(Contract No. DE-AC02-79ER10345), and in part by grants from the Standard Oil Co. of Ohio and Air Products and Chemicals, Inc. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978–1983).

Registry No. 1, 82544-73-8; 2, 82544-74-9; 3, 82544-75-0; RuH(Cl)(CO)$_2$(PPh$_3$)$_2$, 56144-64-0; Ru(CO)$_3$(PPh$_3$)$_2$, 14741-36-7; Na[Co(CO)$_4$], 14878-28-5; RuHCl(CO)(PPh$_3$)$_3$, 16971-33-8; Ru, 7440-18-8; Co, 7440-48-4.

Supplementary Material Available: Tables of derived parameters for the rigid-group atoms of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ (Table A) and structure factors for RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ (Table B) and the ^{31}P{^{1}H} NMR spectrum (Figure A) of a mixture of 2 and 3 (11 pages). Ordering information is given on any current masthead page.

Electrochemical Study of the Oxidative Cleavage of Cobalt–Polyolefin Compounds in Strongly and Weakly Coordinating Solvents

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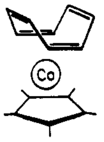
Received May 4, 1982

The oxidation of four cobalt–polyolefin compounds has been studied by direct-current polarography, cyclic voltammetry, and controlled potential coulometry. The compounds studied were (η^5-cyclopentadienyl)- or (η^5-permethylcyclopentadienyl)cobalt compounds of either cyclooctadiene (COD) or cyclooctatetraene (COT). In CH$_3$CN each compound underwent an irreversible oxidation which resulted in cleavage of the polyolefin ligand and production of cobaltocenium ion, Cp$_2$Co$^+$, and Co^{2+}. The reaction was quantitative, and an n value of 1.5 e was measured in agreement with this. In dichloromethane, the cyclooctadiene compounds (COD)CoCp and (COD)Co(C$_5$Me$_5$) gave one-electron reversible oxidations, and an ESR spectrum of (COD)Co(C$_5$Me$_5$)$^+$ was obtained. As the cation radicals decomposed, COD was liberated. Oxidation of either (COT)CoCp or (COT)Co(C$_5$Me$_5$) was irreversible, but cleavage of the Co–COT bond was not responsible for the irreversibility. An unidentified intermediate was formed which reacted over about a 1-h time scale to eventually liberate COT and form Cp$_2$Co$^+$.

Introduction

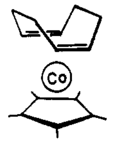
The oxidation of metal–π-olefin complexes has received attention as attempts have been made to activate such complexes toward nucleophilic attack. Strong oxidizing agents such as Br$_2$ or Ce^{4+} usually result in oxidative cleavage of the metal–carbon bonds and have been used for years as reagents to liberate a polyolefin from a metal–polyolefin complex.[1] The more recent work of Connelly and co-workers has shown that milder chemical oxidants (e.g., NO$^+$ or diazonium ions) which produce cation radicals of metal π complexes often lead to compounds in which the polyolefin remains bonded to the metal in a rearranged form. Their studies of the oxidation of iron–cyclooctatetraene compounds have been particularly noteworthy.[2,3]

We became interested in studying the oxidation of cobalt–polyolefin compounds as an outgrowth of our earlier work on these compounds, in which a one-electron *reduction* led to isomerization of the metal–olefin bond.[4] The question then arose as to the nature of the metal–hydrocarbon bond in *electron-deficient*, 17-electron, compounds which might be anodically generated from the neutral starting materials and the ultimate fate of the hydrocarbon as well. The electrochemical results which follow show that cation radicals can be generated by one-electron oxidation of cyclooctadiene (COD) compounds of cyclopentadienylcobalt but that their cyclooctatetraene (COT) analogues undergo rapid reaction to form intermediates in which the COT ring has most likely rearranged, while still remaining bonded to the metal. Ultimately, both (COD)CoCp$^+$ and the Co–COT$^+$ intermediate decompose to yield the free olefin and cobaltocenium ion, Cp$_2$Co$^+$. After this work was completed, a cyclic voltammetry study of cobalt π complex oxidations appeared[5] which included data on one of the four compounds reported below. Our conclusions concerning the oxidation mechanism of (COD)CoCp are in agreement with those reported by Koelle.[5] The four compounds studied are shown in 1–4.



— = H (1)

— = CH$_3$ (2)



— = H (3)

— = CH$_3$ (4)

Experimental Section

Electrochemical techniques, compound preparation, and other experimental factors were as previously described.[4] The supporting electrolyte was 0.1 M Bu$_4$NPF$_6$, and potentials are reported vs. the aqueous saturated calomel electrode (SCE). Bulk electrolysis experiments and transfer of electrolyzed solutions to

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[1] R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, p 52. W. G. Daub, *Prog. Inorg. Chem.*, **22**, 409 (1977).

[2] N. G. Connelly and R. L. Kelly, *J. Organomet. Chem.*, **120**, C16 (1976).

[3] N. G. Connelly, M. D. Kitchen, R. F. D. Stansfield, S. M. Whiting, and P. Woodward, *J. Organomet. Chem.*, **155**, C34 (1978).

[4] J. Moraczewski and W. E. Geiger, *J. Am. Chem. Soc.*, **103**, 4779 (1981).

[5] U. Koelle, *Inorg. Chim. Acta*, **47**, 13 (1981).

[6] Slope of the plot of $-E$ vs. log $[i/(i_d - i)]$, which is 59 mV for a one-electron reversible wave.

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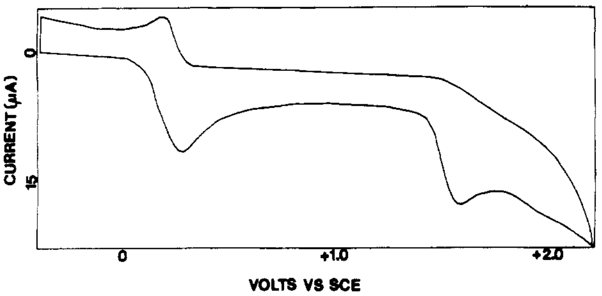

Figure 1. Cyclic voltammetry scan of 5.4 × 10^{-4} M (COT)CoCp in CH_3CN/0.1 M Bu_4NPF_6 at a platinum electrode (v = 78 mV/s).

Table I. Direct Current Polarographic Data for Cyclopentadienylcobalt–Polyolefin Compounds

compd	solv	$E_{1/2}$,[a] V	slope,[b] mV	I[c]
(COT)CoCp (1)	CH_3CN	+0.08	81	5.71
	CH_2Cl_2	+0.22	45	4.15
	THF	+0.27	50	3.67
(COD)CoCp (3)	CH_3CN	+0.02	78	5.40
	CH_2Cl_2	+0.20		

[a] Potentials referred to aqueous saturated calomel electrode. [b] Slope of plot of $-E$ vs. log $[i/(i_d - i)]$. [c] Diffusion current constant, in μA mM^{-1} $mg^{-2/3}$ $s^{1/2}$.

sample tubes for ESR or optical spectroscopy were accomplished in an inert-atmosphere box.

Results

General Electrochemical Behavior. Each of the cyclopentadienylcobalt–diolefin compounds underwent oxidation at a relatively mild potential, i.e., ca. 0 to +0.3 V vs. SCE. The reversibility of the oxidation process varied greatly depending on both the compound and the solvent employed. Oxidation of any of the compounds in acetonitrile led to rapid attack by solvent, with concomitant cleavage of the metal–polyolefin bond and, ultimately, production of cobaltocenium ion as the only organometallic product. In dichloromethane, attack by solvent was not observed, and reaction pathways were characteristic of the radical cations (diene)$CoCp^+$. The most stable cation in this series was (COD)$Co(C_5Me_5)^+$, which was produced by bulk oxidation in CH_2Cl_2 and characterized by ESR spectroscopy.

I. (COT)CoCp (1). (a) In CH_3CN. Oxidation of 1 was highly irreversible at either mercury or platinum electrodes in acetonitrile. Both dc polarography and cyclic voltammetry measurements supported this conclusion, although the cyclic voltammograms are on first glance deceptive concerning the reversibility (Figure 1), a point which will be elaborated on below.

The rising portion of the diffusion-controlled polarographic wave ($E_{1/2}$ = +0.08 V, Table I) was drawn out (slope[6] = 81 mV) and was consistent with an irreversible process. The wave height corresponded to passage of approximately 1.5 e. This figure was arrived at by comparing the diffusion current constant, I, for the oxidation (I_{OX} = 5.71) with that of the previously characterized[4] one-electron reduction wave of this molecule (I_{RED} = 3.77). This value of n = 1.5 e was found to properly describe this oxidation process, for cyclic voltammetry measurements, controlled potential coulometry, and electrolysis product distributions were all found to be consistent with this number.

The appearance of CV scans of this wave depended markedly on scan rate and the extent of the positive-going scan. Scans extended to about +2 V showed not only the anodic peak at +0.28 V (v = 78 mV/s, Figure 1), but also an irreversible wave at E_{p_a} = +1.60 V (some CV data are collected in Table II). This latter peak was apparently due to free COT liberated in the first oxidation step, for cyclooctatetraene has an irreversible oxidation wave at that same potential. In Figure 1, the first oxidation has the *appearance* of a chemically reversible wave, since a cathodic peak was present at E_{p_c} = +0.18 V. However, several points dictate against the cathodic peak arising from reduction of the cation (COT)$CoCp^+$. First, the oxidation of 1 was shown to be irreversible by the fact that its anodic peak potential shifted positive by about 60 mV/tenfold increase in scan rate. Second, the cathodic peak became more dominant when the potential was held positive of the anodic wave for *longer* times, i.e., either in slow CV scans or in scans which extend to far more positive values. When the first oxidation wave was scanned at moderately fast scan rates or without inclusion of the second wave, the first wave was irreversible. The implies that the cathodic wave at +0.18 V arises from a product produced in a chemical reaction *after* the initial irreversible charge transfer step. Koelle[7] has reported that $CpCo(CH_3CN)_3^{2+/+}$ forms a reversible couple with $E°$ = +0.23 V, ΔE_p = 65 mV, which places its cathodic peak at +0.20 V, within experimental error of our observed cathodic wave. This half-sandwich solvent species is also strongly implicated from the bulk electrolytic data (vide infra) which establish that Cp_2Co^+ and Co^{2+} are the ultimate metal-containing products of the oxidation. Hence, the oxidation of (COT)CoCp has the appearance of a reversible wave at slow CV scan rates only because a product, $CpCo(CH_3CN)_3^{2+}$, is being generated which has an $E°$ value very close to the E_{p_a} value for the original compound.

One other important aspect of the linear scan voltammograms concerned the current function, $i_{p_a}/v^{1/2}$, of the oxidation wave, which depended on scan rate. This quantity had a constant value of ca. 0.69 (arbitrary units) at fast scan rates (v > 700 mV/s), but increased at slower scan rates, and at v = 50 mV/s had a value of 1.10, about 1.6 times as great as the fast scan limit. Since the current function was also 0.7 for the one-electron *reduction* wave of this compound, these data show that (a) at fast sweeps, the oxidation is a one-electron process, and (b) over longer times, a kinetic contribution to the current arises from follow-up chemical reactions and subsequent product oxidation. The current function of the free COT wave at +1.55 V does not change over this scan rate variation, indicating that it is liberated *before* the reactions giving rise to the extra oxidation current at the first wave.

Finally, a quantitative determination of electrolysis products was accomplished after bulk electrolysis at either a Pt basket or Hg pool at +0.3 V. In a typical experiment, a 4.4 mM solution of (COT)CoCp initially had a polarographic plateau current of 17 μA for the oxidation wave. Upon electrolysis, 1.57 faraday was liberated as the solution went from dark brown to light yellow. Polarograms after electrolysis showed reductions waves at $E_{1/2}$ = −0.62 V (irreversible by CV), −0.90 V (reversible), and −1.90 V (quasireversible), with plateau currents of 8.0, 3.5, and 20 μA, respectively. In the positive potential region, only the anodic peak at +1.55 V for free COT was present. The reduction wave at −0.62 V was assigned to the two-electron reduction of solvated Co^{2+}, since $Co(BF_4)_2$ had an irreversible wave with the same $E_{1/2}$ value.[8] The reversible wave at −0.90 V was assigned to the one-electron reduction[9]

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[7] U. Koelle, *J. Organomet. Chem.*, **184**, 379 (1980).

[8] Addition of 1,2-bis(diphenylphosphino)ethane, diphos, to the electrolyzed solution resulted in disappearance of the wave at −0.62 V, as also occurred when diphos was added to solutions of $Co(BF_4)_2$.

Table II. Potentials of Oxidation of Cyclopentadienylcobalt-Polyolefin Compounds Measured by Cyclic Voltammetry

compd	solv	electrode	scan rate, mV/s	$E°$ or $E_{\mathrm{p_a}}$, V	comments
(COT)CoCp (1)	CH_3CN	Pt	100	+0.28 ($E_{\mathrm{p_a}}$)	second oxidation wave at $E_{\mathrm{p_a}}$ = +1.56 V (irrev),
	CH_2Cl_2	Pt	200	+0.27 ($E_{\mathrm{p_a}}$)	irrev to v = 1 V/s; no other waves to +1.8 V
(COT)Co(C_5Me_5) (2)	CH_3CN	Pt	400	−0.03 ($E_{\mathrm{p_a}}$)	second oxidation wave at $E_{\mathrm{p_a}}$ = +1.50 V (irrev)
(COD)CoCp (3)	CH_3CN	Pt	200	+0.06 ($E_{\mathrm{p_a}}$)	product wave with $E°$ = +0.24 V due to $CpCo(CH_3CN)_3^{2+/+}$
	CH_2Cl_2	Pt	200	+0.24 ($E°$)	reversible
(COD)Co(C_5Me_5) (4)	CH_2Cl_2	Hg or Pt	160	+0.07 ($E°$)	reversible
				+1.10 ($E_{\mathrm{p_a}}$)	irreversible

of Cp_2Co^+. Cobaltocenium ion was also diagnosed from the UV spectrum of the electrolyzed solution, in which the 262-nm band of Cp_2Co^+ had replaced the 242-nm band of the starting (COT)CoCp compound. Both Cp_2Co^+ and COT are electroactive in the vicinity of −1.9 V,[9,10] and the wave at that voltage is therefore a composite of the two reduction processes $Cp_2Co^{0/-}$ and $COT^{0/2-}$. From the relative heights of the three reduction waves and the known n values for each of the process, it was concluded that for each mole of (COT)CoCp, the oxidation yielded 1 mol of free COT, 0.5 mol of Cp_2Co^+, and 0.5 mol of Co^{2+}. All of the electrochemical data were therefore consistent with the mechanism shown in Scheme I. The terms "fast" and "slow" above refer to the cyclic voltammetry time scale.

Scheme I

$$(COT)CoCp \rightarrow (COT)CoCp^+ + e^-$$

$$\text{fast} \quad (COT)CoCp^+ \rightarrow COT + \text{“}CpCo^{+}\text{”}\ \text{product}$$

$$\text{“}CpCo^{+}\text{”}\ \text{product} + 3CH_3CN \rightarrow CpCo(CH_3CN)_3^+$$

$$\text{slow} \quad CpCo(CH_3CN)_3^+ \rightarrow 0.5Cp_2Co^+ + 0.5Co^{2+} + 0.5e^- + 3CH_3CN$$

$$\text{net} \quad (COT)CoCp \rightarrow COT + 0.5Cp_2Co^+ + 0.5Co^{2+} + 1.5e^-$$

It is necessary to postulate a "$CpCo^{+}$" product (line 2 of Scheme I) because fast CV scans in the vicinity of +0.2 V show no cathodic wave—not even that of $CpCo(CH_3CN)_3^{2+}$. Hence the latter must be formed at a moderate rate from a CpCo-containing intermediate which has already liberated cyclooctatetraene. The "slow" disproportionation reaction is responsible for the n = 1 value for the oxidation at fast sweep rates and the n = 1.5 value in longer experiments (slow sweep rate CV, dc polarography, and bulk coulometry).

(b) In CH_2Cl_2. Changing to the relatively noncoordinating solvent dichloromethane significantly altered the oxidation pathway of 1. A single polarographic wave ($E_{1/2}$ = +0.22 V; I = 4.15[11]) was observed, and this was shown to be irreversible by CV scans at either Hg or Pt at scan rates up to 1000 mV/s. When the scan was extended out to more positive values, *no* wave for free COT was observed.[12] Hence, although the cation of 1 is still very unstable in CH_2Cl_2, its primary reaction does not result in freeing of the COT ligand from the complex. This was confirmed by bulk electrolysis experiments. After exhaustive electrolysis at a platinum basket (n_{app} = 0.83 e) there was only a very small wave for free COT at +1.8 V (Pt electrode). The major wave in the negative potential region was an irreversible one at $E_{1/2}$ = −0.45 V, and only a very small wave attributable to Cp_2Co^+ was present at −0.90 V (Figure 2). Samples of this solution taken for UV analysis had $\lambda_{\max}$ = 252 nm. Over a period of about 2 h after electrolysis, the wave at −0.45 V diminished, and the waves for free COT and Cp_2Co^+ grew in. In a typical experiment, an original 6.3×10^{-4} M solution of 1 had a polarographic oxidation wave of plateau height 1.02 μA. After bulk electrolysis at +0.4 V, the resulting polarogram showed reduction waves at −0.45 (0.60 μA) and −0.90 V (0.05 μA). After 1.5 h, the wave at −0.45 V was 0.25 μA, and the Cp_2Co^+ wave at −0.90 V had increased to 0.30 μA. Eventually, only the wave for cobaltocenium ion was present, and the UV spectrum showed only the 262-nm Cp_2Co^+ band. These "terminal" solutions also were analyzed for free COT by the standard addition method. The height of the COT oxidation wave at +1.8 V was measured by CV scans before and after addition of an aliquot of pure COT. This analysis yielded a value of 0.97 mol of COT released per mol of (COT)CoCp in the original solution.

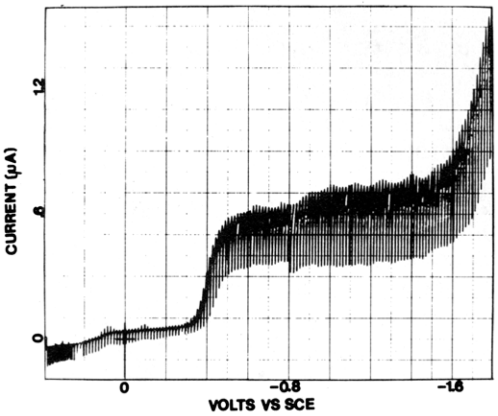

Figure 2. Direct-current polarogram of a solution of 6.3×10^{-4} M (COT)CoCp in CH_2Cl_2/Bu_4NPF_6 after it had undergone bulk electrolysis at +0.4 V.

Thus, the ultimate fate of 1 when oxidized in CH_2Cl_2 is the same as in CH_3CN: release of COT and formation of 0.5 mol of Cp_2Co^+. However, the intermediate which must contain both COT and the CpCo moiety is fairly

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[9] W. E. Geiger, *J. Am. Chem. Soc.*, **96**, 2632 (1974).

[10] B. J. Huebert and D. E. Smith, *J. Electroanal. Chem.*, **31**, 333 (1971). R. D. Allendoerfer and P. H. Rieger, *J. Am. Chem. Soc.*, **87**, 2336 (1965).

[11] For comparison purposes, a I value of 3.11 μA mM^{-1} $mg^{-2/3}$ $s^{1/2}$ was measured for the one-electron process involving the reduction of the nickel–carborane complex $(1,2\text{-}C_2B_9H_{11})_2Ni$ (W. E. Geiger and D. E. Smith, *Chem. Commun.*, 8 (1971)).

[12] In CH_2Cl_2/0.1 M Bu_4NPF_6, free COT exhibited an irreversible oxidation wave at +1.8 V (CV peak potential).

Table III. Cyclic Voltammetry Data for Oxidation of (COD)CoCp in CH_2Cl_2/0.10 M Bu_4NPF_6 at a Platinum Bead Electrode

scan rate, mV/s	44	52	67	111	193	259	333	407	1000
current function[a]	1.13	1.11	1.09	1.05	1.05	1.06	1.04	1.02	1.02
current ratio[b]		0.69		0.80	0.85			0.94	0.99

[a] Anodic peak current/(scan rate)$^{1/2}$: arbitrary units. [b] i_c/i_a (theory: equal to one for a chemically reversible process).

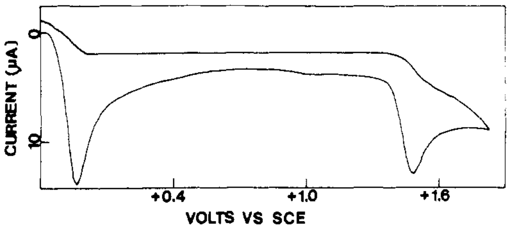

Figure 3. Cyclic voltammetry scan at platinum electrode (v = 400 mV/s) of 7.8 × 10^{-4} M (COT)Co(C_5Me_5) in CH_3CN/Bu_4NPF_6.

long-lived. This intermediate did not react with potential ligands such as triphenylphosphine or bis(diphenylphosphino)ethane and is probably coordinatively saturated.

II. (COT)Co(C_5Me_5) (2). This compound was subjected to a brief investigation. Its anodic behavior in CH_3CN was essentially identical to that of 1. The oxidation was at a less positive potential (E_{p_a} = −0.03 V, Table II) and was irreversible, resulting in liberation of COT (Figure 3). Bulk oxidation at +0.20 V at a mercury pool anode resulted in a color change from light brown to green, but voltammetric scans of the electrolyzed solution using a hmde were dominated by severe adsorption waves, and the detailed mechanism of this oxidation was not pursued.

III. (COD)CoCp (3). (a) In CH_3CN. The overall mechanism of the oxidation of 3 in acetonitrile is analogous to 1: liberation of COD and formation of Cp_2Co^+ and Co^{2+}. This was indicated by a number of electrochemical and analytical measurements. A dc polarogram had an irreversible shape (log slope[6] = 78 mV, $E_{1/2}$ = +0.02 V), and CV scans were irreversible, with the peak potential dependent on scan rate (E_{p_a} = +0.06 at v = 100 mV/s). No wave for free COD was observed because it can neither be oxidized nor reduced in the accessible potential range. The reversible wave for the solvento intermediate, CpCo($CH_3CN)_3{}^{2+/+}$, appeared in the cyclic voltammograms ($E°$ = +0.22 V, ΔE_p = 80 mV). Bulk anodic electrolysis (platinum basket electrode, E_{app} = +0.30 V) gave n = 1.5 e and a resulting polarogram with reduction waves at −0.65 V (Co^{2+}) and at −0.90 and −1.90 V (Cp_2Co^+). The Co^{2+} wave disappeared when phosphine ligands were added to the solution. For example, addition of triphos[13] to the electrolyzed solution turned it dark yellow and gave a new wave at −0.41 V, apparently due to a Co(triphos) complex. Results in THF solution were identical, and the oxidation of 3 in strongly coordinating solvents appears to be identical with that of 1, Scheme I, except that COD is the liberated polyolefin.

(b) In CH_2Cl_2. Direct-current polarograms were subject to maxima which obscured the shape of the wave, so studies of 3 in dichloromethane emphasized cyclic voltammetry and bulk coulometry experiments at platinum electrodes. The oxidation of 3 in CH_2Cl_2 was electrochemically reversible, but the cation was subject to a follow-up reaction after the electron transfer. The ratio of cathodic-to-anodic currents, i_c/i_a (Table III) increased with scan rate until it was 0.99 at a scan rate of 1000 mV/s. The current function (Table III) increased only by about 10% as the scan rate was lowered from v = 1000 to 44 mV/s, making it unlikely that the products of the chemical follow-up reaction also oxidized as they were formed at that potential. The $E°$ value of the process was +0.24 V, and ΔE_p values were about 75 mV at v = 50 mV/s, typical of the values we routinely find for reversible couples in CH_2Cl_2. The anodic peak potential shifted only 20 mV positive over the scan range in Table III, again indicative of a reversible process affected by residual uncompensated resistance problems in the measurements.

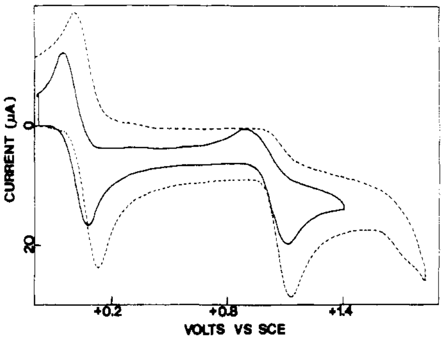

Figure 4. Cyclic voltammetry scans at platinum electrode (v = 300 mV/s) of 7.4 × 10^{-4} M (COD)Co(C_5Me_5) in CH_2Cl_2/Bu_4NPF_6. Dotted line is data at 293 K and solid line data at 258 K.

Bulk electrolysis of 3 at +0.40 V at a platinum gauze resulted in an apparent n value of 1.3 e. During the electrolysis the brown solution turned very pale yellow, and a polarogram of the final solution gave one wave at −0.90 V, which was attributed to Cp_2Co^+ (confirmed by the UV band at 262 nm). From the height of the polarographic wave it was determined by the standard addition method that 0.50 mol of Cp_2Co^+ was formed for every mole of 3 present before oxidation. Cyclooctadiene was analyzed by gas chromatography of samples of the electrolyzed solution: 1.0 mol of 1,5-COD was formed per original mol of 3. All of the above data support Scheme II as describing the oxidation of 3 in this medium. Cleavage of the polyolefin ring appears to occur directly after formation of the radical cation of 3, which has moderate stability in CH_2Cl_2 because it is not subject to attack by solvent, as was seen when CH_3CN was the electrolyte solvent.

Scheme II

$$\text{(COD)CoCp} \rightleftarrows \text{(COD)CoCp}^+ + e^- \quad E° = +0.24\ \text{V}$$

$$\text{(COD)CoCp}^+ \rightarrow \text{1,5-COD} + 0.5\text{Cp}_2\text{Co}^+ + \text{other Co products}$$

IV. (COD)Co(C_5Me_5) (4) In CH_2Cl_2. This compound gave a highly reversible oxidation at $E°$ = +0.07 V (ΔE_p = 65 mV) and a second, irreversible oxidation (Figure 4) at more positive voltages (E_{p_a} = +1.10 V at v = 160 mV/s). The i_c/i_a ratio for the first oxidation was 0.99 at v = 48 mV/s, and the current function and anodic peak potential were constant over the range v = 48–480 mV/s. Under the same conditions, the second (apparently one-electron) wave shifted positive by 40 mV, indicative of an irreversible process. At reduced temperatures, there was an indication (Figure 4) of some chemical reversibility to the second wave, but the dication is in any case highly reactive.

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[13] Triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine.

Bulk oxidation at the first wave (applied E = +0.20 V) was performed at −15 °C. An n value of 1.2 e was obtained as the solution changed from yellow to purple. A voltammogram of the electrolyzed solution taken with a rotating platinum electrode showed the same two waves as in the original solution, except that the first wave was a reduction wave, showing that **4** had been converted into its cation. A sample of this purple solution was removed and frozen for ESR analysis. The frozen solution gave an intense spectrum with cobalt hyperfine lines. A more thorough ESR study of this and other cobalt π complex radicals is underway, but one observation which might be appropriate here is that the major Co hyperfine splitting (ca 55 G) is along the direction of the *high-field g* component. This is the opposite of spectra of d^9 cobalt–polyolefin compounds such as cyclopentadienyl(cyclopentadienone)cobalt(1−) and (COD)CoCp$^-$, in which the dominant Co hfs (140–160 G) lies along the low-field, $g_{\parallel}$, direction.[14,15] Data on paramagnetic cobalt π complexes is certainly rare. The only other d^7 case of which we are aware is that of cobaltocene and its derivatives,[16] but that case involves an orbitally degenerate system and the results are not directly comparable to the results on **4**$^+$. Qualitatively, the ESR spectrum of **4**$^+$ seems to be consistent with an electronic structure of the cation radical in which the cobalt is in the d^7 state, but resolution of the low-field components of the spectrum will be required if serious assignments of electronic structure are to be made.

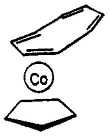
When the solution of the cation was electrolyzed positive of the second wave (E_{app} = +1.2 V), another 0.5 faraday was passed and the solution went from purple to deep blue. After electrolysis, the major electrochemical wave was a reduction at −0.5 V (irreversible). The solution appeared to be air-stable and reacted with either CH_3CN or diphos, but no attempts at product isolation were made.

Discussion

The results show that in a strongly coordinating solvent like CH_3CN, oxidation of these cobalt–polyolefin compounds results in rapid displacement of the polyolefin by solvent, with the eventual organometallic product being the very stable cobaltocenium ion, Cp_2Co^+. The yield of liberated polyolefin is quantitative. In the weak donor solvent CH_2Cl_2, liberation of the polyolefin and formation of Cp_2Co^+ does occur, but the reaction is much slower. For example, the liberation of cyclooctatetraene from **1** is complete within 10^{-2} s in CH_3CN, but it requires about 10^3 s in CH_2Cl_2. The cation radicals of the two cyclooctadiene compounds **3** and **4** are much more stable than those derived from the cyclooctatetraene compounds **1** and **2**, even in CH_2Cl_2. This can be rationalized by recalling that COT ligand is extremely versatile in the manner in which it may bond to a metal.[17,18] Hence, the first reaction of the cation radical (COT)CoCp$^+$ probably involves a fast reorientation of the M–COT bond. This intermediate, of unknown structure, slowly loses COT to form the final products.

Finally, the preferred isomeric forms of the polyolefin ligands in the oxidized compounds must be considered. Unlike the case in its analogous reduction process,[4] the oxidation of (1,5-COD)CoCp does not result in isomerization of the hydrocarbon to the 1,3 isomer. This was proved by gas chromatographic analysis of the solutions produced in bulk anodic oxidations of **3**, which showed that 1,5-COD, but not 1,3-COD, was present in the oxidized solutions.

The question of possible isomerizations involving changes between η^4-1,2,3,4 and η^4-1,2,5,6 modes of bonding of the COT ring to the metal cannot be so readily answered, since the liberated hydrocarbon will be identical in both cases. Associated with this problem is the fact that a *single* oxidation wave was observed for both **1** and **2**, in contrast to the reductions of these compounds, in which waves were observed for both the 1,5 and 1,3 isomers (**1** and **5**, respectively). Electrochemical and NMR measurements have demonstrated that interconversion of the two neutral isomers is slow at room temperature,[4] so a CE mechanism (chemical isomerization preceding electron transfer) cannot account for the absence of a second oxidation wave. The most likely possibilities are that (a) the 1,5 and 1,3 isomers have coincident potentials for oxidation or (b) the cation radical of the more easily oxidized isomer converts rapidly to that of the less easily oxidized isomer. Consider, for example, Scheme III, in which the 1,5 isomer is assumed to have a lower $E°$ potential. Provided that $E°_{1,3} > E°_{1,5}$ and that isomerization of the cation is very fast, a small amount of current flow would catalyze the isomerization of neutral 1,5 isomer to neutral 1,3 isomer at the electrode surface, and a single oxidation wave, at the potential of $E°_{1,3}$, would be observed. What makes this mechanism difficult to test is the added problem that there is another rapid chemical reaction subsequent to electron transfer which makes the overall process irreversible. The question of possible isomeric interconversions in the cation radicals of the cobalt–cyclooctatetraene complexes must still be considered to be open.



5

Scheme III

$$\text{(1,5-COT)CoCp} \rightleftarrows \text{(1,5-COT)CoCp}^+ + e^- \quad E°_{1,5}$$

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

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

Acknowledgment. We are grateful for the support of this work by the National Science Foundation (Grant CHE 80-04242) and for samples of **2** and **4** provided by Dr. John L. Spencer of the University of Bristol.

Registry No. 1, 12110-49-5; **2**, 78063-03-3; **3**, 12184-35-9; **4**, 82595-75-3; **5**, 70810-90-1; Cp_2Co^+, 12241-42-8; (COD)Co(C_5Me_5)$^+$, 82638-71-9; Hg, 7439-97-6; Pt, 7440-06-4.

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