J. Am. Chem. Soc. **1981**, *103*, 4779–4787

Structural Consequences of Electron-Transfer Reactions. 5. Electrochemically Induced Isomerizations of (Cyclooctadiene)- and (Cyclooctatetraene)cobalt Compounds[1a]

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Received December 1, 1980

Abstract: Electrochemical investigations of the reduction of (cycloocta-ene)cyclopentadienylcobalt compounds in nonaqueous solvents are reported. (COT)CoCp (COT = cyclooctatetraene, Cp = η^5-C_5H_5) exists as interconverting 1,5-bonded or 1,3-bonded isomers in solutions of the neutral complex. Both isomers are reducible by one electron, but the radical ion of (1,5-COT)CoCp undergoes rapid and irreversible isomerization to (1,3-COT) $CoCp^-$. Conventional dc polarography, differential pulse polarography, cyclic voltammetry, phase-selective ac polarography, and controlled potential coulometry have been used to characterize these processes. The monoanion (1,3-COT)$CoCp^-$ can be reduced by another electron to an unstable dianion or protonated to yield (cyclooctatriene)CoCp. The pentamethylcyclopentadienyl analogue, (COT)CoC_5Me_5, also undergoes the isomerization process. (1,5-COD)CoCp (COD = cyclooctadiene) undergoes one-electron reduction at a highly negative potential to an anion that, in some solvents, slowly rearranges to (1,3-COD)$CoCp^-$. In DMF the nonconjugated isomer (1,5-COD)$CoCp^-$ is relatively stable. Neutral (1,3-COD)CoCp can be produced in solution by bulk reduction and subsequent reoxidation of (1,5-COD)CoCp, and the rate of isomerization of (1,3-COD)CoCp to (1,5-COD)CoCp was measured. For both COT and COD complexes, the 1,5-bonded isomer is thermodynamically more stable in the neutral compounds and less stable in the anions. Isomerization rates are many orders of magnitude *faster* in the anions.

One of the most interesting aspects of metal π complex chemistry is that a given polyolefin may bond in a number of different ways to a metal. In a gross sense, the nature of the polyolefin–metal bond usually depends on the electronic requirement of the metal (i.e., the EAN rule),[1b] but often there are more subtle forces at play. For example, cyclooctadiene (COD) can donate two pairs of electrons to a variety of transition-metal moieties which require four electrons to achieve the inert-gas configuration, but this fact alone does not determine whether COD bonds as a 1,5-polyolefin or as a 1,3-polyolefin to the metal. In certain cases, the ability of a polyolefin to bond in more than one isomeric form to a given metal moiety has provided the basis for metal-catalyzed isomerizations of the polyolefin, one of the earliest examples in the organometallic literature being the $Fe(CO)_5$-catalyzed isomerization of 1,5-COD to 1,3-COD.[2]

In a general sense, it is important to understand the factors, both electronic and steric, which control the fashion in which unsaturated hydrocarbons bond to metals. This paper, and the one following it, present results on one aspect of this problem, namely, the *effect of metal oxidation state on structural preferences for metal-bonded polyolefins*. We report a series of investigations, using electrochemical techniques, on the reduction of cyclooctatetraene (COT), COD, and, to a lesser extent, cyclooctatriene (COTr) π complexes of cyclopentadienylcobalt (CpCo). The results show that the 8-membered polyolefin rings bond preferentially as four-electron donors through nonconjugated double bonds in the neutral, parent, compounds, (1,5 bonding preferred) but that the polyolefin rearranges to bond through adjacent double bonds (a 1,3-isomer) in the radical anions derived from these parent species. Since the nonconjugated isomer can be regenerated upon reoxidation of the anion, the phenomenon we have discovered may be called *reversible electrochemical isomerization of a metal–hydrocarbon bond*. A brief account of data on the (COT)CoCp compound appeared earlier.[3]

Experiment Section[4]

Chemicals. (COT)CoCp was synthesized in good yield (<50%) by using a procedure which was a hybrid of those reported in the literature.[5,6] Thus, 2 mL (14 mmol) of $CpCo(CO)_2$ (Strem Chemicals) and 2.3 mL (20 mmol) of freshly distilled COT (Aldrich or Strem) were placed in a 50-mL quartz flask containing 10 mL of degassed ethylcyclohexane, and the mixture was refluxed under dinitrogen for 8 h while being stirred and irradiated with a Rayonet Photochemical Reactor (Model RRR-100). After the solution was cooled in a dry ice/ethanol bath, brown (COT)CoCp was separated by filtration and purified by two recrystallizations from pentane and by vacuum sublimation (60 °C (0.1mm Hg)). A melting point of 79–81 °C (lit.[5] 80–81 °C) was obtained. In the preparation of (COD)CoCp, an identical procedure was employed, except that 2.0 mL (20 mmol) of 1,5-cyclooctadiene (Aldrich) was substituted for COT, and the reflux was carried out for 18 h. Sublimation at 70 °C (0.1mmHg) yielded golden yellow crystals, mp 102–104 °C (lit.[7] 102.5 °C). Proton NMR and UV–vis spectra were in accordance with literature.[7-9] (1,3,5-Cyclooctatriene)cyclopentadienylcobalt, (COTr)CoCp, was synthesized in low yield by the literature procedure[7] by using a sample of COTr donated by Organometallics, Inc. (East Hampstead, N.H.). (Pentamethylcyclopentadienyl)cobalt cyclooctatetraene, (COT)CoC_5Me_5, was supplied by Dr. John L. Spencer of the University of Bristol. Each of the cyclopentadienylcobalt cyclooctaene compounds were relatively air-stable, although extend storage (weeks) was done under N_2 at −10 °C, and samples were frequently resublimed to assure purity. 1,3-COD (Chemical Procurement Laboratories) was distilled and Na/K alloy (MSA Research Corp.), and ceric ammonium sulfate (G.F. Smith) was used as received. Sodium napthalenide was prepared by mixing a 1:1 molar ratio of sodium and naphthalene in deoxygenated tetrahydrofuran. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was prepared by metathesis of Bu_4NI (Eastman) and ammonium hexa-

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[1] Green, M. L. H. "Organometallic Compounds", 3rd. ed.; Chapman and Hill: London, 1968.

[2] Arnett, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1961**, *83*, 2954–2955.

[3] Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3407–3408.

[4] The following abbreviations are used throughout: η^5-C_5H_5 (Cp); cyclooctadiene (COD); cyclooctatetraene (COT); cyclooctatriene (COTr); dimethylformamide (DMF); tetrahydrofuran (THF); diffusion current constant ($I_d = i_d/C_0m^{2/3}t^{1/6}$; i_d = polarographic plateau current, m = flow rate of mercury through capillary, t = drop time); cyclic voltammetry (CV); D_0 = diffusion coefficient of electroactive species; k_s = standard heterogeneous electron-transfer rate.

[5] Fritz, H. P.; Keller, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.* **1961**, **16B**, 348.

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[7] Nakamura, A.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 452–453.

[8] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593–3597.

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fluorophosphate (Ozark Mahoning) in acetone, followed by addition of water to precipitate the Bu_4NPF_6. It was recrystallized from 95% ethanol and vacuum dried. Dimethylformamide (Fisher Spectrograde) was vacuum distilled for calcium hydride through an 8-ft column and used immediately after distillation. Both 1,2-dimethyoxyethane (Fisher) and tetrahydrofuran Aldrich Goldlabel) were vacuum distilled from $LiAlH_4$ onto a Na/benzophenone mixture for storage and then distilled as needed. Acetonitrile (Aldrich Spectrograde) was stored in vacuo over CaH_2 and distilled before use. Dichloromethane (Aldrich Spectrograde) was distilled from CaH_2.

Analytical Methods. ^1H NMR data were acquired with a 60-MHz JEOL C-60HL spectrometer, using an internal Me_4Si standard. Vapor-phase chromatography was performed on the Hewlett-Packard Model 5700A gas chromatograph and utilized a thermal conductivity detector. A 6-ft copper column containing 5% squalene on Chromsorb P was used to analyze for hydrocarbons (column temperature 140 °C, injector and detector temperatures 200 °C). With a He flow rate of 60 mL/min, retention times of 7.8, 8.6, and 6.0 min were observed for 1,3-COD, 1.5-COD, and COT, respectively. High-performance liquid chromatography (HPLC) was accomplished with a Waters Model 6000A solvent delivery system and either the Model 450 variable-wavelength UV–vis detector or the Model R401 differential refractometer detector. Most analyses were performed on a C-18M Bondapak reverse-phase column using 70% methanol/water as eluant.

Electrochemical Procedures. Several different electrochemical instruments were employed. Phase-selective ac polarography and differential pulse polarography were performed on a Princeton Applied Research (PAR) Model 170 electrochemistry system. Most conventional dc polarography, cyclic voltammetry, and voltammetry at the rotating platinum electrode experiments were performed on the PAR 173 potentiostat with Model 176 digital coulometer. Waveforms for polarography or cyclic voltammetry were provided by a slow linear ramp or by the Hewlett-Packard Model 3300A function generator. Recordings were made either on a Hewlett-Packard Model 7001A X-Y recorder (scan rates below ca.0.8 V/s) or a Tektronix Model 564B storage oscilloscope. For the assurance of greater accuracy in making current measurements from rapid scan cyclic voltammograms, polaroid pictures from tracings on the storage oscilloscope were made into 8 × 10 prints and measurements were made from the enlarged tracings. Voltammetry experiments employed a conventional three-electrode configuration with a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode, separated from the solution by an agar bridge and a fine frit. The working electrode was either a dropping mercury electrode, a rotating platinum electrode (Sargent Synchronous rotator, 1800 rpm), or a hanging mercury drop electrode. When the platinum button electrode was used, the pretreatment consisted of refluxing the electrode in nitric acid, washing it with water, and then soaking it in a saturated ferrous ammonium sulfate solution in 1 M sulfuric acid. After being washed with water and dried with a tissue, the electrode was inserted into the solution.

For bulk electrolysis experiments a rounded-bottom Metrohm cell (Brinkman) was employed with the anodic and cathodic half-cells separated by a fine frit. The working electrode was either a platinum gauze basket or a mercury pool. A Pt gauze cylinder was used as the auxiliary electrode. When the mercury pool was used as the working electrode, it was situated at the bottom of the cell with the cylindrical auxiliary electrode compartment located above and parallel to the pool a few centimeters away in the solution. The Pt basket, when employed as the working electrode, was in a cocylindrical arrangement in solution with the auxiliary electrode compartment. The SCE in this arrangement was separated from the solution by an agar bridge and a fine frit.

When electrochemical experiments required more rigorous inert atmosphere conditions, they were carried out in a Vacuum Atmosphere Corp. drybox with an H.E.-63-P drytrain. The drybox was used instead of our earlier developed vacuum line techniques[10] because of the large number of manipulations of electrolyzed solutions required in this project.

Low-temperature electrochemical experiments done in the drybox were accomplished by passing nitrogen gas through a copper coil, cooled at liquid-nitrogen temperature. The cooled nitrogen gas was then passed into the drybox via vacuum rubber tubing, through a jacketed Metrohm cell, and then out into the room atmosphere. Two valves were used at the inlet and outlet of the drybox to prevent contamination from the outside air. By regulating the flow rate of nitrogen, we could control the temperature of the solution in the cell to a ±2 °C. Bench-top high-temperature cyclic voltammetry experiments were done by circulating heated water from the Masterline Forma-Temp Jr. Model 2095 bath and circulator through the jacketed Metrohm cell. The temperature in this setup could be regulated to ±1 °C.

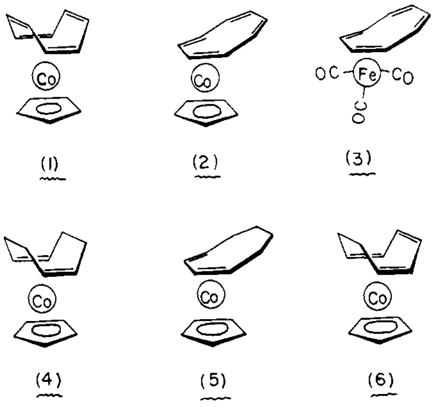

Figure 1. Compounds studied.

Table I. Polarographic $E_{1/2}$ Potentials for Reductions of (Cyclooctaene)cyclopentadienylcobalt Compounds in Nonaqueous Solvents[a]

compd	solvent	$E_{1/2}^{(1)}$	$E_{1/2}^{(2)}$
(COT)CoCp	THF	1,3-isomer: -1.82^b 1,5-isomer: -2.05^b	-2.50
	CH_3CN	1,3-isomer: -1.82^c 1,5-isomer: -2.05^c	-2.50
(COD)CoCp	THF	-2.45	
	CH_3CN	-2.45	
	DMF	-2.35	
(COTr)CoCp	THF	-2.28	

[a] Volts vs. SCE. [b] Combined value of $I_d = 2.37$. [c] Combined value of $I_d = 3.77$.

Results

Structures **1** and **4** are the traditionally accepted structures of the cyclooctatetraene and cyclooctadiene, respectively, π complexes with (η^5-cyclopentadienyl)cobalt.[5-9,11] Frequent mention has been made of the preference for 8-membered carbocyclic polyolefin rings to bond in a tub-like manner to CpCo (as 1,5-dienes), but in a chair-like fashion to $Fe(CO)_3$.[1,8,9] However, in our preliminary communcation[3] we reported that although the tub-like (1,5-COT)CoCp (**1**) is thermodynamically more stable than the 1,3-bonded isomer (**2**), solutions of (COT)CoCp contain both **1** and **2**, in equilibrium, with a ratio of **1**:**2** of about 3:1 at room temperature. In the case of (1,5-COD)CoCp (**4**), we find no evidence of any of the 1,3-isomer **5** in solutions of **4**. However, **5** can be generated through reduction of **4** to its radical anion. The remainder of this paper details our experiments of the electrochemically initiated redox interconversions of 1,3- and 1,5-bonded COT and COD rings on CpCo.

I. Reduction of (COT)CoCp. General Voltammetric Behavior. At first glance, dc polarograms of (COT)CoCp in either THF, CH_3CN, or DMF/0.1 M Bu_4NPF_6 show two reduction waves, each having a diffusion current constant (I_d)[4] appropriate for a one-electron process, at ca. $E_{1/2} = -2.00$ and -2.50 V (table I). Closer inspection of the first wave revealed that it actually is a composite of two waves, with the minor component occurring at the less negative potential (ca. −1.80 V). Voltammetric techniques having higher resolving capabilities showed better separation of the two waves. Scans employing cyclic voltammetry (CV), differential pulse polarography, and phase-selective ac polarography are shown in Figure 2. The small wave is definitiely not an adsorptive prewave, since it obeys the usual criteria for diffusion-controlled mass transport in both dc polarography and CV experiments. Furthermore, idential behavior was observed on both

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(10) Holloway, J. D. L.; Senftleber, F. C.; Geiger, W. E., Jr. *Anal. Chem.* **1978**, *50*, 1010–1013.

(11) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4821–4829.

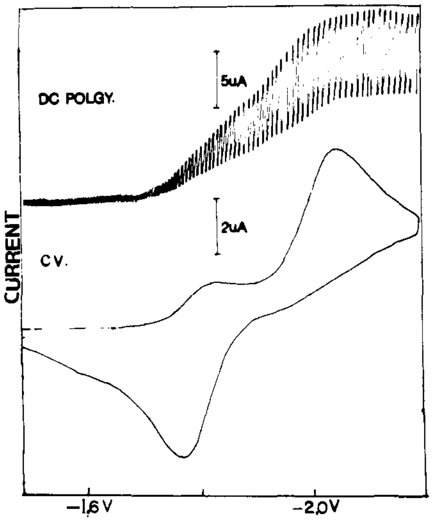

Figure 2. Comparison of techniques of dc polarography (drop time = 2 s) and cyclic voltammetry (CV) (scan rate = 100 mV/s) for a 4 × 10^{-4} M solution of (COT)CoCp in CH_3CN/0.1 M Bu_4NPF_6.

mercury and platinum electrodes.

Combined with NMR data,[3] it is clear that the small wave at -1.8 V must be assigned to reduction of **2**, (1,3-COT)CoCp, and that the wave at -2.00 V arises from reduction of **1**, (1,5-COT)CoCp. It will become clear in the discussion below that the wave at -2.50 V is due to reduction of $\mathbf{2}^-$, and this is detailed in a later section. Electrochemical proof that **1** and **2** are in equilibrium was found by varying the temperature of the solution. At lower temperatures the ratio of **1**:**2** increased dramatically, but the original wave heights were found when the solution was restored to room temperature. Reduction of the minor, 1,3-bonded, isomer **2** is highly reversible. CV scans reversed at the foot of the major isomer wave (ca. -1.9 V) showed an anodic peak coupled to the minor reduction wave, with a peak separation of 60 mV at a scan rate (v) of 0.50 V/s.[3] Reduction of the 1,5-isomer is highly irreversible (Figure 2), but the anodic wave at -1.78 V due to oxidation of $\mathbf{2}^-$ was greatly enhanced in CV scans which included the reduction of **1**. This suggested that the anion of **1** rearranged during the scan reversal to the anion of **2**, which was then reoxidized at the appropriate potential, -1.78 V. Two schemes consistent with the overall mechanism are shown below. Triangular Scheme I assumes that the 1,3-anion is formed in the heterogeneous electron-transfer step from either **2** (reduction reversible) or **1** (reduction irreversible). Square Scheme II assumes finite existence of the 1,5-anion and requires the isomerization $\mathbf{1}^- \rightarrow \mathbf{2}^-$ to occur in a homogeneous reaction subsequent to electron transfer. The essence of the mechanistic question is whether the isomerization occurs subsequent to or concomitant with the heterogeneous electron transfer, and our present data do not allow definition between these two possibilities. Irrespective of any inherent instability of $\mathbf{1}^-$, this anion would be expected to react rapidly in a homogeneous electron-transfer process with **2**, since the $E°$ for the 1,5-isomer is apparently negative of that for the 1,3-isomer. This mechanism could then yield $\mathbf{2}^-$ through two separate routes, (1) and (2). Whatever the microscopic details

$$\text{(1,3-COT)CoCp} + e^- \rightleftarrows \text{(1,3-COT)CoCp}^- \quad (1)$$

$$\text{(1,5-COT)CoCp} + e^- \rightleftarrows \text{(1,5-COT)CoCp}^- \quad (2a)$$

$$\text{(1,5-COT)CoCp}^- + \text{(1,3-COT)CoCp} \rightarrow \text{(1,5-COT)CoCp} + \text{(1,3-COT)CoCp}^- \quad (2b)$$

of the mechanism, the gross feature, namely, the conversion of **1** into **2** by one-electron reduction, was demonstrated unequivocally by rapid multiple scan CV experiments. If continuous triangular waveforms were applied to the electrode, the relative heights of reduction waves for **1** and **2** changed drastically, with the first cathodic peak increasing on second and subsequent cycles. This reflected the fact that the concentrations of **1** and **2** near the electrode surface were no longer identical with those in bulk of solution, since on each scan some of the 1,5-isomer **1** had been converted to the 1,3-isomer **2** by cyclic reduction and reoxidation. After several scans, a steady-state volammogram was obtained in which **1** was present almost exclusively near the electrode surface (Figure 3). The importance of this experiment is that it proves that **1** and **2** give rise to a common reduction product and not different ones that coincidentally oxidize at -1.78 V.

Scheme I

$$\begin{tikzcd}
\mathbf{2} \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon, "e^-"'] & \mathbf{1} \arrow[dl, "e^-"'] \arrow[l, shift left, harpoon] \\
\mathbf{2}^- \arrow[u, shift left, harpoon] &
\end{tikzcd}$$

Scheme II

$$\begin{tikzcd}
\mathbf{2} \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon, "e^-"'] & \mathbf{1} \arrow[l, shift left, harpoon] \arrow[d, "e^-"] \\
\mathbf{2}^- \arrow[u, shift left, harpoon] & \mathbf{1}^- \arrow[l, "k^-"']
\end{tikzcd}$$

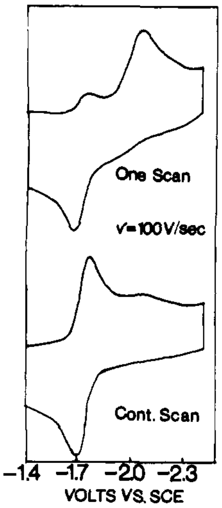

Figure 3. Comparison of single CV scan (top) and steady-state (continuous) CV scan for 5 × 10^{-4} M (COT)CoCo in CH_3CN/0.1 M Bu_4NPF_6 (scan rate = 100 V/s on hanging mercury drop). Reversible couple for $\mathbf{2} \rightleftharpoons \mathbf{2}^-$ predominates in continuous cycle experiment.

Bulk electrochemical reduction at a mercury cathode at -2.20 V in DMF or THF resulted in conversion of the isomer mixture to predominantly that of the 1,3-anion, $\mathbf{2}^-$. One electron was passed (n_{app} = 1.1 e^-) as the color of the solution went from light brown to orange. After electrolysis was complete, removal of the potential resulted in reoxidation of $\mathbf{2}^-$ back to **2**, apparently due to reaction with trace oxygen or other adventitious impurities. As this occurred, CV scans showed reappearance of the curve for **1**, since this is the thermodynamically favored neutral isomer. Within a few minutes the CV wave heights were identical with those observed before electrolysis. Thus, $\mathbf{2}^-$ is extremely sensitive toward oxidation, which is not surprising since it's $E°$ value is about 1 V more negative than that of cobaltocene in the same electrolyte.[12]

Electrochemical Measurement of Equilibrium Constants. At 298 K, the waves for both **1** and **2** display peak currents which are proportional to the square root of the cyclic scan rate, showing that the mass transport of electroactive species is diffusion controlled at this temperature.[13] So, over the time scale of this experiment (ca. 20 s in the low scan-rate range of 50 mV/s), there is not appreciable interconversion of the two neutral isomers, that is, equilibrium is "frozen". This is consistent with room-temperature NMR data.[3] At higher temperatures, the peak current for **2** increases relative to that of **1** due partly to the shift in

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(12) Geiger, W. E. Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2632-2634.

(13) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706-723.

equilibrium in favor of **2**. But before the peak heights were used to measure the temperature dependence of the equilibrium constant, the scan rate dependence of the waves at higher temperatures had to be evaluated.

Theory for linear scan voltammetry involving chemical reaction preceding electron transfer has been worked out in detail.[13,14]

$$\mathbf{2} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{1}$$

$$K = \frac{[\mathbf{1}]}{[\mathbf{2}]} = \frac{[(1,5\text{-COT})\text{CoCp}]}{[(1,3\text{-COT})\text{CoCp}]}$$

This is case III in the paper by Nicholson and Shain;[13] we refer to the case in which the term $(a)^{1/2}/K(l)^{1/2}$ is intermediate (a is a variable proportional to scan rate and l is the sum of the rate constant k_f and k_b in the equilibration reaction). The only difference is that in our case both species involved in the equilibration are electroactive in the region of potential scan. The scan-rate dependence of the peak current values may be viewed as follows. When the potential reaches a value sufficient for reduction of **2**, that is, at the beginning of the first wave, a decrease in the surface concentration of **2** occurs compared to the bulk solution concentration, due to the electrolysis. If the rate constant k_b is high enough, some **1** is converted to **2** in an attempt to maintain the equilibrium concentration of **2**. This "extra" **2** is also electrolyzed, and the net effect is an increase in the peak current for the first wave. In the extreme case of very rapid kinetics, the second wave, due to **1**, could virtually disappear.

If one is to use the peak currents to measure the equilibrium concentrations of **1** and **2**, the scan rate chosen must be rapid enough to outrun the kinetic effects discussed in the preceding paragraph. Accordingly, we employed scan rates of ca. 20 V/s in DMF-solutions of (COT)CoCp over the temperature range 298–343 K (Figure 4) for measurement of the temperature dependence of K. This scan rate was sufficient in each case to outrun the kinetic effects discussed above. Equilibrium concentrations of **1** and **2** were calculated from the peak currents, and a plot of $\ln K$ vs. $1/T$ is shown in Figure 5. A ΔH of −3.2 kcal/mol was calculated from the slope. Because the two voltammetric waves were significantly overlapped, the current contribution at the second wave, for **1**, and had to be adjusted for the current still flowing from the first wave,[15] on the basis of the wave shapes calculated by Nicholson and Shain.[13]

AC Polarographic Measurements: k_s Values of $\mathbf{2} \rightleftarrows \mathbf{2}^-$. Phase-sensitive ac polarographic measurements were made at the dropping mercury electrode in DMF/0.1 M Bu_4NPF_6 on the waves due to the two isomers. The ac response of the first wave, due to (1,3-COT)CoCp, is straightforward, typical of a nearly reversible electron transfer.[17] Peak current (in-phase component) was proportional to square root of the ac frequency over the range 17–600 Hz (107–3768 radians/s, ω). The cotangent of the angle, ϕ, defined by the difference between phases of the applied potential and detected current at the peak potential was also proportional to $\omega^{1/2}$ and passed through unity (ϕ = 45°) when extrapolated to zero frequency (Figure 6). Smith has shown[17] that the slope of such a plot equals $D^{1/2}/2^{1/2}k_s$, and if the diffusion coefficient is known, a heterogeneous electron-transfer rate, k_s, can be calculated. D_0 was calculated[18] from the diffusion current constant of (COT)CoCp in DMF to be 9.1×10^{-6} cm²/s, and this yields a value of k_s = 0.16 cm/s for the electron-transfer rate $\mathbf{2} \rightleftharpoons \mathbf{2}^-$. This is very close to the value (0.24 cm/s) measured for reduction of the closely related compound (1,3-COT)$Fe(CO)_3$ in DMF[19] and is rapid enough to suggest that no drastic structure changes occur in the structure of (1,3-COT)CoCp during its reduction.

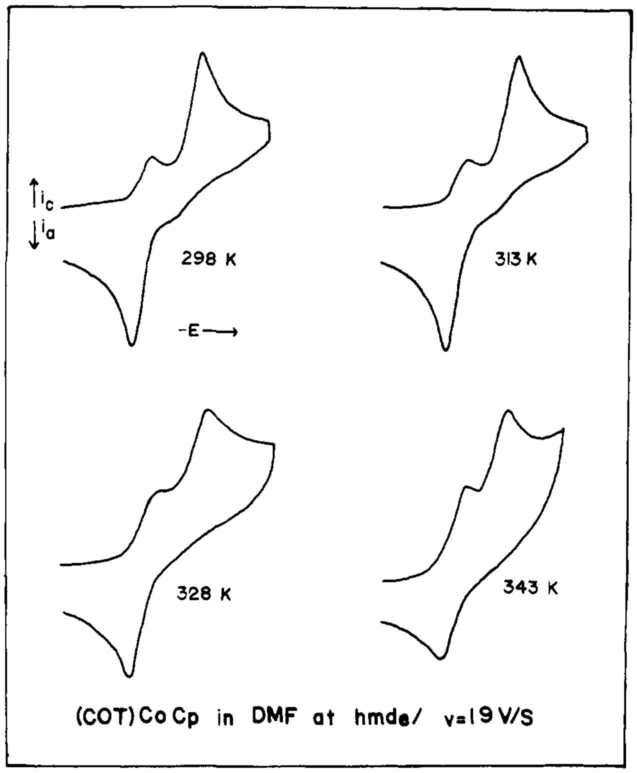

Figure 4. Cyclic voltammetry scans of (COT)CoCp (4×10^{-4} M) at hanging mercury drop in DMF/0.1 M Bu_4NPF_6 at temperatures shown. Potential scans range from −1.4 to −2.2 V.

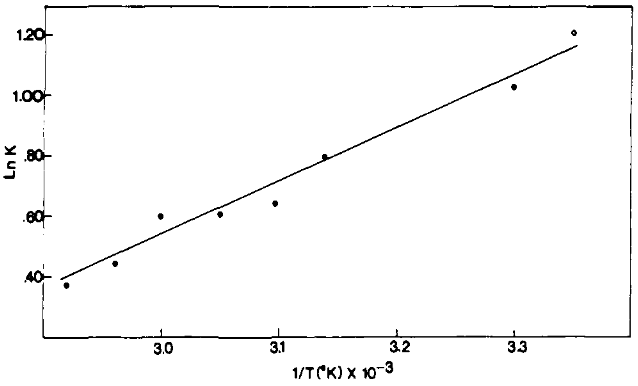

Figure 5. Plot of $\ln K$ vs. $^1/_T$ from variable-temperature CV data for $\mathbf{1} \rightleftharpoons \mathbf{2}$ equilibration.

The height of the ac peak current for the reduction of the 1,5-isomer **1** is much less than that of **2** and the disparity increases at higher frequencies. The cotangent of the phase angle could only be measured over a limited frequency range, since the out-of-phase component was difficult to measure accurately at frequencies above about 200 Hz (see Figure 7). Over this fairly low-frequency range, the $\cot \phi$ vs. $\omega^{1/2}$ plot was linear (Figure 6). Although this behavior coincides with theory for a quasi-reversible charge transfer to a stable product, the irreversible cyclic voltammetry behavior of **1** seems to rule out this interpretation of the ac response. A reviewer has pointed out that a linear $\cot \phi$ vs. $\omega^{1/2}$ plot is also expected in the case of reversible charge

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[14] Keller, H. E.; Reinmuth, W. H. *Anal. Chem.* **1972**, *44*, 1167–1178.

[15] The current function data for a reversible wave (Table I in ref 13) and the Cottrell relationship[16] can be used to calculate the contribution of the first wave at the potential of the current peak of the second wave. For example, 200 mV negative of the peak potential of the wave for **2**, a current equal to 45% of the peak current of **2**, was still flowing. This was subtracted from the measured peak current on the second wave, due to **1**, to yield the true value.

[16] Macdonald, D. B. "Transient Techniques in Electrochemistry"; Plenum Press: New York, 1977; p 72.

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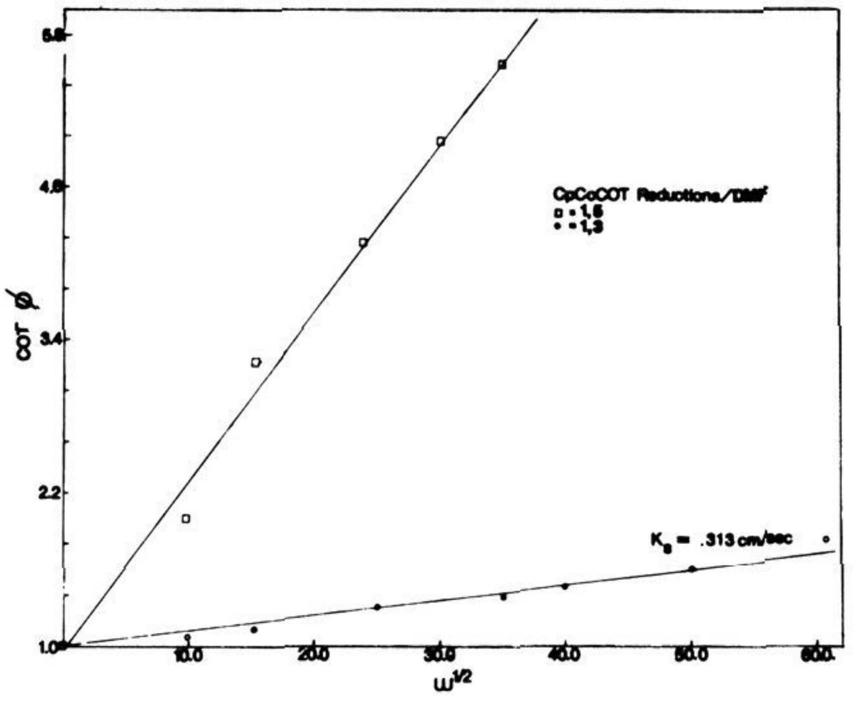


Figure 6. Plot of cot ϕ vs. square root of ac frequency (ω) for two isomers of (COT)CoCp in DMF–0.1 M Bu_4NPF_6: □, 1,5-isomer; ●, 1,3 isomer.

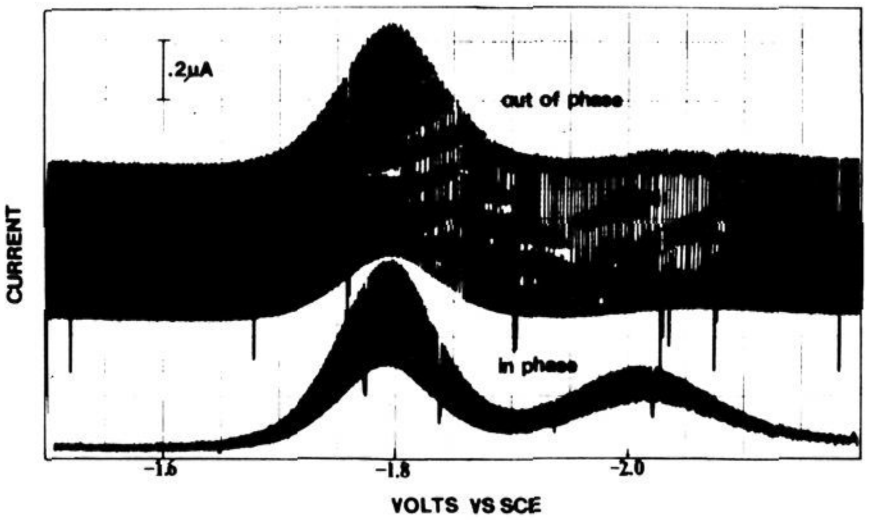


Figure 7. AC polarograms of (COT)CoCp (4.8×10^{-4} M) in DMF/0.1 M Bu_4NPF_6 (frequency = 200 Hz, drop time = 2 s).

transfer followed by a very rapid homogeneous chemical reaction (EC case). This linearity prevails in the low-frequency limit [$\omega \ll k$(isomer)], and this EC model (the chemical reaction being the isomerization of 1^- to 2^-) seems to adequately account for both the CV and ac data. Thus, our data do not allow distinction between isomerization taking place *during* the electron-transfer step and isomerization subsequent to formation of (1,5-COT)-CoCp$^-$. But we can say that if the 1,5-anion has a discrete existence, it is very short indeed.

II. Reduction of (COT)Co(η^5-C_5Me_5). A sample of the pentamethylcyclopentadienyl analogue of (COT)CoCp was obtained from Dr. John Spencer of the University of Bristol. Qualitatively, (COT)Co(C_5Me_5) behaved very much like (COT)CoCp, in that it showed two CV waves, one minor, assigned to the 1,3-bonded isomer **8**, and the other being assigned to the 1,5-bonded isomer **7** in about the same ratio as for the cyclopentadienyl analogues.[20] Both isomers reduce at potentials significantly more negative than their Cp analogues, an effect attributable to the electron-donating property of the methyl groups. On mercury in CH_3CN/0.1 M Bu_4NPF_6, cathodic peak potentials of −2.05 and −2.40 V were noted (v = 0.5 V/s), and, again, a single anodic peak appeared at −1.99 V (Figure 8). As with the Cp analogues, repetitive high speed CV scans (v = 125 V/s) resulted in the reversible couple **8**/**8**$^-$ growing in at the expense and almost total exclusion of the cathodic peak for **7**.

At higher temperatures, the height of the cathodic wave for

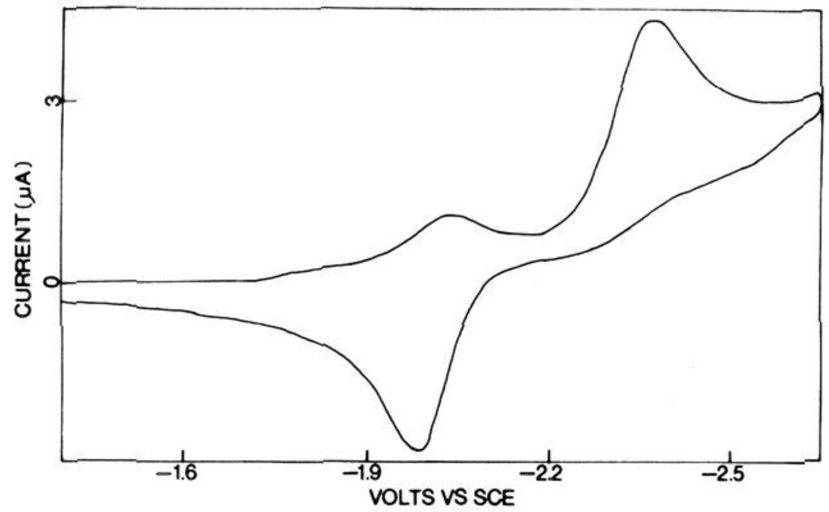
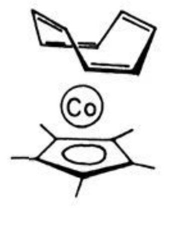


Figure 8. CV scan at mercury drop for 5.0×10^{-4} M (COT)CoC_5Me_5 in CH_3CN/0.1 M Bu_4NPF_6 (scan rate = 0.50 V/s).



(7)

(8)

— = CH_3

8 increased during single-cycle CV experiments, again showing that the 1,5-bonded isomer **7** is thermodynamically favored for the neutral compounds. One attempt to obtain K_{eq} vs. temperature data in DMF solutions, using CV methods outlined previously, failed due to excessive data scatter, and further attempts were frustrated by lack of sufficient sample. Bulk electrolysis in DMF at −2.50 V resulted in passage of one electron and a color change from light brown to red. A CV scan after electrolysis showed mainly the wave for the 1,3-isomer **8**$^-$, clearly the more stable isomer in the anion form. Within a couple of minutes, reaction of the anion with adventitious oxygen or other impurities resulted in oxidation of **8**$^-$ and restoration of the original color and voltammograms of the solution. The very negative reduction potentials of these species make their anions extremely difficult to handle in solution.

Thus it may be concluded that, although the methyl groups on the cyclopentadienyl ring exert an electronic influence over the reduction potentials of the two isomers, there is qualitatively little effect of methyl substitution on the isomeric equilibrium.

III. Reduction and Protonation of the Anion (1,3-COT)CoCp$^-$. As mentioned in Results section I, there is a polarographic wave at $E_{1/2}$ = −2.50 V in nonaqueous solutions of (COT)CoCp. CV scans resolved this wave sufficiently from electrolyte discharge to allow some mechanistic investigations to be made. At slow scan rates the reduction was irreversible, but above about 0.06 V/S an anodic reverse peak began to appear so that at high scan rates these appeared to form a quasi–reversible couple with $E°$ = −2.47 V. This must be ascribed to the process

$$\text{(1,3-COT)CoCp}^- + e^- \rightleftharpoons \text{(1,3-COT)CoCp}^{2-} \quad E° = -2.47 \text{ V}$$

since all evidence shows that at potentials negative of −2 V, it is only the 1,3-bonded isomer which is present in the anionic form at the electrode surface.

The dianion 2^{2-} is subject to a follow-up reaction, yielding a product which itself is reduced at a potential more positive than that at which it is reduced (an ECE mechanism). This results in current values which are increased at slow scan rates, compared to that expected for a one-electron diffusion-controlled reduction. Plots of cathodic current function ($i_p/v^{1/2}$) as a function of scan rate were employed for diagnosis of this mechanism.[21,22] Figure 9 compares the current function data in CH_3CN for the $0 \rightleftharpoons 1-$ waves (combined) with data on the $1- \rightleftharpoons 2-$ wave. The first waves

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(20) NMR data on this compound, at room temperature, establish presence of both the 1,5-isomer [δ 5.8 and 2.7 (4-CH), 1.5 (5-CH_3)] and the 1,3-isomer [δ 5.0 (8-CH, 1.7 (5-CH_3)]: Spencer, J. L.; Firth, S. University of Bristol, personal communication, 1980.

(21) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178–190.

(22) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 190–195.

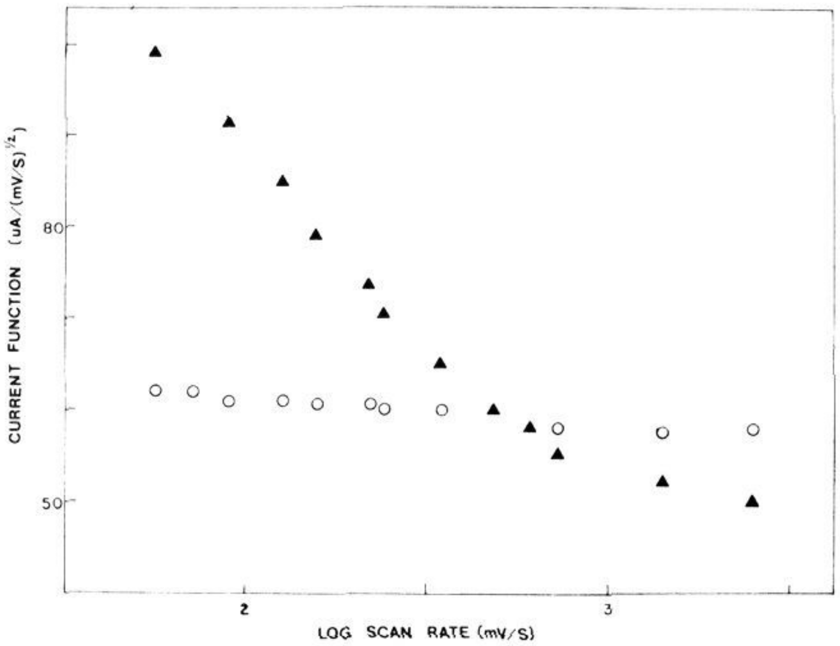

Figure 9. Plot of cathodic current function ($i_p/v^{1/2}$) vs. scan rate (v) for the first reduction wave of (COT)CoCp (two isomer waves combined) (open circles) and second reduction wave (at −2.5 V) (black triangles) (CH_3CN/0.1 M Bu_4NPF_6, mercury drop).

(combined) show the expected invariance for an electrode process involving only electron transfer. The triangles for the second wave show that at high scan rates (above ca. 0.6 V/s) the process simplifies to a one-electron transfer, but at slower scans, a chemical reaction is producing another species which is electroactive at this potential, which consumes at least one additional electron.

The follow-up reaction likely involves the protonation of the dianion $(1,3\text{-COT})CoCp^{2-}$, to produce (*cyclooctatriene*)cyclopentadienylcobalt. The latter fulfills the necessary condition of undergoing reduction at a more positive $E°$ (vide infra) and is probably produced by abstraction of a proton from solvent, adventitious water, or even the electrolyte cation. All these possibilities are well documented in organic electrode reactions.[23] Bulk electrolysis of (COT)CoCp in CH_3CN at a mercury pool at −2.6 V passed several electrons and appeared to result in decomposition of the complex, for a black precipitate fell from solution and only small, mostly ill-defined waves remained in CV scans of the solution itself. One wave at −2.55 V matched that of free 1,3,5-cyclooctatriene in this medium. Evidence thus points to the following process for the most negative reduction wave of (COT)CoCp.

$$(1,3\text{-}C_8H_8)CoCp^- + e^- \rightleftharpoons (1,3\text{-}C_8H_8)CoCp^{2-}$$

$$(1,3\text{-}C_8H_8)CoCp^{2-} + 2H^+ \rightarrow (1,3,5\text{-}C_8H_{10})CoCp$$

$$(1,3,5\text{-}C_8H_{10})CoCp + 2e^- \rightarrow 1,3,5\text{-}C_8H_{10} + Co + 2Cp^-$$

The *monoanion* $(1,3\text{-COT})CoCp^-$ may also be protonated, if a weak acid is added to electrolyte solutions. Thus, if a proton donor such as phenol was added to (COT)CoCp solutions of CH_3CN/0.1 M Bu_4NPF_6, in addition to the cathodic waves at $e_{p_c} = -1.84$ and -2.07 V, a reversible couple appeared at $E° = -2.29$ V, $\Delta e_p = 80$ mV ($v = 0.10$ V/s). A loss in current from the anodic wave at $e_{p_a} = -1.78$ V indicated that the anion $(1,3\text{-COT})CoCp^-$ produced at the electrode was reacting with the phenol to give the new product. The new product was identified as (1,3,5-cyclooctatriene)CoCp by matching its potential with that of an authentic sample of (COTr)CoCp in this medium ($E° = -2.27$ V; $\Delta e_p = 70$ mV at $v = 0.06$ V/s).[24] Thus in the presence of deliberately added acid, the electrolysis mechanism appears to be

$$(1,3\text{- or }1,5\text{-COT})CoCp + e^- \rightleftharpoons (1,3\text{-COT})CoCp^-$$

$$(1,3\text{-COT})CoCp + 2H^+ + e^- \rightleftharpoons (1,3,5\text{-COTr})CoCp$$

and, at more negative potentials

$$(1,3,5\text{-COTr})CoCp + e^- \rightarrow (1,3,5\text{-COTr})CoCp^- \rightarrow \text{unstudied reaction}$$

No evidence for reduction to *cyclooctadiene* cyclopentadienylcobalt was found.

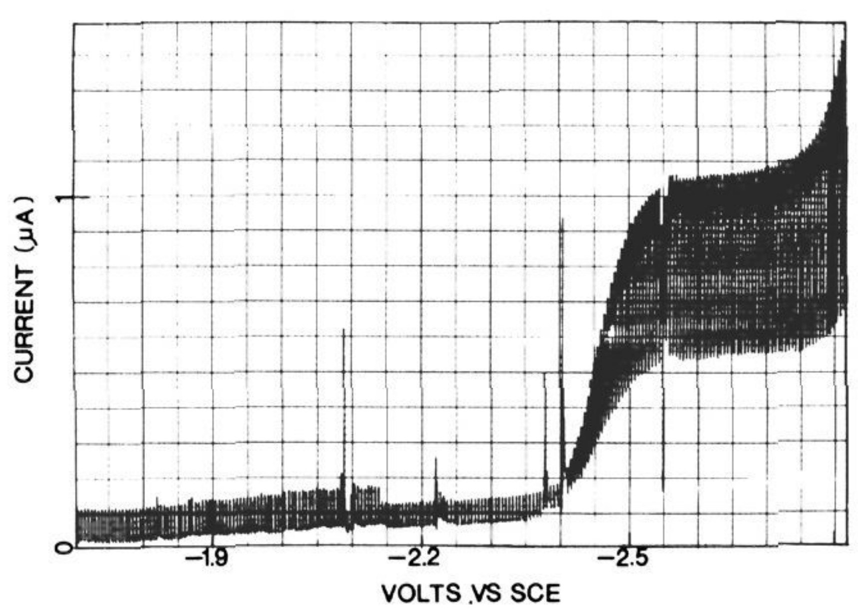

Figure 10. Dc polarogram of 3.8×10^{-4} M (COD)CoCp in CH_3CN/0.1 M Bu_4NPF_6. (drop time = 1 s).

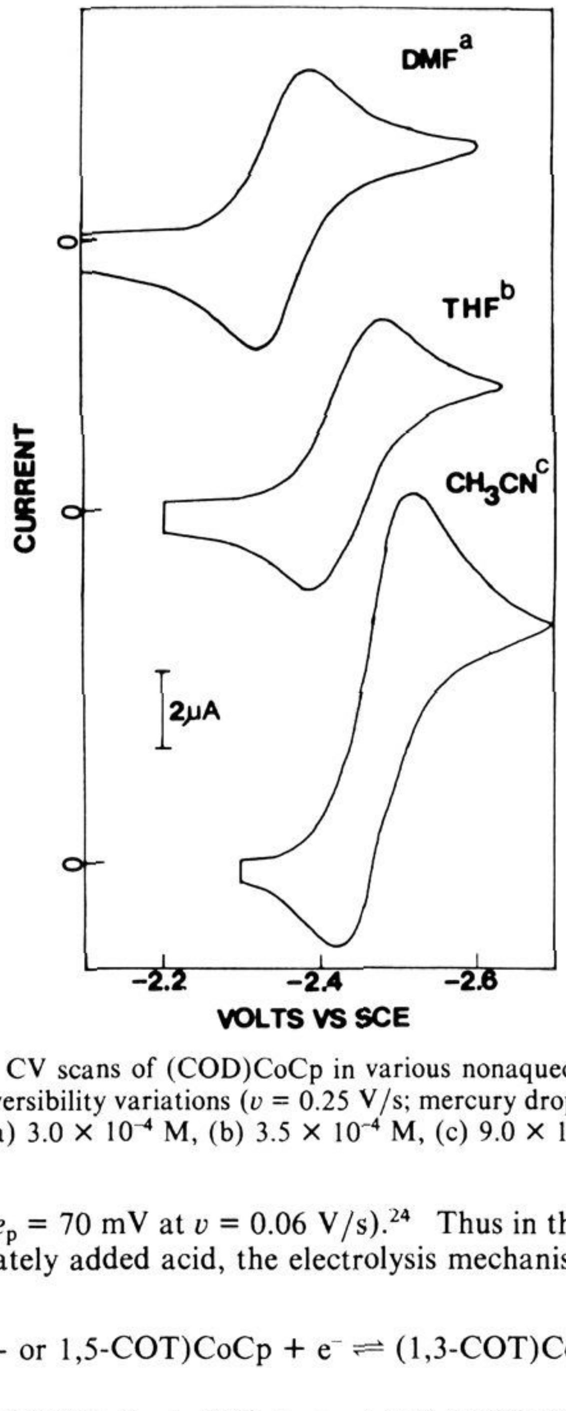

Figure 11. CV scans of (COD)CoCp in various nonaqueous solvents, showing reversibility variations ($v = 0.25$ V/s; mercury drop). Concentrations: (a) 3.0×10^{-4} M, (b) 3.5×10^{-4} M, (c) 9.0×10^{-4} M.

IV. Reductive Isomerization of (1,5-Cyclooctadiene)cyclopentadienylcobalt. Isomerization of a cyclooctadiene ligand in an organometallic compound presents a problem different from that of the metal-bonded cyclooctatetraene ring, because the

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[23] Baizer, M. M., ed. "Organic Electrochemistry"; Marcel Dekker: 1973.

[24] We did not prepare enough $(C_8H_{10})CoCp$ to study it's reduction in depth, but we can at least conclude that the reduction of this compound involves one electron to give an anion radical of moderate stability, for the CV current ratio i_a/i_c was unity at scan rates in excess of 0.75 v/s. This might provide a very convenient way to synthesis of $(C_8H_{10})CoCp$, similar to that reported for $(C_8H_{10})Fe(CO)_3$ by electrolysis of $(COT)Fe(CO)_3$ in aqueous DMF: El Murr, N.; Riveccie, M.; Laviron, E. *Tetrahedron Lett.* **1976**, 3339–3340.

former requires actual movement of hydrogen atoms. Remarkably, we have found that such transformations *can* take place after production of the organometallic anion radical.

(1,5-COD)CoCp (**4**) is a well-known compound which, unlike its COT counterpart, shows evidence only of a 1,5-bound COD ring in its room-temperature NMR spectrum. It is reduced in a single, diffusion-controlled wave (Figure 10) at very negative potentials in a variety of nonaqueous solvents (CH_3CN, THF, DMF, glyme). For example, dc polarography in MeCN gives $E_{1/2} = -2.45$ V (Table I). The height of the polarographic wave and the plot of E vs. $-\log [i/(i_d - i)]$(59-mV slope) were consistent with the reduction being a reversible, one-electron process.

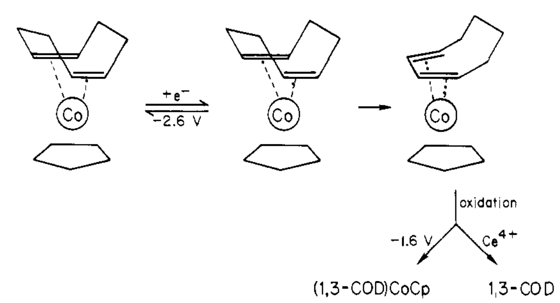
Unlike the COT complex, for which there was virtually no dependence of the reductive behavior on the nature of the solvent, for **4** the stability of the anion was significantly influenced by the solvent employed. The reduction was completely reversible only in DMF, in which $i_a/i_c = 1.0$ and $\Delta e_p = 60$ mV at $v = 0.080$ V/s in CV scans at Hg or Pt electrodes. The cathodic current function was independent of scan rate. CV experiments in other solvents showed the reduction to be less reversible (Figure 11). In both THF and CH_3CN, scan rates in excess of 2 V/s were necessary to outrun the follow-up reaction and obtain a value of i_a/i_c of one. In these two solvents, scanning positive after first going through the reduction wave at -2.5 V revealed small peaks due to a reversible couple at $E° = -1.58$ V ($\Delta e_p = 60$ mV at $v = 0.10$ V/s). The identity of the product giving rise to this new redox couple became the subject of intensive investigation, and it was found to be the isomerized species **5**, (1,3-COD)CoCp.

Bulk electrochemical reduction of the complex was carried out at -2.60 V at a mercury pool cathode in THF. A total of one electron ($n = 1.05$) was passed during the electrolysis. Figure 12 shows two cyclic voltammograms taken at a Pt bead electrode before and after electrolysis. As can be seen from the cyclics the reversible couple at $e_{p_c}(1) = -2.50$ V and $e_{p_a}(1) = -2.40$ V due to (1,5-COD)CoCp was replaced by a reversible couple at $e_{p_c}(2) = -1.62$ V and $e_{p_a}(2) = -1.54$ V. Some decomposition had occurred as a result of the electrolysis as evidenced by a broad oxidation wave at approximately -0.60 V and the decreased current heights in the cyclics of the observed products. A rotating platinum electrode scan showed that the electrolysis product at $E_{1/2} = -1.60$ V was an oxidation wave while the small wave at $E_{1/2} = -2.45$ V was cathodic in nature. Cyclic voltammetry measurements of the wave at $e_{p_c}(2)/e_{p_a}(2)$ show it to be highly reversible with $\Delta E_p = 60$ mV (using a luggin probe plus IR compensation), and plots of $i_p/\nu^{1/2}$ vs. ν were constant, consistent with this new couple being a reversible, one-electron process. Over a period of many hours, the anodic wave at $E_{1/2} = -1.60$ V gradually went away and the reduction wave at $E_{1/2} = -2.45$ V, due to neutral (1,5-COD)CoCp, increased in height along with a minor decomposition peak at $E_{1/2} = -1.90$ V. This experiment showed that (a) the compound with $E° = -1.58$ V was the major product of the slow follow-up reaction of $(1,5\text{-COD})CoCp^-$ and (b) in time, the new product decayed to regenerate the original compound **4**.

The approach taken in formulating the structure of the new product was through analysis of the products of its oxidative cleavage. As part of a study ancillary to this one,[25] we have found that in many cases either anodic oxidation or treatment by oxidants of (polyolefin)CoCp compounds in nonaqueous solvents results in cleavage of the polyolefin, which can be analyzed quantitatively in oxidized solutions by conventional methods. Thus, after oxidation of (1,5-COD)CoCp in CH_3CN by either (a) a slight excess of I_2 or (b) bulk electrolysis positive of its oxidation wave at $e_{p_a} = +0.24$ V, GLC or HPLC analysis of the electrolysis solution gave a quantiative yield of the free 1,5-COD ligand.[26]

If the electrochemically *reduced* solution of (1,5-COD)CoCp (5×10^{-4} M) discussed above was treated with iodine, GLC analysis showed that predominantly 1,3-COD, with some 1,5-COD, was present. Hence, the product at $E° = -1.58$ V was formulated as having the isomerized polyolefin, $(1,3\text{-COD})CoCp^-$. Similarly, electrochemical reduction at -2.6 V followed by oxidation at $+0.50$ V gave a solution containing 1,3-COD. Proper quantification of these experiments was achieved on considerably more concentrated solutions. For example, electrolysis of a 3.5 M solution of (1,5-COD)CoCp in dimethoxyethane/0.1 M Bu_4NPF_6 at -2.6 V at a platinum basket, followed by iodine oxidation gave, by GLC and HPLC analysis, a free COD mixture containing 78% 1,3-COD and 22% 1,5-COD, with a total recovery of 85% of the expected amount (Scheme III).

Scheme III



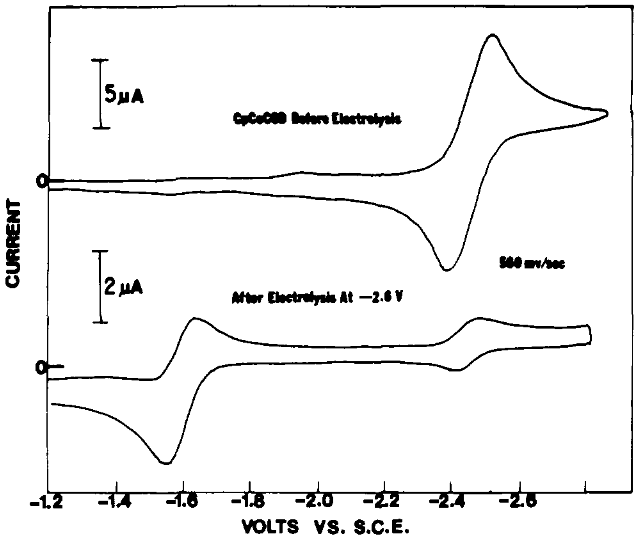


Figure 12. CV scans before electrolysis (top) and after electrolysis (bottom) of (COD)CoCp in THF (platinum electrode, $v = 0.56$ V/s). Scan before electrolysis initiated at 0 V and scan after at -2.8 V.

Chemical redox reagents were also used for the reduction/reoxidation process. Dimethoxyethane solutions of (1,5-COD)CoCp stirred for ca. 0.5 h over Na/K alloy, followed by decantation into a solution containing excess iodine, gave ca. 60% 1,3-COD and 40% 1,5-COD, with a total yield of 75% of theory. These experiments were repeated many times in attempts to minimize recovery of the 1,5-isomer. The limiting factor seems to be the efficiency of conversion of the starting material to its anion. The isomerization of the anion is relatively slow, and it is difficult to keep the extremely reactive anion 4^- from first regenerating **4** by reoxidation. Considering the very negative $E°$ of **4**, over 1.5 V *negative* of that for cobaltocene, these difficulties were not surprising.

V. Comparison of Isomerization Rates of COT- and CODCoCp Compounds. Interconversions of the neutral isomers $4 \rightleftharpoons 5$ is very slow. This allowed us to "trap" neutral (1,3-COD)CoCp, the thermodynamically less stable neutral isomer, by reduction of (1,5-COD)CoCp followed by mild reoxidation of the solution. Thus, a THF solution of (1,5-COD)CoCp was electrolyzed at -2.6 V at a mercury pool, and the resulting $(1,3\text{-COD})CoCp^-$ was then reoxidized at -1.40 V, a potential sufficiently positive to oxidize the anion by one electron, but not positive enough to result in

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[25] Moraczewski, J. Ph.D. Dissertation, University of Vermont, 1980.

[26] The metal-containing product was cobalticinium ion, identified by UV-vis spectroscopy and by electrochemistry.

[27] Unpublished nmr results.

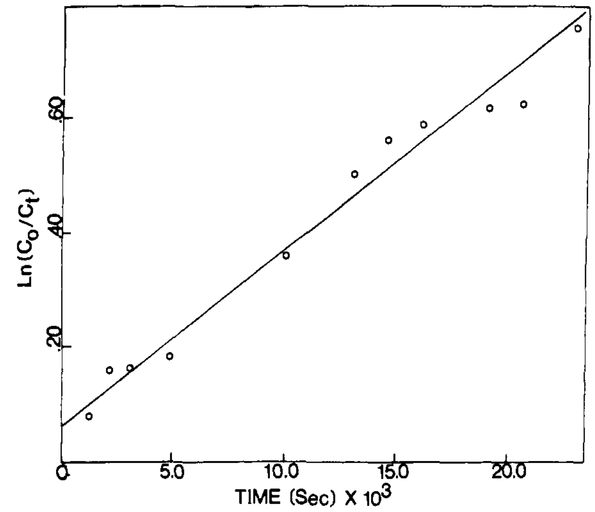


Figure 13. Plot of ln (C_0/C_t) vs. time for isomerization of (1,3-COD)-CoCp prepared in bulk reduction/reoxidation experiment. C_0 = concentration of neutral 1,3-isomer at time = 0 (immediately after reoxidation step), measured from plateau current of rotating platinum electrode voltammogram; C_t = concentration at time *t*.

oxidative cleavage of the hydrocarbon. After this reduction/mild reoxidation cycle, a rotating platinum electrode (RPE) scan of the solution showed the cathodic waves at −1.60 V (major product) and −2.45 V (minor) of *neutral* **5** and **4**, respectively. The heights of these waves were monitored over the course of several hours, as the wave for **5** decreased and that of **4** concomitantly increased. The rate constant for the process

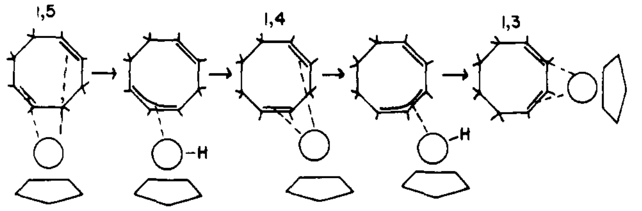
$$\text{(1,3-COD)CoCp} \rightarrow \text{(1,5-COD)CoCp}$$

was measured from a plot (Figure 13) of ln (C_0/C_t) vs. time (C_0 = initial wave height of **5** after reduction/reoxidation; C_t = wave height of (**5**) at time *t*). A rate constant of 3×10^{-5} s^{-1} was calculated. This figure may be compared with that of the COT analogue. This has not been measured at room temperature, but from the NMR spectra at coalescence temperature (ca. 375 K) a rate constant of roughly 30 s^{-1} may be calculated (a more complete, 250-MHz, NMR study is in progress). It is clear that *equilibration of the 1,3-* and *1,5-bonded isomers is many orders of magnitude slower for cyclooctadiene complexes, compared to their cyclooctatetraene analogues.*

A similar conclusion can also be made regarding isomerization rates of the radical anions. We showed above that the isomerization of (1,5-COT)CoCp$^-$ to its 1,3-analgoue was complete in less than 10 ms. A lower limit of k(isomer) $\gg 10^2$ s^{-1} (first-order rate constant assumed) is much more rapid than isomerization of the cyclooctadiene analogue (1,5 COD)CoCp$^-$. In DMF, the 1,5-anion **4**$^-$ was stable for ca. 0.5 h, as showed by bulk electrolysis experiments. For other solvents, in which the anion is less stable (e.g., THF or CH$_3$CN), CV data may be used to calculate an isomerization rate of roughly 0.1 s^{-1}, several orders of magnitude *slower* than the corresponding reaction for the (COT)CoCp anion.

VI. Mechanism of the Isomerizations. Possible mechanistic routes for interconversion of the COT isomers **1** and **2** are several and are in part the subject of the accompanying paper. The reader will see that no definite conclusions are made for the COT case. In the case of the COD compounds, it is easier to see the probable mechanistic route leading to isomerization. We favor the mechanism shown in Scheme IV involving a metal hydride intermediate in which the COD ring bonds as an allyl, three-electron donor, to the metal, with an uncoordinated double bond. This mechanism necessitates going through a 1,4-bonded intermediate, which probably too short-lived for us to detect. This mechanism is similar to those proposed in other studies of metal-polyolefin isomerization.[28-33] In order to account for the much higher rate of isomerization of the anions, compared to the neutral compounds, the extra negative charge in the radical anion must facilitate formation of the allyl-metal hydride intermediate. In DMF, in

Scheme IV



which the 1,5-bonded anion **4** is quite stable, the intermediate must not be stabilized to the same degree as in, e.g., THF, in which the isomerization is much more rapid.

Discussion

Studies of preferred conformations of eight-membered polyolefin rings on metals have been pursued actively since the experiments of Arnet and Pettit,[2] which showed that free 1,5-cyclooctadiene rearranged to the 1,3-isomer when heated in the presence of catalytic amounts of Fe(CO)$_5$. C$_8$H$_{12}$ and C$_8$H$_8$ are known to bond through either conjugated or nonconjugated double bonds to a wide variety of metals and in some cases, both types of coordination may be possible with the same, or at least very similar, metal-containing moiety. There are several such examples pertinent to our study. These include the various reports of 1,3- 1,4-, and 1,5-COD complexes of MX$_2$ (M = Pd or Pt, X = alkyl or halogen)[34] and the rare example of isolable iron-tricarbonyl compounds of either 1,5-COD or 1,3-COD.[35] (1,3-COD)Fe(CO)$_3$ was reported as being less stable to thermal decomposition than the 1,5-isomer, but no interconversions between the two isomers were reported. Very recently there have been quite interesting reports of variations in mode of COD coordination to the Fe(PR$_3$)$_3$ moiety. (COD)Fe(PR$_3$)$_3$ complexes synthesized in metal atom reactors have been reported by groups at Bristol[36] and at Du Pont.[37,38] In the cocondensation reaction of either 1,5- or 1,3-COD, P(OMe)$_3$, and iron, only (1,3-COD)Fe[P(OMe)$_3$]$_3$ is isolated, but the 1,5-isomer presumably forms initially and then rearranges to the more stable 1,3-isomer.[38] Both 1,3- and 1,5-isomers of (COD)Fe(PF$_3$)$_3$ can be isolated, depending on which isomer of the hydrocarbon is used in the cocondensation reaction. Again, no interconversions of the isomers appear to have been reported.

COT, on the other hand, is known to bond exclusively as a 1,3-diolefin to Fe(CO)$_3$[39,40] and Ru(CO)$_3$.[41] η^4-1,3-diolefin coordination of COT to Os(CO)$_3$ has also been found, although a less stable isomer apparently containing an allyl-like COT ring

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has also been reported for (COT)Os(CO)$_3$.[43] It is in the cobalt subgroup that evidence for either 1,5- or 1,3-coordination of η^4-COT occurs, for the same metal, not only in the present work but also previously in that of Smith and Maitlas,[43] who were able to isolate (1,3-COT)MC$_5$Me$_5$ (M = Rh, Ir) from low-temperature reactions of COT^{2-} with [M(C$_5$Me$_5$)Cl$_2$]$_2$. The 1,3-isomers irreversibly arranged to (1,5-COT)MC$_5$Me$_5$ upon warming to room temperature.

Thus, it is apparent that sometimes subtle changes in electronic requirement may have a significant effect on the structural preferences of cyclooctapolyene ligands. The most important contributions of our presently reported work is the discovery that changes in isomeric preferences may accompany changes in electron count (or, if you wish, formal metal oxidation state) of these complexes. This raises the possibility of *control* of isomeric structure through redox chemistry of the organometallic π complex.

The compounds reported in the previous literature, discussed above,[34-43] are all 18-electron species. The isomerizations of (1,5-COT)CoCp$^-$ and (1,5-COD)CoCp$^-$ (both 19-electron species) represent the first data on structural preferences of C$_8$ polyene rings for organometallic *radical ions*. Many questions are raised by these observations, especially concerning the role of the metal in the isomerizations and how the electronic structure[44] of the anions (charge localization, radical character) affects the processes. A further, important, consideration is whether or not this phenomenon of redox-initiated isomerization of nonconjugated to conjugated hydrocarbons will be found to be general for other, smaller or larger, polyolefin rings. These questions are currently under study.

Acknowledgment. We gratefully acknowledge support by the National Science Foundation of this work, and we thank John L. Spencer for his gift of (COT)CoC$_5$Me$_5$.

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Structural Consequences of Electron-Transfer Reactions. 6.[1] Electronic Structures and Structural Preferences of Cyclooctatetraene and Cyclooctadiene Iron and Cobalt Compounds and Their Radical Anions

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Abstract: ESR spectra of (1,3-cyclooctatetraene)CoCp$^-$, -Fe(CO)$_3^-$, and -Fe(CO)$_2$(PPh$_3$)$^-$ were obtained. It is shown by the magnitude of the hyperfine couplings for (1,3-COT)CoCp$^-$ that the odd electron resides in the COT portion of the molecule. Strong evidence for an analogous situation in the Fe complexes is also presented. On the other hand, the ESR spectra for (1,5-cyclooctadiene)CoCp$^-$ and the 1,3-isomer show that the unpaired electron in both cases is predominately metal centered. These findings are corroborated by molecular orbital calculations of the extended Hückel type. Along with a description of the nature of the singly occupied orbital in these reduced species, details of the geometric structure are presented. The relative ease of reduction and pathways interconverting the 1,3- and 1,5-isomers of (COT)CoCp are also given.

Cyclooctatetraene (COT) and cyclooctadiene (COD) are common ligands in organometallic chemistry. Much of their chemistry has been investigated with an emphasis on the mode of coordination to the transition-metal and the fluxional properties of some of the compounds.[3] Complexes of COT from η^8 to η^2 are known. This engenders a variety of geometries that the COT ligand can adopt. An elegant description of this has been given by Guggenberger and Schrock.[4] COT itself is tub-shaped.[5] Reduction to the dianion flattens the ring[6] to D_{8h} symmetry in accord with the prediction by Hückel's rule. One of the more interesting observations made is that even when an 8-membered ring (e.g., COT or COD) is restricted by the 18-electron rule to η^4 coordination, the ligand may bond either as a chelating 1,5-diene (η^4-1,2,5,6 bonding, through nonadjacent double bonds) or as a conjugated 1,3-diene (η^4-1,2,3,4 bonding). The electronic factors which govern the favored mode of bonding are not known. We have recently discovered that the total number of electrons possessed by the metal π complex can have a determining effect on whether the 1,5- or 1,3-bonded isomer is favored.[1,7] In particular, half-occupancy of the lowest unoccupied molecular orbital (LUMO) of (COT)CoCp or (COD)CoCp (Cp = η^5-C$_5$H$_5$) by one-electron reduction of the neutral compounds facilitates conversion of the 1,5-isomer to the 1,3-isomer. Obviously, the

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[1] Part 5: Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.*, preceding paper in this issue.

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