Acyclic Redox Responsive Anion Receptors containing Amide Linked Cobalticinium Moieties

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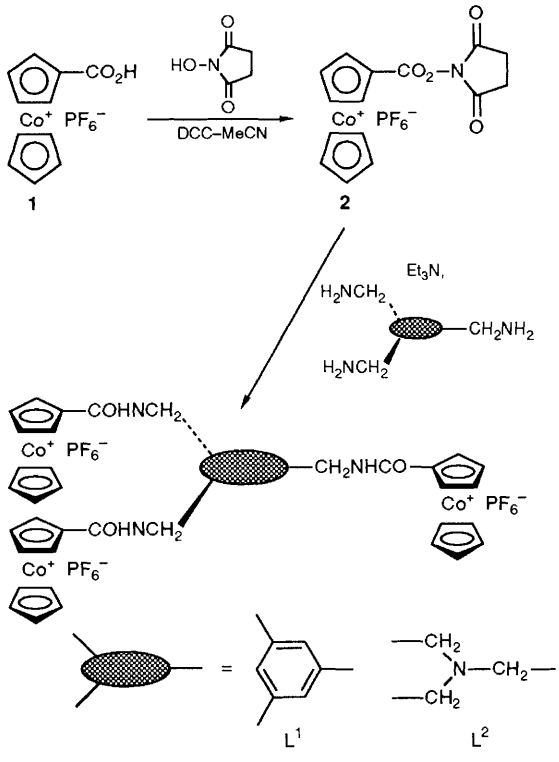
New acyclic redox responsive anion receptors containing amide linked cobalticinium moieties are prepared; preliminary anion coordination studies reveal that the combination of a positively charged cobalticinium unit together with an amide N–H group are the essential components for the molecular and electrochemical recognition of anionic guest species

The molecular recognition of anionic guest species by positively charged or electron-deficient neutral abiotic organic receptor molecules is a relatively new area of chemical investigation.[1] This is somewhat surprising in view of the ubiquitous role anionic substrates play in chemical and biochemical processes. Only a few classes of anion receptor have been reported including Lewis acid-containing ligands,[2] ammonium quaternary salts,[3] protonated polyamines[4] and guanidines.[5] We report here the syntheses, anion coordination and electrochemical studies of novel acyclic anion receptors containing the redox-active, pH-independent positively charged cobalticinium moiety and demonstrate that the simple combination of a cobalticinium unit together with an amide N–H group are the essential components for anion recognition.

We have previously reported[6] that an ester linked poly-



DCC = 1,3-dicyclohexylcarbodiimide

Scheme 1

cobalticinium macrocyclic ligand can bind and electrochemically detect the bromide guest anion, whereas simple acyclic cobalticinium 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.

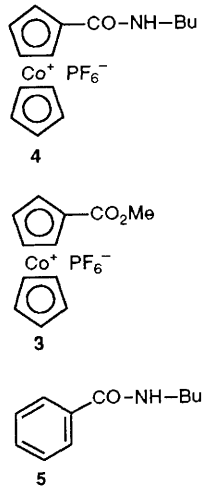
The reaction of carboxycobalticinium hexafluorophosphate **1**[7] with *N*-hydroxysuccinimide gave the activated ester **2** in excellent yield. This new synthon has proved much more stable than the corresponding acid chloride derivative.[7] The reaction of three moles of **2** with 1,3,5-triaminomethylbenzene[4d] and tris(2-aminoethyl)amine in the presence of triethylamine gave respectively the new acyclic tripodal receptors L^1 and L^2 in 65 and 60% yields (Scheme 1).†

The addition of tetrabutylammonium chloride to deuteriated acetonitrile ^1H NMR solutions of L^1 and L^2 resulted in remarkable shifts of the respective protons of both receptors. 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 one equivalent of chloride. These results suggest a significant –CO–NH···Cl^- hydrogen bonding interaction is contributing to the overall anion complexation process.[8] Subsequent ^1H NMR titration studies in CD_3CN and [$^2H_6$]dimethyl sulphoxide ([$^2H_6$]DMSO) with Cl^-, Br^- and NO_3^- produced titration curves suggesting 1 : 1 L : anion stoichiometry in all cases. Interestingly, with F^- and

† All new compounds gave spectroscopic and analytical data in accordance with assigned structures. For L^1: δ_H (CD_3CN) 4.50 (d, 6H, *J* 6 Hz), 5.66 (s, 15H), 5.75 (t, 6H, *J* 2 Hz), 6.05 (t, 6H, *J* 2 Hz), 7.28 (s, 3H) and 7.70 (br t, 3H, *J* 2 Hz). δ_{13C} (CD_3CN) 44.22, 84.95, 87.08, 87.21, 95.14, 126.9, 140.43 and 162.56. *m/z* (FAB) 1100 $(M - PF_6)^+$.

For L^2: δ_H (CD_3CN) 2.73 (t, 6H *J* 6 Hz), 3.42 (q, 6H, *J* 6 Hz), 5.68 (s, 15H), 5.71 (t, 6H, *J* 2 Hz), 6.02 (t, 6H, *J* 2 Hz) and 7.42 (br t, 3H, *J* 2 Hz). δ_{13C} (CD_3CN) 39.37, 54.67, 84.95, 86.92, 87.24, 95.49 and 162.77. *m/z* (FAB) 1081 $(M - PF_6)^+$.

For **7**: δ_H ($CDCl_3$) 3.8 (s, 6H), 3.9 (s, 6H), 5.1 (s, 4H), 5.5 (s, 4H) and 9.04 (br s, 2H). *m/z* (FAB) 547 $(M - BPh_4)^+$.



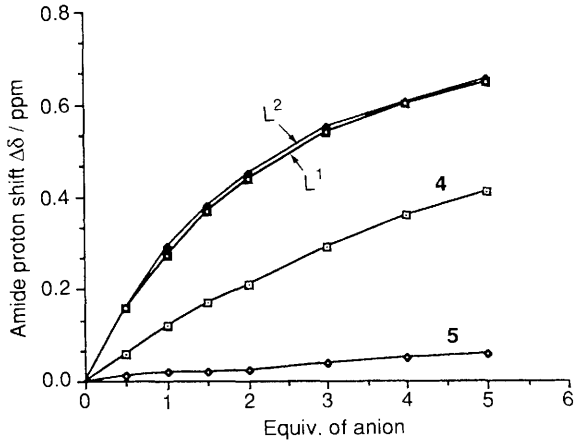


Fig. 1 Comparison of ^1H NMR titration curves of L^1, L^2, **4** and **5** with Cl^- in [$^2H_6$]DMSO solution

L^1 the titration curve indicates that a 2 : 1 solution complex is formed. Negligible shifts were observed under identical experimental conditions with cobalticinium hexafluorophosphate itself or the ester derivative **3**. However, the simple monoamide substituted cobalticinium derivative **4** did exhibit some significant solution interactions with halide anions. Fig. 1 displays a comparison of ^1H NMR titration curves of L^1, L^2, **4** and aryl amide **5** with Cl^- guest anion in [$^2H_6$]DMSO solution. These results imply that it is the unique combination of the positively charged cobalticinium moiety *and* the appending amide N–H unit, which can form a favourable hydrogen bond with a coordinated anion guest, are the essential components for successful anion complexation.

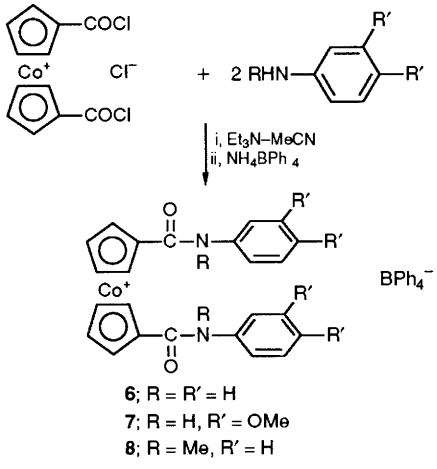
To test this hypothesis further a series of simple acyclic cobalticinium–amide containing derivatives **6–9** were prepared in very good yields, (Scheme 2) and solution ^1H NMR complexation studies with Cl^- and Br^- anions investigated. Remarkable shifts of the amide N–H and respective host protons were again observed. Fig. 2 for example, shows the titration curve of **7** 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 ^1H NMR titration experiment gave the same result, negating the possibility for a simple anion exchange process. In addition, it is also noteworthy that if the amide proton is replaced by a methyl or methylene group, as in the case of compounds **8** and **9** no solution shifts of the host are observed under analogous experimental conditions.

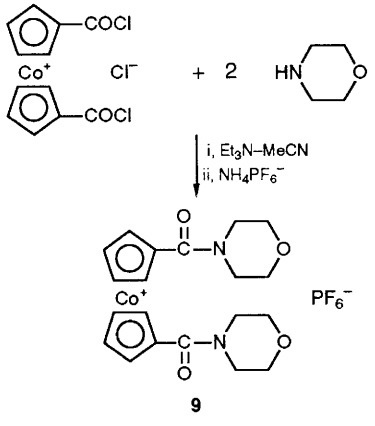
The electrochemical properties of compounds L^1, L^2 and **6–9** were investigated in acetonitrile using cyclic voltammetry

Table 1 Electrochemical data

	L^1	L^2	**3**	**4**	**6**	**7**	**8**	**9**
$E_{1/2}V^a$	−0.74[b]	−0.75[b]	−0.45	−0.74	−0.55	−0.52	−0.50	−0.60
$\Delta E(F^-)^c$/mV	55[d]	60[d]	<5	—	—	—	<5	<5
$\Delta E(Cl^-)^c$/mV	30	30	<5	30	35	30	<5	<5
$\Delta E(Br^-)^c$/mV	—	—	<5	45	60	55	<5	<5

[a] Obtained in MeCN 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] Three electron reduction process as determined by coulometric experiments. [c] Cathodic shift in reduction potential produced by the presence of anions (4 equivalents) added as their ammonium or tetrabutylammonium salts. [d] Values obtained in DMSO solution.





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Scheme 2

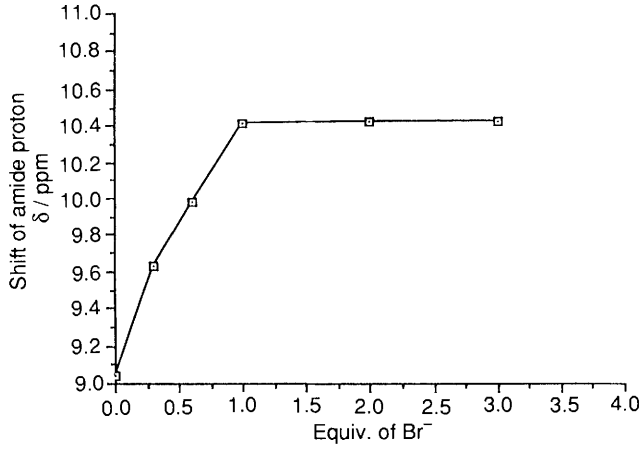

Fig. 2 ^1H NMR titration curve of **7** and Br^- in $CDCl_3$ solution

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 summarised in Table 1.

Only in the case where the cobalticinium 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.

In conclusion, these preliminary anion coordination studies have revealed that relatively simple, easily prepared, acyclic cobalticinium derivatives containing amide N–H groups can coordinate and electrochemically recognise 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.

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