dependences of the rate constant on steric and electronic characteristics of R and L. Electron-releasing ligands L on the metal center should promote reaction when there is a net withdrawal of electrons from the metal center in the transition state. Increased steric requirement at either the metal or the group donor is expected to slow the reaction by impeding the effective approach of reactants. A higher electron affinity of the group donor molecule should speed up the reaction. Such an effect is observed for PhSSPh as compared to the alkyl disulfides (Table III). However, we noted above that the S–S bond energy in PhSSPh is only about 55 kcal/mol as compared with 74 kcal/mol for MeSSMe. This difference in bond energy also accounts for the faster reaction of the phenyl compound.

In summary, the reactions of transition-metal carbonyl radicals with RSSR provide an efficient synthetic pathway for forming thiolate–metal carbonyl complexes.[19] The group transfer reaction rates are influenced by the electronic and steric characteristics of ligands on the metal in the same manner as observed for halogen atom transfer processes. The rate constants fit a two-parameter free energy relationship wherein the electronic and steric parameters are represented. Finally, the group transfer rate constants are observed to be very sensitive to the steric properties of the alkyl groups bound to sulfur.

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Unusual Oxidative Behavior of $(\eta^5\text{-}C_5R_5)M(CO)_2$ ($R = H, CH_3$; $M = Rh, Co$) Complexes at Mercury and Platinum Electrodes†

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The electrochemical oxidative behavior of a series of cyclopentadienyl and pentamethylcyclopentadienyl carbonyl complexes of rhodium and cobalt is described. The voltammetric, polarographic, and coulometric data from the oxidations of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$, and $(\eta^5\text{-}C_5(CH_3)_5)Rh(CO)_2$ are reported. The electrochemical experiments were conducted in methylene chloride at platinum and mercury electrodes. The cyclopentadienyl complexes $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ exhibited oxidative behavior dependent on electrode material. At a platinum-bead electrode there was evidence that the organometallic solute adsorbs to the electrode surface, while at a hanging-mercury-drop electrode it was found that mercuric chloride formed at the surface of the electrode at potentials greater than 0.200 V vs. SCE. This $HgCl_2$ reacts with the solute to form an insoluble Lewis acid–base adduct, $[Cl_2Hg]\cdot[M(CO)_2(\eta^5\text{-}C_5H_5)]$, where M = Rh, Co. These adducts were also formed from the homogeneous oxidation of the organometallic solute with $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$, but only when mercury was present in the solution. The pentamethylcyclopentadienyl complexes $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$ and $(\eta^5\text{-}C_5(CH_3)_5)Rh(CO)_2$ were found to undergo chemically reversible one-electron oxidations to relatively stable cation radicals at both platinum and mercury electrodes. There was no evidence of either pentamethylcyclopentadienyl complex reacting with the mercuric chloride. Extended Hückel calculations were conducted on all four complexes. Correlations were seen between the experimental observations and Hückel predictions of adduct formation and radical stability.

Introduction

Among the cyclopentadienyl derivatives of organometallic complexes, monomeric carbonyl species with the general formula $(\eta^5\text{-}C_5H_5)M(CO)_{n-x}(L)_x$ are of particular interest because of their catalytic importance in a number of organic syntheses.[1-9] We report here the unusual oxidative behavior of a series of cyclopentadienyl and pentamethylcyclopentadienyl dicarbonyl derivatives of rhodium and cobalt: $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ (I), $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (II), $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$ (III), and $(\eta^5\text{-}C(CH_3)_5)Rh(CO)_2$ (IV). (The $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5(CH_3)_5$ rings will be abbreviated as Cp and Cp′, respectively.)

The main thrust of recent research on π-bonded polyolefin organometallic complexes has centered on the chemistry of their paramagnetic derivatives. These radical systems have been suggested as possible catalytic intermediates and/or transition states for important synthetic and industrial processes.[3,4,7-10] The rate at which the metal center undergoes nulceophilic substitution has been shown to control catalytic efficiency.[4,9-11] Therefore, investigations have been primarily concerned with developing processes that enhance the susceptibility of the metal center to nucleophilic substitution reactions. Kochi has reported that the rate of nucleophilic substitution at the metal center increases substantially for complexes with the general formula $CpMn(CO)_{3-x}(L)_x$, when the complexes are oxidized to their cation radicals.[12] Also of interest are the independent observations of Connelly[13] and McKinney[14] that $CpRh(CO)(PR_3)$ complexes undergo one-electron-oxidation reactions to cation radicals, which dimerize to form bimolecular fulvalene dications.[6] Other important studies include the extended Hückel theoretical determinations by Hofmann on the plausibility of 16-electron organometallic intermediates being involved in catalytic processes[15] and the work of Casey on the effect of substitution at the metal center on the η number of a π-bonded polyolefin ring.[16] Finally,

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† This paper is dedicated to the memory of Dr. Dorothy Z. Gennett, an extremely remarkable scholar and colleague who will be missed by us all.

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of equal importance are investigations concerned with the homogeneous reactions of neutral complexes with electrode-generated species. There are a number of possible reactions or series of reactions, which can occur before, during, or after electron transfer in the bulk of the solution, in the diffusion layer, or at the electrode surface.[17,18]

This investigation contains an evaluation of the oxidative behavior of complexes I–IV. particularly notable was the peculiar electrochemical response of complexes I and II at the different electrode materials in methylene chloride solutions. The platinum electrode exhibited strong adsorption behavior, while at mercury electrodes the voltammetric response was found to be the direct result of a series of homogeneous reactions taking place near the electrode surface. Similar electrode effects have been reported by Bond et al., for a series of isoelectronic iron carbonyl complexes.[19] We report the isolation and characterization of the oxidative electrochemical product for complexes I and II at mercury electrodes. The complex formed was the result of a Lewis acid–base reaction between a solvent–electrode precursor species, $HgCl_2$, and the organometallic solute, either $CpRh(CO)_2$ or $CpCo(CO)_2$. This homogeneous Lewis acid–base reaction and unusual electrochemical behavior were not observed for complexes III and IV. In fact, the pentamethylcyclopentadienyl derivatives both undergo reversible one-electron oxidations to a relatively stable cation radical. The diversity of the electrochemical and homogeneous behavior was quite unexpected considering the known chemical similarities for complexes I–IV.[11,17,20] These experimental observations of adduct formation and radical stability were found to correlate with the theoretical predictions of extended Hückel molecular orbital calculations.[21]

Experimental Section

Routine electrochemical experiments described were carried out under an atmosphere of argon. Controlled-potential electrolysis experiments were performed inside a Vacuum Atmospheres inert-gas chamber equipped with a Model 372 Dri-train and adapted for low temperature. An IBM Model EC/225 voltammetric analyzer was employed as a potentiostat. Low-temperature experiments were conducted in a cell where the working compartment was temperature controlled and the reference compartment was kept at room temperature. The temperature of the working compartment in the electrochemical cells was controlled to ±1 °C with a Forma Scientific Model 2067 temperature bath and circulator. All potentials were recorded vs. an aqueous saturated calomel electrode. The base electrolyte was always 0.1 M tetrabutylammonium hexafluorophosphate. The compounds, I–IV, were 0.3–1.0 mM for voltammetric/polarographic experiments and 0.5–2.0 mM for controlled-potential electrolysis experiments. Glass-distilled Spectrograde Burdick and Jackson methylene chloride was dried over calcium hydride and vacuum-distilled before use.

The compounds $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, and $(\eta^5\text{-}C_5(CH_3)_5)Rh(CO)_2$ were purchased from Strem Chemical Co. The compounds $(\eta^5\text{-}C_5(CH_3)_5)Co(CO)_2$, $[HgCl_2]\cdot[(\eta^5\text{-}C_5H_5)Co(CO)_2]$, and $[HgCl_2]\cdot[(\eta^5\text{-}C_5H_5)Rh(CO)_2]$ were synthesized according to literature procedures.[22-24] All of the compounds were stable indefinitely when stored inside the drybox.

The platinum-bead electrodes were pretreated by (1) refluxing in concentrated nitric acid for 10 min, (2) rinsing with distilled water, (3) submerging the electrode in a 1.0 M sulfuric acid solution saturated with ferrous ammonium sulfate, and (4) rinsing with distilled water, matting dry, and using. Hanging-mercury-drop electrodes were prepared according to literature procedures.[25]

Table I. Oxidation Potentials Observed for Cobalt and Rhodium Complexes in This Study[a-c]

	platinum			mercury		
	E_{pa}	E_{pc}	$E°$	E_{pa}	E_{pc}	$E°$
$CpRh(CO)_2$ (I)	1.00	0.290[d]		0.507	0.433	0.470[e]
$CpCo(CO)_2$ (II)	0.960	0.590[d]		0.380	0.305	0.343[e]
$Cp'Co(CO)_2$ (III)	0.432	0.362	0.397	0.432	0.355	0.394
$Cp'Rh(CO)_2$ (IV)	0.520	0.040		0.520	-0.020	

[a] Cyclic voltammetric data in methylene chloride. [b] Potentials in volts referenced to the aqueous saturated calomel electrode. [c] Scan rate 0.200 V/s. [d] Exhibited adsorptive behavior. [e] These potentials are not $E°$ but $(E_{pa} - E_{pc})/2$.

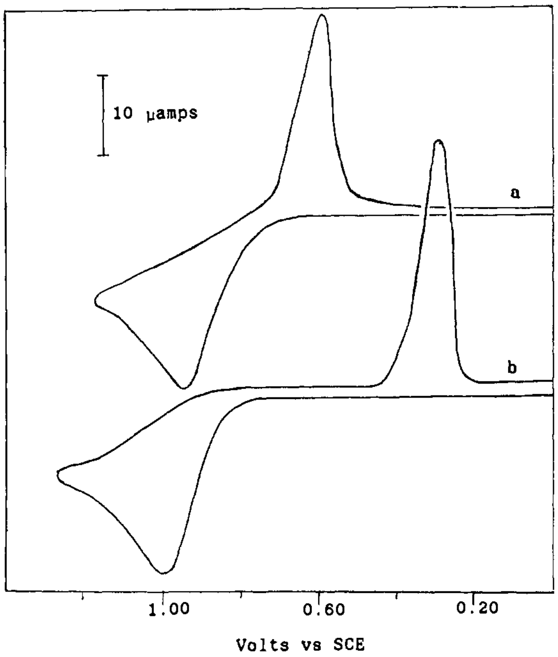

Figure 1. Cyclic voltammograms of ca. 8.1×10^{-4} M $CpCo(CO)_2$ (a) and $CpRh(CO)_2$ (b) in CH_2Cl_2–0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (scan rate 0.200 V/s; $T = 298$ K; Pt electrode).

Infrared spectra were recorded on a Perkin-Elmer PE 298 spectrophotometer and calibrated against the adsorption of polystyrene at 1601 cm^{-1}. Proton NMR spectra were recorded on a JEOL FX 90Q spectrometer.

Results

A summary of the electrochemical behavior in methylene chloride for complexes I–IV is presented in Table I. All electrochemical experiments were performed in methylene chloride because of the known formation of solvento complexes, $CpM(Solv)_3^+$, in other electrochemical solvents such as tetrahydrofuran, acetonitrile, and dimethylformamide.[26,27]

Electrochemistry of $CpRh(CO)_2$ and $CpCo(CO)_2$. Immediately apparent from Table I is the effect of electrode material on the potentials and reversibility of the oxidation reactions for complexes I and II. Cyclic voltammetry at a platinum-bead electrode showed the oxidations of $CpRh(CO)_2$ and $CpCo(CO)_2$ were complicated by adsorption at the electrode surface evidenced by the unusual waveform of the cathodic peaks in voltammograms a and b of Figure 1. This adsorption behavior limited our electrochemical analysis of I and II at platinum surfaces. In marked contrast was the apparently reversible, uncomplicated oxidative behavior of I and II at the hanging-mercury-drop electrode, HMDE (Figure 2, voltammograms a and b). Evaluation of the voltammetric data at the HMDE for both I and II found the cathodic to anodic peak

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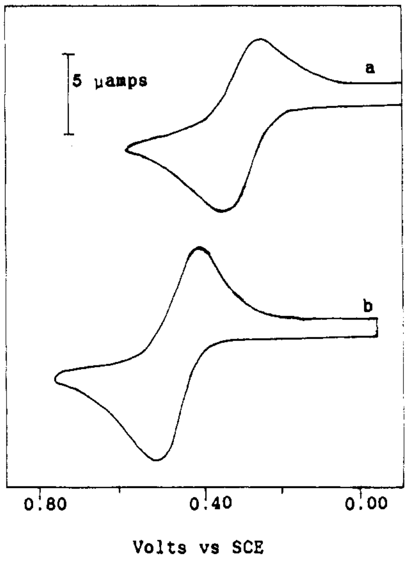

Figure 2. Cyclic voltammograms of ca. 8.1 × 10^{-4} M $CpCo(CO)_2$ (a) and $CpRh(CO)_2$ (b) in CH_2Cl_2–0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (scan rate 0.200 V/s; T = 298 K; HMDE).

current ratios to be approximately unity and the peak separation to range from 70 to 80 mV for scan rates between 0.050 and 5.00 V/s. These data seemed to indicate that the oxidation was a chemically reversible one-electron process. Further evaluation of the experimental data for the oxidative electron transfer showed that the current function, $i_{pa}/v^{1/2}$, was not constant over the scan-rate range. Also of significance was the effect of electrode history on electrochemical behavior; subsequent scans using the same mercury drop lead to a broadening of both the cathodic and anodic peaks. Finally, a maximum was observed in the dc polarogram approximately 320 mV positive of the half-wave potential. These data are consistent with an electron-transfer process complicated by chemical reactions at or near the electrode surface. Remarkably, this unusual electrochemical response was the same for both the rhodium and cobalt cyclopentadienyl compounds. The only difference between the oxidation reactions of complexes I and II at mercury was the magnitude of the oxidation potentials (Table I).

Controlled-potential electrolysis of the cyclopentadienylrhodium complex I in CH_2Cl_2 with an E_{app} value of 0.55 V at a stirred-mercury-pool electrode resulted in a yellow compound precipitating out of solution. The measured number of coulombs for this oxidation was irreproducible. This variability is assumed to be a consequence of electrolyzing the mercury electrode, not the organometallic solute (vide infra). Analysis of the yellow product showed it to be diamagnetic, to be unstable in nonaqueous electrochemical solvents, and to decompose at temperatures greater than 98 °C. An infrared spectrum of the yellow compound (KBr pellet) found carbonyl stretches at 2099, 2050, and 2022 cm^{-1} and an HgCl stretch at 266 cm^{-1}. A proton NMR spectrum of an *o*-chloroaniline solution containing the yellow product showed a doublet at 5.20 ppm vs. Me_4Si ($I_{Rh} = {}^1/_2$). These physical and spectroscopic data were found to be in excellent agreement with the values reported for the Lewis acid–base adduct $[Cl_2Hg]\cdot[RhCp(CO)_2]$.[23,24,28,29] Comparison of the spectroscopic behavior of the electrochemically and chemically synthesized[23] Lewis acid–base adduct confirmed the above results.[11] These experimental results were highly unexpected considering the results reported by Connelly[13] and McKinney[14] for a very similar compound, $CpRh(CO)(P(C_6H_5)_3)$. Electrochemical oxidation of this complex in methylene chloride at platinum electrodes formed a dimeric fulvalene dication derivative, $[(C_5H_4)_2Rh_2(CO)_2(P(C_6H_5)_3)_2]^{2+}$, and homogeneous oxidation by silver ions formed a silver-bridged, trinuclear, cationic complex, $\{[CpRh(CO)(P(C_6H_5)_3)]_2Ag\}^+$.[13]

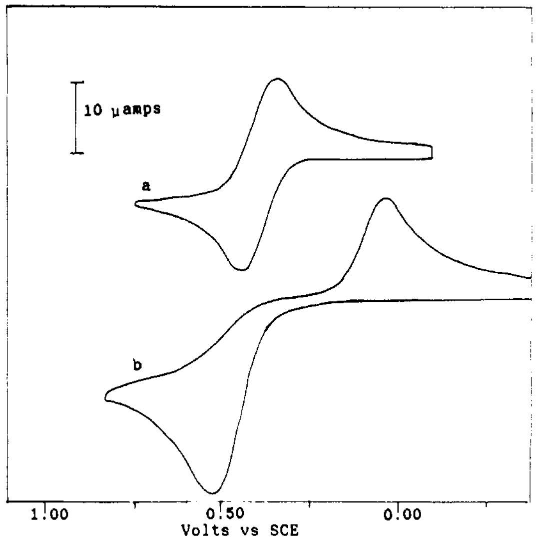

Figure 3. Cyclic voltammograms of ca. 7.7 × 10^{-4} M $Cp'Co(CO)_2$ (a) and $Cp'Rh(CO)_2$ (b) in CH_2Cl_2–0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (scan rate 0.200 V/s; T = 273 K; Pt electrode).

The cobalt derivative II had electrolytic behavior very similar to that of the rhodium compound I. Controlled-potential electrolysis with an E_{appl} value of 0.45 V at a stirred-mercury-pool electrode resulted in the precipitation of an orange solid. This is different from the yellow product isolated for the rhodium complex. Coulometric data were again irreproducible as with I, due to the oxidation of the mercury electrode (vide infra). The orange product had chemical behavior very similar to that of the electrolysis product from the rhodium complex. It was diamagnetic, it decomposed or was insoluble in nonaqueous electrochemical solvents, and the crystals decomposed at temperatures greater than 88 °C. An infrared spectrum of the orange product showed carbonyl stretches at 2072, 2040, and 2023 cm^{-1} and an HgCl stretch at 239 cm^{-1}. A proton NMR spectrum of an *o*-chloroaniline solution containing the orange product showed a peak at 5.10 ppm vs. Me_4Si. These data are consistent with the literature and our laboratory values obtained for the Lewis acid-based adduct $[Cl_2Hg]\cdot[CoCp(CO)_2]$.[25,30] These results were highly unexpected considering the reports of a stable monocation radical for similar phosphine-substituted cobalt complexes with the general formula $CpCo(CO)(PR_3)$.[31,32]

The homogeneous redox reaction of the oxidizing ferrocenium complex $[(Cp)_2Fe][PF_6]$ with complexes I and II was also informative. Ferrocenium ion, with $E°$ = 0.43 V, should partially oxidize complex I and completely oxidize complex II according to our mercury electrode electrochemical data (Table I). However, no reaction occurred for either complex with the ferrocenium ion.[31] When mercury was added to the reaction mixture containing either complex I or II and the ferrocenium ion, the respective insoluble yellow or orange product formed. The spectroscopic and physical properties of these solids were identical with those of the Lewis acid–base adducts formed during heterogeneous electrolysis.

Electrochemistry of $Cp'Co(CO)_2$. The pentamethylcyclopentadienyl derivatives of cobalt and rhodium, complexes III and IV, exhibited quite different electrochemical behavior at the platinum and mercury electrodes compared with the behavior of their respective nonmethylated counterparts.

In cyclic voltammetry experiments of the cobalt derivative III at a platinum-bead or hanging-mercury-drop electrode, for any scan rate between 0.050 and 5.00 V/s, the current function was found to be constant, the anodic to cathodic peak separation was

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shown to be a consistent 70 mV, and the cathodic to anodic peak current ratio was approximately unity (voltammogram a, Figure 3). These data are consistent with III undergoing an electrochemically and chemically reversible one-electron oxidation. This radical stability was totally unexpected considering the results of adduct formation for the cyclopentadienylcobalt complex II.

Low-temperature (−20 °C) controlled-potential electrolysis of III in CH_2Cl_2 was conducted at a large platinum basket with $E_{appl} = 0.500$ V. (Results for the mercury-pool electrode were identical with those for the platinum basket.) The solution changed color from golden yellow to deep red. A plot of ln *i* vs. *t* was linear for the electrolysis data, confirming the oxidation was diffusion-controlled. The value of 1.05 electrons determined by coulometry verified the oxidation to be a one-electron process. Cyclic and rotating-electrode voltammetry at a platinum electrode of the electrolyzed solution showed that only the cation radical of III, $[Cp'Co(CO)_2]^{\bullet+}$ ($E°$ and $E_{1/2}$ equal to 0.395 and 0.390 V, respectively), was present in solution. The current levels for the reduction of the cation radical were only 5% lower then the current levels for the original oxidation reaction. An ESR spectrum of the frozen electrolyzed solution was obtained, establishing the paramagnetism of the electrolysis product. Disappointingly, only a single broad line with no coupling to the cobalt ($I_{Co} = {}^7/_2$) was observed. These ESR results are consistent with those seen for $[CpCo(CO)(P(C_6H_{11})_3)]^{+}$.[31] The cation radical proved to be thermally unstable in solution, decomposing to a blue color at temperatures greater than 0 °C and to a green color on exposure to air. Further analyses of the blue and green products proved to be inconclusive. However, this decomposition behavior corresponds well with the behavior reported for the cation radical $[Cp'Co(CO)P(C_6H_5)_3]^{\bullet+}$.[31] The infrared spectrum after electrolysis showed that the solution contained a mixture of products. Even attempts using FTIR instrumentation proved incapable of obtaining spectra before decomposition.

The bulk reduction of the cation radical of III back to the neutral species was achieved with an 85% reconversion. The conditions for the reelectrolysis of the radical were the same as for the original oxidation except that the E_{app} value equaled 0.100 V.

Homogeneous oxidation reactions of complex III with $[(Cp)_2Fe][PF_6]$ in methylene chloride induced the same color changes as the bulk electrolysis. The infrared spectra were comparable to those of the electrolytic solution with the mixture of products in solution.

Electrochemistry of $Cp'Rh(CO)_2$. Cyclic voltammetry at a scan rate of 0.200 V/s of the rhodium pentamethylcyclopentadienyl derivative IV in CH_2Cl_2 at a platinum-bead electrode shows an oxidation wave at $E_{pa} = 0.520$ V and a subsequent reduction wave at $E_{pc} = 0.040$ V (voltammogram b, Figure 3). At any scan rate from 0.05 to 5.00 V/s no reverse cathodic current was seen for the anodic oxidation wave. This waveform with its large cathodic to anodic peak separation is typical of an electrochemically and chemically irreversible heterogeneous electron-transfer reaction.

Controlled-potential electrolysis of IV in CH_2Cl_2 at −30 °C with $E_{appl} = 0.60$ V was done at a large platinum-basket electrode. The color changed from yellow to bright orange. The ln *i* vs. *t* plot was linear, showing the process to be diffusion-controlled. Coulometric data for the electrolysis indicated that 0.93 electron was removed, showing the oxidation to be a one-electron process. Cyclic and rotating-electrode voltammetry experiments at platinum of the electrolyzed solution verified the existence of a complex with an irreversible reduction at $E_{pc} = 0.040$ V (scan rate 0.200 V/s) and $E_{1/2} = 0.020$ V (0.005 V/s). The current levels were 80% of the original oxidation. This orange solution proved to be even more unstable then the radical solution of III. The electrolysis product decomposed to a pink and then brown color when warmed to temperatures greater than −20 °C. Bulk reduction of the electrolyzed species at −0.050 V, with subsequent electrochemical analysis, showed that the starting material IV was regenerated to within 70% of the original concentration. The neutral starting material was confirmed by its infrared spectrum. These data are strong evidence that the oxidation for IV is a chemically reversible one-electron process that is electrochemically irreversible. Using Nicholson theory, we can calculate an electron-transfer rate of $k_s = 2 \times 10^{-4}$ cm/s (±10%), resulting from the 480-mV peak separation at 0.200 V/s.[33] This slow electron-transfer rate is well within the range of an electrochemically irreversible process, greater than 10^{-2} cm/s, and indicates that there is a large activation barrier to electron transfer. This barrier is probably caused by a drastic structural rearrangement of the cation.

An extremely important experimental observation was that at no time during any of our experiments on the pentamethylcyclopentadienyl complexes was there evidence to suggest that complicating chemical reactions were occurring at the electrode surface. In fact neither the neutral nor the cationic radical species of III or IV underwent the Lewis acid-base reaction that was observed for complexes I and II.

Discussion

The apparently reversible oxidation reactions of the cyclopentadienyl derivatives I and II at mercury electrodes are proposed to be caused by the following series of heterogeneous and homogeneous reactions occurring at or near the electrode–solvent interface. The first process involves the oxidation of the mercury electrode to either the mercurous, Hg^+, or mercuric, Hg^{2+}, ion. The next step actually involves a series of reactions ooccurring in very rapid succession. The first is the reaction of the mercury ions with methylene chloride to form mercuric chloride, $HgCl_2$. The methylene type species formed by this reaction, either "CH_2Cl^{+}" or "CH_2^{2+}", for Hg^+ and Hg^{2+}, respectively, are assumed to react with solvent molecules. There is no experimental evidence to suggest that either of these "methylene-like" species react with the organometallic solute. In most experiments the mercuric chloride formed at the electrode surface would be in minimal concentrations and would not be involved in any chemical or electrochemical reactions. However, our experiments have shown that a Lewis acid–base reaction occurs between the mercuric chloride and the organometallic solute (complexes I and II), resulting in the formation of an insoluble Lewis acid–base adduct. This reaction removes the mercuric chloride from the electrode–solvent interface, causing more mercuric chloride to be produced, which is again removed by the reaction with the organometallic solute. This equilibrium process continues until the all of the organometallic solute is depleted from the solution. The rates of the above reactions are very rapid on the time scale of the electrochemical experiments. This causes the overall process to apparently behave as a one-step, concerted electron-transfer process.

The observed voltammetric behavior of the oxidation of I and II at mercury electrodes can be explained by the following processes occurring at the mercury surface. These processes are different from those presented by Bond, who postulated that a mercury-stabilized cationic complex was formed.[19] The oxidation of the mercury electrode, caused by the aforementioned equilibrium process, passes substantial anodic current. The $HgCl_2$ formed by the reaction with the solvent is known to adsorb to the electrode surface.[34] The organometallic solute diffuses to the electrode surface and reacts with $HgCl_2$, forming the Lewis acid–base adduct $[Cl_2Hg]\cdot[MCp(CO)_2]$, where M = Rh, Co. Initially, this removal of $HgCl_2$ induces more mercury to be oxidized and causes an increase in anodic current. This current is a direct result of the diffusion-controlled movement of organometallic solute to the electrode surface. Therefore, a maximum current will be achieved in the voltammetry experiment; however, in this case the maximum, i.e., diffusion control, only occurs for the first cyclic scan. The adsorption maxima observed in dc polarography show that the insoluble Lewis acid–base adduct is adsorbing on the mercury electrode surface. This adsorption of the adduct to the electrode surface will inhibit the electron transfer at, and diffusion to, the electrode surface. The observed broadening of the voltammetric peaks with subsequent scans at the HMDE substantiates this. The reverse cathodic current associated with the anodic wave on the

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first scan is assumed to be caused by the reduction of Hg^{2+} back to neutral mercury. The source of the Hg^{2+} would be from the reduction of the mercuric ion present in the Lewis acid–base adduct $[Cl_2Hg]\cdot[MCp(CO)_2]$. This reduction of the adduct causes the organometallic starting material to be regenerated. We wish to restress that the rates of the electron-transfer and homogeneous reactions have to be quite rapid in order to obtain the pseudoreversible one-electron oxidative behavior we have observed. The electrolysis reaction at the stirred-mercury-pool electrode proceeds until all of the solution is depleted because the stirring action constantly renews the electrode surface, thereby minimizing pacification of the electrode surface.

The important consequence of these homogeneous reactions is that they have caused an underpotential to occur for the oxidation of mercury in a methylene chloride solution.

Lewis acid–base adduct formation for the pentamethylcyclopentadienyl complexes III and IV was not observed. In an explanation of this result two contributing factors are considered: (1) What is the steric effect of the methyl groups on the approach of $HgCl_2$ to the metal center? (2) What is the availability of the metal's highest occupied orbital, necessary for the orbital–orbital overlap with the lowest unoccupied molecular orbital of $HgCl_2$, for Lewis acid–base adduct formation? The X-ray crystal structure data on complexes III[22] and IV[35] and on the two acid–base adducts[29,30] show that the steric hindrance to adduct formation upon ring methylation will be minimal. This is because the methyl groups are pointed slightly up and away from the methyl carbonyl moiety hence not hindering the mercuric chloride, which can only approach the metal center from the carbonyl side of the molecule.[23,24,29]

In order to evaluate the orbital effects on adduct formation, extended Hückel molecular orbital calculations were conducted on complexes I–IV.[21] The geometric parameters used in the calculations were obtained from X-ray crystallographic data.[22,24,29,30,35] The theoretical calculations show that upon methylation the carbon atoms in the ring π system become more positive by an average of 0.05, the central metal atom becomes more negative by 0.08, and the carbonyl oxygens and carbons become more negative by 0.03 and 0.02, respectively (all values ± 0.01). Intuitively, it is expected that the pentamethylcyclopentadienyl derivatives would be stronger Lewis bases because of the higher electron density at the metal center compared to that in the cyclopentadienyl derivatives. However, this increase in anionic charge caused by the forward donation of electron density from the ring π system to the metal center induces additional back-donation of metal electron density to the carbonyl ligands. These interactions have changed the bonding throughout the entire molecule. Consequently, even though there is greater electron density at the metal center the occupied orbitals containing the Lewis base electrons are less available for adduct formation because of the interactions between the molecular orbitals of the ring and carbonyl π systems. The infrared data show that the carbonyl bands for III and IV have shifted to lower frequencies compared to those for I and II,[20] indicative of more back-bonding, i.e., double bond, character between the metal and the carbonyl carbon for III and IV. These changes in orbital availability cause an effective decrease in Lewis basicity for III and IV. We proposed that this decrease in basicity is the major factor inhibiting adduct formation between the methylated ring complexes (III and IV) and the mercuric chloride.

Conclusions

Electrochemists have always been concerned that homogeneous reactions of the electrolyte, solvent, or electrode material would affect electron-transfer reactions and cause results that could be easily misinterpreted. In fact, our results, along with those of Bond,[19] have shown that a series of homogeneous reactions can actually mimic the redox behavior of an uncomplicated reversible electron transfer. These results emphasize the need to evaluate even apparently reversible electron-transfer reactions cautiously and critically. In the literature there have been reports of reversible oxidations at mercury in methylene chloride for π-bonded polyolefin transition-metal complexes similar to those in this investigation.[36-39] We feel that these data should be reevaluated in light of the results reported here. It is not our intent to imply that every reversible oxidation reported is in fact a series of homogeneous reactions, but it now seems obvious that redox processes at mercury electrodes should be evaluated with the utmost care.

Additionally, we have seen that our experimental results on adduct formation and radical stability correlated with the predictions of extended Hückel theory calculations. We believe future investigations that concentrate on comparing the theoretical predictions of extended Hückel molecular orbital calculations with experimental redox reactions will be useful in evaluating the electrochemical behavior of molecules.

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