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An Electrochemical Study of the Protonation Site of the Cobaltocene Anion and of Cyclopentadienylcobalt(I) Dicarbollides

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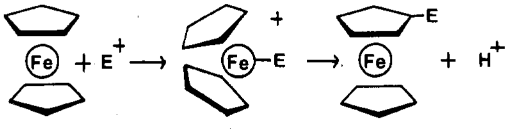
The reaction of electrochemically generated Co(I) π complexes with phenol in nonaqueous solvents has been studied by dc polarography, cyclic voltammetry, differential pulse polarography, and bulk electrolysis. Deuterium-labeling experiments establish that the protonation of the cobaltocene anion takes place directly at the ligand and does not involve a metal hydride intermediate. Cyclopentadienylcobaltacarboranes reduced to the Co(I) state also react with phenol in what seems to be a parallel pathway.

Introduction

The role played by the metal in the reactions of metallocenes has been an important and often controversial subject. Structures like **1**, involving direct bonding of a reacting ligand to the metal, have often been assumed to be involved in metallocene reactions, particularly in the electrophilic substitution reactions of ferrocene.[1-3] The most widely studied reaction seems to be the protonation of ferrocene, for which NMR evidence for **1** (E = H) is obtained. Discussions of this reaction can be found in ref 4–9.



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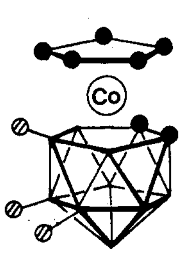
Protonation reactions of other, more electron-rich, metallocenes have been studied without much success, due partly to the tendency of these compounds to undergo oxidation in acidic media. The protonation of nickelocene, $(C_5H_5)_2Ni$, in trifluoroacetic acid has recently been shown to occur directly at the cyclopentadienyl ligand to form $(C_5H_5)Ni(C_5H_6)^+$, without intervention of a Ni–H intermediate.[10]

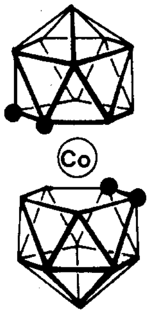
Cobaltocene is also an electron-rich metallocene, but its treatment with acids generally leads to formation of $(C_5H_5)_2Co^+$ or to decomposition.[11-13] In contrast to the behavior of ferrocene, attempts to carry out electrophilic substitution on cobaltocene have been unsuccessful. However, electrophilic addition reactions are known to occur.[13] Knowledge of the site of electrophilic attack on Cp_2Co is of central interest to attempts to rationalize the differences in reactivity of the Fe and Co metallocenes. This paper reports a new approach to the problem, in which we first reduce the cobalticinium ion (**2**) by two electrons to the cobaltocene anion, Cp_2Co^-, and then allow the anion to react with weak acids added to the solution. All of the data are consistent with the attack taking place directly at the ligand, with no metal hydride intermediate. Data on analogous cobalt dicarbollide complexes **3–5** are also included.

Experimental Section

Cobalticinium hexafluorophosphate was made by stirring an air-saturated solution of cobaltocene in benzene over 20% aqueous HCl for 3 h. The aqueous layer was filtered and an excess of KPF_6 in water added. The resulting $Cp_2Co^+PF_6^-$ was filtered and recrystallized from acetone/ethanol. Cyclopentadienyl(cyclopentadiene)cobalt, $CpCoC_5H_6$, and its deuterated analogue $CpCoC_5H_5D$ were made from Cp_2Co^+ and $LiAlH_4$ (or $LiAlD_4$) by the method of Green and co-workers.[14] The cobaltacarboranes[15] (π-cyclopentadienyl)(π-1,2-dicarbollyl)cobalt (**3**, $CpCoB_9C_2H_{11}$), bis(π-1,2-dicarbollyl)cobaltate [**4**, $(B_9C_2H_{11})_2Co^-$, Et_4N^+ salt], and $(B_9C_2H_8Br_3)CoCp^-$, Et_4N^+ salt (**5**), were obtained from Professor M. F. Hawthorne. **2–5** are all air-stable yellow Co(III) compounds, whereas $CpCoC_5H_6$ is air-sensitive, particularly in solution.



3,5



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● = CH
⊘ = H in 3
⊘ = Br in 5

Tetra-*n*-butylammonium hexafluorophosphate was used as supporting electrolyte (0.1 or 0.2 M) for all electrochemical experiments. It was made by metathesis of Bu_4NI and NH_4PF_6 in acetone/water and recrystallized several times from 95% ethanol. *N,N*-Dimethylformamide (DMF) was Spectro Grade. 1,2-Dimethoxyethane (glyme) and tetrahydrofuran (THF) were distilled from the potassium ketyl of benzophenone or from $LiAlH_4$ to ensure dryness and eliminate peroxides. Electrochemical solutions were purged with prepurified nitrogen which was passed over an oxygen-scavenging catalyst and through pure solvent before entering the cell. Standard Metrohm or H-cells were used for electrolyses. A Princeton Applied Research (PAR) Model 173 potentiostat with Model 179 digital coulometer, or the PAR Model 170 electrochemistry system, was used for voltammetry and coulometry. The aqueous saturated calomel electrode was used as reference electrode. Other electrochemical procedures were as previously reported.[16]

Results and Discussion

Reversibility of the Co(II)/Co(I) Reductions. Each of the compounds **2–6** undergoes two separate one-electron reductions involving a Co(III) ⇌ Co(II) ⇌ Co(I) reduction (Figure 1). Substitution of a dinegatively charged dicarbollide ligand for the cyclopentadienide ligand in **2–4** results in a negative shift in $E_{1/2}$ values, but the bromo-substituted compound **5** is the easiest of all to reduce (Table I). The Co(III) ⇌ Co(II) reductions have all been noted elsewhere,[15,17-21] and it is the Co(II) ⇌ Co(I) couple which is of interest here.

The second reduction wave of each compound [Co(II) ⇌ Co(I)] is a diffusion-controlled, reversible, one-electron process. This was established from the heights of the waves (I_d values), slopes of the dc polarographic waves (ca. 60 mV),[22] cyclic voltammetry peak separations (see ref 23), current functions[24,25] (constant vs. scan rate), and i_a/i_c ratios[26,27] (near unity at slow scan rates) in cyclic voltammetry (CV). There were nuances of change in some of these parameters when the solvent was varied. For example, CV scans on mercury in glyme for Cp_2Co/Cp_2Co^- gave i_a/i_c ratios greater than unity

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Table I. Voltammetric Data for Cobalt π Complexes

		Co(III) $\rightleftarrows$ Co(II)[a]		Co(II) $\rightleftarrows$ Co(I)[b]		
compd	solvent	$E_{1/2}$[d]	i_{p_a}/i_{p_c}[c] (V^f)	$E_{1/2}$[d]	i_{p_a}/i_{p_c}[e] (V^f)	E_{p_c}(protonated product)[c]
Cp_2Co^+	glyme	−0.81	1.00 (50)	−1.90	1.14 (50)	−2.30
$CpCo(B_9C_2H_{11})$	glyme	−1.19	1.00 (200)	−2.21	0.97 (200)	−2.70
	THF	−1.18	1.01 (100)	−2.23	1.00 (100)	
$CoCo(B_9C_2H_8Br_3)$	THF	−0.78	1.05 (50)	−1.84	1.10 (50)	−2.28
$Co(B_9C_2H_{11})_2$	glyme	−1.38	1.00 (60)	−2.38	1.02 (60)	
	THF	−1.43	1.01 (100)	−2.45	1.00 (100)	...

[a] First reduction wave. [b] Second reduction wave. [c] Peak potential of cathodic wave observed after addition of phenol to solution. [d] Dc polarographic half-wave potential in volts vs. aqueous saturated calomel electrode. [e] Ratio of anodic-to-cathodic currents in cyclic voltammetry, calculated by method of ref 27. [f] ν = scan rate in mV/s.

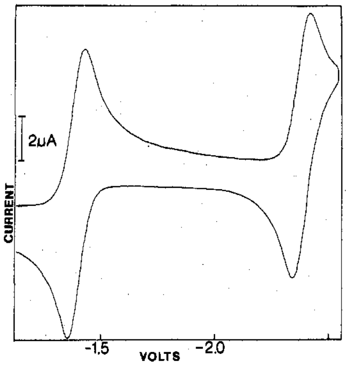


Figure 1. Cyclic voltammogram at a hanging mercury drop electrode of 4×10^{-4} M $(B_9C_2H_{11})_2Co^-$ in glyme; scan rate 100 mV/s.

(ca. 1.1–1.2 at slow scan rates), indicating perhaps that weak adsorption of the anion occurs in this solvent.[28] It has already been pointed out[29] that Cp_2Co^- undergoes a follow-up reaction (not a protonation) in CH_3CN but is stable in glyme[29] and in DMF.[30] Protonations of the Co(I) species were therefore carried out in glyme, THF, and DMF in order to ensure that no other side reactions were occurring. Thus, we investigated the electrochemical characteristics of solutions of the cobalt compounds to which weak acids were added, at the potential of the second wave. The follow-up reactions which occurred were due to reaction of the acids with the Co(I) species Cp_2Co^-, $CpCo(B_9C_2H_{11})^{2-}$, $CpCo(B_9C_2H_8Br_3)^{2-}$, or $(B_9C_2H_{11})_2Co^{3-}$.

Effect of Acids on Co(II) $\rightleftharpoons$ Co(I) Reduction. The reaction of Cp_2Co^- with acids is extremely facile. The cobaltocene anion is rapidly protonated by weak acids such as phenols or benzoic acid. When a few milligrams of phenol was added to a glyme solution, i_a/i_c values for the $Cp_2Co^{0/-}$ wave dropped well below unity and a new wave appeared at about −2.3 V which was more prominent at slower scan rates. This wave was at the same potential as the known two-electron reduction of cyclopentadienyl(cyclopentadiene)cobalt, $CpCoC_5H_6$ (**6**).[31] Although phenol itself does not exhibit a wave in this solvent, it has the effect of making the potential of the electrochemical background discharge more positive and increases the current base line after about −2.3 V. This made it difficult to quantify the amount of current for the $CpCoC_5H_6$ wave by CV and dc polarography, in other than a qualitative sense. Consequently, we used differential-pulse polarography, which yielded a well-resolved peak-shaped curve (Figure 2), for quantitative analysis of the $CpCoC_5H_6$ wave.

Thus in the presence of phenol, the reduction of cobaltocene is an ECE process [(A)–(C)] in which $CpCoC_5H_6$ is formed

$$\text{(A)} \quad Cp_2Co + e^- \rightleftharpoons Cp_2Co^- \quad E_{1/2} = -1.89\ \text{V}$$

$$\text{(B)} \quad Cp_2Co^- + C_6H_5OH \rightarrow CpCoC_5H_6 + C_6H_5O^-$$

$$\text{(C)} \quad CpCoC_5H_6 + 2e^- \rightarrow \text{products} \quad E_{1/2} = -2.30\ \text{V}$$

(step B) and subsequently reduced at a more negative potential (step C). Confirmation of the ECE process was found in the drop-time dependence of the ratio of the wave at −2.3 V to that at −1.9 V in either normal- or differential-pulse polarography. At longer drop times, the relative height of the more negative wave increased, as greater time was available for the protonation (B) to occur. These data allowed us to measure the rate of the protonation reaction by using a modification of the method of Nicholson et al.[32] These authors calculated the interrelationships for an ECE mechanism between drop time, rate constant of the intervening chemical reaction, and the height of the dc polarographic wave (i_k), compared to the height obtained in the absence of the reaction (i_d).

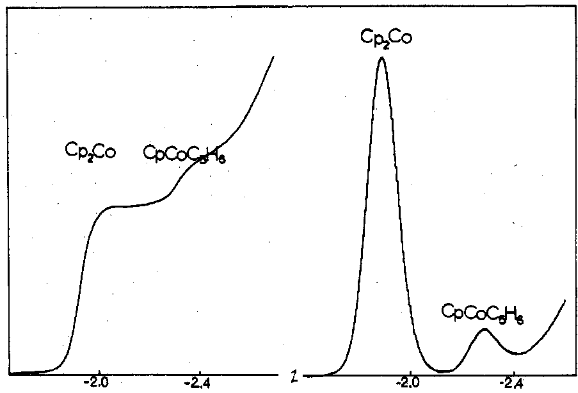


Figure 2. Left: Dc polarogram (only trace of current maxima shown) of Cp_2Co^+ in glyme with phenol added. The wave at about −2.3 V is due to $CpCoC_5H_6$. Right: Differential pulse polarogram of same solution.

The ratio i_k/i_d and the drop time are then used to calculate the rate constant, k_{app}, of the chemical reaction. Since our most accurate current–potential data were obtained by using differential-pulse polarography (DPP) (vide ante), we sought to adapt this method to our DPP measurements to obtain a rate constant. Although no theoretical treatment has appeared for the study of an ECE process by DPP, there should be a correspondence between i_k, the total height of the dc polarographic wave due to the two electron-transfer steps (E_1CE_2), and the sum of the peak currents of the two DPP waves for E_1 and E_2. Consequently we used, in place of i_k/i_d, the value $(i_1 + i_2)/i_1$, where i_1 and i_2 were the peak currents at −1.9 and −2.3 V, respectively.[33] Under these assumptions, we calculated values of $k_{app}t$ (Table II) and plotted average values against concentration of phenol (Figure 3). This analysis gave a pseudo-first-order rate constant of k_{app} = 29[phenol] $L^2/(mol^2\ s)$ for the protonation of Cp_2Co^-. This rate constant should be viewed as an approximate number, since the calculations were not based on a rigorous model. However, the point to be made is that the cobaltocene anion reacts fairly rapidly even with a weak acid like phenol.

Metal vs. Ligand Protonation Site of Cp_2Co^-. Although the above data establish that Cp_2Co^- is protonated at one of the cyclopentadienyl rings, they do not eliminate the possibility

Table II. Differential Pulse Polarography Data Used To Calculate Rate of Protonation Reaction of Cp_2Co^- with Phenol[a]

[phenol], mM	t,[b] s	i_k/i_d[c]	$k_{app}t$,[d] L^2/mol^2	k_{app}, $L^2/(mol^2\ s)$
3.0	0.5	1.02 (5)	0.05	0.10
3.0	1.0	1.04 (5)	0.10	0.10
3.0	2.0	1.07	0.15	0.07
3.0	5.0	1.12 (5)	0.28	0.06
5.1	0.5	1.04 (5)	0.10	0.20
5.1	1.0	1.05 (5)	0.12	0.12
5.1	2.0	1.12	0.28	0.14
5.1	5.0	1.21	0.51	0.10
8.1	0.5	1.06	0.12	0.24
8.1	1.0	1.12	0.27	0.27
8.1	2.0	1.21	0.52	0.26
8.1	5.0	1.34	0.98	0.20

[a] Glyme solution, 0.1 M Bu_4NPF_6, 5.4×10^{-4} M $Cp_2Co^+PF_6^-$. DPP parameters: pulse width 25 mV, sampling duration 15 ms. [b] Mechanically controlled drop time. [c] Ratio of the sum of the peak heights at −1.9 and −2.3 V to that at −1.9 V (corrected for the 2e reduction at −2.3 V: see text). [d] The apparent rate constant ($k_{app}t$ is derived from the i_a/i_c value and the working curve from Table I of ref 32.

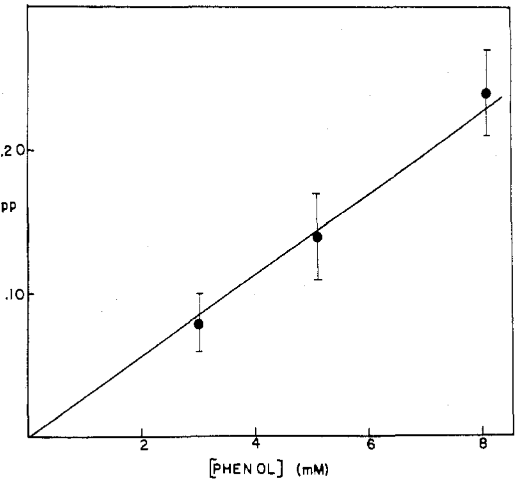
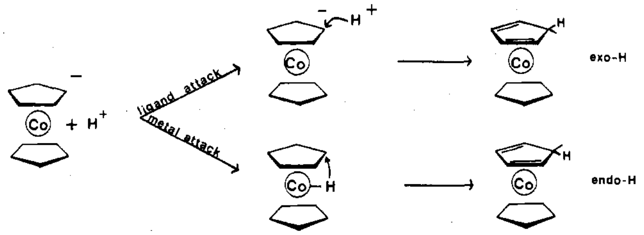


Figure 3. Apparent rate constant for the protonation of Cp_2Co^- calculated from differential-pulse polarography data, plotted against phenol concentration. Error bars give standard deviation.

that a metal hydride intermediate like **1** may mediate the process.

If the metal hydride intermediate is involved the incoming proton must occupy a position endo to the metal. In principle, direct attack upon the ligand could yield either an exo or endo product, but steric considerations strongly favor exo attack.[10,34–38] The stereochemistry of the proton addition was probed by reaction of the cobaltocene anion with D_2O. As shown below, only the exo-deuterated product was isolated.



Since stereospecific exo attack can result only from direct attack upon the ligand, it must be concluded that there is no evidence for a metal hydride intermediate in the Cp_2Co^- protonation.

Bulk Electrolysis of Cobaltocene in Presence of Acids: Isolation of $CpCoC_5H_5D$. **6** or its deuterated analogue, $CpCoC_5H_5D$, can be isolated in quantitative yield by working up an electrolyzed solution of cobaltocene in DMF/water, with use of inert-atmosphere techniques. Thus, electrolysis of 200 mg of $Cp_2Co^+PF_6^-$ at −2 V in 40 mL of DMF containing 5% H_2O and 0.2 M Bu_4NPF_6 passed 2.1 equiv of electrons ($Cp_2Co^+ \rightarrow Cp_2Co^-$) and resulted in a deep red solution. After addition of a large amount of water, ether was used to extract the red $CpCoC_5H_6$. The ether layer was washed first with a K_2CO_3 solution and then by water, dried ($MgSO_4$), and evaporated, yielding 100 mg (90%) of $CpCoC_5H_6$, which was identified by its NMR and IR spectra.[14] A similar result was obtained in DMF/phenol solutions (58 mg of Cp_2Co^+, 40 mg of phenol). After electrolysis at −2 V a virtually quantitative yield of $CpCoC_5H_6$ was obtained by an isolation procedure similar to that described for the DMF/water electrolysis. The cyclopentadiene product could also be obtained from aqueous ethanol electrolysis of Cp_2Co^+, but in lower yield.[39]

$CpCoC_5H_5D$ was isolated after the electrolysis of Cp_2Co^+ in DMF/5% D_2O at −2 V. The infrared spectrum of the compound showed four peaks in the vicinity of 2050 cm^{-1} and showed no bands in the 2750-cm^{-1} region ($CpCoC_5H_6$ gives a strong band at 2742 cm^{-1}).[14] Thus the spectrum was identical with that reported[14] for $CpCoC_5H_5D$ prepared by the action of $LiAlD_4$ on Cp_2Co^+. These bands fall at an unusual energy and hence were originally thought to arise from close proximity of an endo hydrogen or deuterium to the metal.[14] However, later structural determinations[40–42] on substituted $CpCoC_5H_5R$ compounds showed conclusively that the 2750-cm^{-1} band was only present when there is an exo C–H. Since this band is absent in our $CpCoC_5H_5D$, this shows that the proton addition results exclusively in the exo product and gives strong support to the statement that *electrophilic addition of a proton to Cp_2Co^- does not involve the metal* in any direct way.

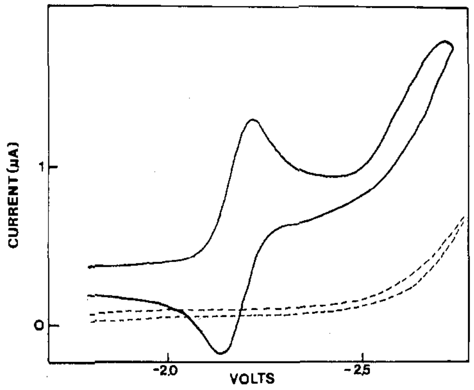


Figure 4. Cyclic voltammetry scans of a glyme solution at a hanging mercury drop electrode at 50 mV/s scan rate: dotted line, phenol added; solid line, phenol plus $CpCo(B_9C_2H_{11})$.

Voltammetry of Co(I) Carboranes in Presence of Acid. As noted previously, the cobaltacarboranes **3**–**5** formed stable Co(I) species in THF or glyme as a dianion (**3** and **5**) or a trianion (**4**). The mixed-sandwich compounds **3** and **5** are protonated by acids with the protonation product giving a wave about 0.5 V more negative than for the Co(II) $\rightleftharpoons$ Co(I) couple.

Consider the cyclic voltammetry data for $CpCo(B_9C_2H_{11})$ in glyme/phenol (Figure 4). The i_a/i_c values for the second reduction dropped below 1 and a new wave (irreversible) appeared at $e_{p_c} = -2.70$ V, barely resolved from background. The wave is more prominent at slower scan rates, indicating its kinetic character, controlled by the rate of the protonation. Similar results were obtained with the bromo-substituted mixed-sandwich $CpCo(B_9C_2H_8Br_3)$ (Figure 5). In this case, all the waves were shifted to less negative values due to the electron-withdrawing nature of the bromo substituent, and the product peak came at $e_{p_c} = -2.28$ V. The height of the product peak was, again, kinetically controlled.[43]

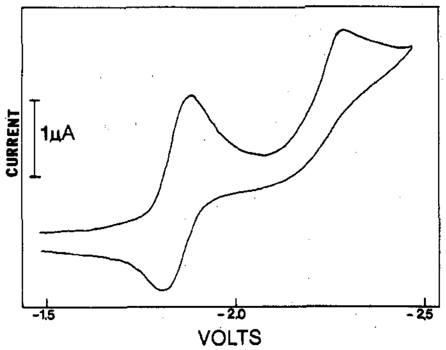


Figure 5. Cyclic voltammogram of $CpCo(B_9C_2H_8Br_3)$ in THF at a hanging mercury drop after addition of phenol. Prior to addition of phenol, the wave at −2.3 V was not present. Scan rate 50 was mV/s.

Thus, the reduction mechanisms of Cp_2Co^+, $CpCo(B_9C_2H_{11})$, and $CpCo(B_9C_2H_8Br_3)$ in the presence of added acids are strikingly similar. Each exhibits a kinetically controlled, irreversible, wave 0.4–0.5 V negative of the Co(II) $\rightleftharpoons$ Co(I) couple. Since the wave for the cobaltocene case involves protonation of the Cp ligand, we assume that the protonation of the cyclopentadienyl cobaltacarboranes also involves attack at the cyclopentadienyl ring, rather than at the dicarbollide cage, and results in the compounds $(C_5H_6)Co(B_9C_2H_{11})^-$ and $(C_5H_6)Co(B_9C_2H_8Br_3)^-$.

Attempts were made to learn if the bis(dicarbollide) Co(I) species $Co(B_9C_2H_{11})_2^{3-}$ was protonated under similar conditions, but our efforts were frustrated by the very negative potential needed to form this species, leaving insufficient potential range in which to look for the protonated product wave.

Conclusion

Electrophilic attack at the cobaltocene anion proceeds directly at the ligand and does not involve a metal-bonded intermediate, at least when the proton is the electrophile. Protonation of cyclopentadienylcobaltacarboranes probably follows the same route, with electrophilic attack at the Cp ring favored over the carborane cage.

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Registry No. **2**, 12241-42-8; **3**, 37100-20-2; **4**, 11078-84-5; **5**, 55760-46-8; **6**, 33032-03-0; Cp_2Co, 1277-43-6; Cp_2Co^-, 55917-09-4; $CpCo(B_9C_2H_{11})^-$, 51850-04-5; $CpCo(B_9C_2H_{11})^{2-}$, 70749-39-2; $CpCo(B_9C_2H_8Br_3)^-$, 70775-24-5; $CpCo(B_9C_2H_8Br_3)^{2-}$, 70788-24-8; $Co(B_9C_2H_{11})_2^{2-}$, 51850-08-9; $Co(B_9C_2H_{11})_2^{3-}$, 51850-08-9; $(C_5H_6)Co(B_9C_2H_{11})^-$, 70788-25-9; $(C_5H_6)Co(B_9C_2H_8Br_3)^-$, 70788-26-0.

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(22) Slope of the plot of $-E$ vs. log $[i/(i_d - i)]$.
(23) In more conductive solvents like DMF or acetone, peak separations were near 60 mV, but in THF and glyme they tended to be a minimum of about 70–75 mV, indicative of the high resistance and concomitant iR loss in the ether solvents.
(24) The cathodic current function is defined as the cathodic peak current divided by the square root of scan rate. It is constant for an uncomplicated diffusion-controlled electron transfer (see ref 25).
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