_6]^+$. NMR (CD_3CN): ^1H, δ 2.73 (6 H, t, J = 5.9, CH_2–N), 3.42 (6 H, q, J = 5.9, CH_2NHCO), 5.68 (15 H, s, cp H), 5.71 (6 H, t, J = 2.1, cp H), 6.02 (6 H, t, J = 2.1, cp H) and 7.42 (3 H, br t, J = 2.1 Hz, NHCO); ^{13}C, δ 39.37, 54.67, 84.95, 86.92, 87.24, 95.49 and 162.77 (Found: C, 38.4; H, 3.6; N, 4.8. Calc. for $C_{39}H_{42}Co_3F_{18}N_4O_3P_3$: C, 38.2; H, 3.5; N, 4.6%).

(Butylaminocarbonyl)cobaltocenium hexafluorophosphate (L^3). An acetonitrile solution (25 cm^3) of butylamine (0.19 g, 2.6 mmol), and triethylamine (0.26 g, 2.6 mmol) was added dropwise to a solution of **2** (1 g, 2.1 mmol) in dry acetonitrile (25 cm^3) under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 18 h and the solvent removed *in vacuo*. The crude product was purified using column chromatography (alumina, 10% methanol) to give L^3 as a yellow solid (0.88 g, 97% yield). Mass spectrum (FAB): m/z 288 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 0.95 (3 H, t, J = 7.2, CH_3), 1.38 (2 H, m, CH_2), 1.55 (2 H, m, CH_2), 5.67 (5 H, s, cp H), 5.72 (2 H, t, J = 2.1, cp H), 6.07 (2 H, t, J = 2.1 Hz, cp H) and 7.29 (1 H, s, CONH).

(Benzylaminocarbonyl)cobaltocenium hexafluorophosphate (L^4). Activated ester **2** (0.28 g, 0.59 mmol) was dissolved in dry acetonitrile (30 ml) and stirred under nitrogen. A solution of benzylamine (0.065 g, 0.62 mmol) and triethylamine (0.061 g, 0.60 mmol) in dry acetonitrile (5 cm^3) was added dropwise and the resulting mixture left stirring at room temperature for 15 h. The solvent was removed *in vacuo* to leave a semi-solid which was washed with water (10 cm^3), filtered and dried to give L^4 (0.23 g, 86% yield). Mass spectrum (FAB): m/z 322 $[M - PF_6]^+$. NMR (CD_3CN): ^1H δ 4.60 (2 H, s, CH_2), 5.64 (5 H, s, cp H), 5.73 (2 H, t, J = 2.1, cp H), 6.07 (2 H, t, J = 2.1 Hz, cp H), 7.33–7.39 (m, 5 H, aryl H) and 7.64 (1 H, s, CONH); ^{13}C, δ 44.5, 85.0, 86.9, 87.1, 128.5, 128.8 and 129.7 (Found: C, 45.2; H, 3.7; N, 3.5. Calc. for $C_{18}H_{17}CoF_6NOP$: C, 45.3; H, 3.6; N, 3.0%).

(Phenylaminocarbonyl)cobaltocenium hexafluorophosphate (L^5). Carboxycobaltocenium hexafluorophosphate **1** (0.5 g, 1.32 mmol) was dissolved in dry acetonitrile (40 cm^3) and aniline (0.13 g, 1.40 mmol) and 1,3-dicyclohexylcarbodiimide (0.31 g, 1.52 mmol) added to the solution. The reaction mixture was stirred for 18 h at room temperature, filtered and the solvent removed *in vacuo*. The solid residue was washed with dichloromethane and dried to give an orange-red powder (0.48 g, 80% yield). Mass spectrum (FAB): m/z 308 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 5.75 (5 H, s, cp H), 5.79 (2 H, t, J = 2.1, cp H), 7.22 (1 H, t, J = 7.5, aryl H), 7.42 (2 H, t, J = 7.5, aryl H), 7.72 (2 H, d, J = 7.5 Hz, aryl H) and 8.83 (1 H, s, CONH) (Found: C, 45.0; H, 3.3; N, 3.6. Calc. for $C_{17}H_{15}CoF_6NO$: C, 45.0; H, 3.1; N, 3.3%).

[(4-Aminophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate (L^6). This compound was prepared following the method for L^5 using **1** (0.3 g, 0.8 mmol), 1,4-phenylenediamine (0.095 g, 0.8 mmol) and 1,3-dicyclohexylcarbodiimide (0.2 g, 0.9 mmol) in dry acetonitrile (20 cm^3). The product was purified by column chromatography on Sephadex LH20 using acetonitrile as eluent to give a red powdery solid (0.24 g, 65% yield). Mass spectrum (FAB): m/z 324 $[M - PF_6]^+$. NMR (CD_3CN): δ 4.20 (2 H, s, aryl NH_2), 5.73 (5 H, s, cp H), 5.77 (2 H, t, J = 2.1, cp H), 6.17 (2 H, t, J = 2.1, cp H), 6.67 (2 H, d, J = 6, aryl H), 7.39 (2 H, d, J = 6 Hz, aryl H) and 8.57 (1 H, s, CONH) (Found C, 44.2; H, 3.9; N, 6.3. Calc. for $C_{17}H_{17}CoF_6N_2OP$: C, 43.6; H, 3.4; N, 6.0%).

[(4-Nitrophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate (L^7). This compound was prepared following the method for L^5 using **1** (0.38 g, 1.0 mmol), 4-nitroaniline (0.15 g, 1.1 mmol) and 1.3-dicyclohexylcarbodiimide (0.25 g, 1.21 mmol). After washing with dichloromethane and hot methanol the product was obtained as a pale yellow powder (0.25 g, 50% yield). Mass spectrum (FAB): m/z 353 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 5.77 (5 H, s, cp H), 5.83 (2 H, t, J = 2.1, cp H), 6.25 (2 H, t, J = 2.1, cp H), 7.97 (2 H, d, J = 9, aryl H), 8.28 (2 H, d, J = 9 Hz, aryl H) and 9.17 (1 H, s, CONH) (Found: C, 41.0; H, 2.9; N, 5.3. Calc. for $C_{17}H_{14}CoF_6N_2O_3P$: C, 41.0; H, 2.8; N, 5.6%).

[(4-Hydroxyphenyl)aminocarbonyl]cobaltocenium hexafluorophosphate (L^8). This compound was prepared following the method for L^5 using **1** (0.38 g, 1.0 mmol), 4-aminophenol (0.11 g, 1.0 mmol) and 1,3-dicyclohexylcarbodiimide (0.23 g, 1.1 mmol). The crude product was washed with dichloromethane and recrystallised from methanol to give L^8 (0.35 g, 75% yield). Mass spectrum (FAB): m/z 324 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 5.74 (5 H, s, cp H), 5.78 (2 H, t, J = 2.1, cp H), 6.21 (2 H, t, J = 2.1, cp H), 6.85 (2 H, d, J = 9, aryl H), 7.53 (2 H, d, J = 9 Hz, aryl H) and 8.79 (1 H, s, CONH) (Found: C, 40.4; H, 3.3; N, 2.9. Calc. for $C_{17}H_{15}CoF_6NO_2P \cdot 2H_2O$: C, 40.4; H, 3.8; N, 2.8%).

[(4-Methoxyphenyl)aminocarbonyl]cobaltocenium hexafluorophosphate (L^9). This compound was prepared following the procedure for L^5 using **1** (0.38 g, 1 mmol), *p*-anisidine (0.13 g, 1.1 mmol) and 1,3-dicyclohexylcarbodiimide (0.23 g, 1.1 mmol) in dry acetonitrile (40 cm^3) to give L^9 (0.26 g, 52% yield). Mass spectrum (FAB): m/z 338 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 3.60 (3 H, s, OCH_3), 5.75 (5 H, s, cp H), 5.79 (2 H, t, J = 2.1, cp H), 6.22 (2 H, t, J = 2.1, cp H), 6.96 (2 H, d, J = 9, aryl H), 7.62 (2 H, d, J = 9 Hz, aryl H) and 8.90 (1 H, s, CONH) (Found: C, 43.9; H, 3.4; N, 2.9. Calc. for $C_{18}H_{17}CoF_6NO_2P$: C, 43.2; H, 3.4; N, 2.8%).

[(4-Chlorophenyl)aminocarbonyl]cobaltocenium hexafluorophosphate (L^{10}). Analogous synthetic procedure to L^5 using **1**

(0.38 g, 1.0 mmol), 4-chloroaniline (0.13 g, 1.0 mmol) and 1,3-dicyclohexylcarbodiimide (0.22 g, 1.2 mmol) in dry acetonitrile. The crude product was purified by column chromatography on Sephadex using methanol–acetonitrile (1 : 1) as eluent to give L^{10} as a yellow crystalline powder (0.23 g, 47% yield). Mass spectrum (FAB): *m/z* 342 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 5.72 (5 H, s, cp H), 5.80 (2 H, t, J = 2.1, cp H), 6.22 (2 H, t, J = 2.1, cp H), 7.42 (2 H, d, J = 7.5, aryl H), 7.74 (2 H, d, J = 7.5 Hz, aryl H) and 8.95 (1 H, s, CONH) (Found: C, 42.1; H, 3.1; N, 3.1. Calc. for $C_{17}H_{14}ClCoF_6NOP$: C, 41.8; H, 2.9; N, 2.9%).

1,1′-*Bis*[(3,4-*dimethoxyphenyl*)*aminocarbonyl*]*cobaltocenium tetraphenylborate* (L^{12}). 3,4-Dimethoxyaniline (0.83 g, 5.4 mmol) and triethylamine (1.5 g, 12 mmol) were dissolved in dry acetonitrile (40 cm^3) and a solution of 1,1′-bis(chlorocarbonyl)-cobaltocenium chloride **3** (1.24 g, 2.7 mmol) in dry acetonitrile (20 cm^3) was added dropwise. The resulting mixture was stirred at room temperature overnight and the solvent removed *in vacuo*. The crude product was dissolved in water and an excess of NH_4BPh_4 added to precipitate the product as a brown-red solid (2.96 g, 79% yield). Mass spectrum (FAB): *m/z* 547 $[M - BPh_4]^+$. ^1H NMR ($CDCl_3$): δ 3.82 (3 H, s, OMe), 3.90 (3 H, s, OMe), 5.10 (2 H, t, J = 2.1, cp H), 5.59 (2 H, t, J = 2.1, cp H), 6.84 (1 H, d, J = 7 Hz, aryl H), 6.9–7.5 (22 H, m, aryl H and BPh_4) and 9.04 (1 H, s, CONH) (Found: C, 69.6; H, 5.5; N, 3.1. Calc. for $C_{52}H_{48}BCoN_2O_4$: C, 70.1; H, 5.6; N, 3.2%).

1,1′-*Bis*[(N-*methyl*-N-*phenyl*)*aminocarbonyl*]*cobaltocenium hexafluorophosphate* (L^{13}). This compound was prepared following the method for L^{12} using *N*-methylaniline (0.44 g, 4.1 mmol), triethylamine (0.45 g, 4.0 mmol) and **3** (0.95 g, 2.1 mmol) in dry acetonitrile (200 cm^3). The crude product was purified using Sephadex column chromatography (MeCN eluent) to give after addition of an excess amount of NH_4PF_6, L^{13} as a yellow solid (0.66 g, 53% yield). Mass spectrum (FAB): *m/z* 456 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 3.40 (6 H, s, Me), 5.39 (2 H, t, J = 2.1 Hz, cp H) and 7.2–7.3 (10 H, m, aryl H) (Found: C, 55.1; H, 4.1; N, 4.3. Calc. for $C_{24}H_{24}CoF_6N_2O_2P$: C, 52.0; H, 4.0; N, 4.7%).

1,1′-*Bis*(*morpholinocarbonyl*)*cobaltocenium hexafluorophosphate* (L^{14}). An analogous procedure to the preparation of L^{12} was employed using morpholine (0.35 g, 4.1 mmol), triethylamine (1.5 g, 12 mmol) and **3** (0.93 g, 2.0 mmol) in dry acetonitrile (100 cm^3). After removal of the solvent *in vacuo* the crude product was purified using Sephadex column chromatography (MeCN eluent) to give after addition of an excess amount of NH_4PF_6, L^{14} as a yellow powder (1.64 g, 71%). Mass spectrum (FAB): *m/z* 415 $[M - PF_6]^+$. ^1H NMR (CD_3CN): δ 3.4–3.7 (16 H, m, NCH_2), 5.55 (2 H, t, J = 2.1, cp H) and 5.80 (2 H, t, J = 2.1 Hz, cp H) (Found: C, 43.3; H, 4.9; N, 6.0. Calc. for $C_{20}H_{24}CoF_6NO_4P$: C, 42.8; H, 4.3; N, 5.0%).

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