

# Electrochemistry of Metallocenes at Very Negative and Very Positive Potentials. Electrogeneration of 17-Electron $\text{Cp}_2\text{Co}^{2+}$ , $\text{Cp}_2\text{Co}^{2-}$ , and $\text{Cp}_2\text{Ni}^{2-}$ Species

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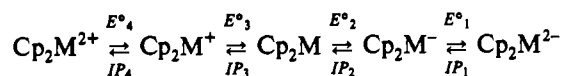
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Cyclic voltammetry (CV) with Pt ultramicroelectrodes and coulometry were used to study the electrooxidation of the  $\text{Cp}_2\text{Co}^+$  cation in liquid  $\text{SO}_2/(\text{TBA})\text{AsF}_6$  solution in the temperature range from  $-70$  to  $+25$  °C. The  $\text{Cp}_2\text{Co}^+$  cation was shown to undergo reversible one-electron oxidation with formation of the  $\text{Cp}_2\text{Co}^{2+}$  dication, which is stable on the CV time scale. The chemical and electrochemical reversibility of  $\text{Cp}_2\text{Co}^+$  oxidation suggests retention of the sandwich structure in the dication. The  $E^\circ$  value for the  $\text{Cp}_2\text{Co}^{+/2+}$  redox couple is  $+3.15$  V (vs SCE) and the rate constant of heterogeneous electron transfer is  $\geq 0.03 \pm 0.01$  cm/s. Electrochemically generated in the  $\text{THF}/(\text{TBA})\text{PF}_6$  medium at  $T < -60$  °C,  $\text{Cp}_2\text{Co}^-$  and  $\text{Cp}_2\text{Ni}^-$  anions, at  $E < -3.1$  V, are reduced to  $\text{Cp}_2\text{Co}^{2-}$  and  $\text{Cp}_2\text{Ni}^{2-}$  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  $E^\circ$  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.<sup>1,2</sup> The existence of a linear relationship between the standard potential values ( $E^\circ_j$ ) of all possible redox reactions of homo- and heteroligand sandwich complexes and metal ionization potentials ( $IP_j$ ) has been established and justified.<sup>2-5</sup> This relationship is based on the fact that the frontier orbitals of sandwich complexes are predominantly metal-based,<sup>6</sup> and the  $E^\circ_j$  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  $IP_j$  value.<sup>2,3</sup> Thus, for the redox couples



( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), the equation

$$E^\circ_j \text{ (V vs SCE)} \cong -4.16 + 0.11IP_j \quad (1)$$

is valid, where  $-4.16$  is a constant characteristic of the Cp ligand and  $j = 1-4$ .<sup>2-5</sup> Equation 1 makes it possible to estimate the values of the redox potentials of  $\text{Cp}_2\text{Co}^{2+/+}$  and  $\text{Cp}_2\text{Co}^{-/2-}$  couples, which previously have not been observed. According to eq 1 the  $E^\circ$  values for the  $\text{Cp}_2\text{Co}^{2+/+}$  and  $\text{Cp}_2\text{Co}^{-/2-}$  redox couples can be estimated as  $>+2$  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<sup>7</sup> 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,  $\text{SO}_2$  is a very useful solvent for the study of electrooxidation processes accompanied by the generation of strong electrophiles. For example, the  $\text{Cp}_2\text{Fe}^+$  and  $\text{Cp}^*\text{Fe}^+$  cations ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) can be reversibly oxidized to the corresponding dications at very positive potentials in  $\text{SO}_2$ .<sup>8</sup> 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.<sup>9,10</sup> Thus, in a THF medium, one-electron reversible reductions are observed for benzene to the radical anion at  $E^\circ = -3.38$  V vs SCE at  $-90$  °C,<sup>11</sup> and for  $\text{Cp}_2\text{Fe}$  to  $\text{Cp}_2\text{Fe}^-$ ,<sup>10</sup> and using ultramicroelectrodes and low-temperature techniques, the  $\text{Cp}_2\text{Ru}^{0/-}$  ( $E^\circ = -3.48$  V vs SCE) and  $\text{Cp}_2\text{Os}^{0/-}$  ( $E^\circ = -3.44$  V vs SCE) couples can be observed.<sup>2,9,12</sup> Thus,  $\text{SO}_2$  and THF were chosen here to study the redox reaction of  $\text{Cp}_2\text{Co}$  at very positive and very negative potentials. Preliminary results of these studies have been briefly reported previously ( $\text{Cp}_2\text{Co}^{2+/+}$ <sup>13,14</sup> and  $\text{Cp}_2\text{Co}^{-/2-}$ <sup>10</sup>).

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## Experimental Section

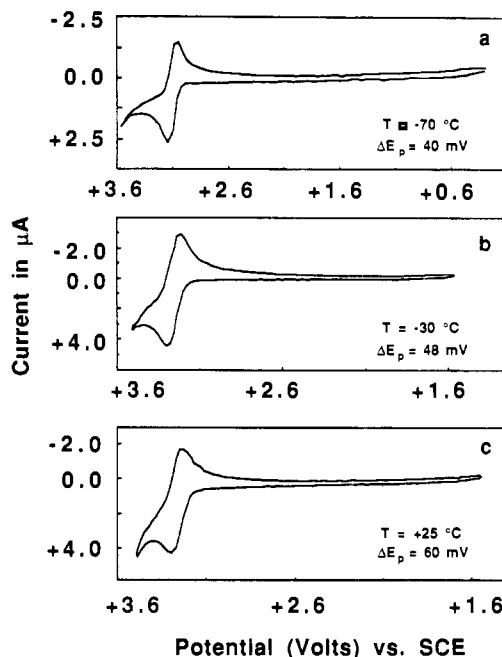
**Chemicals.** Tetra-*n*-butylammonium hexafluoroarsenate, (TBA)AsF<sub>6</sub>, was prepared from an aqueous solution of tetra-*n*-butylammonium bromide (SACHEM, Austin, TX) to which an equivalent amount of aqueous lithium hexafluoroarsenate (Ozark-Mahoning, Pennwalt Corp., Tulsa, OK) was added. The resulting (TBA)AsF<sub>6</sub> 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*-butylammonium hexafluorophosphate, (TBA)PF<sub>6</sub>, (Fluka) was used as received.

Bis(cyclopentadienyl)cobalt hexafluoroarsenate, Cp<sub>2</sub>CoAsF<sub>6</sub>, was prepared by ion exchange from Cp<sub>2</sub>CoPF<sub>6</sub>, which was dissolved in water with a minimum amount of EtOH added. This solution was then percolated through a Dowex-1-chloride (1X8–200, Aldrich Chemical Co.) ion exchange column. Cp<sub>2</sub>CoAsF<sub>6</sub> was obtained when an aqueous solution of LiAsF<sub>6</sub> 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 Cp<sub>2</sub>CoAsF<sub>6</sub>. After being dried under vacuum at 90 °C for 48 h, the solid was found to melt at 346 °C (while Cp<sub>2</sub>CoPF<sub>6</sub> melted at 336 °C). Cobaltocene and Cp<sub>2</sub>CoPF<sub>6</sub> 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 counterelectrode, and a reference electrode). All potentials are reported vs a silver quasireference electrode (AgQRE), which was prepared by dipping a Ag wire in 1 M HNO<sub>3</sub>, rinsing it in water and acetone, and drying it at –70 °C. Potentials given below are referenced to the aqueous saturated calomel electrode (SCE) by measuring the AgQRE potential with respect to the 9,10-diphenylanthracene (DPA/DPA<sup>•+</sup>) couple. The compound to be studied was weighed and placed in the sample container. The cell was placed on the vacuum line and heated in a silicone oil bath to 120 °C while under vacuum (typically (2–6) × 10<sup>–6</sup> Torr) for at least 24 h. Anhydrous SO<sub>2</sub> gas (Matheson Gas Products, Houston, TX) (99.99%) was purified by washing with concentrated sulfuric acid and percolated through a P<sub>2</sub>O<sub>5</sub> column and then a Woelm B-super 1 Alumina (Woelm Phara) column packed on glass wool. SO<sub>2</sub> was condensed into the cell at –70 °C (propanol/dry ice bath).

The working electrodes were of Pt wire, 0.5 mm and 0.25 mm in diameter, sealed in Pyrex glass tubing. The ultramicroelectrode was prepared from 25-μm Pt wire (Alfa Products/Thiokol) that was washed with 30% nitric acid, dried overnight, and then placed in a 19-cm-long, 1-mm-i.d. Pyrex tube that was sealed at one end.<sup>15–17</sup> The open ended tube was connected to a vacuum line and heated with a helix heating coil for 1 h, so that any impurities on the Pt surface were desorbed. After high-temperature vacuum cleaning, the wire was sealed by increasing the heating coil temperature. The sealed end of the electrode was polished with sandpaper until the wire cross-section was exposed and then was successively polished with 6-, 1-, and 0.25-μm diamond paste (Buehler Ltd, Lake Bluff, IL). Electrical connection to the Pt wire was made with silver paint to a copper wire. All CV waves were corrected for the solvent background and charging current, and for later waves, the currents were measured from the estimated decaying faradaic current of the preceding wave following usual practice.<sup>18</sup>

Controlled potential coulometry was carried out in a three-compartment cell separated with medium-porosity glass frits. The quasireference electrode was placed in the working compartment and was separated from it by a fine porosity glass frit. The working electrode was a 2.5 × 4 cm Pt gauze and the counterelectrode was a 1 cm<sup>3</sup> piece of reticulated vitreous carbon. The solution was continuously stirred magnetically with a Teflon-coated stirring bar, and the cell was thermostated at –45 °C with an FTS Systems cryostat while submerged in an 2-propanol bath.



**Figure 1.** Cyclic voltammograms of a 13 mM solution of Cp<sub>2</sub>CoAsF<sub>6</sub> in SO<sub>2</sub>/(TBA)AsF<sub>6</sub> at a 500-μm Pt electrode: (a) 5 V/s, –70 °C; (b) 10 V/s, –30 °C; (c) 10 V/s, 25 °C.

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)PF<sub>6</sub> 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 air and moisture. 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 counterelectrode. 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 Cp<sub>2</sub>Fe<sup>0/+</sup> or Cp\*<sub>2</sub>Fe<sup>0/+</sup> 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 digital oscilloscope, Model 3001 (Norland 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.

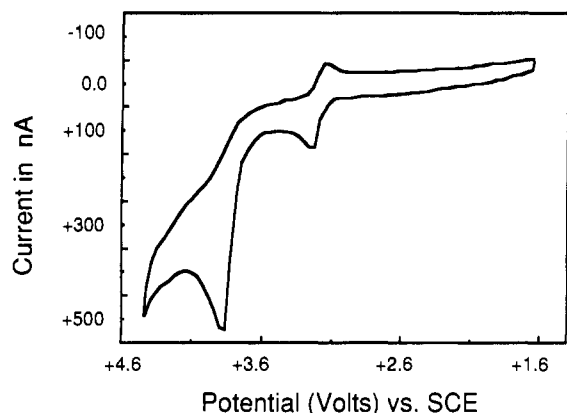
## Results and Discussion

**Oxidation.** A typical cyclic voltammogram for the oxidation of Cp<sub>2</sub>Co<sup>2+</sup> at a 500-μm Pt electrode in liquid SO<sub>2</sub> at –70 °C and scan rate of 5 V/s is shown in Figure 1a. The formal potential, E<sup>o</sup>, was estimated from the anodic (E<sub>p</sub><sup>a</sup>) and cathodic (E<sub>p</sub><sup>c</sup>) peak potentials as

$$E^{\circ} \approx (E_p^a + E_p^c)/2 \quad (2)$$

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, ΔE<sub>p</sub>, 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

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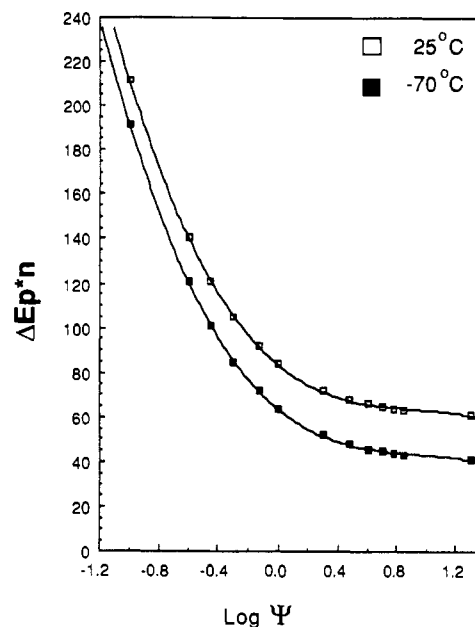
**Figure 2.** Cyclic voltammograms of a 13 mM solution of  $\text{Cp}_2\text{CoAsF}_6$  in  $\text{SO}_2/(\text{TBA})\text{AsF}_6$  at a 25- $\mu\text{m}$  Pt electrode at  $-30$  V,  $v = 10$  V/s.

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- $\mu\text{m}$  Pt electrodes, respectively. Similarly, the peak separation obtained at  $-70$  °C was 43 and 36 mV for 500- and 25- $\mu\text{m}$  Pt electrodes, respectively. The theoretical peak separation at  $-70$  °C for a Nernstian wave is 40 mV. Thus, the  $\text{Cp}_2\text{Co}^+$  cation undergoes a one-electron oxidation to the  $\text{Cp}_2\text{Co}^{2+}$  dication. The chemical and electrochemical reversible character of the  $\text{Cp}_2\text{Co}^+$  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  $\text{Cp}_2\text{CoAsF}_6$  was prepared in 35 mL of a 0.15 M  $(\text{TBA})\text{AsF}_6/\text{SO}_2$  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 1.31 mA to the background level of  $19$   $\mu\text{A}$ . The total number of coulombs passed was 6.89 C (vs 6.76 C expected for a one-electron reaction). Thus,  $n_{\text{app}}$  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  $\text{Cp}_2\text{Co}^{2+}$  showed  $\lambda_{\text{max}} \approx 410$  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  $\text{Cp}_2\text{Co}^{2+}$  at higher temperatures. However, the reversible CV curves at 25 °C suggest that the decomposition of  $\text{Cp}_2\text{Co}^{2+}$  is slow on the CV time scale.

A second anodic wave ( $E_p^a \approx +3.8$  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- $\mu\text{m}$ -diameter Pt electrode at scan rates of up to 200 V/s. Thus, further  $\text{Cp}_2\text{Co}^{2+}$  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 potentials of the second wave,  $\text{PF}_6^-$  irreversibly oxidizes in a  $(\text{TBA})\text{AsF}_6/\text{SO}_2$  solution,<sup>19</sup> so that the second wave could be the result of traces of  $\text{PF}_6^-$  ions in the  $\text{Cp}_2\text{CoAsF}_6$  sample during preparation (see Experimental Section). We feel that this explanation is unlikely because the height of the second wave is large compared with that of the first.

The heterogeneous rate constant,  $k^\circ$ , for the oxidation process  $\text{Cp}_2\text{Co}^+/\text{Cp}_2\text{Co}^{2+}$  was estimated for a 10.6 mM solution by means of CV as proposed by Nicholson,<sup>20</sup> i.e., from a plot of  $\Delta E_p$  vs  $v$ . The peak potential separation was obtained at  $-70$  °C for scan rates



**Figure 3.** Nicholson plot of  $\Delta E_p \cdot n$  vs  $\log \Psi$  at 25 °C and corrected data at  $-70$  °C.

**Table I.** Peak Separation and Kinetic Data for  $\text{Cp}_2\text{Co}^+$  Obtained with Pt Disk Microelectrodes in  $\text{SO}_2^a$

$2r, \mu\text{m}$	$v, \text{V/s}$	$\Delta E_p, \text{V}$	$\log \Psi$	$\Psi$	$k^\circ, \text{cm/s}$
500	5	97	-0.419	0.38	0.026
	10	117	-0.575	0.27	0.025
	20	133	-0.684	0.21	0.028
	50	172	-0.907	0.12	0.027
25	5	67	-0.052	0.89	0.060
	20	107	-0.500	0.32	0.043
	50	147	-0.770	0.17	0.036
	100	234	-1.17	0.067	0.020

<sup>a</sup> Average rate constant =  $0.03 \pm 0.01$  cm/s.

from 1 to 200 V/s. Nicholson's working curve corrected to this temperature and values of  $\Delta E_p$  vs  $\log \Psi$  obtained from these curves are shown in Figure 3. The  $k^\circ$  values are obtained from the definition of  $\Psi^{20}$

$$\Psi = (RT/\pi N F v D_{\text{ox}})^{1/2} [(D_{\text{ox}}/D_{\text{red}})^{1/2}]^{\alpha} k^\circ \quad (3)$$

or, if the diffusion coefficients of reduced and oxidized species are assumed to be equal, from

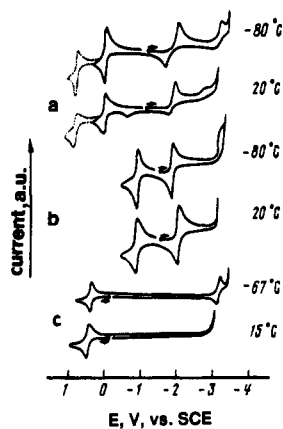
$$\Psi = (RT/\pi N F v D_{\text{ox}})^{1/2} k^\circ \quad (4)$$

$D_{\text{ox}}$  was obtained from steady-state cyclic voltammograms at a 25- $\mu\text{m}$  Pt ultramicroelectrode ( $i_{\text{ss}} = 4nrFD_{\text{ox}}c$ ,<sup>15</sup> where  $r$  = electrode radius and  $c$  = bulk concentration of  $\text{Cp}_2\text{CoAsF}_6$ ) and was found to be  $5.1 \times 10^{-6}$   $\text{cm}^2/\text{s}$ . Typical data for the determination of  $k^\circ$  for both 25- and 500- $\mu\text{m}$  Pt electrodes are shown in Table I. The average value and standard deviation obtained for  $k^\circ$  was found to be  $0.03 \pm 0.01$  cm/s. This value should be taken as a lower limit. We have recently found that transient CV measurements, even at an ultramicroelectrode and with careful  $iR$ -compensation, can still be perturbed by uncompensated solution resistance effects when the heterogeneous rate constant is high.<sup>21</sup> This could be a problem with this measurement. For example, the  $k^\circ$  value for the isoelectronic and isostructural  $\text{Cp}_2\text{Fe}^{0/+}$  couple (with the same  $d^{5/6}$  redox transition) is equal to ca. 3.7 cm/s in MeCN at 25 °C, although significantly lower values (perhaps also due to uncompensated resistance) have been reported.<sup>21</sup> It seems unlikely that the true value of  $k^\circ$  for  $\text{Cp}_2\text{Co}^{0/+}$  is 2 orders of magnitude lower.

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**Figure 4.** Cyclic voltammograms of 1 mM solutions of metallocenes in THF/0.05 M (TBA)PF<sub>6</sub> at different temperatures and scan rates: (a) Cp<sub>2</sub>Ni,  $v = 0.1$  V/s, Hg and Pt (dashed line) electrodes; (b) Cp<sub>2</sub>Co,  $v = 0.1$  V/s, Pt electrode; (c) Cp<sub>2</sub>Fe,  $v = 0.05$  V/s, Pt electrode. Current is given in arbitrary units which differ for different metallocenes and temperatures.

**Table II.**  $E^\circ$  Values for Cp<sub>2</sub>M<sup>2+/+0/-2-</sup> Redox Couples in THF and Gas-Phase Ionization Potentials ( $IP_j$ , eV) of Corresponding Metals

Cp <sub>2</sub> M	T, °C	$E^\circ, ^a$ V			
		Cp <sub>2</sub> M <sup>2+/+</sup> ( $IP_4$ )	Cp <sub>2</sub> M <sup>+0</sup> ( $IP_3$ )	Cp <sub>2</sub> M <sup>0/-</sup> ( $IP_2$ )	Cp <sub>2</sub> M <sup>-2-</sup> ( $IP_1$ )
Cp <sub>2</sub> Ni	+20	0.81 (54.9)	0.01 (35.2)	-1.85 (18.2)	
	-40	0.81	0.01	-1.84	-3.04 (7.6)
	-80	0.81	0.01	-1.84	-3.13
Cp <sub>2</sub> Co	+22		-0.90 (33.5)	-2.04 (17.1)	
	-47		-0.90	-1.91	-3.18 (7.9)
	-70	3.15 <sup>c</sup> (51.3)			
	-80		-0.90	-1.86	-3.20
Cp <sub>2</sub> Fe	+15		0.45 (30.6)		
	-42	2.03 <sup>d</sup> (54.8)	0.45	-3.06 (16.2)	
	-90		0.45	-3.00	

<sup>a</sup>  $E^\circ = (E_p^a + E_p^c)/2$ , vs SCE. <sup>b</sup>  $E_p^c$  values. <sup>c</sup> In SO<sub>2</sub>; this work. <sup>d</sup> In SO<sub>2</sub>, 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 Cp<sub>2</sub>Ni (a) and Cp<sub>2</sub>Fe (c) under the same conditions. The  $E^\circ$  values of Cp<sub>2</sub>M<sup>2+/+0/-2-</sup> 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 Cp<sub>2</sub>Co<sup>-2-</sup> and Cp<sub>2</sub>Ni<sup>-2-</sup> 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  $\Delta E_p = 2.30RT/F$  values for reversible one-electron-transfer reactions at corresponding temperatures, except for that of Cp<sub>2</sub>Ni<sup>0/-</sup> (Figure 4a), which is larger, probably because of a slow charge-transfer process.<sup>22</sup> For ferrocene, one cannot detect the Cp<sub>2</sub>Fe<sup>-2-</sup> redox couple (or a simultaneous electron-transfer, bond rupture process) because this peak is beyond the potential for supporting electrolyte discharge.

Estimation of  $E^\circ$  values for CpM<sup>-2-</sup> 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  $E^\circ$  estimation by eq 1 (which is  $\pm 0.1$  V)<sup>5</sup> and peak distortion due to interference

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

d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	d <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	d <sup>10</sup>
Ti <sup>a</sup>	Ti <sup>-a,c</sup>	V <sup>-</sup>	Cr <sup>-</sup>	Mn <sup>-b</sup>	Fe <sup>-</sup>	Co <sup>-</sup>	Co <sup>2-</sup> <sup>a</sup> (?)	Ni <sup>2-</sup> <sup>a</sup> (?)
Zr <sup>a</sup>	Zr <sup>-a,c</sup>	Cr	Mn <sup>b</sup>	Fe	Ru <sup>-a</sup>	Rh <sup>-a</sup>	Ni <sup>-</sup>	
Hf <sup>a</sup>	Hf <sup>-a,c</sup>	Mn <sup>+b</sup>	Re	Ru	Os <sup>-a</sup>	Ni		
V <sup>+</sup>	V	Re <sup>+</sup>	Fe <sup>+</sup>	Os	Co			
	Cr <sup>+</sup>	Fe <sup>2+</sup>	Ru <sup>+</sup>	Co <sup>+</sup>	Rh			
			Os <sup>+</sup> <sup>a</sup>	Rh <sup>+</sup>	Ni <sup>+</sup>			
			Co <sup>2+</sup> <sup>a</sup>	Ni <sup>2+</sup>				

<sup>a</sup> Identified by means of low-temperature voltammetry or ultramicroelectrode techniques. <sup>b</sup> Cp<sup>\*</sup><sub>2</sub>M. <sup>c</sup> See ref 2.

with supporting electrolyte discharge. The absence of anodic response for the peak at -3.18 V is evidence of instability of Cp<sub>2</sub>Co<sup>-2-</sup> (and Cp<sub>2</sub>Ni<sup>-2-</sup>, Figure 4a) even at low temperature, perhaps because of simultaneous (concerted) electron-transfer and bond rupture processes.<sup>23</sup>

In addition to the possibility of electrochemically generating Cp<sub>2</sub>M<sup>2-</sup> species at low temperatures, the stability of the products of the redox reactions of metallocenes is increased considerably. For example, the Cp<sub>2</sub>Ni<sup>-</sup> anion, which is unstable at room temperature and decomposes with formation of Cp<sup>-</sup> and CpNi,<sup>24</sup> 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 (SO<sub>2</sub>, 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 Cp<sub>2</sub>M<sup>0/+</sup> redox couples known previously, the Cp<sub>2</sub>M<sup>0/-</sup>, Cp<sub>2</sub>M<sup>-2-</sup>, and Cp<sub>2</sub>M<sup>+2+</sup> redox reactions have been demonstrated. The experimentally detected redox forms of the metallocenes are shown in Table III.<sup>2</sup> In a previous study,<sup>21</sup> this table appeared as an inverted triangle whose height was determined by the number of known metallocenes and their ions with the d<sup>6</sup> 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 early transition metal metallocenes and the highly reactive Cp<sub>2</sub>M<sup>-</sup>, Cp<sub>2</sub>M<sup>-2-</sup>, and Cp<sub>2</sub>M<sup>2+</sup> ions.

The  $E^\circ$  values for Cp<sub>2</sub>M<sup>-2-</sup> (M = Co, Ni) are in good agreement with eq 1. On the other hand, the  $E^\circ$  value for the Cp<sub>2</sub>Co<sup>0/+</sup> couple (+3.15 V) deviates from the linear correlation ( $E^\circ$  calculated from eq 1 = 1.48 V) in the direction of positive potentials, according to the peculiar characteristics of the d<sup>5/6</sup> transition in the redox series for metallocenes. Similar significant deviations from eq 1 are also characteristic of the  $E^\circ$  values for (arene)<sub>2</sub>Cr<sup>+2+</sup> redox couples.<sup>25</sup> These effects probably are connected with changes in the frontier orbital scheme during the course of the electron-transfer reaction.<sup>25</sup> The nonbonding  $a_{1g}$  orbital in ferrocene is known to be located above the  $e_{2g}$  orbitals (ground state  $e_{2g}^4 a_{1g}^2$ ), while in the ferrocenium cation, the opposite sequence is observed ( $e_{2g}^2 a_{1g}^3$ ).<sup>26</sup> This difference apparently hinders the oxidation of ferrocene. It is quite likely that a similar situation also exists for the Cp<sub>2</sub>Co<sup>+2+</sup> redox couple, i.e., the oxidation of the cation to the dication entails a redistribution of the frontier orbitals.

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