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ANION RECOGNITION BY AMIDE-LINKED PYRIDYL AND PYRIDINIUM SUBSTITUTED COBALTICINIUM RECEPTORS

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Abstract—New acyclic mono- and 1,1′-bis-amide-linked pyridyl and pyridinium substituted cobalticinium ligands have been prepared. ^{1}H NMR anion coordination studies reveal that these ligands form 1 : 1 stoichiometric solution anion complexes with halides, HSO_4^- and $H_2PO_4^-$. Stability constant determinations suggest that the pyridinium cobalticinium derivatives form stronger chloride anion complexes than their pyridyl analogues. Cyclic voltammetric investigations show that all these new cobalticinium derivatives electrochemically recognize halide, HSO_4^- and $H_2PO_4^-$ guest anions.

The realization that anionic substrates play many essential roles in chemical and biochemical processes has been the stimulus for increased research activity in anion coordination chemistry.[1] During the last few years, a variety of abiotic anion receptors have been reported, including Lewis-acid-containing ligands,[2] ammonium quaternary salts,[3] protonated polyammonium macrocycles[4] and guanidinium.[5] We have recently described the first redox-responsive class of anion receptor based on the redox-active, pH-independent, positively charged cobalticinium moiety and demonstrated that the simple combination of the positively charged cobalticinium unit, together with an amide (CO—NH) group, are the ubiquitous components for anion recognition.[6] In order to gain more knowledge concerning the effects of increased positivity on anion binding properties of amide substituted cobalticinium derivatives, we report here the syntheses, coordination and electrochemical anion recognition properties of a variety of new mono- and 1,1′-bis-amide substituted pyridyl cobalticinium receptors. These ligands can be further modified to contain additional regions of positive charge by either (i) coordinating, via the pyridyl nitrogen, a Lewis acid transition metal or (ii) quaternizing the pyridyl nitrogen to produce alkyl-pyridinium derivatives and consequently enhance the strength of anion complexation in a cooperative fashion.

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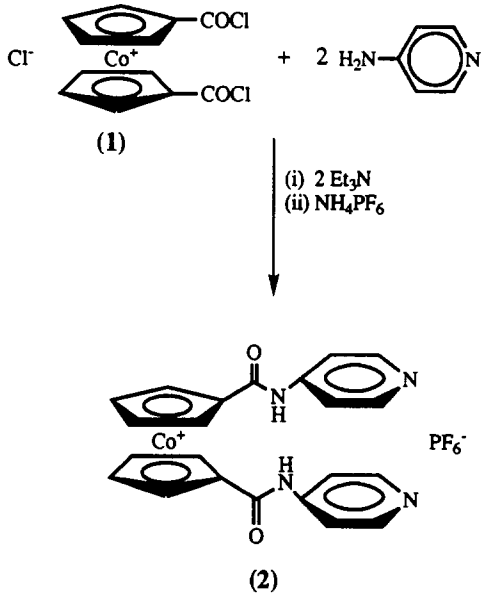
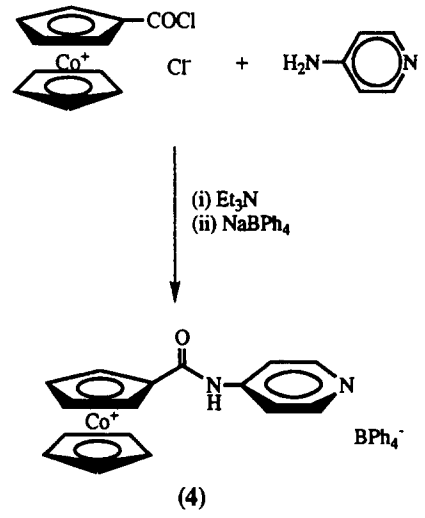
RESULTS AND DISCUSSION

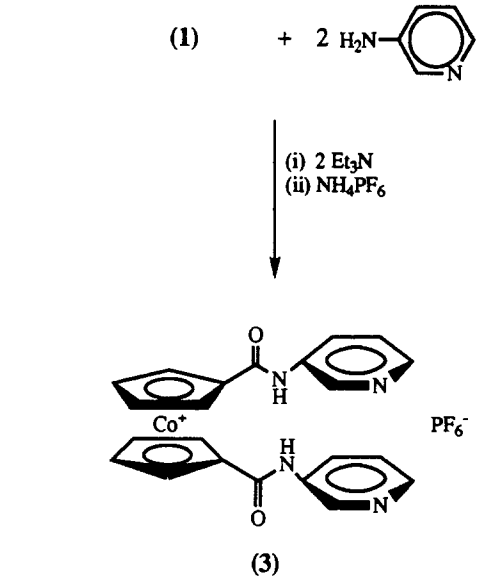
Ligand syntheses

The condensation of 1,1′-bis(chlorocarbonyl) cobalticinium chloride (**1**)[7] and two equivalents of the appropriate amino-substituted pyridine in the presence of triethylamine gave crude products which were purified via conversion to their hexafluorophosphate salts (**2** and **3**) (Scheme 1). An analogous synthetic procedure was used to prepare 1-(4-pyridylaminocarbonyl) cobalticinium tetraphenylborate (**4**) via the reaction of chlorocarbonyl cobalticinium chloride[7] and one equivalent of 4-aminopyridine and $NaBPh_4$ (Scheme 2). Refluxing ligands **2** and **4** in methyl iodide, dissolving the crude products in water and addition of excess amounts of NH_4PF_6 precipitated the respective quaternized receptors (**5** and **6**) in high yields (Scheme 3). All these new compounds gave spectroscopic and analytical data in accordance with assigned structures (see Experimental section).





Scheme 2.



Scheme 1.

Transition metal complexes of **2** *and* **4**

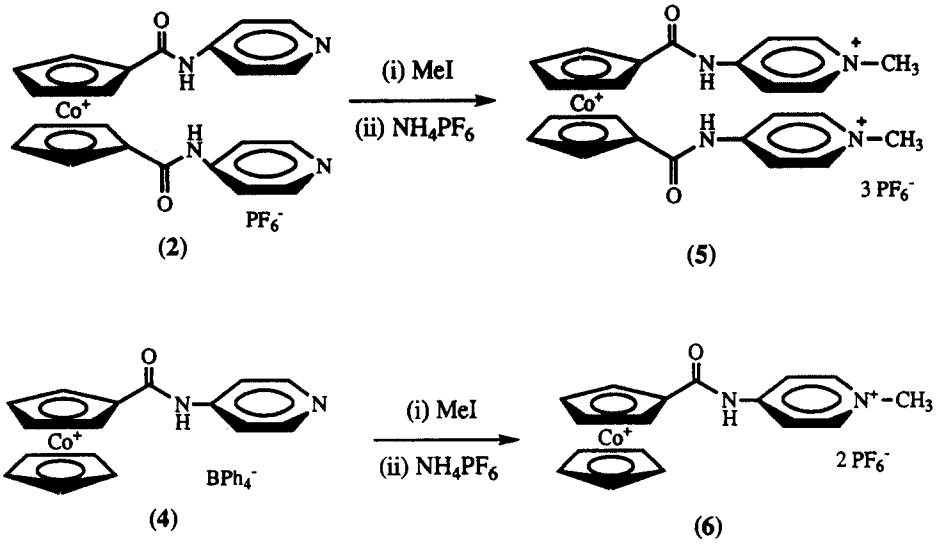
Fabbrizzi and co-workers[8] have recently demonstrated that 3-ferrocenyl pyridine was able to form complexes with platinum(II) via reaction with K_2PtCl_4. Using analogous preparative methodology, the reactions of **2** and **4** with K_2PtCl_4 in methanol–water solvent mixtures produced golden yellow powders whose elemental analyses suggested the desired products (**7** and **8**) had been isolated (Scheme 4). Unfortunately, both complexes were found to be insoluble in all common organic solvents and this thwarted further characterization and anion coordination investigations. Attempts were also made at producing ruthenium(II) complexes of **2** and **4** via reactions with $(bipy)_2RuCl_2 \cdot 2H_2O$; however, although ^1H NMR spectra implied complex formation, numerous purification procedures failed to isolate the target products.

Anion coordination studies—^1H NMR titrations

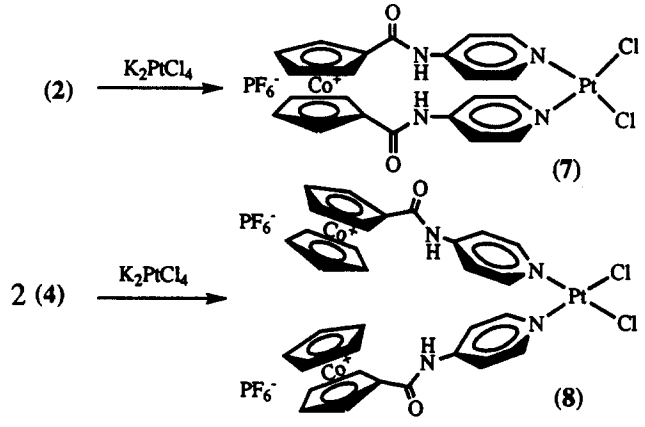
The addition of tetrabutylammonium salts ($Bu_4N^+X^-$, X = halide, HSO_4^-, $H_2PO_4^-$) to deuterated acetonitrile ^1H NMR solutions of **2–6** resulted in remarkable shifts of the respective protons of all receptors. As observed with simple aryl- and alkyl-amide substituted cobalticinium receptors,[6] substantial downfield shifts of the amide protons were noteworthy. For example, with **3** an amide proton shift of 1.4 ppm was observed on addition of one equivalent of chloride anion. The resulting titration curve (Fig. 1) suggested a 1 : 1, **3** : Cl^- solution stoichiometric complex. Unfortunately, in many cases, however, precipitation problems were encountered in the acetonitrile solvent and consequently complete titration curves could only be obtained in deuterated DMSO solutions (Fig. 2). As a consequence of the more polar solvent system, the relative magnitudes of anion guest-induced proton perturbations of the respective cobalticinium receptor were reduced; however, the titration curves suggest 1 : 1 receptor : anion stoichiometry in all cases (Fig. 2).

Stability constant determinations

The computer programme EQNMR[9] was used to calculate stability constants from the ^1H NMR titration data in DMSO and the results are sum-



Scheme 3.



Scheme 4.

marized in Table 1. Disappointingly, in the case of $H_2PO_4^-$ and HSO_4^- anions the percentage calculated error associated with each stability constant was found to be too large (i.e. $> \pm 30\%$) to give a meaningful quantitative result.

It is interesting that the addition of an extra positive charge via quaternization of this class of amide-linked pyridyl substituted cobalticinium ligand does in fact enhance the strength of anion complexation. For example, **4** binds chloride with a log K of 1.3 and its quaternized analogue **6** exhibits a log K value of 2.3 for the same anionic guest. It is also noteworthy that the magnitudes of log K values for mono- and bis-substituted cobalticinium receptors are similar [for example, **2**: log K (Cl^-) = 1.7; **3**: log K (Cl^-) = 1.3].

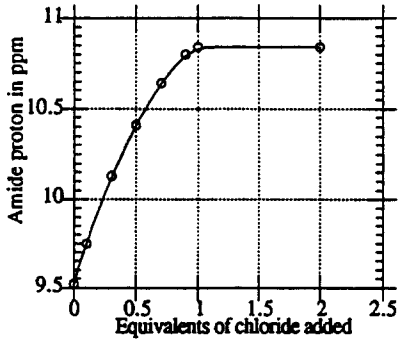


Fig. 1. ^1H NMR titration curve of **3** and Cl^- in CD_3CN.

Electrochemical anion recognition studies

The electrochemical properties of these new acyclic cobalticinium derivatives were investigated in acetonitrile using cyclic voltammetry with Bu_4NBF_4 as the supporting electrolyte. Each compound exhibited a reversible redox reduction wave in the -0.6 to -1.0 V region (vs Ag^+/Ag electrode). The quat-

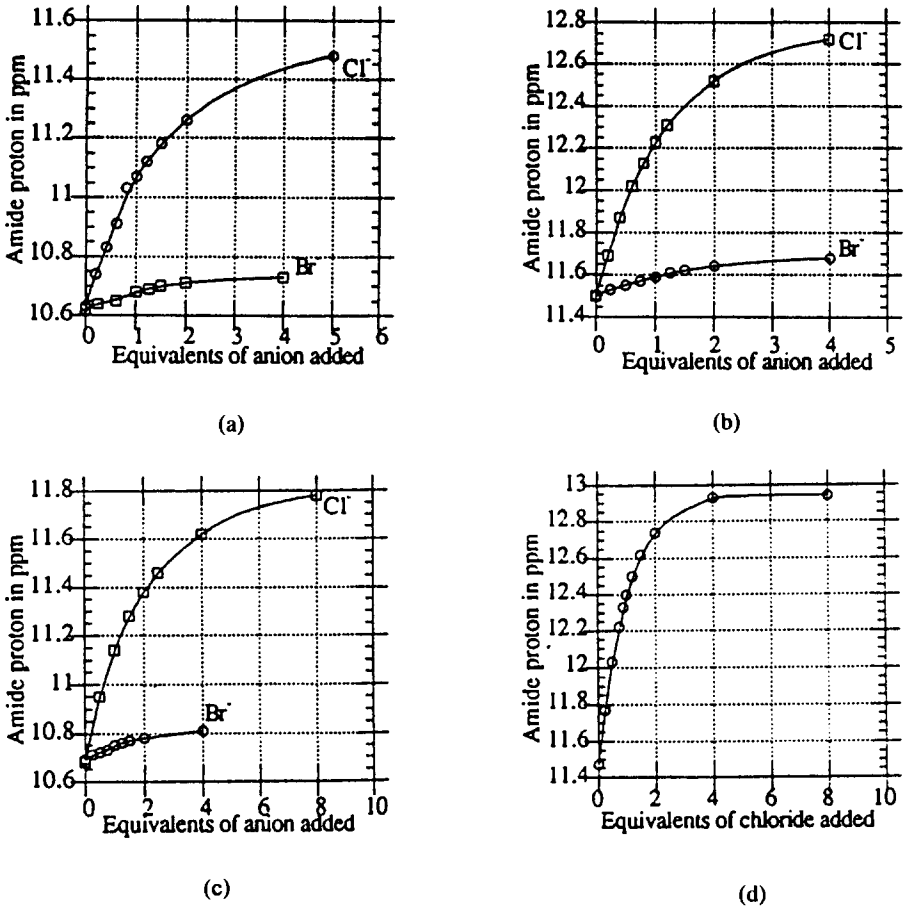


Fig. 2. ^{1}H NMR titration curves in DMSO. (a) Ligand **2** and Cl^-, Br^-; (b) **4** and Cl^-, Br^-; (c) **5** and Cl^-, Br^-; (d) **6** and Cl^-.

ernized receptors **5** and **6** display slightly more anodic redox potentials compared with their unquaternized analogues, the additional positive centres within these ligands making reduction more favourable. Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions, and the results are summarized in Table 2. In the case of Cl^-, HSO_4^- and $H_2PO_4^-$, significant one-wave cathodic shifts of up to 300 mV were produced with **3** and $H_2PO_4^-$.

Table 1. Stability constant data

Ligand	Anion	Solvent	Log K^a
2	Cl^-	DMSO	1.7
2	Br^-	DMSO	1.8
3	Cl^-	CH_3CN	4.0
4	Cl^-	DMSO	1.3
4	Br^-	DMSO	1.5
5	Cl^-	DMSO	2.1
5	Br^-	DMSO	1.8
6	Cl^-	DMSO	2.3

[a] Errors <20%.

The evolution of a new redox wave at much more cathodic potentials ($\Delta E = 400$ mV for **5** and F^-) resulted on the addition of F^- to electrochemical solutions of **5** and **6**, suggesting that the respective fluoride anion complex is kinetically inert on the timescale of the electrochemical experiment. Figure 3 shows the cyclic voltammograms of the electrochemical titration experiment between **5** and fluoride anions at a scan rate of 150 mV s^{-1}. At sub-stoichiometric equivalents of F^- anion, two redox waves are observed corresponding to the free receptor **6** and the **6**·F^- complex (Fig. 3). On addition of $\geqslant 1$ equivalent of F^-, the redox wave due to the free receptor **6** disappears and only that of the fluoride complex remains.

CONCLUSION

New acyclic mono- and 1,1′-bis-amide-linked pyridyl and pyridinium substituted cobalticinium

Table 2. Electrochemical data

Ligand	$E_{1/2}$/V[a]	Anion	$\Delta E(A^-)$/mV[b]
2	−0.76	$H_2PO_4^-$	290
3	−0.73	$H_2PO_4^-$	300
4	−0.97	$H_2PO_4^-$	185
4	—	HSO_4^-	50
4	—	F^-	200
4	—	Cl^-	50
5	−0.60	F^-	400[c]
5	—	Cl^-	30
6	−0.90	$H_2PO_4^-$	260
6	—	HSO_4^-	85
6	—	F^-	240[c]

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} Bu_4NBF_4 as supporting electrolyte. Solutions were 2×10^{-3} mol dm^{-3} in ligand and potentials were determined with reference to Ag^+/Ag electrode.

[b] Cathodic one-wave shift in reduction potential produced by presence of anions (up to 4 equiv.) added as their tetrabutylammonium salts.

[c] Evolution of new redox wave cathodically shifted.

receptors have been synthesized. ^1H NMR anion coordination studies reveal that these ligands form 1 : 1 stoichiometric solution anion complexes with halides, HSO_4^- and $H_2PO_4^-$. Stability constant determinations with Cl^- suggest the pyridinium cobalticinium derivatives form relatively stronger chloride complexes than the unquaternized analogues, a consequence of the introduction of an additional positively charged centre into the cobalticinium ligand framework. Electrochemical anion recognition investigations showed that all these amide-linked cobalticinium receptors undergo substantial cathodic perturbations of the respective cobalticinium/cobaltocene redox couples in the presence of halide, HSO_4^- and $H_2PO_4^-$ guest anions.

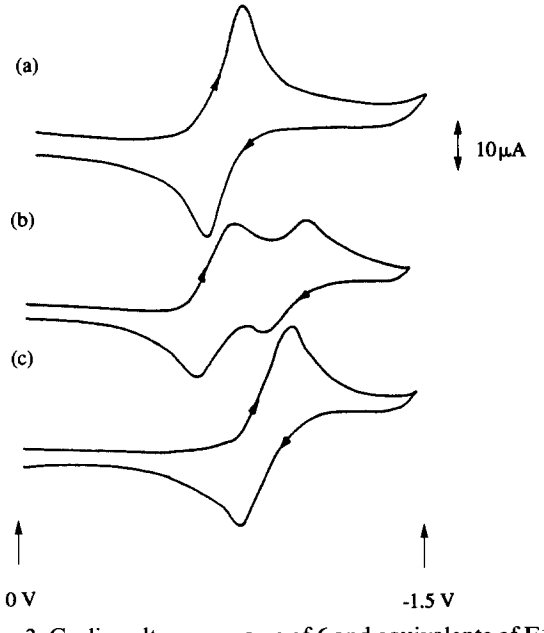


Fig. 3. Cyclic voltammograms of **6** and equivalents of F^- added in CH_3CN with Bu_4NBF_4 as electrolyte. (a) Ligand **6**; (b) **6** + 0.5 equiv. F^-; (c) **6** + ⩾1 equiv. F^-.

EXPERIMENTAL

Instrumentation

IR spectra were recorded on a Perkin–Elmer 1710 FTIR instrument (4000–400 cm^{-1}) as KBr discs. NMR 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 4 Å 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: 1,1′-bis(chlorocarbonyl)cobalticinium chloride (**1**)[7] and chlorocarbonyl cobalticinium chloride.[7]

1,1′-*Bis*(4-*pyridylaminocarbonyl*)*cobalticinium hexafluorophosphate* (**2**)

A solution of 4-aminopyridine (0.5 g, 5.2 mmol) and triethylamine (0.53 g, 5.3 mmol) was made up in dry CH_3CN (60 cm^3) and stirred under nitrogen at room temperature. To this was added a solution of 1,1′-bis(chlorocarbonyl)cobalticinium hexafluorophosphate (**1**; 1.2 g, 2.6 mmol) in CH_3CN (60 cm^3) dropwise and under nitrogen. On addition, the colour of the solution changed from colourless to green and a yellow precipitate formed. The mixture was allowed to stir for 12 h, and the yellow

solid was isolated by filtration as the crude product (1.1 g, 1.9 mmol; yield: 74%). The crude product was taken up in hot water and excess NH_4PF_6 was added. On cooling, the pure product formed as a fine bright yellow powder which was isolated by filtration and dried in quantitative yield.

^{1}H NMR (DMSO): δ 6.12 (t, J = 1.74 Hz, 4H, CpH), 6.52 (t, J = 1.68 Hz, 4H, CpH), 7.55 (d, J = 4.95 Hz, 4H, PyrH), 8.40 (d, J = 4.89 Hz, 4H, PyrH), 10.62 (s, 2H, NH). ^{13}C NMR (75.42 MHz, DMSO): δ 85.7 (CpCH); 87.1 (CpCH); 94.6 (CpC—C=O); 115.0, 149.9 (PyrCH); 145.0 (Pyr CN); 160.1 (C=O). FTIR (cm^{-1}): 3400 (NH), 1693 (C=O), 836 (PF_6^-). Found: C, 45.5; H, 3.5; N, 8.9. Calc. for $C_{22}H_{18}N_4O_2CoPF_6$: C, 46.0; H, 3.2; N, 9.8%. FABMS: m/z 429 $[M-PF_6]^+$.

1,1′-*Bis*(3-*pyridylaminocarbonyl*)*cobalticinium hexafluorophosphate* (**3**)

A solution of 3-aminopyridine (0.2 g, 2.12 mmol) was made up in dry CH_3CN (50 cm^3) and stirred under nitrogen at room temperature. To this was added a solution of 1,1′-bis(chlorocarbonyl) cobalticinium hexafluorophosphate (**1**; 0.5 g, 1.1 mmol) in CH_3CN (60 cm^3) dropwise and under nitrogen. On addition, the colour of the solution changed from colourless to green and a khaki green precipitate formed. The mixture was allowed to stir for 2 h, and the green solid was isolated by filtration, washed with CH_3CN (10 cm^3), and dried as a dark green powder (0.35 g, 0.61 mmol; yield: 55%).

^{1}H NMR (CD_3CN): δ 5.98 (t, J = 2.0 Hz, 4H, CpH), 6.34 (t, J = 2.3 Hz, 4H, CpH), 7.68 (t, J = 5.4 Hz, 2H, PyrH), 8.35 (d, J = 6.3 Hz, 2H, PyrH), 8.42 (d, J = 6.3 Hz, 2H, PyrH), 9.06 (s, 2H, PyrH), 9.52 (s, 2H, NH). ^{13}C NMR (75.42 MHz, DMSO): δ 85.7 (CpCH); 87.4 (CpCH), 93.6 (Cp C—C=O); 125.7, 132.1, 136.3, 136.6 (PyrCH); 140.8 (PyrCN); 160 (C=O). FTIR (cm^{-1}): 3400 (NH), 1671 (C=O), 843 (PF_6^-). FABMS: m/z 429 $[M-PF_6]^+$.

1-(4-*Pyridylaminocarbonyl*)*cobalticinium tetraphenylborate* (**4**)

A solution of 4-aminopyridine (0.216 g, 2.3 mmol) and triethylamine (0.23 g, 2.3 mmol) was made up in dry CH_3CN (50 cm^3) and stirred under nitrogen at room temperature. To this was added a solution of (chlorocarbonyl)cobalticinium hexafluorophosphate (0.89 g, 2.25 mmol) in CH_3CN (60 cm^3) dropwise and under nitrogen. On addition, the colour of the solution changed from colourless to golden brown and a fine brown precipitate formed. The mixture was allowed to stir for 12 h, the brown solid was removed by filtration and the golden yellow filtrate was evaporated to yield the crude product as a golden semi-solid. The crude product was purified by column chromatography using Sephadex LH20 and CH_3CN–methanol (4 : 1) as eluting solvent. Three fractions were collected: brown, golden yellow and bright yellow. The two yellow fractions from the column were further purified by dissolving the fractions in hot water and adding a saturated solution of $NaBPh_4$. On cooling, the product precipitated as a bright yellow crystalline powder (0.69 g, 1.5 mmol; yield: 66%).

^{1}H NMR (DMSO): δ 5.91 (s, 5H, CpH), 5.99 (t, J = 1.83 Hz, 2H, CpH), 6.43 (t, J = 1.83 Hz, 2H, CpH), 6.79 (t, J = 6.84 Hz, 4H, BPh_4^-), 6.92 (t, J = 6.84 Hz, 8H, BPh_4^-), 7.17 (s, 8H, BPh_4^-), 7.73 (d, J = 4.89 Hz, 2H, PyrH), 8.55 (d, J = 4.86 Hz, 2H, PyrH), 10.68 (s, 1H, NH). FABMS: m/z 309 $[M-PF_6]^+$. Found: C, 76.3; H, 5.3; N, 4.2. Calc. for $C_{40}H_{34}N_2OCoB$: C, 76.5; H, 5.5; N, 4.5%.

1,1′-*Bis*(4-N-*methylpyridylaminocarbonyl*) *cobalticinium trishexafluorophosphate* (**5**)

1,1′ - Bis(4 - pyridylaminocarbonyl)cobalticinium hexafluorophosphate (**2**; 0.14 g, 0.24 mmol) was taken up in iodomethane (10 cm^3) and allowed to reflux under nitrogen for 24 h, during which time the colour of the suspension changed from yellow to orange. The solvent was removed and a fine orange precipitate was isolated. This solid was dissolved in hot water and a saturated solution of NH_4PF_6 was added to precipitate the product as a fine yellow powder (0.148 g, 0.17 mmol; yield: 69%).

^{1}H NMR (DMSO): δ 4.24 (s, 6H, CH_3), 6.19 (t, J = 1.83 Hz, 4H, CpH), 6.57 (t, J = 1.41 Hz, 4H, CpH), 8.06 (d, J = 5.82 Hz, 4H, PyrH), 8.74 (d, J = 6.3 Hz, 4H, PyrH), 11.5 (s, 2H, NH). ^{13}C NMR (75.42 MHz, CD_3CN): δ 48.1 (CH_3); 87.3 (CpCH); 89.2 (CpCH); 89.2 (CpCH); 94.5 (CpC—C=O), 117.1, 147.0 (PyrCH); 151.8 (PyrCN); 162.5 (C=O). FTIR (cm^{-1}): 3391 (NH), 1603 (C=O), 830 (PF_6^-). Found: C, 31.3; H, 2.7; N, 6.2. Calc. for $C_{24}H_{24}N_4O_2CoP_3F_{18}$: C, 32.2; H, 2.7; N, 6.3%. FABMS: m/z 459 $[M-3PF_6]^{3+}$, 604 $[M-2PF_6]^{2+}$, 749 $[M-PF_6]^+$.

1-(4-N-*Methylpyridylaminocarbonyl*)*cobalticinium bishexafluorophosphate* (**6**)

1-(4-Pyridylaminocarbonyl)cobalticinium hexafluorophosphate (**4**; 0.05 g, 0.11 mmol) was taken up in iodomethane (10 cm^3) and allowed to reflux under nitrogen for 24 h, during which time

the colour of the suspension changed from yellow to yellow–orange. The solvent was removed and a fine yellow precipitate was isolated. This solid was dissolved in hot water and a standard solution of NH_4PF_6 was added to precipitate the product as a fine yellow powder in both cases (0.0385 g, 6.27×10^{-5} mol; yield: 57%).

^{1}H NMR (DMSO): δ 4.24 (s, 3H, CH_3), 5.96 (s, 5H, CpH), 6.07 (t, $J = 1.7$ Hz, 2H, CpH), 6.46 (t, $J = 1.6$ Hz, 2H, CpH), 8.20 (d, $J = 6.3$ Hz, 2H, PyrH), 8.76 (d, $J = 6.5$ Hz, 2H, PyrH), 11.45 (s, 1H, NH). ^{13}C NMR (75.42 MHz, CD_3CN): δ 47.9 ($\underline{C}H_3$); 85.7, 87.7, 87.8 (Cp$\underline{C}$H); 93.0 (Cp$\underline{C}$—C=O); 116.7, 117.2 (Pyr$\underline{C}$H); 143.2 (Pyr$\underline{C}$N); 146.8 (C=O). FTIR (cm^{-1}): 3350 (NH), 1703 (C=O), 837 (PF_6^-). Found: C, 32.1; H, 2.8; N, 4.6. Calc. for $C_{17}H_{17}N_2OCoP_2F_{12}$: C, 33.2; H, 2.8; N, 4.6%. FABMS: m/z 324 $[M-PF_6]^+$.

1,1′-*Bis*(4-*pyridylaminocarbonyl*)*cobalticinium dichloroplatinate hexafluorophosphate* (7)

This preparation was based on the procedure used by Fabbrizzi and co-workers.[8] A solution of 1,1′ - bis(4 - pyridylaminocarbonyl)cobalticinium hexafluorophosphate (**2**; 0.052 g, 9×10^{-5} mol) in methanol (30 cm^3) was stirred at room temperature. To this was added a solution of K_2PtCl_4 (0.036 g, 8.7×10^{-5} mol) in methanol–water (1:2; 5 cm^3) and the mixture was allowed to stir for 1 week. The product was isolated by filtration as a golden yellow powder (0.053 g, 6.3×10^{-5} mol; yield: 72%).

FTIR (cm^{-1}): 3300 (NH), 1638 (C=O), 831 (PF_6^-). Found: C, 32.1; H, 2.5; N, 6.7%. Calc for $C_{22}H_{18}N_4O_2Cl_2PtCoPF_6$: C, 31.4; H, 2.2; N, 6.7%.

Bis(1-4-*pyridylaminocarbonyl*)*cobalticinium dichloroplatinate bishexafluorophosphate* (8)

This preparation was based on the procedure used by Fabbrizzi and co-workers.[8] A solution of 1-(4-pyridylaminocarbonyl)cobalticinium hexafluorophosphate (**4**; 0.036 g, 7.9×10^{-5} mol) in hot methanol (30 cm^3) was stirred. To this was added a solution of K_2PtCl_4 (0.016 g, 3.85×10^{-5} mol) in methanol–water (2:1; 10 cm^3), the colour of the mixture changed from pale yellow to orange yellow and was allowed to stir for 1 week. The product was isolated by filtration as a yellow powder (0.026 g, 2.2×10^{-5} mol; yield: 57%).

FTIR (cm^{-1}): 3216 (NH), 1697 (C=O), 870 (PF_6^-). Found: C, 31.4; H, 2.4; N, 4.6. Calc. for $C_{32}H_{28}N_4O_2Cl_2PtCo_2P_2F_{12}$: C, 32.7; H, 2.4; N, 4.8%.

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