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The synthesis and complexation of a cobaltocenium-based redox-active cryptand containing the phenanthroline unit

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Abstract

The synthesis and characterization of a cobaltocenium-based redox-active cryptand **3** containing a phenanthroline unit is described. Complex formation (with Ca^{2+}) was studied by $^{1}H/^{13}C$-NMR, and the effects of complexation on the redox properties of **3** were monitored by cyclic voltammetry. The fluorescence spectra of the complexes of **3** and its ferrocene analogue (**4**) with Eu^{3+} are also reported, and the low intensity of the fluorescence in each case attributed to carbonyl coordination of Eu^{3+} rather than metallocene quenching. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cobaltocenium; Redox-active cryptand; Phenanthroline unit

1. Introduction

The synthesis, structure, electrochemistry and complex formation of cryptands containing metallocene units have attracted considerable attention in recent years [1–3]. These redox-active compounds are potentially useful as sensors for the detection and quantitative estimation of metal cations by electrochemical techniques [4] as catalysts in a variety of reactions [5] and possibly as voltage-regulated optical switches [6,7]. With respect to the latter application, all the compounds synthesized so far have contained ferrocene, a potential fluorescence quencher, as the electroactive unit. This paper describes the synthesis, complexation, electrochemical and photochemical properties of an analogous system containing the cobaltocenium unit. Compound **3** was prepared in 26% isolated yield by the condensation of the tetraazamacrocycle (**1**) with cobaltocenium diacid chloride (**2**); a route based on the synthesis of the analogous ferrocene cryptand **4** [6].

2. Results and discussion

2.1. NMR data

2.1.1. Cryptand 3

n.b. The numbering is not systematic but has been chosen to coincide with that used in Ref. [6] in the interpretation of NMR data.

It is clear from the complexity of the ^{1}H- and ^{13}C-NMR spectra that the molecule is unsymmetrical which means that in common with all compounds of this type examined so far [6,8–11] the carbonyl groups are *trans* to each other when observed on the NMR time scale. In particular, the ^{13}C spectrum consists of 32 separate signals comprised of four NCH_2 carbons, four OCH_2 carbons, eight cobaltocenium CH carbons, two cobaltocenium (*ipso*) carbons, six phenanthroline CH carbons, six (*ipso*) phenanthroline carbons and two carbonyl carbons. Likewise, the ^{1}H-NMR reflects the unsymmetrical structure by, for example, showing eight cobaltocenium proton multiplets, two widely-spread AB quartets for 7_{AB} and 20_{AB}, six phenanthroline protons (as two sets of double doublets and an AB quartet) and complex patterns for the NCH_2 and OCH_2 protons of the aliphatic chain. The application of COSY 45, the DEPT technique and $^{1}H/^{13}C$ heteronuclear correlation

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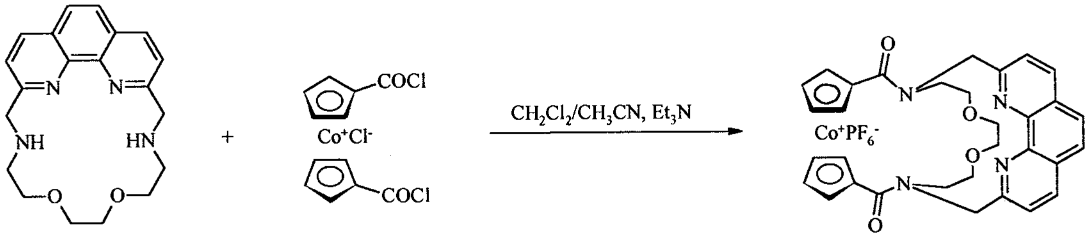

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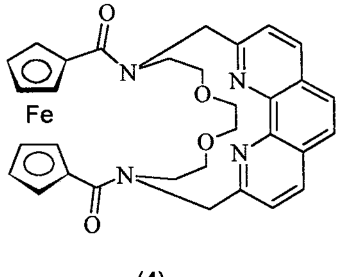

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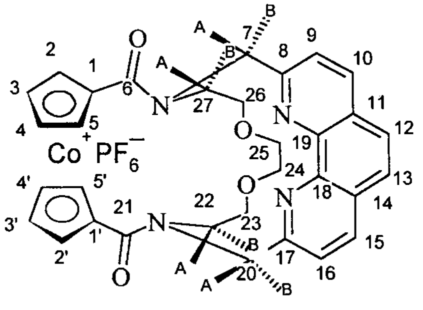

(3)

spectroscopy, enabled an almost unambiguous assignment of all the NMR data to be achieved (Table 1). The keys to the assignment are as follows. In the ^{1}H-NMR spectrum one cobaltocenium proton is at unusually low field (7.85 ppm) and this is assumed to be H-2 *cis* to the phenanthroline group and *cis* to C-6 thus placing the proton in the anisotropic deshielding cone of the carbonyl function. With this much assumed, the COSY-45 and ^{1}H/^{13}C correlation spectra enable the assignment of all the protons and carbons around the cyclopentadiene rings. Secondly, if it is assumed, as suggested by models, that H_{7B} and H_{22B} lie in the deshielding zones of the C-6 carbonyl and a cyclopentadiene unit, respectively, then the two AB quartets can be assigned completely. Finally, by assuming that the carbon atoms *trans* to the carbonyl groups are at the lowest fields in the ^{13}C spectrum [12], C-7, C-20 and C-22–C-27 can also be assigned. Thus the only slight ambiguity lies in the assignment of protons 9–16 and 23–26 and in the case of the ^{13}C data, the assignment of 8–19. One is tempted to assume that carbon atoms, 8–12 and 19 are at lower field than their respective counterparts (13–18) and that likewise protons 9, 10 and 12 are at a lower field than H-13, 15 and 16. Although the assumption is a reasonable one, it should be treated with caution since it may represent an over-interpretation of the data.

2.1.2. *Complex of **3** with Ca^{2+}*

^{1}H and ^{13}C solution NMR was used to study complex formation of **3** with a number of cations. For example, the addition of one equivalent of Ca^{2+} to a solution of **3** caused a dramatic change in both the ^{1}H and ^{13}C spectra of the host molecule. Thus the phenanthroline protons were shifted slightly downfield and were seen as two unequally populated sets of two doublets and a singlet. The integrated ratio of each set was ca. 3:2 with the higher field set predominating. This is reminiscent of the ferrocene analogue [6] and is due to the formation of a mixture of 2:1 and 1:1 host: Ca^{2+} complexes with the former predominating in a molar ratio of 64:36. The low field cyclopentadiene proton of

Table 1
^{1}H- and ^{13}C-NMR data on cryptand **3**

^{1}H		^{13}C	
Assignment	δ (ppm)	Assignment	δ (ppm)
10/15	8.40 (d/d)	10/15	138.6; 137.9
12/13	7.94 (ABq)	12/13	128.1; 127.2
9/16	7.65 (d/d)	9/16	122.6, 124.1
		8,17,18,19	158.5,157.7,147.0, 146.5
		11/14	129.8, 129.4
		6/21	165.1: 164.0
		1/1′	105.4; 97.4
2	7.86	2	88.9
3	5.55	3	87.6
4	5.85	4	87.3
5	6.00	5	86.0
2′	6.45	2′	89.8
3′	5.90	3′	88.9
4′	5.90	4′	87.7
5′	6.12	5′	88.1
7A	4.44	7	55.0
7B	5.96		
20A	4.43	20	56.0
20B	5.13		
22A	2.89 (m)	22	48.1
22B	4.77		
27A	3.40	27	53.5
27B	4.23		
23AB	2.44 (A) 3.22 (B)	23	69.2
24AB	2.92 (A) 3.33 (B)	24	71.2
25AB	2.79 (A) 3.33 (B)	25	71.8
26AB	3.62 (A) 3.68 (B)	26	71.0

the host at 7.85 ppm was now found in the conventional cyclopentadiene region (5.8–6.6 ppm) where two sets of four cobaltocenium CH signals were observed again in the integrated ratio of ca. 3:2. The two AB quartets associated with the CH_2 groups at C-7 and C-20 were also observed in more conventional positions (4.9/3.35 for the 2:1 complex and 4.5/3.55 for 1:1 stoichiometry) again in the same ratio of 3:2. The remainder of the proton spectrum was inevitably rather complex, but, in general, confirmed the analysis. Addition of a second equivalent of Ca^{2+} ion merely changed the ratio of 2:1 vs. 1:1 complexes so that the latter predominated in a ratio of 3:2 (i.e. 60% 1:1 complex) (Table 2a). The assignments are based on the reasonable assumption that the lower field sets of protons are due to the 1:1 complex where the charge density of the cation would be more pronounced. The ^{13}C spectra of the Ca^{2+} complexes serve to confirm these conclusions. At a molar ratio of 1:1, two unequally populated sets of ^{13}C signals were observed. Each set consisted of 16 signals comprised of two NCH_2 carbons, two OCH_2 carbons, four cobaltocenium CH carbons, one *ipso*-cobaltocenium carbon, three phenanthroline CH carbons, three-*ipso*-phenanthroline carbons and one carbonyl carbon (Table 2b). The data are consistent with the existence of a plane of symmetry within both complexes which, in common with previous studies, implies that the carbonyl groups within the host molecules are now *cis* to each other and *involved in the coordinative bonding* with the Ca^{2+} ion. This is emphasized by the observation that the carbonyl carbon signals of the complexes are observed at 167.7 and 169 ppm, whereas the carbonyl groups of the host appear at 164 and 165 ppm.

2.2. Cyclic voltammetry (CV)

Cyclic voltammetry of the ligand alone and in the presence of Ca^{2+} was carried out in acetonitrile with TBAP as the supporting electrolyte (Fig. 1). Clearly, complexation with Ca^{2+} causes an anodic shift of 170 mV, but equally there was always a discernible amount of free ligand available even at a four equivalent excess of $[Ca^{2+}]$ over [ligand]. This is emphasized by the deconvolution plots (dI_1/dt and dI_1/dE vs. E) (Fig. 2a and b), which also show that the CV waves are only quasi-reversible since the oxidation and reduction peaks do not coincide but are dispersed approximately 10 mV either side of the $E_{1/2}$ value (at -690 mV). All three CV traces show that in the case of the complexed systems, the oxidation wave of the free ligand in the mixture is at a much lower intensity than the reduction wave which implies that in the reduced form of the electroactive center (Co^{2+}) the ligand binds Ca^{2+} strongly, but on oxidation the Ca^{2+} is, to some extent, released prior to reduction. This conclusion is corroborated by the observation that the intensity of the reduction wave of the complex is less than that of the oxidation wave. The CV as a whole is reminiscent of that observed with the ferrocene analogue (**4**) and Mg^{2+} [6], although the comparison is somewhat tenuous, since the latter was necessarily acquired with propylene carbonate as solvent. With Ca^{2+} and **4**, only an “averaged” wave was observed (with a maximum shift of ca. 150 mV), which implies a weaker complex than that observed with **3**. Again the comparison has to be viewed with caution in view of the different solvent systems.

2.3. Fluorescence spectra

Ultraviolet irradiation of complexes of **4** with Eu^{3+} (Fig. 3b), Tb^{3+}or Yb^{3+} produced only weak fluorescence in the expected visible region of the spectrum. The low level of fluorescence was ascribed either to

Table 2
Data on the 1:1 and 2:1 (host:guest) complexes formed by **3** and calcium triflate

2:1 (Host:Ca^{2+})		1:1 (Host:Ca^{2+})	
δ	Assignment	δ	Assignment [a]
(a) ^{1}H-NMR			
8.40 ($J=8.2$)	H 10/15	8.67 ($J=8.2$)	H 10/15
7.86 (s)	H 12/13	8.12 (s)	H 12/13
7.62 ($J=8.2$)	H 9/16	7.99 ($J=8.2$)	H 9/16
6.45 (m)	cp	6.61 (m)	cp
6.30 (m)	cp	6.45 (m)	cp
5.93 (m)	cp	5.98 (m)	cp
5.87 (m)	cp	5.93 (m)	cp
4.91/3.99	AB q (7/20)	5.87/4.503	AB q (7/20)
4.00–1.35 (multiplets)	OCH_2 /NCH_2 chain	3.99, 3.541 (m)	NCH_2
		3.25, 2.454 (m)	OCH_2 (23/26)
		2.801, 1.53 (m)	OCH_2 (24/25)
(b) ^{13}C-NMR			
52.7, 55.7	$2\times NCH_2$	55.7, 53.3	C7/20; C22,27
67.4, 69.7	$2\times OCH_2$	69.8, 67.3	C24/25; C23,26
86.3, 86.7, 87.7, 90.8,	$4\times$CoCH	91.1, 89.0, 86.8, 86.2	$4\times$CoCH (5,2,4,3)
99.4	1/1′	99.8	1/1′
125.6, 127.9, 140.9	phen CH	141.2, 128.1, 125.9	10/15; 12/13; 9/16
129.1, 145.2, 160.8	phen C	160.2, 144.9, 130.0	8,17,18,19; 11,14
167.7	C=O	168.6	C = O

[a] In the order shown against each chemical shift.

quenching by the ferrocene unit *or* to coordination of the cations by the carbonyl oxygens, thus distancing the fluorescent ion from the phenanthroline unit and hence inhibiting energy transfer. A similar set of results was obtained using the cobaltocenium cryptand **3** and hence the reported spectra (Fig. 3a, b and Table 3) are restricted to the results with Eu^{3+}. The cobaltocenium ligand (**3**) was designed to distinguish between quenching by the metallocene unit and distancing by carbonyl coordination and since the cobaltocenium unit, an 18-electron system, would not be expected to quench fluorescence, it is likely that the latter explanation is

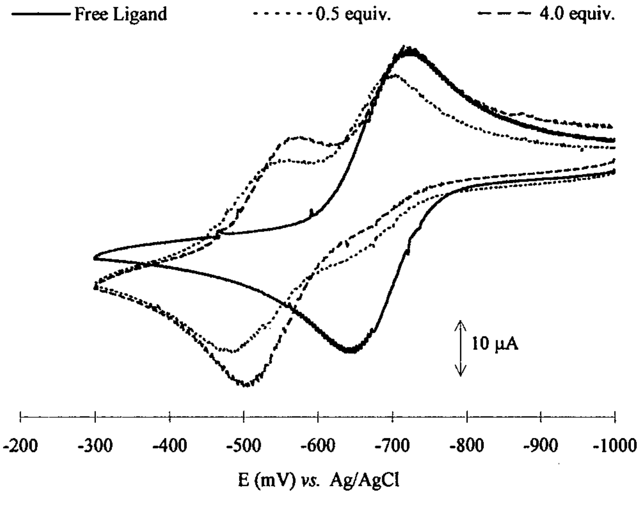

Fig. 1. Cyclic voltammetry traces on **3** and its complexation with Ca^{2+}.

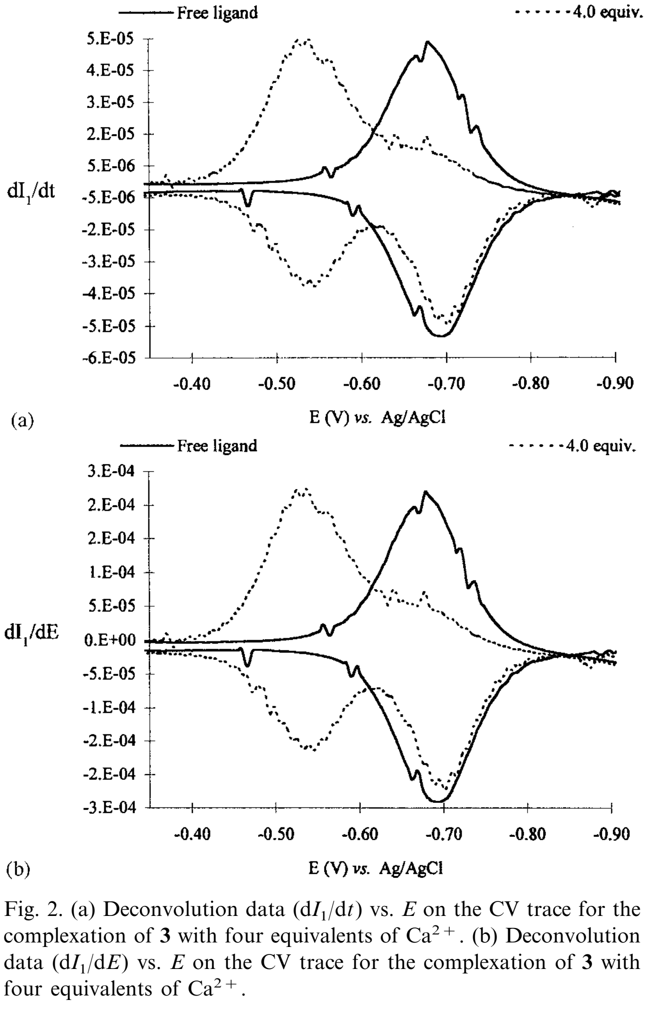

Fig. 2. (a) Deconvolution data (dI_1/dt) vs. E on the CV trace for the complexation of **3** with four equivalents of Ca^{2+}. (b) Deconvolution data (dI_1/dE) vs. E on the CV trace for the complexation of **3** with four equivalents of Ca^{2+}.

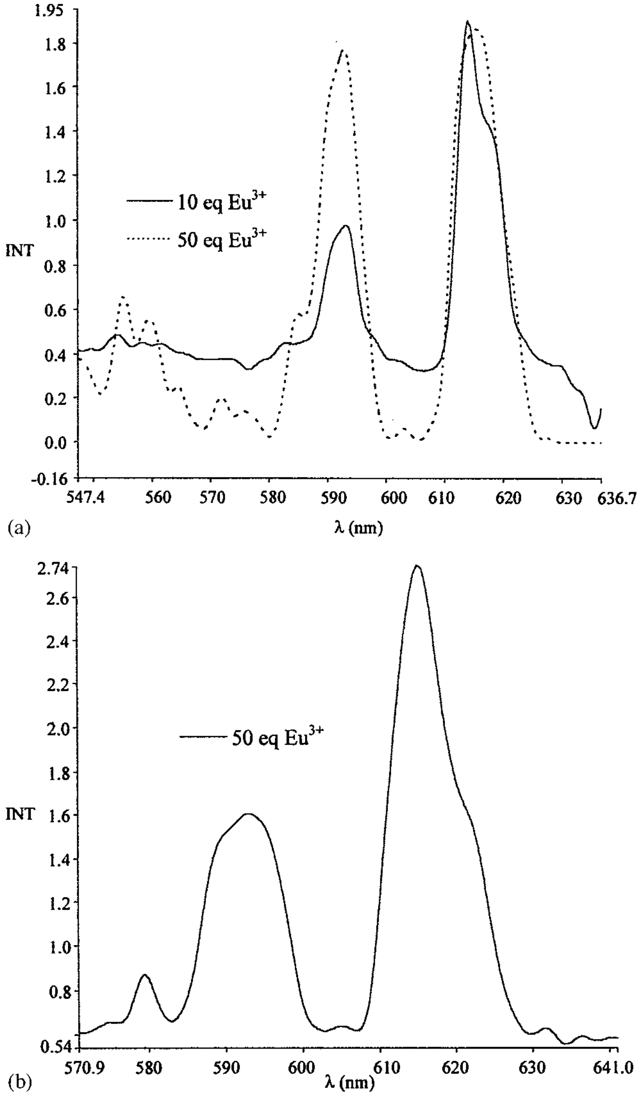

Fig. 3. (a) Luminescence spectra for the complexes of **3** with Eu^{3+} at 10 equivalents excess and 50 equivalents excess of Eu^{3+}. (b) Luminescence spectra for the complexes of **4** with Eu^{3+} at 50 equivalents excess of Eu^{3+}.

correct a conclusion which is reinforced by the ^{13}C-NMR data on the complexes.

3. Experimental

^{1}H-NMR spectra were recorded on a Bruker AM-360 spectrometer or on a Bruker AMX-400 spectrometer operating at 360.13 (or 400.14) MHz for ^{1}H and 90.6 (or 100.6) MHz for ^{13}C-NMR. Chemical shifts (δ) are given in parts per million (ppm) downfield from Me_4Si as internal standard. ^{13}C-DEPT (distortionless enhancement of polarization transfer) spectra were recorded using the 135° pulse sequence, giving positive signals for CH_3 and CH, negative signals for CH_2 and no signal for quaternary (*ipso*) carbon atoms. High resolution fast-atom-bombardment mass spectrometry (HRMS-FAB) was performed at the ULIRS Mass Spectrometry Facility, School of Pharmacy on a VG ZAB-SE instrument using VG Opus software (resolution 8–10 K). Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer using NaCl plates (neat) or KBr discs (KBr). Elemental analyses were determined by the microanalytical service at University College London. Thin layer chromatographic (TLC) analyses were performed on aluminum oxide 60 F_{254} neutral on aluminum sheets with a 0.2 mm layer thickness (Merck), using 5% $MeOH–CH_2Cl_2$ as eluent. Preparative chromatography columns were packed with alumina [neutral, type 507C, Fluka, (0.05–0.15 mm; pH 7.0 ± 0.5)], or silica gel 60 (F_{254}, 0.035–0.070 mm, Merck). Solvents were dried and purified prior to use and stored under nitrogen over class 4 Å molecular sieves (4–8 mesh). CH_2Cl_2, MeCN and Et_3N were all distilled under nitrogen from calcium hydride. MeCN for electrochemistry was dried prior to use as indicated above and tetrabutylammonium perchlorate (TBAP) was purchased from Fluka and used without further purification.

Cyclic voltammograms were recorded using an EG&G Princeton Applied Research Versastat™ potentiostat and the current-potential traces analyzed using EG&G 270/250 Research Electrochemistry Software. The data were recorded using either a platinum or a glassy carbon (diameter, 0.3 cm) working electrode, a platinum counter electrode and a Ag/AgCl reference electrode (at 0.222 V). The working electrodes were polished with alumina at frequent intervals. An MeCN solution (containing 0.2 M TBAP as supporting electrolyte) of the ligand (at ca. 2 mmol) was placed in the unsealed one-compartment cell and degassed by bubbling with Ar prior to each recording. An Ar atmosphere was maintained above the solution while the experiments were in progress. Addition of calculated quantities of calcium triflate solution was accompanied by stirring, but recordings were made on the unstirred solutions.

Table 3
Fluorescence data on the complexes formed between Eu^{3+} and cryptands **3** and **4**; $\lambda_{exc} = 338$ nm

Eu^{3+}	Co^{+} (cryptand, **3**) 1.2 mM, $\lambda_{ex} = 338$ nm	Eu^{3+}	Fe (cryptand, **4**) 1.5 mM, $\lambda_{ex} = 338$ nm
10 eq	593 (0.98), 614 (1.91)	–	–
50 eq	555 (0.66), 560 (0.56), 593 (1.77), 616 (1.86)	50 eq	579.5 (0.87), 593 (1.61), 615 (2.75)

Fluorescence spectra were measured with a Perkin–Elmer Luminescence Spectrometer LS50B and analyzed with FL WinLab Version 2.01 Software using either the default scan or time drive methods. The excitation and emission slits were 10 and 2.5 nm, respectively. Fluorescence spectra (excited at 338 nm) of the ligands (1.2–1.5 mM) and complexes with Eu^{3+} were measured in MeCN at room temperature.

3.1. Preparation of calcium trifluoromethanesulfonate

Trifluoromethanesulfonic acid (0.89 g, 5.92 mmol) dissolved in dry MeCN (1 ml) was added to a suspension of $CaCO_3$ (0.3 g, 2.96 mmol) in dry MeCN (4 ml) with stirring. After 15 min, insoluble starting material was filtered off and the filtrate was evaporated to dryness. The product was dried under vacuum (130 °C, $6.0–7.0 \times 10^{-2}$ mbar) for 2 h to give a white crystalline solid (0.71 g, 64%).

*3.2. Preparation of cryptand **3***

A creased, round-bottomed, three-necked flask was charged under N_2 with a mixture of dry CH_2Cl_2 (250 ml), dry CH_3CN (250 ml), and Et_3N (0.40 ml, 2.84 mmol). The diazamacrocycle [13] (0.10 g, 0.28 mmol) was dissolved in CH_2Cl_2 (250 ml) and cobaltocenium chloride diacid chloride [11] (0.10 g, 0.30 mmol) was dissolved in CH_3CN (250 ml). The two solutions were added to the stirred contents of the flask simultaneously over 6 h using electrically powered syringes and the mixture was left stirring for 15 h. The suspension was filtered and the filtrate concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (50 ml), washed with 0.1 M aqueous NaOH and 10% aqueous $NH_4^+PF_6^-$, before drying over $MgSO_4$. The solvent was removed under reduced pressure and the yellow residue was purified by flash chromatography on silica (CH_2Cl_2:CH_3OH) to give a yellow oil that was dissolved in a minimum of CH_3CN. Upon dropwise addition to ether (20 ml), a yellow solid precipitated (53.0 mg, 26%). HRMS-FAB for $C_{32}H_{30}O_4N_4Co$, M_{calcd} 593.1621, M_{obs} 593.1549. Anal. Found: C, 52.27; H, 4.11; N, 7.54. Calc.: C, 52.05; H, 4.09; N, 7.59%.

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