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Electrochemistry of Metallocenes at Very Negative and Very Positive Potentials.
Electrogeneation of 17-Electron Cp2Co2+, Cp2Co2−, and Cp2Ni2− Species

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Cyclic voltammetry (CV) with Pt ultramicroelectrodes and coulometry were used to study the electrooxidation of the Cp2Co+ cation in liquid SO2/(TBA)AsF6 solution in the temperature range from -70 to +25 °C. The Cp2Co+ cation was shown to undergo reversible one-electron oxidation with formation of the Cp2Co2+ dication, which is stable on the CV time scale. The chemical and electrochemical reversibility of Cp2Co+ oxidation suggests retention of the sandwich structure in the dication. The $E^o$ value for the Cp2Co2+/+ redox couple is +3.15 V (vs SCE) and the rate constant of heterogeneous electron transfer is $k_{e-} = 10.03 \pm 0.01$ cm/s. Electrochemically generated in the THF/(TBA)PF6 medium at $T < -60$ °C, Cp2Co- and Cp2Ni- anions, at $E < -3.1$ V, are reduced to Cp2Co2− and Cp2Ni2− dianions (or are reduced with simultaneous electron transfer and bond rupture); these dianions are unstable on the CV time scale for $T$ down to -100 °C. The relationship between the $E^o$ values of redox reaction of metallocenes and the ionization potentials of the corresponding metals is discussed.

Introduction

The redox behavior of sandwich complexes has been the subject of many investigations.1,2 The existence of a linear relationship between the standard potential values ($E^o$) of all possible redox reactions of homo- and heteroligand sandwich complexes and metal ionization potentials ($IP$) has been established and justified.2-5 This relationship is based on the fact that the frontier orbitals of sandwich complexes are predominantly metal-based, and the $E^o$ values for the electron-transfer reaction in the series of sandwich complexes involving precisely the HOMO and LUMO should in fact reflect the change in the oxidation state of the metal, whose measure is the $IP$ value.2 Thus, for the redox couples

$$E^o_j (V vs \text{SCE}) = -0.16 + 0.111IP_j$$

(1)

is valid, where -0.16 is a constant characteristic of the Cp ligand and $j = 1-4$.2-5 Equation 1 makes it possible to estimate the values of the redox potentials of Cp2Co2+/+ and Cp2Co2−/− couples, which previously have not been observed. According to eq 1 the $E^o$ values for the Cp2Co2+/+ and Cp2Co2−/− redox couples can be estimated as $>4.2$ V and $<$-3 V, respectively, and are outside of the "potential windows" of most solvents suitable for electrochemical studies.

Liquid sulfur dioxide containing a suitable supporting electrolyte is an excellent solvent for the electrochemical generation of reactive cations due to low nucleophilicity, ability to solvate ionic compounds as well as covalent substrates, and an anodic range up to about +6 V vs SCE. Thus, SO2 is a very useful solvent for the study of electrooxidation processes accompanied by the generation of strong electrophiles. For example, the Cp2Fe+ and Cp*pFe+ cations (Cp*p = p5-C5Me5) can be reversibly oxidized to the corresponding dications at very positive potentials in SO2.8 On the other hand, tetrahydrofuran (THF), because of its low electrophilicity, is one of the best solvents for the study of reduction processes at very negative potentials, especially at low temperatures when the potential window is extended to -3.5 V vs SCE.9,10 Thus, in a THF medium, one-electron reversible reductions are observed for benzene to the radical anion at $E^o = -3.38$ V vs SCE at -90 °C,11 and for Cp2Fe to Cp2Fe2− and using ultramicro-electrodes and low-temperature techniques, the Cp2Ru0+/− ($E^o = -3.48$ V vs SCE) and Cp2Os0+/− ($E^o = -3.44$ V vs SCE) couples can be observed.9,12 Thus, SO2 and THF were chosen here to study the redox reaction of Cp2Co at very positive and very negative potentials. Preliminary results of these studies have been briefly reported previously (Cp2Co2+/+ 13,14 and Cp2Co2−/− 10).

Experimental Section

**Chemicals.** Tetra-n-butylammonium hexafluorarsenate, (TBA)AsF₆, was prepared from an aqueous solution of tetra-n-butylammonium bromide (SACHEM, Austin, TX) to which an equivalent amount of aqueous lithium hexafluorarsenate (Ozark-Mahoning, Pennwalt Corp., Tulsa, OK) was added. The resulting (TBA)AsF₆ crystals were filtered at 0 °C and redissolved in a minimum amount of hot ethyl acetate to which 10% (v/v) diethyl ether was added. The recrystallization was repeated twice and the isolated product was dried under vacuum at 120 °C for 72 h (mp 245–246 °C). Tetra-n-butyrammonium hexafluorophosphate, (TBA)PF₆ (Fluka) was used as received.

Bis(cyclopentadienyl)cobalt hexafluorarsenate, Cp₂CoAsF₆, was prepared by ion exchange from Cp₂CoPF₆ which was dissolved in water with a minimum amount of EtOH added. This solution was then percolated through a Dowex-1-chloride (1X–200, Aldrich Chemical Co.) ion exchange column. Cp₂CoAsF₆ was obtained when an aqueous solution of LiAsF₆ was added to the effluent of the column. The precipitate was filtered and then redissolved in acetone to which ethyl acetate was added (10%, v/v). This solution was then refrigerated to yield the yellow crystals of Cp₂CoAsF₆. After being dried under vacuum at 90 °C for 48 h, the solid was found to melt at 346 °C (while Cp₂CoPF₆ melted at 336 °C). Cobaltocene and Cp₂CoPF₆ were received from the Institute of Organometallic Compounds, Russian Academy of Sciences, and were used without additional purification.

**Procedure.** Before each experiment in the sulfur dioxide medium, a sufficient amount of supporting electrolyte was added to the cell to yield a concentration of 0.15 M. CV experiments were performed in a single-compartment cell (fitted with five working ultramicroelectrodes, one counter electrode, and a reference electrode). All potentials are reported vs a silver quasireference electrode (AgQRE), which was prepared by a salt bridge that had a graphite rod sealed in a glass tip and was filled with a solution of supporting electrolyte to prevent contamination of the reference electrode. The working electrode was polished with diamond paste (down to 0.5-1 μm in diameter) before solvent distillation. This procedure excludes contamination of the reference electrode was kept at room temperature during the low-temperature measurements. All potentials are given in V vs SCE and are referred to the Cp₂FeO⁺/Cp*₂FeO⁺ couples whose potentials are +0.44 and 0.00 V vs SCE, respectively.

THF was distilled from sodium benzophenone immediately prior to use, under argon, into a special buret with supporting electrolyte salt and then was transferred into a previously dried, in vacuo, and argon-filled low-temperature electrochemical cell without contact with air. The (TBA)PF₆ was first dried in the buret by melting it in vacuo immediately before solvent distillation. This procedure excludes contamination of the sample solution by traces of water and chloride ions. For low-temperature measurements, this electrochemical cell was thermostated with ethanol cooled with liquid nitrogen in a Dewar vessel. The cell was equipped with a 1-mm-diameter Pt disk working electrode, a Ag/AgCl/4 M LiCl(aq) reference electrode, and a Pt foil or wire counter electrode. The working electrode was polished with diamond paste (down to 0.5–1 μm in diameter) before use. The reference electrode was separated from the test solution by a salt bridge that had a graphite rod sealed in a glass tip and was filled with a solution of supporting electrolyte to prevent contamination of the solution studied by traces of water and chloride ions. The aqueous reference electrode was kept at room temperature during the low-temperature measurements. All potentials are given in V vs SCE and are referred to the Cp₂FeO⁺/Cp*₂FeO⁺ couples whose potentials are +0.44 and 0.00 V vs SCE, respectively.

**Apparatus.** Electrochemical measurements were made with a PAR (Princeton Applied Research, Princeton, NJ) Model 175 universal programmer and PAR Model 173 potentiostat with a 179 digital coulometer. All measurements were made with feedback IR-drop compensation. All current-potential curves were obtained with a Norland programmer and PAR Model 173 potentiostat with a 179 digital coulometer. All measurements were made with feedback IR-drop compensation. All current-potential curves were obtained with a Norland digital oscilloscope, Model 3001 (Noriland Corp., Fort Atkinson, WI) with a minimum acquisition time of 100 ns/point. In THF at low scan rates (v < 0.5 V/s) a Houston Instruments Model RE x-y recorder was used.

**Results and Discussion**

**Oxidation.** A typical cyclic voltammogram for the oxidation of Cp₂Co²⁺ at a 500-μm Pt electrode in liquid SO₂ at -70 °C and scan rate of 5 V/s is shown in Figure 1a. The formal potential, $E^0$, was estimated from the anodic ($E_p^a$) and cathodic ($E_p^c$) peak potentials as

$$E^0 \approx \frac{E_p^a + E_p^c}{2}$$

and is equal to +3.17 V vs SCE. Also shown in Figure 1 are CV curves at -30 and +25 °C at a scan rate of 10 V/s (parts b and c of Figure 1, respectively). The peak separation, $\Delta E_p$, observed in Figure 1a–c is identical to that expected for Nernstian behavior at these temperatures. For all of these waves, the ratio of cathodic
to anodic peak currents was essentially one. The average $E^\circ$ values obtained at -70 °C were +3.17 and +3.15 V vs SCE for 100- and 25-μm Pt electrodes, respectively. Similarly, the peak separation obtained at -70 °C was 43 and 36 mV for 500- and 25-μm Pt electrodes, respectively. The theoretical peak separation at -70 °C for a Nernstian wave is 40 mV. Thus, the Cp$_2$Co$^+$ oxidation undergoes a one-electron oxidation to the Cp$_2$Co$^{2+}$ dication. The chemical and electrochemical reversible character of the Cp$_2$Co$^{2+}$ oxidation strongly indicates retention of the sandwich structure in the dication.

Controlled potential electrolysis was also employed to confirm the reaction stoichiometry and probe the longer term stability of the product. A 2 mM solution of Cp$_2$CoAsF$_6$ was prepared in 35 mL of a 0.15 M (TBA)AsF$_6$/SO$_2$ solution at -45 °C. When a constant potential of +3.6 V vs SCE was applied, the anodic current decayed from an initial value of 1.3 mA to the background level of 19 μA. The total number of coulombs passed was 6.89 C (vs 6.76 C expected for a one-electron reaction). Thus, $n_{app}$ is essentially one. The electrolyzed solution was a deep blue color. A sample was transferred under vacuum and sealed in a 1-cm glass cuvette, and the absorbance spectrum for Cp$_2$Co$^{2+}$ showed $\lambda_{max} = 410$ nm. The cuvette was then allowed to warm to room temperature. A color change from deep blue to light burgundy was observed upon warming, and the absorbance maximum of this solution was about 500 nm. Because the solution was so intensely colored, a reliable measurement could not be obtained.

The color change suggests instability of the Cp$_2$Co$^{2+}$ at higher temperatures. However, the reversible CV curves at 25 °C suggest that the decomposition of Cp$_2$Co$^{2+}$ is slow on the CV time scale.

A second anodic wave ($E_{p^*} = +3.8$ V vs SCE) was observed when the potential scan was extended to +4.4 V (Figure 2). This wave was totally irreversible at a 25-μm-diameter Pt electrode at scan rates of up to 200 V/s. Thus, further Cp$_2$Co$^{2+}$ oxidation is a chemically irreversible process, proceeding with the consumption of more than two electrons and is probably accompanied by sandwich structure destruction. Note also that around +3.7 V vs SCE, a burgundy was observed upon warming, and the absorbance maximum of this solution was 410 nm. Because the solution was so intensely colored, a reliable measurement could not be obtained.

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Figure 4. Cyclic voltammograms of 1 mM solutions of metallocenes in THF/0.05 M TBA PF6 at different temperatures and scan rates: (a) Cp2Ni, v = 0.1 V/s, Hg and Pt (dashed line) electrodes; (b) Cp2Co, v = 0.1 V/s, Hg electrode; (c) Cp2Fe, v = 0.05 V/s, Pt electrode. Current is given in arbitrary units which differ for different metallocenes and temperatures.

Table II. E° Values for CpM2+/+0/-/2- Redox Couples in THF and Gas-Phase Ionization Potentials (IP) of Corresponding Metals

<table>
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<tbody>
<tr>
<td>Cp2Ni</td>
<td>+20</td>
<td>0.81 (54.9)</td>
<td>0.01 (35.2)</td>
<td>-1.85 (18.2)</td>
<td>-3.04 (7.6)</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>0.01</td>
<td>-1.84</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>Cp2Co</td>
<td>+22</td>
<td>-0.90 (33.5)</td>
<td>-2.04 (17.1)</td>
<td>-1.91</td>
<td>-3.18 (7.9)</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>-0.90</td>
<td>-1.86</td>
<td>-3.20</td>
<td></td>
</tr>
<tr>
<td>Cp2Fe</td>
<td>+15</td>
<td>0.45 (30.6)</td>
<td>0.45</td>
<td>-3.06 (16.2)</td>
<td>-3.00</td>
</tr>
<tr>
<td></td>
<td>-90</td>
<td>0.45</td>
<td>-3.00</td>
<td></td>
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</table>

E° = (E° + E°)/2, vs SCE. E° values in THF; this work. E° values in SO2; ref 8.

Reduction. The cyclic voltammograms for the reduction of cobaltocene in THF at different temperatures are shown in Figure 4b. Figure 4 also shows the voltammograms of Cp2Ni (a) and Cp2Fe (c) under the same conditions. The E° values of Cp2M2+/+0/-/2- redox couples are summarized in Table II. All waves approximately followed a linear peak current vs square root of scan rate dependence and were of about the same height, suggesting all are one-electron waves. Accurate analysis of the most negative waves, i.e., those attributed to the Cp2Co+/+ and Cp2Ni+/2- reactions, were complicated by overlap with the supporting electrolyte discharge process. However, after subtraction of the background current, these waves showed approximate one-electron heights. The peak separation values for the corresponding couples of cathodic and anodic peaks are very close to ∆E = 2.30RT/F values for reversible one-electron-transfer reactions at corresponding temperatures, except that for Cp2Ni+/2- (Figure 4a), which is larger, probably because of a slow charge-transfer process. For ferrocene, one cannot detect the Cp2Fe+/2- redox couple (or a simultaneous electron-transfer, bond rupture process) because this peak is beyond the potential for supporting electrolyte discharge.

Estimation of E° values for CpM2+/+ redox couples by eq 1 results in values of ~3.29 V (Co) and ~3.32 V (Ni), in good agreement with the experimental values (Table II). The differences between the experimental and calculated data can probably be attributed to uncertainties in the E° estimation by eq 1 (which is ±0.1 V) and peak distortion due to interference with supporting electrolyte discharge. The absence of anodic response for the peak at ~3.18 V is evidence of instability of Cp2Co2- (and Cp2Ni2-) at low temperature, perhaps because of simultaneous (concerted) electron-transfer and bond rupture processes.

In addition to the possibility of electrochemically generating Cp2M2+ species at low temperatures, the stability of the products of the redox reactions of metallocenes is increased considerably. For example, the Cp2Ni+ anion, which is unstable at room temperature and decomposes with formation of Cp and CpNi, is quite stable at ~80 °C for the CV time scale (peak at ca. -1.8 V, Figure 4a). The large peak separation is probably due to slow charge transfer.

Conclusion

Five redox states from dication to dianion were identified for the first time from the cyclic voltammetry of cobaltocene and nickelocene. By use of low-temperature solvents (SO2, THF) and ultramicroelectrode techniques, the working potential range can be expanded to permit studies not possible at traditional temperatures and conventional electrodes. In addition to the Cp2M0+/+ redox couples known previously, the Cp2M0/-, Cp2M2+/+ and Cp2M2+/+ redox reactions have been demonstrated. The experimentally detected redox forms of the metallocenes are shown in Table III.2 In a previous study,21 this table appeared as an inverted triangle whose height was determined by the number of known metallocenes and their ions with the d6 electronic configuration associated with the high stability of these 18-electron closed-shell complexes. However, the form of the table must now be expanded to include the metastable transition metal metallocenes and the highly reactive Cp3-, Cp3M+, and Cp3M2+ ions.

The E° values for Cp2M+/2- (M = Co, Ni) are in good agreement with eq 1. On the other hand, the E° value for the Cp2Co0+/+ couple (+3.15 V) deviates from the linear correlation (E° calculated from eq 1 = 1.48 V) in the direction of positive potentials, according to the peculiar characteristics of the d5/6 transition in the redox series for metallocenes. Similar significant deviations from eq 1 are also characteristic of the E° values for (arene)2Cr+/+ redox couples.25 These effects probably are connected with changes in the frontier orbital scheme during the course of the electron-transfer reaction.25 The nonbonding d1 orbital in ferrocene is known to be located above the e2g orbital (ground state e2g); while in the ferrocenium cation, the opposite sequence is observed (e2g).26 This difference apparently hinders the oxidation of ferrocene. It is quite likely that a similar situation also exists for the Cp2Co+/+ redox couple, i.e., the oxidation of the cation to the dication entails a redistribution of the frontier orbitals.

Acknowledgment. The support of this research by grants from the National Science Foundation (NSF 9214480) and the Robert A. Welch Foundation is gratefully acknowledged.


Table III. Experimentally Proposed Metallocene Ions in Terms of the Electrostatic Configurations of the Metal

<table>
<thead>
<tr>
<th>d°</th>
<th>d1</th>
<th>d2</th>
<th>d3</th>
<th>d4</th>
<th>d5</th>
<th>d6</th>
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<tr>
<td>Ti°</td>
<td>Ti°</td>
<td>V°</td>
<td>Cr</td>
<td>Mn±</td>
<td>Fe°</td>
<td>Co°</td>
<td>Co2°</td>
</tr>
<tr>
<td>Zr°</td>
<td>Zr°</td>
<td>V°</td>
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<td>Mn±</td>
<td>Fe°</td>
<td>Ru°</td>
<td>Rh°</td>
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<td>HF°</td>
<td>V°</td>
<td>Re</td>
<td>Os°</td>
<td>Ni°</td>
<td>Pt°</td>
<td>Pt°</td>
</tr>
<tr>
<td>V°</td>
<td>V°</td>
<td>Re</td>
<td>Fe°</td>
<td>Os</td>
<td>Co</td>
<td>Co°</td>
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<tr>
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<td>Os°</td>
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<td>Co°</td>
<td>Rh°</td>
<td>Co°</td>
<td>Ni°</td>
<td>Ni°</td>
<td>Ni°</td>
</tr>
</tbody>
</table>

*Identified by means of low-temperature voltammetry or ultramicroelectrode techniques. See ref 2.