

Preparation and Redox Properties of Novel Polymerizable Pyrrole- and Allyl-Functionalized Cobaltocenium Monomers and Siloxane-Based Cobaltocenium Polymers

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A series of novel cobaltocenium complexes functionalized with electrochemically and chemically polymerizable pyrrole or allyl substituents, [$\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{NC}_4\text{H}_4\}\text{PF}_6$ (**1**), [$\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{NC}_4\text{H}_4\}_2\text{Co}\text{PF}_6$ (**2**), [$\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{NHC}_6\text{H}_4\text{NC}_4\text{H}_4\}\text{PF}_6$ (**3**), [$\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{NHCH}_2\text{CH}=\text{CH}_2\}\text{PF}_6$ (**4**), and [$\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2\}\text{PF}_6$ (**5**), have been prepared via condensation reactions. In a similar way, the siloxane-based polymer **6** and the block copolymer **8**, in which the amide-linked cobaltocenium moieties are incorporated in the polymer backbone either as a part of the main polymer chain or as pendant side groups, as well as the dimetallic model complex [$\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\}_2\text{O}\text{PF}_6$] (**7**), were prepared and characterized. The molecular structure of the pyrrole-containing cobaltocenium **1** has been determined by a single-crystal X-ray diffraction study. Cyclic voltammetric studies show that the stability of the electrogenerated anionic species depends on the solvent and the nature of the cyclopentadienyl substituents. Gold, platinum, and glassy-carbon electrodes have been successfully modified by electrochemical polymerization of the pyrrole-functionalized monomers **1–3**, in acetonitrile solutions, resulting in detectable electroactive cobaltocenium polymer films persistently attached to the electrode surfaces. Glassy-carbon electrodes coated with films of the hydrophobic, siloxane-based, cobaltocenium-containing block copolymer **8** show redox activity in aqueous solutions when an ionic surface-active agent is added to the film.

Introduction

Metallocene-based polymers are an important category of polymeric materials, which have attracted increasing attention in the past few years, because of the significantly different properties they possess in comparison to conventional polymers.¹ These include thermal stability, novel redox characteristics, nonlinear optical (NLO) effects, magnetic properties, and liquid crystalline behavior. Likewise, metallocene-containing polymers are interesting materials for the modification of electrode surfaces that can be used for practical applications and fundamental studies.

In general, two main strategies have been employed for the synthesis of metallocene-containing polymers.

The first approach involves the use of chemically polymerizable metallocenyl monomers, which can be homo- or copolymerized. On the other hand, the incorporation of metallocenes in preformed organic or inorganic polymers constitutes a very facile and versatile access to novel organometallic macromolecules. An alternative, less exploited approach involves the electrochemical polymerization of metallocene derivatives containing appropriate functional groups, directly onto electrode surfaces. This is a simple and effective method, which provides control of the properties of the resulting polymer, including its conductivity, permeability, and redox properties.

In this regard, molecules based on pyrrole have been the subject of increasing interest in recent years, since this chemical function appears exceptionally convenient for achieving electropolymerization in the production of electrodes modified by electroactive polymeric films.² The pyrrole group is polymerized by an oxidative polymerization mechanism that proceeds through an electrochemically accessible radical cation intermediate.

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(1) For excellent recent reviews on metallocene-based polymers see: (a) Peckham, T. J.; Gómez-Elipse, P.; Manners, I. In *Metallocenes*; Togni, A., Halterman, R., Eds.; Wiley-VCH: Weinheim, Germany, 1998; p 756. (b) Nguyen, P.; Gomez-Elipse, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (c) Gonsalves, K. E.; Chen, X. In *Ferrocenes: Homogeneous Catalysis-Organic Synthesis-Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

(2) For reviews on functionalized pyrroles see for example: (a) Deronzier, A.; Moutet, J.-C. *Coord. Chem. Rev.* **1996**, *147*, 339. (b) Deronzier, A.; Moutet, J.-C. *Acc. Chem. Res.* **1989**, *22*, 249. (c) Curran, D.; Grimshaw, J.; Perera, S. D. *Chem. Soc. Rev.* **1991**, *20*, 391.

Although a wide variety of transition-metal complexes with pyrrole groups have been prepared, pyrrole monomers containing organometallic entities remain restricted to a few examples. To the best of our knowledge, the only examples of pyrroles functionalized with organometallic redox-active centers reported until now contain the ferrocene unit.³ However, only a few of these ferrocene-containing pyrrole derivatives form electroactive polymer films by direct anodic electropolymerization. Cobaltocenium also constitutes an excellent organometallic moiety to functionalize pyrrole systems in order to achieve a rapid and direct deposition of the resulting cobaltocenium polymers onto the electrode surface. Cobaltocenium is a highly stable, positively charged complex that undergoes a reversible monoelectronic reduction to yield the uncharged, 19-electron cobaltocene.^{4–9} In contrast to the well-developed chemistry of ferrocene-containing polymers, the incorporation of the analogous, isoelectronic cobaltocenium system into polymeric structures has been explored to a much lesser extent.¹⁰ This is probably because the preparation of cobaltocenium derivatives is considerably more difficult, since the cobaltocenium nucleus, once formed, will not undergo electrophilic substitution.¹¹

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(4) For recent examples of cobaltocenium derivatives see for example refs 4–9: (a) Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106. (b) Herberich, G. E.; Englert, U.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1998**, *17*, 4769.

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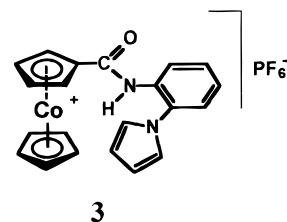
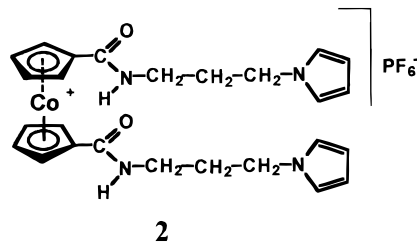
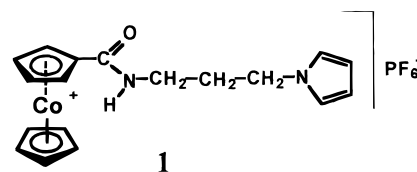
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As a part of our research on new redox-active polymeric¹² and dendritic¹³ organometallic systems, we report here the synthesis and redox behavior of the first examples of electropolymerizable cobaltocenium monomers containing pyrrole groups, together with closely related cobaltocenium derivatives functionalized with allyl groups, which are potential candidates to prepare polymers via addition reactions. Likewise, novel siloxane-based polymers containing cobaltocenium salts, as well as a siloxane-bridged dimetallic model compound, prepared by a similar synthetic route, are also described.

Results and Discussion

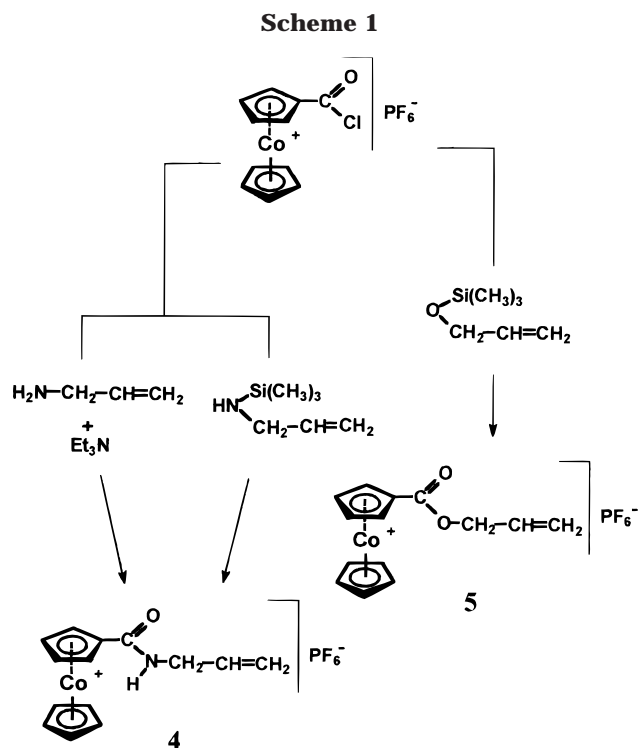
Synthesis of the Pyrrole- and Allyl-Functionalized Cobaltocenium Monomers. The synthetic route used to functionalize cobaltocenium moieties with pyrrole derivatives takes advantage of condensation reactions of the hexafluorophosphate salts of (chlorocarbonyl)cobaltocenium and 1,1'-bis(chlorocarbonyl)cobaltocenium with amine-containing pyrroles. Recently, we have used successfully a similar condensation strategy to prepare a series of cobaltocenium-functionalized dendrimers,¹⁴ which in combination with β -cyclodextrins constitute a novel type of host-guest system in which the formation of high-molecular-weight supramolecular assemblies is driven by the electrochemical reduction of the dendrimers.

The condensation reactions of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Cl}\}]\text{PF}_6$ and $[\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Cl}\}_2\text{Co}]\text{PF}_6$ with 1-(3-aminopropyl)pyrrole and 1-(2-aminophenyl)pyrrole, in chloroform solutions, at room temperature, and in the presence of triethylamine as the base to neutralize the acidic byproduct, afford the monosubstituted cobaltocenium salts **1** and **3**, as well as the difunctional derivative **2**. The reactions are slightly exothermic and



take place rapidly, affording the desired cobaltocenium

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complexes in relatively high yields. In addition, Et_3NHCl , which is formed as a byproduct, is more soluble than the final reaction products in CHCl_3 so that the isolation of the desired pyrrole-containing cobaltocenium complexes was facilitated. After appropriate purification, the pyrrole-functionalized compounds were isolated as air-stable yellow (**1** and **3**) and greenish (**2**) crystalline solids.

A similar condensation reaction was performed by reacting allylamine with $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Cl}\}]\text{PF}_6$, which after purification yielded the desired allyl-functionalized, amide-linked cobaltocenium **4** (Scheme 1). In this case, we have also attempted an alternative synthetic route which involves a condensation reaction between *N*-(trimethylsilyl)allylamine and (chlorocarbonyl)cobaltocenium hexafluorophosphate in chloroform, at room temperature. *N*-trimethylsilyl-substituted amines are known to be one of the most reactive classes of organosilane compounds and react with a variety of electrophiles, such as carboxylic acid chlorides, yielding the corresponding condensation products.¹⁵ This route has several advantages over the conventional amine route described above. In particular, the condensation with the *N*-silylated amine proceeds under neutral reaction conditions, as it avoids the liberation of HCl generated in the absence of the silyl group. In addition, the liberated trimethylsilyl chloride byproduct is highly volatile and easy to remove from the reaction mixture, and thus the desired amide-linked cobaltocenium salt **4** was cleanly obtained. In a similar way, the reaction of *O*-(trimethylsilyl)allyl alcohol with (chlorocarbonyl)cobaltocenium hexafluorophosphate, under the same reaction conditions, also afforded the desired ester-linked product **5** (Scheme 1), which was isolated in high yield as large yellow needles.

The structures of the novel cobaltocenium derivatives were straightforwardly determined on the basis of

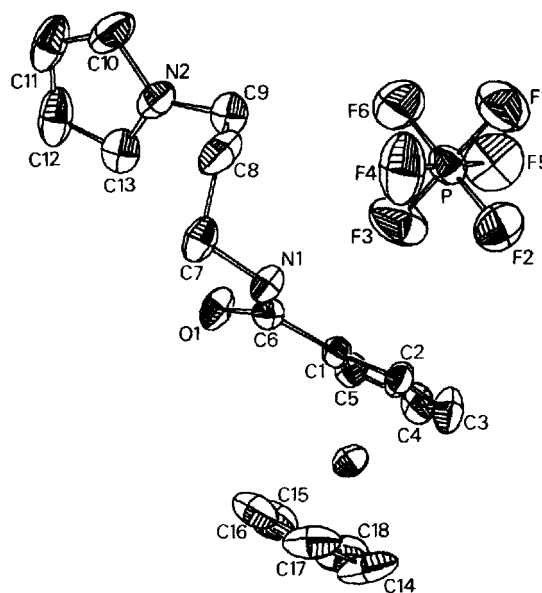


Figure 1. Molecular structure of the pyrrole-functionalized cobaltocenium **1**.

infrared spectroscopy, ^1H and ^{13}C NMR spectra, mass spectrometry, and elemental analysis. Compound **1** was further characterized by X-ray diffraction studies (see below). ^1H NMR spectra of **1–5** (in acetone- d_6) show in all cases the pattern of resonances characteristic of cobaltocenium derivatives in the expected region, along with the proton resonances due to the organic groups in the side chain. Thus, for example, for the pyrrole-functionalized derivatives, two apparent triplets corresponding to the α - and β -protons are observed, which are centered at about 6.1 and 6.7 ppm for **1** and **2** and at 6.3 and 7.1 ppm for **3**. Likewise, the allyl group in **4** and **5** gives rise to an AA'KLM spin system pattern in the ^1H NMR spectra. The AA' part due to the methylene consists of a multiplet centered at 3.99 and 4.88 ppm for **4** and **5**, respectively. The three signals of the allyl part include two close pseudoquartets for both $=\text{CH}_{\text{trans}}$ and $=\text{CH}_{\text{cis}}$ and a multiplet for the methine proton. The FAB mass spectra of compounds **1–5** provided confirmation for the structural assignments and showed in all cases the peak corresponding to the loss of the counterion, together with several informative peaks assignable to reasonable fragmentation products (see Experimental Section).

X-ray Structure of 1. Single crystals of the pyrrole-functionalized cobaltocenium derivative **1** suitable for an X-ray diffraction study were grown by slow diffusion of cyclohexane into a concentrated solution of the compound in acetonitrile. The molecular structure of **1** is shown in Figure 1. Table 1 lists a summary of cell constants and data collection parameters for the analysis of **1**.

The structure of **1** consists of discrete cations and hexafluorophosphate anions. The two cyclopentadienyl rings are planar and are nearly parallel to one another (dihedral angle 2.41°). An unusual feature of this molecule is that the cyclopentadienyl rings are almost completely eclipsed, in contrast with what is observed for carboxycobaltocenium hexafluorophosphate¹⁶ and other cobaltocenium derivatives.^{6a,9} The Co–C(cyclo-

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Table 1. Crystal and Refinement Data for $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{o})\text{Nh}(\text{CH}_2)_3\text{NC}_4\text{H}_4\}]\text{PF}_6$ (1**)**

formula	$\text{CoC}_{18}\text{ON}_2\text{PF}_6\text{H}_{20}$
mol wt	484.27
cryst dimens, mm	$0.10 \times 0.15 \times 0.40$
cryst habit and color	prismatic yellow
cryst syst	orthorhombic
space group	<i>Pbca</i> (No. 61)
cell dimens	
<i>a</i> , Å	21.885(3)
<i>b</i> , Å	10.10(1)
<i>c</i> , Å	17.960(3)
$\alpha = \beta = \gamma$ (deg)	90.0
<i>Z</i>	8
<i>V</i> , Å ³	3970(4)
<i>D</i> _{calcd} , g cm ⁻³	1.62
<i>F</i> (000)	1968
temp, K	295
diffractometer	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo K α ($\lambda = 0.71069$ Å)
scan technique	$\omega/2\theta$
2θ range, deg	1–52
data collected	$0 \leq h \leq 26, 0 \leq k \leq 12,$ $0 \leq l \leq 22$
no. of unique data	4374
no. of obsd rflns, $I > 3\sigma(I)$	1912
<i>R</i> _{int}	
decay	<1%
std rflns	3/45
μ (Mo K α), cm ⁻¹	10.1
transmissn range	0.65–0.90
weighting scheme	unit
max and av shift/error	0.01, 0.001
max residual, e Å ⁻³	0.2
$R = \sum(F_o - F_c) / \sum F_o $	0.062
$R_w = (\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$	0.064
GOF (<i>F</i>)	1.2
no. of refined params	262
rfln/param ratio	7.3

pentadienyl ring) distances are in the range 1.989(12)–2.036(10) Å, which are essentially similar to those found in $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{COOH}\}]\text{PF}_6$.¹⁶ Other bond distances and angles found in **1** do not differ significantly from those of other cobaltocenium complexes.

Solution Redox Behavior of Monomers 1–5. The electrochemical behavior of the new cobaltocenium derivatives **1–5** has been investigated in dichloromethane, acetonitrile, and dimethylformamide (DMF) solution with *n*-Bu₄NClO₄ as supporting electrolyte.

The cyclic voltammograms (CVs) of the pyrrole-functionalized cobaltocenium monomers **1–3** in DMF solutions, over the range 0.0 to –2.0 V vs SCE, show two reversible processes (waves A and B in Figure 2a) characterized by peak-to-peak potential splittings (ΔE_p) of about 65–70 mV and essentially equal cathodic and anodic peak currents. Furthermore, both electrochemical processes are diffusion-controlled with the peak current linearly proportional to the square root of the scan rate, *v*. Potentiostatic coulometry and comparisons of limiting currents, obtained from rotating-disk-electrode (RDE) voltammograms with that of the unsubstituted cobaltocenium hexafluorophosphate indicate two successive one-electron transfers. The two observed reduction waves can be easily assigned to the two successive one-electron reductions of the cobaltocenium moiety. These results indicate that for compounds **1–3**, in DMF solutions, reversible processes take place, and stable neutral and monoanionic species are formed in the time scale of the CV experiments.

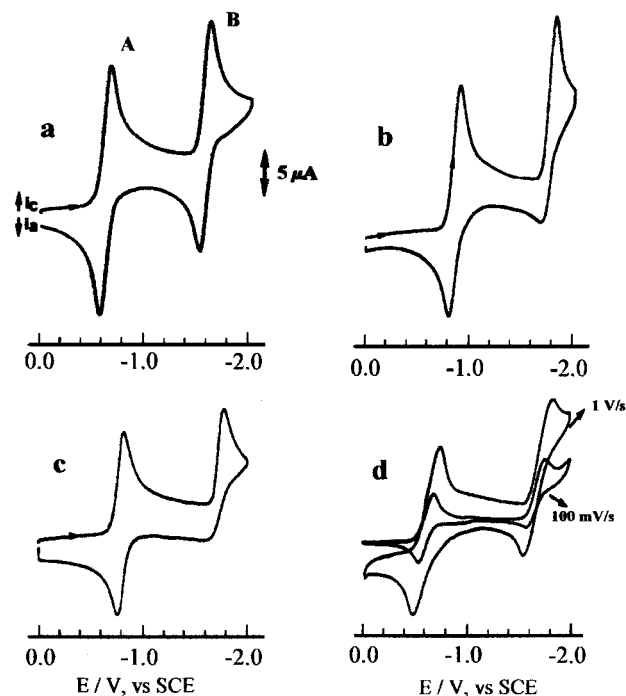


Figure 2. Cyclic voltammograms of (a) **1** in DMF, (b) **1** in CH₃CN, (c) **4** in DMF, and (d) **4** in CH₂Cl₂. Unless otherwise indicated, the scan rate is 100 mV s⁻¹.

When the electrochemical reduction of **1** and **2** was effected in acetonitrile (see Figure 2b), the $i_{p,a}/i_{p,c}$ value for the second process, at slow scan rates, is less than 1 and the cathodic current is higher than the diffusion-controlled reversible value. In addition, at high scan rates the current function ($i_p/v^{1/2}$) for this wave reaches a limiting value that is the same as that of the uncomplicated first reduction process but increases at slower scan rates. These results are consistent with an ECE mechanism in which the electrogenerated anion could react with the solvent to give a product with a less negative reduction potential. A similar behavior has been observed by Geiger for the cobaltocene reduction in acetonitrile solution, in which the formation of the ring-addition intermediate $\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^4\text{-C}_5\text{H}_5\text{CH}_2\text{-CN}\}$ is postulated.¹⁷

The redox behavior, in DMF as solvent, of the allyl-functionalized cobaltocenium compounds **4** and **5** is different from that described above for the pyrrole derivatives **1–3**. The second reduction at about –1.6 V vs SCE is irreversible, as shown by the absence of the corresponding anodic peak in the reverse scan (see Figure 2c). However, in CH₂Cl₂ at high scan rates these compounds show partially chemically reversible reductions (Figure 2d), the $i_{p,a}/i_{p,c}$ ratio being close to 1. The instability of the monoanionic species generated in the reduction of **4** and **5** could be related to the nature of the substituents on the cyclopentadienyl ring.

Redox potential values for the new cobaltocenium compounds **1–5** together with the observed values for the unsubstituted cobaltocenium hexafluorophosphate are indicated in Table 2. The electron-withdrawing effect exerted by the carbonyl groups is clearly evident in the substantial positive shift observed in the half-

(17) Geiger, W. E. in *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; p 683.

Table 2. Redox Potentials (V, vs SCE) of the Cobaltocenium Complexes and Polymers^a

compd	solvent	$E_{1/2}(A/A')$	$E_{1/2}(B/B')$	$E_p(B)$
1	DMF	-0.68	-1.62	
	CH ₃ CN	-0.60		-1.59
2	DMF	-0.53	-1.43	
	CH ₃ CN	-0.58		-1.56
3	DMF	-0.65	-1.53	
4	DMF	-0.69		-1.70
	CH ₂ Cl ₂	-0.70		-1.68
5	DMF	-0.61		-1.57
	CH ₂ Cl ₂	-0.62		-1.70
6	DMSO	-0.61	-1.48	
7	DMF	-0.69	-1.66	
8	DMF	-0.65	-1.71	
[η^5 -C ₅ H ₅] ₂ Co]PF ₆	DMF	-0.88	-1.85	

^a At a glassy-carbon electrode.

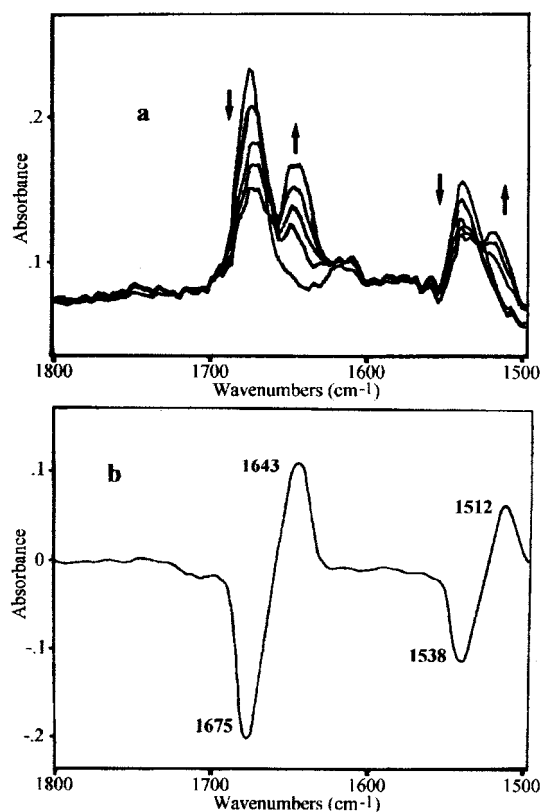


Figure 3. (a) Infrared spectral changes observed upon reduction of **4** in CH₂Cl₂/*n*-Bu₄NPF₆ at -1.0 V vs Ag pseudoreference electrode in the spectroelectrochemical cell. (b) FTIR absorbance difference spectrum of the starting **4** and the electrogenerated reduction product.

wave potential value of monomers **1–5** in comparison to the $E_{1/2}$ value of pure cobaltocenium. Therefore, the reduction of the new functionalized cobaltocenium compounds **1–5** is thermodynamically easier than that of [η^5 -C₅H₅]₂Co]PF₆.

The formation of the neutral cobaltocene species, generated by the monoelectronic reduction of the cationic species **1–5**, has been evidenced by infrared spectroelectrochemical experiments. As an example, Figure 3 shows the spectral changes that accompany the controlled-potential reduction of **4** in CH₂Cl₂/*n*-Bu₄NPF₆, in the thin-layer cell, at room temperature. With the application of a reductive potential, the amide I ν (C=O) band at 1675 cm⁻¹, corresponding to the cationic compound **4**, decreases in intensity while a new carbonyl band corresponding to the electrogenerated neutral

cobaltocene grows in isospectically at 1643 cm⁻¹, indicating a clean conversion. The shift to a lower frequency in this ν (C=O) band is produced because the reduction of the cobaltocenium unit of **4** inductively increases the electron density on the amide group directly attached to the cyclopentadienyl ring, resulting in a loss of strength in the C=O bond.

Electropolymerization of Pyrrole-Functionalized Cobaltocenium Monomers. Figure 4a shows the cyclic voltammogram of the pyrrole-containing cobaltocenium monomer **1** in acetonitrile solution containing 0.1 M *n*-Bu₄NClO₄, at a gold electrode, between -1.1 and +1.5 V vs SCE. The potential was first scanned in the negative region, and the cyclic voltammogram shows the reversible redox system A/A' corresponding to the monoelectronic reduction of the cobaltocenium moiety to the neutral cobaltocene. Upon scan reversal, a large irreversible oxidation peak, C, appears at +1.26 V vs SCE, which could be assigned to the oxidation of the pyrrole group. In fact, this oxidation takes place at a potential value, which is in close agreement with that observed for the free 1-(aminopropyl)pyrrole ligand, under the same experimental conditions (+1.22 V vs SCE). The subsequent cyclic voltammogram shows an important increase in the peak current corresponding to the cobaltocenium/cobaltocene redox couple. At the same time, a new peak of lower intensity D appears at the foot of the cobaltocenium reduction. Likewise, in the anodic region, an irreversible peak E is observed, which could be associated with the oxidation of the pyrrole group.

Figure 4b shows the evolution of the cyclic voltammogram of **1** during repeated potential scans over the range -1.0 to +1.7 V vs SCE. The increase in the current for the previously described cobaltocenium/cobaltocene system upon continuous scanning indicates that electrochemical polymerization of the monomer **1** rapidly occurs and that an electroactive polymeric film grows on the electrode surface. Furthermore, in the positive region, the wave centered at +1.26 V vs SCE, corresponding to the oxidation of the pyrrole group, grew in magnitude only during the early stages of deposition and it reached an apparent steady-state value. At the same time, the prepeak associated with this oxidation becomes more anodic as the film grows. Similar prepeaks have been observed for some N-substituted pyrroles with large groups, and they have been related to the oxidation of polypyrrole.¹⁸ The intensity of the prepeak in the negative voltage region increases upon cycling, and its potential shifts gradually to negative values and finally merges with the reduction peak of the cobaltocenium. This prepeak is ascribable to the mediated reduction of the polypyrrole through the reduced form of the cobaltocenium group.^{18a,c}

After a period of scanning in a rigorously deaerated solution of monomer **1**, the electrodes thus coated were removed from the monomer-containing solution, rinsed with acetonitrile to remove any adhering solution, and dried in air. Inspection of the electrode reveals the presence of an insoluble colored (reddish brown) film.

(18) (a) Cosnier, S.; Deronzier, A.; Moutet, J.-C. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *207*, 315. (b) Daire, F.; Bedioui, F.; Devynck, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *224*, 95. (c) Cosnier, S.; Deronzier, A.; Moutet, J.-C. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *193*, 193.

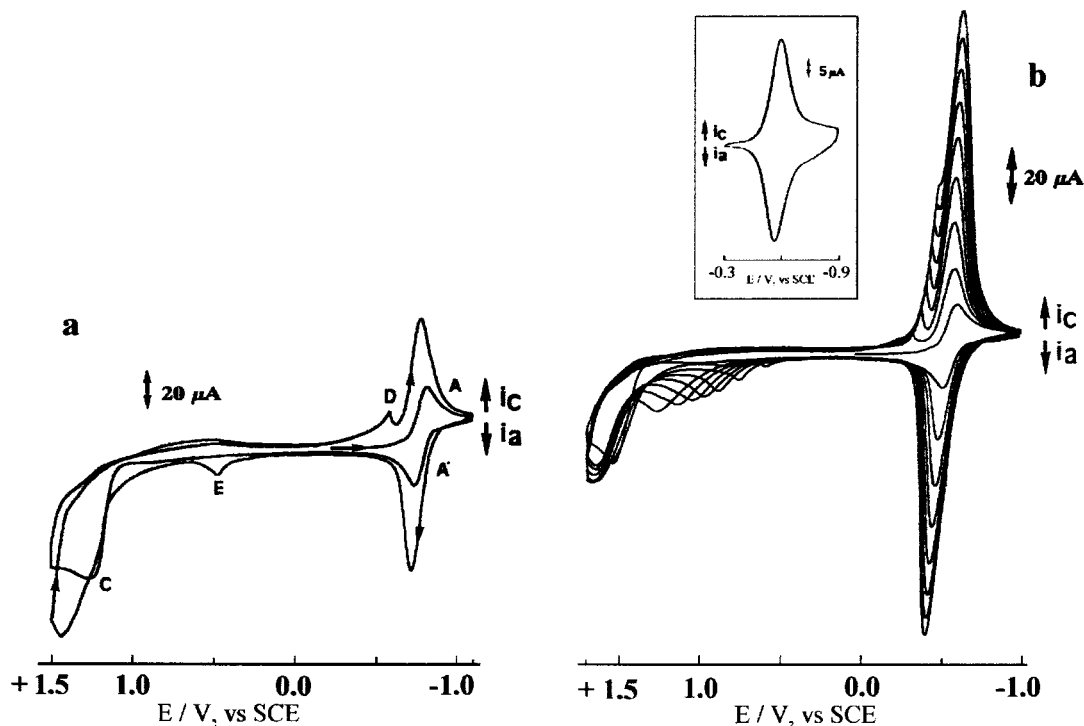


Figure 4. (a) Cyclic voltammograms, at a gold electrode, of **1** in $\text{CH}_3\text{CN}/0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4$, at a scan rate of 100 mV s^{-1} . (b) Evolution of the cyclic voltammogram during the oxidative electropolymerization of monomer **1** by repeated potential scans (nine cycles) on a gold electrode in $\text{CH}_3\text{CN}/0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4$. The inset shows the cyclic voltammogram of a Au electrode modified with a film of poly-**1**, measured in $\text{CH}_3\text{CN}/0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4$.

The voltammetric response of electrodes modified with cobaltocenium-containing polymer films was examined in acetonitrile and aqueous electrolyte solutions. A cyclic voltammogram of a gold electrode modified with an electropolymerized film of monomer **1**, obtained in a clean acetonitrile solution containing only supporting electrolyte, is shown in the inset of Figure 4b. A well-defined redox process corresponding to the cobaltocenium/cobaltocene system is observed at -0.6 V , which is virtually identical with the redox potential of the monomer **1** in solution. The redox wave is symmetric and characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with the potential sweep rate.¹⁹ For polymer films examined at scan rates lower than 100 mV s^{-1} , a peak splitting ΔE_p of 10 mV , for the redox couple, was observed and the $i_{p,a}/i_{p,c}$ ratio was close to unity. These voltammetric features unequivocally indicate the surface-confined nature of the electroactive cobaltocenium-containing polypyrrole film. The surface coverage of electroactive cobaltocenium sites in the film, Γ , was determined from the integrated charge of the cyclic voltammetric wave, resulting in a value of $6 \times 10^{-9} \text{ mol/cm}^2$. A similar electrochemical behavior is observed for films of poly-**1** examined in an aqueous electrolyte solution. A remarkable feature of electrodes modified with electropolymerized films of **1** is that they are extremely durable and reproducible either in acetonitrile or aqueous electrolyte solutions. In addition, the above-described results are essentially the same for platinum and glassy-carbon electrodes.

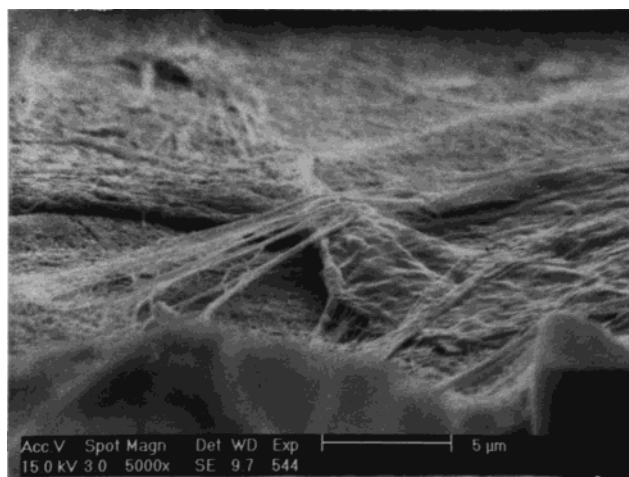


Figure 5. Scanning electron micrograph of a polymer film, obtained by electropolymerization of **1** (25 cycles) on a platinum-wire electrode.

The microstructure of a film of poly-**1** obtained by anodic polymerization of the pyrrole-functionalized monomer **1** on a platinum wire (0.25 mm of diameter) was examined by scanning electron microscopy (SEM). The SEM micrograph in Figure 5 shows that the cobaltocenium-containing polymeric film has a compact morphology of crossed fibers.

The pyrrole-functionalized cobaltocenium monomers **2** and **3** can be also electropolymerized under similar experimental conditions. In the case of the difunctional monomer **2**, the presence of two polymerizable pyrrole substituents attached to the cyclopentadienyl rings does not seem to increase the efficiency of the electropolymerization process. Electropolymerized films of the cobaltocenium-functionalized monomers **2** and **3** showed

(19) (a) Murray, R. W. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Techniques of Chemistry XXII; Wiley: New York, 1992; p 1. (b) Abruña, H. D. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Dekker: New York, 1988; Vol 1, p 97.

similar voltammetric responses and similar stabilities to the redox processes.

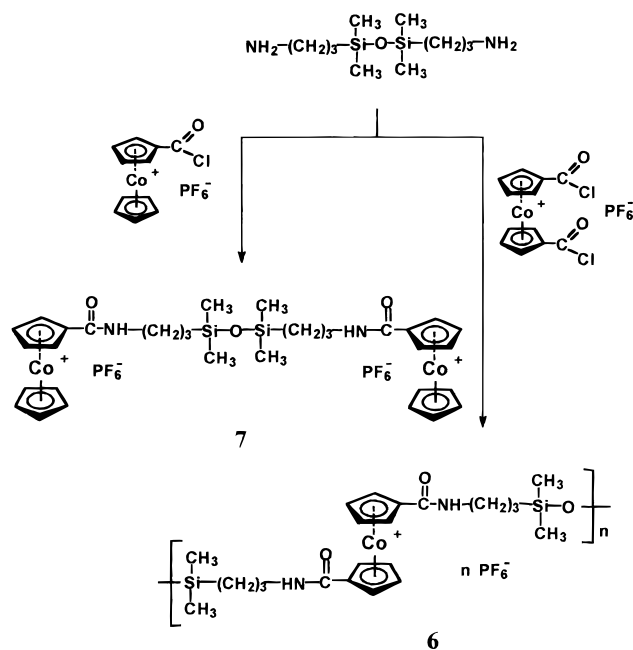
In conclusion, cobaltocenium-containing polypyrrole homopolymers can be readily formed as stable films on the electrode surfaces by electrochemical polymerization of monomers **1–3**. It is interesting to note that this result contrasts with the electrochemical polymerization of related N-substituted pyrrole ferrocene derivatives, which can be grown as stable films only by copolymerization with 1-methylpyrrole.^{3d} The ease of preparation, rapid polymerization rates, and electrochemical stability either in aqueous and organic solvents make these pyrrole-based cobaltocenium polymer films potentially useful for applications in the fields of electrocatalysis and molecular recognition of anions.

Synthesis and Electrochemistry of Siloxane-Based Cobaltocenium Polymers. In the past few years our group has been interested in the synthesis of siloxane-based redox-active organometallic polymers. Thus, we have reported siloxane polymers containing ferrocene, $[(\eta^5\text{-C}_5\text{R}_4)\text{Fe}(\text{CO})(\mu\text{-CO})]_2$ ($\text{R} = \text{H, Me}$), as well as $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_3]$ moieties, which exhibit interesting redox properties.^{12d,12e} Due to its resistance to strong oxidizing agents and interesting electrochemical behavior, cobaltocenium is an attractive moiety to incorporate into polymeric backbones.¹⁰ To the best of our knowledge, polysiloxane polymers containing cobaltocenium units have not been prepared so far. With this in mind, we are now particularly interested in the possibility of obtaining cobaltocenium-containing polysiloxane materials, where the interesting electrochemical and chemical features of this organometallic moiety are combined with the unique and valuable properties of siloxane backbones.

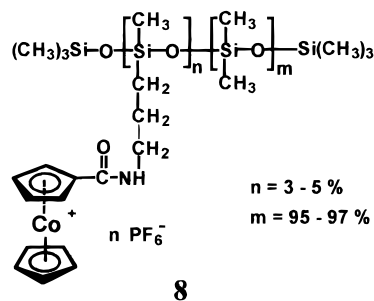
We have prepared two different types of siloxane-based cobaltocenium-containing polymers. The polycondensation of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate was effected under the same reaction conditions as those used to prepare compounds **1–3** and afforded polymer **6**, with a backbone consisting of alternating dimethylsiloxane segments and cobaltocenium moieties bonded through amide linkages (see Scheme 2). The reaction has been carried out using the minimum volume of solvent to dissolve the starting products. These high-concentration conditions were used to ensure maximization of the intermolecular condensation relative to the intramolecular cyclization process. Polymer **6** was isolated as a shiny greenish solid, which was found to be essentially insoluble in most common organic solvents. The high insolubility of this material precluded a complete characterization. Nevertheless, it was found to be partially soluble in DMSO, and thus, NMR characterization of the more soluble fraction could be performed.

Likewise, the condensation reaction of the same difunctional amine with the hexafluorophosphate salt of (chlorocarbonyl)cobaltocenium, in CHCl_3 solution, at room temperature and in the presence of Et_3N , affords the siloxane-bridged dimetallic model compound **7**, which has been prepared in order to aid the spectroscopic and electrochemical characterization of the polymers.

Scheme 2



On the other hand, reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Cl}\}]\text{PF}_6$ with amino(propyl)methyl(3–5%)–dimethylsiloxane(95–97%) copolymer, as a source of the NH_2 functionality, allows facile access to the block copolymer **8**, consisting of a poly(dimethylsiloxane) chain, in which pendant amide-linked cobaltocenium moieties are randomly distributed along the flexible methylsiloxane backbone. After purification, polymer **8** was isolated as a yellow gum, which hardens and solidifies on standing.



The dimetallic model compound **7** as well as the polymeric cobaltocenium salts **6** and **8** were structurally characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy as well as by elemental analysis and yielded data consistent with the assigned structures. The ^1H NMR spectrum of **7** showed the resonances of the cyclopentadienyl rings at 6.35, 5.98, and 5.91 ppm as well as resonances assigned to the $\text{CH}_2\text{CH}_2\text{CH}_2$ groups at 3.35, 1.67, and 0.61 ppm. The integration ratio of these resonances was consistent with the assigned structure. Broad, less well-resolved resonances were found in the ^1H NMR spectra of both polymers **6** and **8** compared to those of the corresponding model compound **7** but were also consistent with the presence of backbones containing amide-linked cobaltocenium moieties and dimethylsiloxane segments. For the cobaltocenium-substituted copolymer **8**, the ^1H NMR spectrum, together with elemental analysis, was important for the estimation of the degree of cobaltocenium functionalization. Thus,

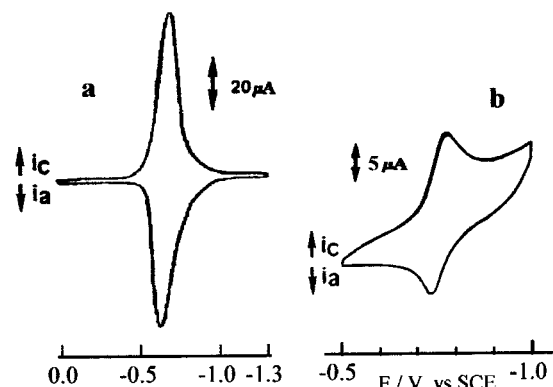


Figure 6. Cyclic voltammograms of (a) a film of polymer **8** evaporatively deposited on a glassy-carbon electrode, measured in $\text{CH}_3\text{CN}/0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4$, and (b) a film of polymer **8** + sodium *n*-dodecylbenzenesulfonate deposited on a glassy-carbon electrode, measured in $\text{H}_2\text{O}/1 \text{ M KCl}$.

satisfactory results were obtained when integration of the cobaltocenium and methyl protons was used, indicating that all the pendant amine groups in the siloxane chains have been derivatized with cobaltocenium moieties. The ^{13}C NMR spectra of **6–8** showed the expected resonances for the carbon atoms in the molecules in their different chemical environments. The ^{29}Si NMR spectra of both dimer **7** and polymer **6** show the expected single resonance centered at about 8.3 ppm corresponding to the dimethylsiloxane segment. Likewise, in the ^{29}Si NMR of the block copolymer **8**, in addition to the resonances corresponding to the two different polysiloxane blocks at -18.82 and -21.87 ppm, a small resonance was also detected at 7.33 ppm, which was assigned to the terminal OSiMe_3 units of the polymer chain.

The electrochemical reduction of the dimetallic model compound **7** and polymer **8** in DMF solutions is similar to that observed for the pyrrole derivatives **1** and **2**, and the corresponding redox potentials are indicated in Table 2. In the case of the model compound **7**, two simultaneous, but independent, one-electron transfers are associated with each reduction wave. This result indicates the noninteracting character of the two equivalent electroactive cobaltocenium moieties in the compound.

The redox properties of the polymer **8** have been also studied as films evaporatively deposited on electrode surfaces from a polymer-containing CH_2Cl_2 solution. The polymer films were characterized by cyclic voltammetry in fresh acetonitrile solutions containing only supporting electrolyte. The deposited films exhibit reproducible, well-defined reversible redox responses, owing to the cobaltocenium/cobaltocene system, characteristic of surface-confined redox couples (Figure 6a). It is also interesting to note the redox response of films of the block copolymer **8** in aqueous solution. In the CV of glassy-carbon electrodes modified with a film of **8**, measured in $\text{H}_2\text{O}/\text{KCl}$, only background current was observed, indicating that the redox reaction of the cobaltocenium moieties does not occur in the polymer film. The absence of redox waves in an aqueous medium is probably related to the highly hydrophobic character of the poly(dimethylsiloxane) polymer backbone, which hinders the diffusion of water and electrolyte ions into the polymer film. However, when an ionic surface-active agent such as sodium dodecylbenzenesulfonate or dode-

cyltrimethylammonium bromide was added to the polymer film, the diffusion through the polymer film is allowed and well-defined anodic and cathodic waves (see for example Figure 6b), due to the reduction of the cobaltocenium moieties in the polymer, appeared.

Summary

We have synthesized new cobaltocenium complexes containing electrochemically and chemically polymerizable pyrrole and allyl substituents. Electrode surfaces can be readily coated with stable and electroactive cobaltocenium polymeric films upon oxidative electrochemical polymerization of the new pyrrole-functionalized monomers **1–3**, resulting in detectable electroactive material persistently attached to the electrode surfaces. In addition, we have prepared novel redox-active, siloxane-based cobaltocenium polymers and block copolymers. Electrodes coated with films of the hydrophobic siloxane-based copolymer **8** show redox activity in acetonitrile and also in an aqueous solution when an ionic surface-active agent is added to the film. Work is now focused on detailed studies of the applications of electrodes modified with cobaltocenium-containing polymer films in the fields of molecular recognition and electrocatalysis.

Experimental Section

Materials and Equipment. All reactions were performed under an inert atmosphere (prepurified N_2 or 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 . The hexafluorophosphate salts of 1-(chlorocarbonyl)cobaltocenium and 1,1'-bis(chlorocarbonyl)cobaltocenium were prepared as described in the literature.²⁰ 1-(3-aminopropyl)pyrrole was prepared by reduction of 1-(2-cyanoethyl)pyrrole²¹ with lithium aluminum hydride in diethyl ether. The product was purified by distillation at $65\text{--}70$ °C/1.5 Torr. The following silicon-containing products were purchased from Petrarch Systems: *N*-(trimethylsilyl)allylamine, *O*-(trimethylsilyl)allyl alcohol, 1,3-bis(aminopropyl)-1,1,3,3-tetramethyldisiloxane, and (aminopropyl)methyl(3–5%)dimethylsiloxane(95–97%) copolymer. Allylamine and 1-(2-aminophenyl)pyrrole were obtained from Aldrich and used as received. Infrared spectra were recorded on a Bomem MB-100 FTIR spectrometer. NMR spectra were recorded on a Bruker-AMX (^1H , 300 MHz; ^{13}C , 75.43 MHz; ^{29}Si , 59.3 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) with reference to internal tetramethylsilane (SiMe_4) or to residual solvent resonances for ^1H and ^{13}C NMR (CDCl_3 : ^1H , δ 7.27 ppm; ^{13}C , δ 77.0 ppm). ^{29}Si NMR spectra, referenced externally to tetramethylsilane, were recorded with inverse-gated proton decoupling in order to minimize nuclear Overhauser effects. In some cases the solutions contained 0.015 M $\text{Cr}(\text{acac})_3$ in order to reduce T_1 's. FAB mass spectral analyses were conducted on a VG Auto Spec mass spectrometer equipped with a cesium ion gun. 3-Nitrobenzyl alcohol (M_n) were obtained with an Osmomat 070 vapor-pressure osmometer. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain.

(20) Sheats, J. E.; Rausch, M. D. *J. Org. Chem.* **1970**, *35*, 3254.

(21) Patterson, J. M.; Brasch, J.; Drenchko, P. *J. Org. Chem.* **1962**, *27*, 1652.

Electrochemical Measurements. Cyclic voltammetric experiments were performed on either a BAS CV-27 potentiostat or a PAR 362 potentiostat. Coulometric measurements were made with a PAR 362 potentiostat and a PAR 379 digital coulometer. A PAR 377A coulometry cell system fitted with a platinum-gauze working electrode was used. Electrochemical measurements were performed in acetonitrile and dichloromethane (both freshly distilled from calcium hydride under nitrogen) and in dimethylformamide (distilled in vacuo and stored over 4 Å molecular sieves). The supporting electrolyte was in all cases tetra-*n*-butylammonium perchlorate (Fluka), which was purified by recrystallization from ethyl acetate and dried at 60 °C under vacuum. It was used in a concentration of 0.1 M in all cyclic voltammetric measurements. A conventional sample cell operating under an atmosphere of prepurified nitrogen was used for cyclic voltammetry. All cyclic voltammetric experiments were performed using a platinum-disk working electrode, a gold-disk electrode, or a glassy-carbon-disk working electrode (for the three of them $A = 0.070 \text{ cm}^2$), each of which was polished prior to use with either 1 μm diamond paste (Buehler) or 0.05 μm alumina/water slurry and rinsed thoroughly with purified water and acetone. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counter electrode. Solutions for cyclic voltammetry were typically 1.0 mM in the redox-active species and were deoxygenated by purging with prepurified nitrogen. No *iR* compensation was used. The modification of electrode surfaces by electropolymerization of the pyrrole-functionalized monomers **1–3** was effected by electrochemical cycling as described earlier in the text. The preparation of electrodes coated with evaporatively deposited films of polymer **8** was accomplished by micropipetting a few microliters of a dichloromethane solution of the polymer containing about 1 mg/mL of the polymer onto the platinum or glassy-carbon electrode surface and allowing the solvent to evaporate to dryness. Infrared spectral changes during thin-layer bulk electrolyses were measured by using a spectroelectrochemical cell as described previously.^{12e} Infrared data were collected with a Bomem MB-100 FTIR spectrometer. Bulk electrolyses were controlled by a PAR 362 potentiostat.

X-ray Structure Determination Technique. A summary of the fundamental crystal data is given in Table 1. A yellow crystal of prismatic shape and dimensions $0.10 \times 0.15 \times 0.40 \text{ mm}^3$ was coated with an epoxy resin and mounted on an Enraf-Nonius CAD4 diffractometer with a monochromatic Mo K α radiation source ($\lambda = 0.71069 \text{ \AA}$). The cell dimensions were refined by least-squares-fitting the θ values of 25 accurate centered reflections within a 2θ range of $13\text{--}27^\circ$. Data were collected at 295 K using the $\omega\text{--}2\theta$ scan technique to a maximum $2\theta = 52^\circ$, from (0,0,0) to (26,12,22) to yield 4374 unique reflections; among them 1912 were considered observed, having $I > 3\sigma(I)$. The stability of the crystal was monitored every 100 reflections using 3 standard reflections; no significant decay of their intensities was observed. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Co and P were taken from ref 22. The position of the heavy atom was obtained from the Patterson function. The rest of the structure was solved by means of Fourier synthesis. An empirical absorption correction²³ was applied at the end of the isotropic refinements. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by the molecular geometry. A final refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms. Since no trends in ΔF vs F_o or $(\sin \theta)/\lambda$ were observed, no special weighting scheme has been applied. Final difference synthesis showed no significant

electron density. Most of the calculations were carried out with the X-ray 80 system.²⁴

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)NH(CH}_2\text{)}_3\text{NC}_4\text{H}_4\}]\text{-PF}_6$ (1**).** 1-(3-Aminopropyl)pyrrole (0.40 g, 3.2 mmol) and triethylamine (0.40 g, 3.9 mmol) were dissolved in 20 mL of dry chloroform and added dropwise under a nitrogen atmosphere to (chlorocarbonyl)cobaltocenium hexafluorophosphate (1.00 g, 2.5 mmol) in 30 mL of dry chloroform with stirring. The reaction mixture was stirred at room temperature overnight. After this time, the precipitate formed was separated by filtration, washed several times with CHCl_3 in order to remove small amounts of the triethylamine hydrochloride byproduct, and dried under vacuum. Compound **1** was isolated as an air-stable yellow solid. Yield: 0.80 g, 65%. Recrystallization can be effected by slow diffusion of cyclohexane in a concentrated solution of **1** in acetonitrile. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{CoN}_2\text{O}_2\text{PF}_6$: C, 44.62; H, 4.16; N, 5.79. Found: C, 44.52; H, 4.14; N, 5.62. FT-IR (KBr, cm^{-1}): $\nu(\text{NH})$, 3325; amide I, 1644; amide II, 1561; amide III, 1305, 830, 557. ^1H NMR (acetone- d_6 , 300 MHz): δ 2.07 (q, 2H, CH_2), 3.37 (t, 2H, $\text{CH}_2\text{-NH}$), 4.04 (t, 2H, NCH_2), 5.95 (s, 5H, C_5H_5), 5.98 (t, 2H, C_5H_4), 6.02 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 6.33 (t, 2H, C_5H_4), 6.76 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 8.09 (s, 1H, C(O)NH). ^{13}C NMR (acetone- d_6 , 75.43 MHz): δ 31.94 (CH_2), 38.37 (CH_2NH), 47.60 (NCH_2), 85.96 (C_5H_4), 86.71 (C_5H_4), 87.10 (C_5H_5), 108.62 ($\text{C}_4\text{H}_4\text{N}$), 121.25 ($\text{C}_4\text{H}_4\text{N}$), 162.15 (C(O)NH). MS (FAB; m/z (%)): 339.1 ($[\text{M} - \text{PF}_6]^+$, 100.0), 274.1 ($[\text{M} - \text{PF}_6 - \text{NC}_4\text{H}_4]^+$, 3.5), 188.0 ($[\text{M} - \text{PF}_6 - \text{C(O)NH(CH}_2\text{)}_3\text{NC}_4\text{H}_4]^+$, 4.9).

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_4\text{C(O)NH(CH}_2\text{)}_3\text{NC}_4\text{H}_4\}_2\text{Co}]\text{PF}_6$ (2**).** This compound was prepared similarly to compound **1**, starting from 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.00 g, 2.2 mmol), 1-(3-aminopropyl)pyrrole (0.61 g, 4.9 mmol), and triethylamine (0.75 g, 7.4 mmol). In this case, after evaporation of the solvent under vacuum, the resulting crude product was dissolved in CH_2Cl_2 and the solution washed with water in order to dissolve the triethylamine hydrochloride byproduct. The organic phase was separated and dried over anhydrous MgSO_4 . The solvent was removed under vacuum, to give 0.98 g (70% yield) of pure **2**, which was isolated as a bright greenish solid. Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{CoN}_4\text{O}_2\text{PF}_6$: C, 49.20; H, 4.67; N, 8.93. Found: C, 49.28; H, 4.77; N, 9.01. FT-IR (KBr, cm^{-1}): $\nu(\text{NH})$, 3417, 3239; amide I, 1660; amide II, 1551; amide III, 1300; PF_6^- , 840, 557. ^1H NMR (acetone- d_6 , 300 MHz): δ 2.10 (q, 2H, CH_2), 3.42 (t, 2H, CH_2NH), 4.00 (t, 2H, NCH_2), 5.98 (t, 2H, C_5H_4), 6.03 (t, 2H, C_5H_4), 6.11 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 6.71 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 7.46 (s, 1H, C(O)NH). ^{13}C NMR (chloroform- d , 75.43 MHz): δ 30.54 (CH_2), 38.43 (CH_2NH), 47.59 (NCH_2), 85.39 (C_5H_4), 86.67 (C_5H_4), 94.96 (C_5H_4), 108.48 ($\text{C}_4\text{H}_4\text{N}$), 120.68 ($\text{C}_4\text{H}_4\text{N}$). MS (FAB; m/z (%)): 489.2 ($[\text{M} - \text{PF}_6]^+$, 30.3).

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)NHC}_6\text{H}_4\text{NC}_4\text{H}_4\}]\text{-PF}_6$ (3**).** Compound **3** was prepared similarly to compound **1**, by reacting $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)Cl}\}]\text{PF}_6$ (1.00 g, 2.5 mmol), 1-(2-aminophenyl)pyrrole (0.45 g, 2.8 mmol), and triethylamine (0.40 g, 3.9 mmol). Purification of the reaction product was achieved in this case by redissolving the yellow crude product in acetone and the desired complex was precipitated by addition of *n*-hexane. Yield: 0.58 g (45%). Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{CoN}_2\text{O}_2\text{PF}_6$: C, 48.64; H, 3.50; N, 5.41. Found: C, 48.83; H, 3.36; N, 5.31. FT-IR (KBr, cm^{-1}): $\nu(\text{NH})$, 3268; amide I, 1653; amide II, 1538; amide III, 1303; PF_6^- , 836, 557. ^1H NMR (acetone- d_6 , 300 MHz): δ 5.88 (s, 5H, C_5H_5), 6.03 (t, 2H, C_5H_4), 6.33–6.36 (t, 2H, C_5H_4), 6.33–6.36 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 7.06 (t, 2H, $\text{C}_4\text{H}_4\text{N}$), 7.42–7.49 (m, 3H, $\text{C}_6\text{H}_4\text{N}$), 7.77 (m, 1H, $\text{C}_6\text{H}_4\text{N}$), 9.43 (s, 1H, C(O)NH). ^{13}C NMR (acetone- d_6 , 75.43 MHz): δ 85.17 (C_5H_4), 86.94 (C_5H_4), 87.32 (C_5H_5), 110.60 ($\text{C}_4\text{H}_4\text{N}$), 122.85 ($\text{C}_4\text{H}_4\text{N}$), 127.66 ($\text{C}_6\text{H}_4\text{N}$), 128.08 ($\text{C}_6\text{H}_4\text{N}$), 128.48 ($\text{C}_6\text{H}_4\text{N}$), 128.66 ($\text{C}_6\text{H}_4\text{N}$). MS (FAB; m/z (%)): 373.2 ($[\text{M} - \text{PF}_6]^+$, 100.0).

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216.1 ([M - PF₆ - NHC₆H₄NC₄H₄]⁺, 7.0), 188.1 ([M - PF₆ - C(O)NHC₆H₄NC₄H₄]⁺, 10.6).

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)NHCH}_2\text{CH}=\text{CH}_2\}\text{PF}_6\text{ (4)}$. Two condensation methods were used for the preparation of the compound **4**.

Method 1. Allylamine (0.14 g, 2.5 mmol) and triethylamine (0.30 g, 2.9 mmol) were dissolved in dry chloroform and added dropwise under nitrogen to (chlorocarbonyl)cobaltocenium (0.80 g, 2.0 mmol), in chloroform. The reaction mixture was stirred at room temperature overnight. A precipitate was formed during this time, which was separated by filtration, thoroughly washed with CHCl₃, and dried under vacuum to afford **4** as a yellow crystalline solid. Yield: 0.45 g (53%).

Method 2. A solution of *N*-(trimethylsilyl)allylamine (0.30 g, 2.3 mmol) in chloroform was added with stirring under nitrogen to (chlorocarbonyl)cobaltocenium (0.80 g, 2.0 mmol) also in chloroform. Stirring was continued for 5 h. The resulting yellow precipitate was filtered off, washed with chloroform, and dried under vacuum. Yield: 0.59 g (65%). Anal. Calcd for C₁₄H₁₅CoNOPF₆: C, 40.30; H, 3.63; N, 3.36. Found: C, 40.35; H, 3.53; N, 3.27. FT-IR (KBr, cm⁻¹): ν(NH), 3322, 3353; amide I, 1650; amide II, 1551; amide III, 1241; PF₆⁻, 835, 557. ¹H NMR (acetone-*d*₆, 300 MHz): δ 3.99 (m, 2H, CH₂), 5.14 (dq, 1H, CH=CH₂ (cis)), 5.25 (dq, 1H, CH=CH₂ (trans)), 5.94 (m, 1H, CH=CH₂), 5.95 (s, 5H, C₅H₅), 6.03 (t, 2H, C₅H₄), 6.37 (t, 2H, C₅H₄), 8.15 (s, 1H, C(O)NH). ¹³C NMR (acetone-*d*₆, 75.43 MHz): δ 42.89 (CH₂), 84.97 (C₅H₄), 85.12 (C₅H₅), 86.35 (C₅H₄), 95.67 (C₅H₄), 116.60 (CH=CH₂), 135.14 (CH=CH₂). MS (FAB; *m/z* (%)): 272.1 ([M - PF₆]⁺, 100.0).

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)OCH}_2\text{CH}=\text{CH}_2\}\text{PF}_6\text{ (5)}$. Compound **5** was prepared following method 2, starting from (chlorocarbonyl)cobaltocenium (1.00 g, 2.5 mmol) and *O*-(trimethylsilyl)allyl alcohol (0.70 g, 5.3 mmol). From the reaction mixture a yellow solid was filtered, which after drying under vacuum was identified as **5**. The filtrate was cooled to -30 °C, and yellow crystals of pure **5** were also isolated. Yield: 0.90 g (86%). Anal. Calcd for C₁₄H₁₄CoO₂PF₆: C, 40.20; H, 3.35. Found: C, 40.26; H, 3.10. FT-IR (KBr, cm⁻¹): ν(C=O), 1730; PF₆⁻, 832, 557. ¹H NMR (acetone-*d*₆, 300 MHz): δ 4.88 (m, 2H, CH₂), 5.35 (dq, 1H, CH=CH₂ (cis)), 5.48 (dq, 1H, CH=CH₂ (trans)), 6.05 (s, 5H, C₅H₅), 6.10 (m, 1H, CH=CH₂), 6.12 (t, 2H, C₅H₄), 6.40 (t, 2H, C₅H₄). ¹³C NMR (acetone-*d*₆, 75.43 MHz): δ 67.46 (CH₂), 86.48 (C₅H₄), 87.37 (C₅H₅), 87.99 (C₅H₄), 90.05 (C₅H₄), 119.51 (CH=CH₂), 132.69 (CH=CH₂), 163.79 (C(O)O). MS (FAB; *m/z* (%)): 273.1 ([M - PF₆]⁺, 100.0), 233.0 ([M - PF₆ - CH₂CH=CH₂]⁺, 6.6).

Synthesis of Polymer 6. A dry, deoxygenated chloroform solution of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (0.68 g, 2.7 mmol) and freshly distilled triethylamine was added to 1,1'-bis(chlorocarbonyl)cobaltocenium (1.25 g, 2.7 mmol) in chloroform. After a few minutes with stirring, a slight increase of the temperature was observed and a green solid immediately appeared. The reaction mixture was stirred overnight. The precipitate was collected by filtration, washed thoroughly with chloroform to remove the triethylamine hydrochloride, and dried in vacuo. Polymer **6** was isolated as a green solid (1.1 g). Anal. Calcd for [C₂₂H₃₄CoN₂O₃Si₂PF₆]_{*n*}: C, 41.63; H, 5.40; N, 4.42. Found: C, 40.98; H, 5.02; N, 4.36. FT-IR (KBr, cm⁻¹): ν(NH), 3314; amide I, 1650; amide II, 1552; amide III, 1292; PF₆⁻, 559. ¹H NMR (acetone-*d*₆, 300 MHz): δ 0.05 (s, 6H, SiCH₃), 0.52 (m, 2H, CH₂Si), 1.54 (m, 2H, CH₂),

3.19 (m, 2H, NHC₆H₅), 5.89 (br, 2H, C₅H₄), 6.34 (br, 2H, C₅H₄), 8.31 (br, 1H, C(O)NH). ¹³C NMR (dimethyl sulfoxide-*d*₆, 75.43 MHz): δ 1.43 (SiCH₃), 16.27 (CH₂Si), 23.79 (CH₂), 43.53 (NHCH₂), 86.15 (C₅H₄), 88.0. (C₅H₄), 95.56 (OC-C₅H₄), 161.16 (CO). ²⁹Si NMR (dimethyl sulfoxide-*d*₆, 59.3 MHz): δ 8.30.

Synthesis of $[\{\eta^5\text{-C}_5\text{H}_5\}\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{C(O)NH(CH}_2\text{)}_3\text{Si(CH}_3\text{)}_2\}\text{PF}_6\text{]}_2\text{(7)}$. (Chlorocarbonyl)cobaltocenium (1.00 g, 2.5 mmol) was added to a chloroform solution, previously stirred at room temperature, of triethylamine (0.51 g, 5.0 mmol) and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (0.31 g, 1.2 mmol). The reaction mixture was stirred overnight. Subsequently, a precipitate was collected by filtration, washed several times with chloroform to remove small amounts of triethylamine hydrochloride, and dried in vacuo. Dimer **7** was isolated as a yellow solid. Yield: 0.57 g (47%). Anal. Calcd for C₃₂H₄₄Co₂N₂O₃Si₂P₂F₁₂: C, 39.66; H, 4.54; N, 2.89. Found: C, 38.97; H, 4.32; N, 2.74. FT-IR (KBr, cm⁻¹): ν(NH), 3428, 3322; amide I, 1643; amide II, 1557; amide III, 1305; PF₆⁻, 559. ¹H NMR (acetone-*d*₆, 300 MHz): δ 0.09 (s, 6H, SiCH₃), 0.61 (m, 2H, CH₂Si), 1.67 (m, 2H, CH₂), 3.35 (q, 2H, NHC₆H₅), 5.91 (s, 5H, C₅H₅), 5.98 (t, 2H, C₅H₄), 6.35 (t, 2H, C₅H₄), 8.16 (t, 1H, C(O)NH). ¹³C NMR (dimethyl sulfoxide-*d*₆, 75.43 MHz): δ 1.22 (SiCH₃), 16.05 (CH₂Si), 23.72 (CH₂), 43.30 (NHCH₂), 84.74 (C₅H₄), 86.49 (C₅H₄), 86.71 (C₅H₅), 95.01 (OC-C₅H₄), 161.89 (CO). ²⁹Si NMR (dimethyl sulfoxide-*d*₆, 59.3 MHz): δ 8.34. MS (FAB; *m/z* (%)): 823.0 ([M - PF₆]⁺, 100.0), 678.0 ([M - 2PF₆]⁺, 34.7).

Synthesis of Polymer 8. Polymer **8** was prepared by starting from (chlorocarbonyl)cobaltocenium (1.00 g, 2.5 mmol) and (aminopropyl)methyl(3-5%)-dimethylsiloxane(95-97%) copolymer (6.9 g) in a chloroform solution in the presence of triethylamine. After evaporation of the solvent under vacuum, the resulting residue was purified by repeated treatment with dichloromethane/acetonitrile. Polymer **8** was isolated as a yellow viscous oil which solidified on standing. Anal. Calcd for *n* = 5% and *m* = 95%: C, 33.95; H, 7.19; N, 0.73. Found: C, 34.07; H, 6.81; N, 0.80. *M_n* (VPO, THF): 4900. FT-IR (KBr, cm⁻¹): ν(NH), 3420, 3320; amide I, 1641; amide II, 1561; PF₆⁻, 558. ¹H NMR (acetone-*d*₆, 300 MHz): δ 0.14 (s, 99H, SiCH₃), 0.64 (m, 2H, CH₂Si), 1.71 (m, 2H, CH₂), 3.36 (m, 2H, CH₂NH), 5.93 (s, 5H, C₅H₅), 6.00 (m, 2H, C₅H₄), 6.37 (m, 2H, C₅H₄), 8.01 (br, 1H, NH). ¹³C NMR (acetone-*d*₆, 75.43 MHz): δ 1.02, 1.43 (SiCH₃), 15.03 (CH₂Si), 23.36 (CH₂), 43.13 (NHCH₂), 84.6 (C₅H₄), 86.56 (C₅H₄), 86.73 (C₅H₅), 95.31 (OC-C₅H₄), 161.49 (CO). ²⁹Si NMR (acetone-*d*₆, 59.3 MHz): δ 7.33, -19.78, -22.43.

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Supporting Information Available: Tables of all bond distances and angles, torsion angles, displacement parameters, and atomic coordinates for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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