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Reaction of (Chlorocarbonyl)metallocenes of Iron and Cobalt with 1,4-Diaminobutane: Synthesis of a Heterobimetallic Ferrocene−Cobaltocenium Complex

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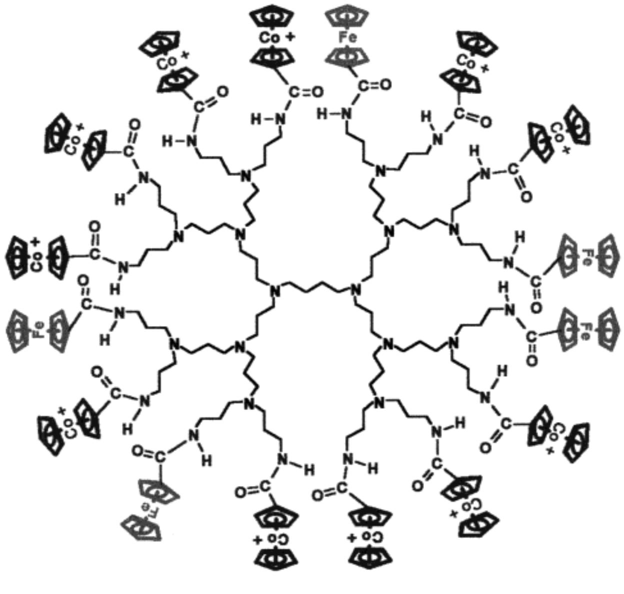
Summary: The reactivity differences of the neutral and cationic metallocenes (chlorocarbonyl)ferrocene and the salt of (chlorocarbonyl)cobaltocenium, when reacted with 1,4-diaminobutane, is presented. This reaction afforded the heterobimetallic complex $[\{\eta^5\text{-}C_5H_5\}Co\{\eta^5\text{-}C_5H_4\}(CO)NH(CH_2)_4NH(CO)\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\}][PF_6]$ ***(4)*** *as the major product, as well as the homobimetallic* $[\{\eta^5\text{-}C_5H_5\}Co\{\eta^5\text{-}C_5H_4\}(CO)NH(CH_2)_2]_2[PF_6]_2$ ***(5)*** *and only traces of* $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4\}(CO)NH(CH_2)_2]_2$ ***(6)***, *and constitutes a useful model approach for the synthesis of heteromultimetallic dendrimers. These compounds have been characterized by* ^1H *and* ^{13}C *NMR, IR spectroscopy, and fast atom bombardment mass spectrometry (FAB-MS) and elemental analyses. The molecular structure of compound* ***4*** *was ascertained by X-ray crystallography. The electrochemical behavior of* ***4*** *and* ***5*** *has been studied by cyclic voltammetry.*

Introduction

It is well-known that one of the most valuable synthetic approaches to organometallic polymers is based on condensation reactions.[1] Research in this area was catalyzed by the observation that many organometallic halides possess a high degree of covalent character within their composite structure and that they can behave like an organic chloride in many reactions such as hydrolysis, amidation, and esterification.[2] In particular, the highly efficient reactions of mono- and difunctional (chlorocarbonyl)ferrocene and (chlorocarbonyl)cobaltocenium derivatives with molecules containing reactive NH_2 or OH groups are attracting renewed attention in the last few years, as they have provided access to interesting examples of redox-active macromolecules such as ferrocenyl and cobaltocenium polymers,[3] dendritic poly(metallocenes),[4,5] and neutral and cationic anion-receptor multimetallic systems[5a,6] as well as ferrocene-containing liquid-crystalline materials.[7]

In a recent preliminary communication we have reported novel peripherally heterogeneous dendrimers containing ferrocene and cobaltocenium units located simultaneously at the surface of the dendritic structure, which have been prepared via condensation reactions.[8] In these syntheses we were most intrigued by the fact that the reaction of equimolar amounts of (chlorocarbonyl)ferrocene and the salt of (chlorocarbonyl)cobaltocenium, with diaminobutane-based dendritic molecules containing a controlled number of terminal NH_2 groups, did not lead to an equimolar ferrocene/cobaltocenium loading. In fact, a common feature in the resulting metallodendrimers, such as **1**, was a significantly higher loading of cobaltocenium units than of ferrocene moi-



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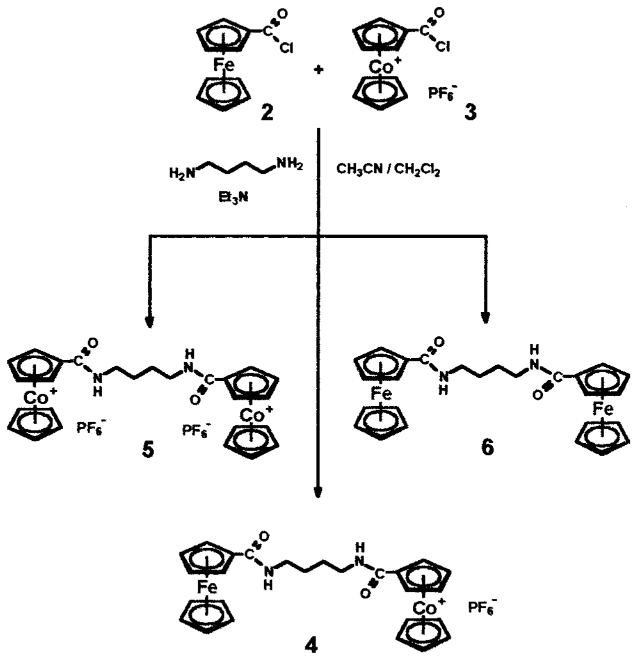
Scheme 1



eties. This observation prompted us to take a close look at the reactivity difference of both (chlorocarbonyl)-metallocenes in such condensation reactions.

In this context, we decided to study the stoichiometric reaction of (chlorocarbonyl)ferrocene, and the salt of (chlorocarbonyl)cobaltocenium with 1,4-diaminobutane as a model reaction, and the results are reported here.

Results and Discussion

As shown in Scheme 1, it would be expected that the reaction of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4COCl\}$ (**2**) and $[\{\eta^5\text{-}C_5H_5\}Co\{\eta^5\text{-}C_5H_4COCl\}][PF_6]$ (**3**) with 1,4-diaminobutane would afford an equimolar mixture of the three bimetallic species **4**−**6**. Our main aim with this reaction was to prepare the heterobimetallic complex **4**, which serves as a useful model compound to facilitate the structural and electrochemical characterization of related heterometallic dendrimers of higher nuclearity.[8]

In our first attempt, stoichiometric amounts of **2** and **3** were reacted simultaneously with the diamine in the presence of triethylamine to scavenge the HCl formed, and using a 1/1 CH_2Cl_2/CH_3CN mixture as solvent, in which both starting metallocenes **2** and **3** were soluble. This reaction gave a mixture of the two bimetallic complexes **4** and **5**, as indicated by ^1H NMR spectroscopy, which were carefully separated by column chromatography on Sephadex-LH and isolated in 9% and 32% yields, respectively. Surprisingly, the formation of the biferrocenyl complex **6** was not observed. The absence of **6** as well as the significant difference in the yields of **4** and **5** suggest that **3** exhibits an increased reactivity toward the amine groups in comparison to the neutral ferrocene derivative **2**, presumably due to the positive charge of the cobaltocenium moiety.

With the aim of increasing the yield of the desired heterobimetallic complex **4**, we evaluated the effect of changing the order of addition of reagents. In this way, a CH_2Cl_2 solution of **2** was added to a vigorously stirred solution of 2 equiv of 1,4-diaminobutane in a large volume of CH_2Cl_2 also containing triethylamine. Subsequently, a solution containing **3** in CH_3CN was also added to the reaction mixture. These reaction conditions allow the condensation of **2** with the amine to take place before the addition of **3** and render more difficult the formation of the homobimetallic **5** and **6**, thus giving preferentially **4** as the major product. By this procedure **4** and **5** were obtained as orange and yellow crystalline solids in 48% and 8% yields, respectively, and only trace amounts of **6** were observed.

The successful chromatographic separation as well as the identities of **4** and **5** were confirmed by ^1H and ^{13}C NMR, fast atom bombardment mass spectrometry (FAB-MS), and elemental analyses. The ^1H NMR spectrum of **4** shows resonances at 5.8−6.4 ppm typical of the cyclopentadienyl protons in cobaltocenium salts, downfield from the ferrocenyl protons, which are observed at 4.1−4.8 ppm. These two sets of resonances show a 1:1 ratio of integrated intensity which is consistent with the simultaneous presence of a ferrocenyl and a cobaltocenium unit in **4**. In addition, two equally integrating signals are observed at 8.98 and 7.85 ppm, attributable to the amide protons adjacent to the cobaltocenium and ferrocenyl moieties, respectively. In contrast, the NMR spectral features of **5** are in accordance with its symmetrical structure and show the presence of the cobaltocenium, amide, and methylene groups. The most intense ions in the FAB mass spectrum of **4** and **5** occur at *m*/*z* 515 and 663, respectively, and are attributable in both cases to the loss of a PF_6^- anion. In the spectrum of **5** the ion corresponding to the loss of two PF_6^- anions is also observed at *m*/*z* 518.

The heterobimetallic structure of **4** was corroborated via an X-ray crystallographic analysis. Orange crystals of **4** suitable for crystallographic analysis were obtained by slow diffusion of cyclohexane into an acetone solution of the compound. The molecular structure of **4** is illustrated in Figure 1, and crystallographic data are given in Table 1. In the structure of **4** the diaminobutane bridge adopts a bent conformation and the metallocenes are oriented almost perpendicular to one another. The cyclopentadienyl rings in both metallocenes are planar and nearly parallel and exhibit an almost eclipsed conformation. The Co−C and Fe−C (cyclopentadienyl ring) distances and amide bonds do not differ significantly from those of other cobaltocenium and ferrocene complexes.[6]

The redox properties of **4** and **5** were investigated by cyclic voltammetry in CH_3CN solution. The electrochemical behavior of **4** is in accordance with the heterobimetallic nature of the compound. The cyclic voltammogram shown in Figure 2 reveals two reversible redox waves of equal intensity, with formal potential values of +0.56 and −0.75 V vs SCE, which are clearly assigned to the one-electron oxidation of the ferrocenyl unit and the one-electron reduction of the cobaltocenium moiety, respectively. These potential values are considerably more positive than the corresponding processes for $(\eta^5\text{-}C_5H_5)_2Fe$ (+0.40 V in CH_3CN) and $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ (−0.94 V in CH_3CN). This is due to the strong electron-withdrawing effect of the amide groups when bound directly to the cyclopentadienyl rings, making the

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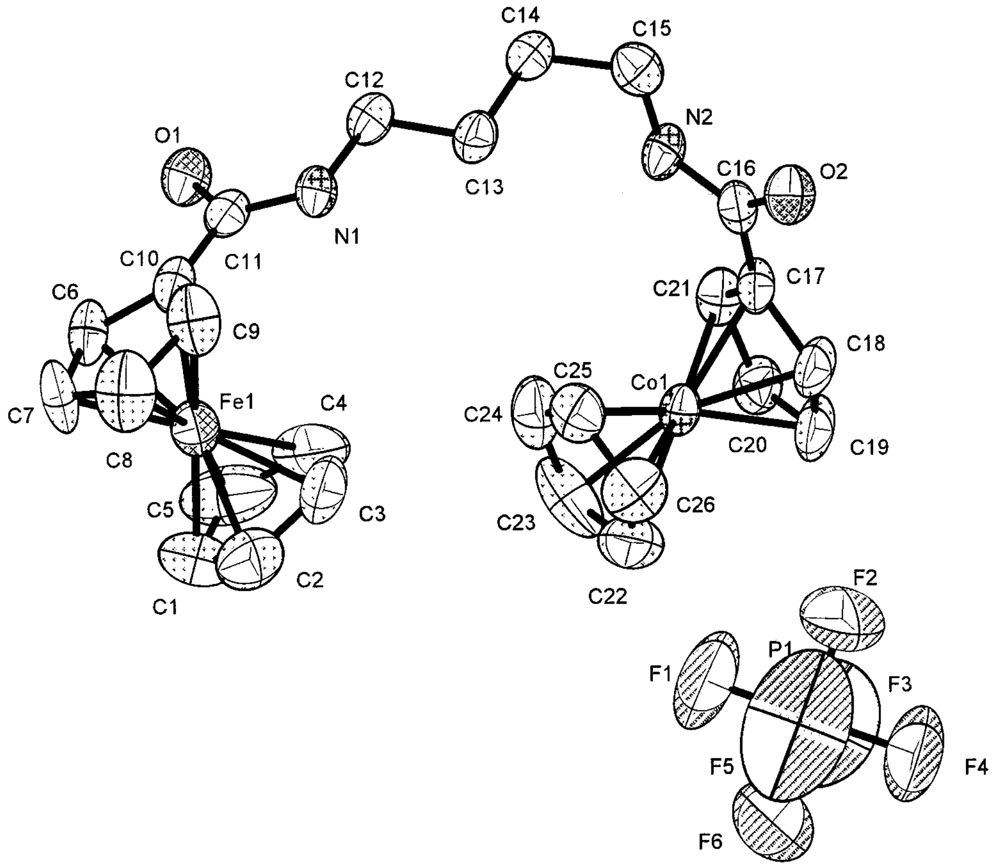

Figure 1. Molecular structure of the heterobimetallic compound **4** (50% thermal ellipsoids). Selected bond lengths (Å) and bond angles (deg): Cent$_{C(1)-C(5)}$−Fe(1) = 1.634(11), Cent$_{C(6)-C(10)}$−Fe(1) = 1.641(9), Cent$_{C(17)-C(21)}$−Co(1) = 1.639(8), Cent$_{C(22)-C(26)}$−Co(1) = 1.651(9), C(10)−C(11) = 1.490(10), C(16)−C(17) = 1.494(10); C11−N1−C12 = 121.9(6), C16−N2−C15 = 124.0(6), N(1)−C(11)−C(10) = 118.3(6), N(2)−C(16)−C(17) = 116.1(6).

Table 1. Crystal Data and Structure Refinement for 4

formula	$C_{26}H_{28}CoFeN_2O_2PF_6$
fw	660.25
cryst syst	monoclinic
space group	$C2/c$
a (Å)	9.9848(10)
b (Å)	23.903(2)
c (Å)	22.614(3)
β (deg)	98.162(9)
V (Å^3)	5342.5(9)
Z	8
calcd density (g/cm^3)	1.642
abs coeff (mm^{-1})	10.419
radiation	graphite-monochromated Cu Kα (λ = 1.541 78 Å)
F(000)	2688
θ range for data collection (deg)	3.70−57.13
limiting indices	$-1 \le h \le 10$, $-1 \le k \le 26$, $-24 \le l \le 24$
no. of rflns collected	4530
no. of indep rflns	3552
R_{int}	0.0328
max, min transmissn	0.5313, 0.1806
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3552/0/407
goodness of fit on F^2	1.030
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0820, 0.2160
R1,[a] wR2[b] (all data)	0.0974, 0.2336
extinction coeff	0.00001(3)
largest diff peak and hole (e/Å^3)	0.903 and −0.621

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

oxidation of the ferrocene unit and the reduction of the cobaltocenium moiety in **4** thermodynamically more difficult and easier, respectively, than those of unsubstituted metallocenes. In the case of the homobimetallic **5** a single reversible process is observed at −0.78 V vs SCE corresponding to the simultaneous one-electron reduction of the two noninteracting cobaltocenium moieties.

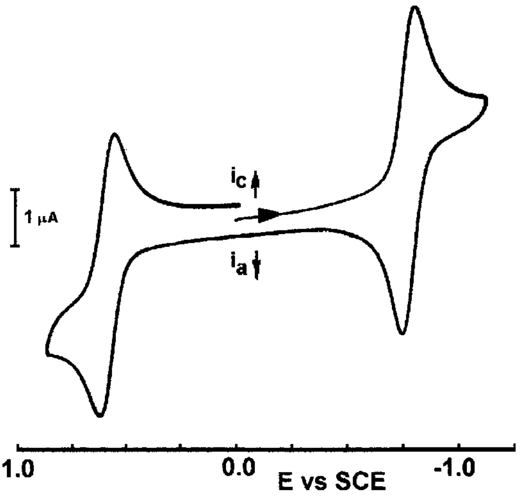

Figure 2. Cyclic voltammogram of the heterobimetallic compound **4** in CH_3CN (scan rate 100 mV s^{-1}).

The novel mixed ferrocene−cobaltocenium compound **4** constitutes one of the rare examples of derivatives containing the two most stable organometallic redox-active systems in the same molecule.[9] The facile synthetic approach described here can be extended further to prepare novel types of heteromultimetallic dendritic molecules and polymers. We are currently working toward this end.

Experimental Section

Materials and Equipment. All reactions were performed under an inert atmosphere (prepurified Ar) using standard Schlenk techniques. Solvents were dried by standard procedures over the appropriate drying agents and distilled immediately prior to use. Triethylamine (Merck) was distilled over KOH under N_2. (Chlorocarbonyl)ferrocene[10] and the hexafluorophosphate salt of (chlorocarbonyl)cobaltocenium[11] were prepared as described in the literature. 1,4-Diaminobutane was obtained from Aldrich and used as received. Chromatographic separations were performed with the use of Sephadex LH-20 (Fluka). NMR spectra were recorded on a Bruker-AMX spectrometer. Chemical shifts are reported in parts per million (δ) with reference to residual solvent resonances. FAB mass spectral analyses were conducted on a VG Auto Spec mass spectrometer equipped with a cesium ion gun. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain.

Cyclic voltammetric experiments were performed on a BAS CV-27 potentiostiat, using a conventional three-electrode cell (Pt, Pt, SCE) and operating under an atmosphere of prepurified nitrogen. Solutions were typically 1.0 mM in the redox-active species, and the supporting electrolyte (used in a concentration of 0.1 M) was tetra-*n*-butylammonium hexafluorophosphate (Fluka). No *iR* compensation was used.

X-ray Crystal Structure Determination. A suitable orange crystal of **4** of prismatic shape and dimensions 0.02 × 0.45 × 0.2 mm was located and mounted on a glass fiber with silicone cement in air and placed on a Siemens P4 diffractometer. Unit cell parameters were determined by least-squares analysis of 47 reflections with $11.62° < 2\theta < 30.03°$. Data were collected at 296 K using continuous $\omega-2\theta$ scans. The stability of the crystal was tested every 50 reflections with 3 check reflections that showed only random fluctuations in intensity during data collection. The intensities were corrected for Lorentz and polarization effects. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[12] Calculations were performed using Bruker SHELXTL for NT, version 5.10, a system of programs refining on F^2. The structure was solved by direct methods, and there were no unusual features of this refinement. The hydrogen atom positions were calculated with fixed isotropic contributions at their calculated positions determined by molecular geometry. An absorption correction using an empirical model based on reflection measurements at different azimuthal angles and/or measurements of equivalent reflections was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the final difference map was equivalent to 0.903 e/Å^3 and was located 1.250 Å from F6.

Reaction of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4COCl\}$ (2) and $[\{\eta^5\text{-}C_5H_5\}Co\{\eta^5\text{-}C_5H_4COCl\}][PF_6]$ (3) with 1,4-Diaminobutane. Method A. 2 (1.76 g, 7.08 mmol) and **3** (2.81 g, 7.08 mmol) were dissolved in CH_2Cl_2/CH_3CN (1:1, 100 mL) under an argon atmosphere, at room temperature. To this solution was added dropwise 1,4-diaminobutane (0.62 g, 7.03 mmol) and Et_3N (2 mL, 14.35 mmol) in 1/1 CH_2Cl_2/CH_3CN (40 mL), and the mixture was stirred at room temperature for 18 h. After this time the resulting mixture was filtered, the solvent was removed under vacuum, and the residue was purified by column chromatography on Sephadex LH-20. Using CH_3CN as eluent, an orange band was separated and a yellow band was eluted with a 1:1 mixture of $CH_3CN/EtOH$. After solvent removal, redissolution of each of the solids in small quantities of water, and dropwise addition of aqueous ammonium hexafluorophosphate to both solutions, **4** and **5** were obtained as crystalline orange (0.43 g), and yellow (1.8 g) solids, respectively.

Method B. A solution of **2** (0.75 g, 3 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise to a stirred solution of 1,4-diaminobutane (0.27 g, 3 mmol) and triethylamine (1 mL, 7 mmol) in CH_2Cl_2 (250 mL). Stirring was continued for 15 min, the solution was concentrated to 200 mL under vacuum, and CH_3CN (100 mL) was added. A solution of **3** (1.2 g, 3 mmol) in a mixture of CH_3CN (40 mL) and CH_2Cl_2 (20 mL) was added. The reaction mixture was stirred at room temperature overnight and then concentrated under vacuum. After the mixture was cooled to −30 °C, the crystalline triethylamine hydrochloride precipitate formed was filtered off and the solvent removed by evaporation. The residue was redissolved in CH_3CN and subjected to column chromatography. Elution with CH_3CN afforded an orange solid, which was then dissolved in a small quantity of water and aqueous ammonium hexafluorophosphate added dropwise, producing **4** as a crystalline orange solid (0.95 g). A yellow band was then eluted using $CH_3CN/EtOH$ (7:3), which after treatment with aqueous ammonium hexafluorophosphate afforded **5** as a yellow solid (0.20 g).

Characterization data for **4** are as follows. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ 8.98 (t, 1H, CONH[Cb]), 7.85 (t, 1H, CONH[Fc]), 6.32 (t, 2H, C_5H_4[Cb]), 5.91 (t, 2H, C_5H_4[Cb]), 5.83 (s, 5H, C_5H_5[Cb]), 4.77 (t, 2H, C_5H_4[Fc]), 4.31 (t, 2H, C_5H_4[Fc]), 4.13 (s, 5H, C_5H_5[Fc]), 3.28 (m, 2H, CH_2NHCO[Cb]), 3.20 (m, 2H, CH_2NHCO[Fc]), 1.57 (m, 4H, NCH_2CH_2). ^{13}C NMR (125.4 MHz, [D_6]DMSO, 25 °C): δ 169.7, 162.0 (CO), 94.9 (C_5H_4[Cb]), 86.8 (C_5H_5[Cb]), 86.5, 85.1 (C_5H_4[Cb]), 77.8, 70.6 (C_5H_4[Fc]), 70.1 (C_5H_5[Fc]), 69.1 (C_5H_4[Fc]), 39.3, 27.9, 27.1 (CH_2). IR: amide I 1656 cm^{-1}, amide II 1536 cm^{-1}. FAB-MS: *m*/*z* (%) 515.2 (100) $[M - PF_6^-]^+$. Anal. Calcd for $C_{26}H_{28}FeCoN_2O_2PF_6$: C, 60.60; H, 5.48; N, 5.44. Found: C, 60.51; H, 5.39; N, 5.51. Cb = $C_5H_4CoC_5H_5$, Fc = $C_5H_4FeC_5H_5$.

Characterization data for **5** are as follows. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ 9.13 (t, 2H, CONH), 6.38 (t, 4H, C_5H_4), 5.92 (t, 4H, C_5H_4), 5.85 (s, 10H, C_5H_5), 3.27 (m, 4H, CH_2NHCO), 1.62 (m, 4H, NCH_2CH_2). ^{13}C NMR (125.4 MHz, [D_6]DMSO, 25 °C): δ 162.1 (CO), 94.7 (C_5H_4), 86.8 (C_5H_5), 86.5, 85.0 (C_5H_4), 39.8, 27.1 (CH_2). IR: amide I 1642 cm^{-1}, amide II 1551 cm^{-1}. FAB-MS: *m*/*z* (%) 518.2 (100) $[M - 2PF_6^- + H^+]^+$. Anal. Calcd for $C_{26}H_{28}Co_2N_2O_2P_2F_{12}$: C, 60.24; H, 5.44; N, 5.40. Found: C, 60.10; H, 5.35; N, 5.50.

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Supporting Information Available: Tables of complete bond distances and angles, torsion angles, displacement parameters, and atomic coordinates for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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