be calculated by the same procedure employed for $Pt(PEt_3)_3$.

$$\ln\left[\frac{1}{f^2[PtL_2]_0}\left(\frac{1}{\gamma^2}-\frac{1}{\gamma}\right)\right] = \ln\frac{K_s+1}{K_d{}^0K_s} + \frac{P}{[H_2O]_0} + \ln\left(1+\frac{1}{K_0(K_s+1)[H_2O]_0}\right) \quad (23)$$

The K values ($1/K_d + 1/K_dK_0[H_2O]_0$ for $Pt(PEt_3)_3$, $1/K_d + 1/K_dK_s + 1/K_dK_sK_0[H_2O]_0$ for $Pt[P(i\text{-}Pr)_3]_3$) at $[H_2O]_0$ of 5.549 M estimated from the slope of Fuoss plots (eq 21 and Figure 7) were 2.2 (0.7) × 10^2 M^{-1} for $Pt(PEt_3)_3$ and 9.2 (2.0) × 10^2 M^{-1} for $Pt[P(i\text{-}Pr)_3]_3$. These are in fair agreement with the respective values of 2.6 (0.2) × 10^2 and 9.9 (2.0) × 10^2 M^{-1} calculated on the basis of K_0, K_d, and K_s values assessed (see text).

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Electron-Transfer Reactions of Metallocenes. Influence of Metal Oxidation State on Structure and Reactivity

John D. L. Holloway and William E. Geiger, Jr.*

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05401.

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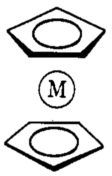
Abstract: Vacuum- and low-temperature electrochemical techniques have been used to characterize the redox pathways of Cp_2V (Cp = η^5-cyclopentadienyl), Cp_2Cr, Cp_2Ni, Cp_2VCl_2, and $CpNi(\eta^3\text{-}C_5H_7)$. The pure metallocenes show an electron-transfer series of three or four members. The nickelocene anion, a d^9, 21-electron species, was shown to be a reduction intermediate, stable in DMF at −60 °C, and $CpNi(\eta_3\text{-}C_5H_7)$ was but a minor product of the bulk reduction of nickelocene. The heterogeneous electron-transfer rate was abnormally slow for the nickelocene reduction, suggesting that a structural distortion and/or a change in solvation occurs to relieve the high metal electron density. Vanadocene was oxidized in two one-electron steps, only the first of which was reversible. It is unlikely that there are gross changes in structure in going from vanadocene to the vanadocene cation, but the irreversibility of the second oxidation suggests the formation of $Cp_2V(THF)_2{}^{2+}$ for the d^1 species.

Introduction

The bis(η^5-cyclopentadienyl)metals, the "metallocenes" (**1**), are the prototype of organometallic π complexes, and have been widely studied since the discovery of ferrocene in 1951.[1] One of the most interesting aspects of these molecules is their ability to form compounds in violation of the 18-electron rule so commonly employed in organometallic chemistry.[2] Neutral compounds of the familiar sandwich structure are known for all first-row transition metals between V (15 valence electrons) and Ni (20 valence electrons). Because of this ability to accommodate a variable d-orbital occupancy, these compounds appeared to be likely candidates for investigation of electron-transfer reactions of organometallic π compounds. Electron-transfer series encompassing four or more members have been



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reported for metal chelates in which at least some of the redox steps can be described as primarily involving ligand orbitals.[3] But the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the metallocenes are largely metal based.[4] Thus electron-transfer reactions of the metallocenes should represent bona fide changes in metal oxidation state.

Several metallocenes, predominantly those less air sensitive, have been studied by one or another electrochemical technique, since the redox reactions of these compounds were discovered almost immediately after their synthesis.[5,6] But for over 20 years, the only reversible electron-transfer processes reported for metallocenes involved oxidation of the neutral compounds. Thus, the electrochemical oxidation of Cp_2Fe (to Cp_2Fe^+),[5,7,8] Cp_2Co (to Cp_2Co^+),[5,9,10] and Cp_2Ni (to Cp_2Ni^+ and Cp_2Ni^{2+})[6,10-13] and chemical oxidation of Cp_2Cr (to Cp_2Cr^+)[14] have been reported. More recently, the cobaltocene *anion* was reported independently by El Murr and co-workers[15] and by Geiger.[16,17] El Murr has extended these studies to the reduction of substituted cobaltocenes[18] and has also explored the synthetic utility of the cobaltocene anion.[19,20]

The present paper represents an attempt at a general study of metallocene electron-transfer reactions, with special emphasis on Cp_2V, Cp_2Cr, and Cp_2Ni. Attempts have been made to characterize not only the electron-transfer process but also the nature of reactions following the electron transfer. One goal of this research was to find out how electron rich or electron deficient a metallocene had to become before undergoing a significant change in structure. It appears from our results on the reversibility of these redox processes that structure and/or solvation changes occur upon formation of d^1 (Cp_2V^{2+}) or d^9 (Cp_2Ni^-) metallocenes, but intermediate electronic structures (d^2 to d^8) support the ring-coplanar structure (**1**) at least in the absence of strongly coordinating solvents or other ligands. A preliminary account of some of this work has appeared.[21]

Experimental Section

All electrochemical experiments except those requiring subambient temperatures were carried out under vacuum conditions using procedures previously described.[22] For the low-temperature work, a cell similar to that described by Van Duyne[23] was employed. This cell utilized a coaxial arrangement of the working and auxiliary electrodes and had a Luggin probe as a reference electrode compartment into which an aqueous saturated calomel electrode was inserted.

Several electrochemical instruments were used to carry out the measurements, but most work involved either the Princeton Applied Research (PAR) Models 170 or 173 potentiostats. Coulometry was accomplished with the PAR Model 179 digital coulometer. Waveforms for cyclic voltammetry were generated with a Hewlett-Packard Model 3300A function generator, and voltammograms were recorded on a Hewlett-Packard *X-Y* recorder (Model 7001A) or Tektronix Model 564B storage oscilloscope. Low-temperature work used a Lauda Model KB-20 thermostat system to circulate coolant through the jacket of the electrochemical cell. Inert atmosphere transfers were performed in a Vacuum Atmospheres Corp. drybox.

$CpNiC_5H_7$ was obtained from Professor M. D. Rausch at the University of Massachusetts at Amherst. Metallocenes were obtained from commercial sources and purified by vacuum sublimation (Cp_2Ni and Cp_2Cr, Alfa; Cp_2V, Research Inorganic). Cp_2VCl_2, obtained from Alfa, was used without further purification. *N,N*-Dimethylformamide (Fisher Spectrograde) (DMF) was distilled from CaH_2 under vacuum (ca. 0.1 mmHg) through an 8-ft column and used immediately after distillation. Tetrahydrofuran (THF) from Aldrich (Gold Label) was flash distilled from $LiAlH_4$ into a flask containing potassium and benzophenone and subjected to several freeze/pump/thaw cycles at 10^{-6} mmHg. As long as the deep purple color of the benzophenone ketyl was present, the solvent was appropriately free of water and oxygen. The solvent was directly distilled into the vacuum cell for an experiment. All electrolyte solutions were 0.1 M in tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte. The electrolyte was prepared by metathesis of tetrabutylammonium iodide and ammonium hexafluorophosphate in acetone, followed by precipitation by addition of water. It was recrystallized three times from 95% ethanol and vacuum dried.

Table I. Polarographic $E_{1/2}$ Values[a] for Metal π Complexes

A. Metallocenes

compd	solvent	$2+ \rightleftharpoons 1+$[b]	$1+ \rightleftharpoons 0$	$0 \rightleftharpoons 1-$	ref
Cp_2V	THF	+0.59[c,d]	−0.55	−2.74	this work
Cp_2Cr	CH_3CN		−0.67	−2.30	this work
Cp_2Fe	CH_3CN		+0.31		7
Cp_2Co	CH_3CN		−0.94	−1.88	17
Cp_2Ni	CH_3CN	+0.74[c]	−0.09	−1.66[d]	this work, 11

B. Other Compounds

compd	solvent	$E_{1/2}$ (ox)	$E_{1/2}{}^1$ (red)	$E_{1/2}{}^2$ (red)	$E_{1/2}{}^3$ (red)
$CpNiC_5H_7$	THF	+0.6[d]	−2.45[d]		
Cp_2VCl_2	THF	+0.24[d]	−0.29	−1.54[d]	−2.74

[a] Volts vs. saturated calomel electrode. Drop time 2–5 s. [b] Charge on compound. [c] Anodic peak potential. [d] Irreversible.

Results

Half-wave potentials for all compounds studied are collected in Table I.

Vanadocene. This is the most electron-deficient metallocene which retains the ferrocene-like structure (**1**) with coplanar cyclopentadienyl rings. It has just 15 valence electrons in excess of the argon core, yet it is easily oxidized, in two one-electron steps. The first oxidation of Cp_2V in THF occurs with an $E_{1/2}$ of −0.55 V and gives a diffusion-controlled polarographic wave, although it is subject to a maximum of the first kind. Cyclic voltammetry (CV) measurements at either a hanging mercury drop electrode (HMDE) or a platinum bead gave values of i_c/i_a of unity, independent of scan rate. This established the stability of the vanadocene cation, Cp_2V^+, formed in the process. Bulk coulometry on the first oxidation confirmed it to be a one-electron process ($n_{app} = 1.03\ e^-$).

Measurement of the heterogeneous electron-transfer rate, k_s, for the Cp_2V oxidation was hampered by uncompensated resistance effects typical of measurements in THF. The design of the vacuum cell made it difficult to construct a luggin probe to minimize resistance effects. The reference probe used a fine frit at its terminus to help guard against decomposition of this very reactive metallocene and this exaggerated the resistance problem. Two experiments were done to get a qualitative idea of the electrochemical reversibility of the $Cp_2V \rightleftharpoons Cp_2V^+$ couple. First, ferrocene was added to a Cp_2V solution and CV scans were taken of the oxidation waves of both. At $v = 0.10$ V/s, the peak spread for $Cp_2Fe^{+/0}$ was 115 mV and for $Cp_2V^{+/0}$ was 140 mV, a 25-mV difference. Ferrocene undergoes a highly reversible oxidation in THF (unpublished observations) as well as in other solvents, and a k_s value of 0.7 cm s^{-1} has been reported[24] for methanol solutions. Assuming this k_s value in THF also, and ascribing the extra 25-mV peak spread for Cp_2V to quasi-reversibility of the electron transfer, one can use the method of Nicholson[25] to calculate a lower limit of k_s as about 0.01 cm s^{-1}. In another experiment, Cp_2V in THF was investigated in the drybox using a Metrohm cell and luggin probe.[26] Although the voltammetry was not as clean as observed in the vacuum cell, it was noted that a 60-mV separation was obtained at $v = 0.10\ V\ s^{-1}$ for the $Cp_2V^{0/+}$ couple.

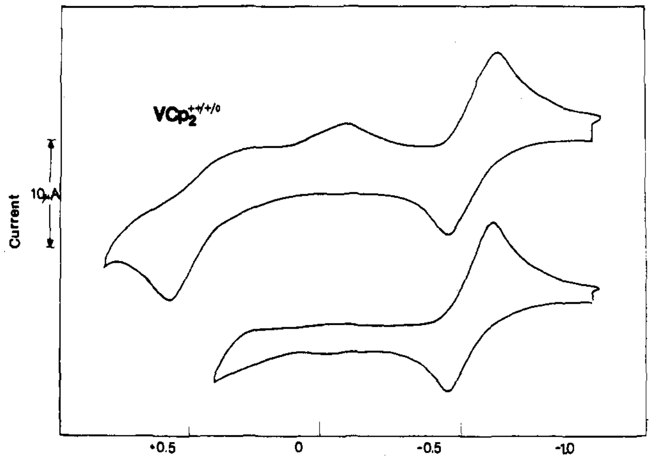


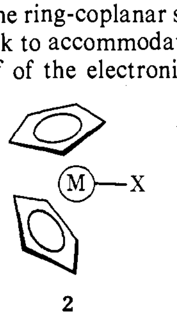
Figure 1. Cyclic voltammogram of vanadocene in THF/Bu_4NPF_6 at Pt electrode, scan rate = 100 mV s^{-1}. Bottom scan shows first oxidation, whereas top scan shows both oxidations and the wave at ca. −0.1 V due to a product arising from decomposition of Cp_2V^{2+}

Thus, the vanadocene oxidation is quite reversible, and the change from V^{II} to V^{III} does not appear to involve a major structural change, such as bending back of the Cp rings as in **2.** This possibility is discussed in greater detail below.

The second oxidation of vanadocene is highly irreversible. Figure 1 demonstrates a CV scan for both oxidations at a platinum electrode. The second oxidation is of one-electron height, showing that Cp_2V^{2+} is initially formed, but then undergoes a rapid reaction. The peak potential was +0.59 V at a scan rate of 0.1 V s^{-1}. Multiple CV scans between −0.3 and +0.7 V resulted in the buildup of a small amount of a reversible couple at ca. −0.14 V. This product wave only arises when the second oxidation of vanadocene is scanned (Figure 1) and must arise from the decomposition reaction of Cp_2V^{2+}.

Vanadocene is reduced at a very negative potential, $E_{1/2} = -2.74$ V, with a diffusion-controlled polarographic plateau current approximately equal to that of the one-electron oxidation wave. A plot of $-E$ vs. log $[i/(i_d - i)]$ gave a straight line of slope 74 mV. Although this value is above that of a reversible one-electron process (59 mV), it is in the same range as other waves of known reversible behavior studied in our cell in THF. Cyclic voltammetry scans at a HMDE just barely allowed resolution of the reduction peak, because of the proximity of the wave to the electrolyte discharge. An anodic peak was observed in the reverse sweep of the cyclic voltammogram showing the reduction to be chemically reversible. Thus, the reduction of vanadocene proceeds by a one-electron reversible process to Cp_2V^-.

Vanadocene Dichloride. Very highly oxidized metallocenes do not retain the ring-coplanar structure (**1**). Instead, the Cp rings bend back to accommodate other electron-donating ligands in relief of the electronic strain. Structures **2** and **3**



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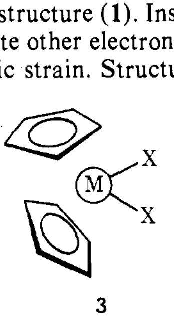

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demonstrate typical structures in which either one or two additional ligands are incorporated. The literature in this area is quite extensive and the reader is referred to other sources for leading references.[4,27-30] Clearly, in the oxidation of vanadocene, the possibility of formation of the bent structures must be considered. In the case of anodic oxidation, in THF, the extra ligands would most likely be THF molecules. One approach to this problem is to investigate the vanadocene oxidation in the presence of small amounts of a coordinating ligand to see whether this leads to a change in electrochemical behavior. A convenient way of doing this seemed to be to reduce vanadocene dichloride, Cp_2VCl_2 (**3**, X = Cl), by two electrons to produce a solution of Cp_2V containing a 2:1 ratio of chloride to vanadocene:

$$Cp_2VCl_2 + 2e^- \rightleftharpoons Cp_2V + 2Cl^- \qquad (1)$$

This has been the speculated reduction pathway in the polarographic and CV studies of Dessey et al.[31] and Bond et al.[32] Our investigations on this reduction (in THF) present confirming evidence for this overall mechanism, but differ in details of the stepwise mechanism leading to the final product, vanadocene. Previous studies in other solvents (dimethoxyethane[31] and acetone[32]) agreed that the reduction of Cp_2VCl_2 (two observed waves) proceeded by the following mechanism:

$$\left.\begin{aligned} &Cp_2VCl_2 + e^- \rightleftharpoons Cp_2VCl_2^- &(2)\\ &Cp_2VCl_2^- \rightarrow Cp_2VCl + Cl^- &(3)\end{aligned}\right\}\ \text{first wave}$$

$$Cp_2VCl + e^- \rightarrow Cp_2V + Cl^- \qquad \text{second wave} \qquad (4)$$

Our polarographic studies on this compound show three reduction waves at −0.29, −1.54, and −2.74 V, of approximately equal height. Only the second wave was irreversible by CV. The third wave, which had not been previously reported, corresponds to the reduction of Cp_2V, and confirms that vanadocene is produced by electrolysis at the second wave.

We find, however, that $Cp_2VCl_2^-$ is stable when produced by electrolysis at the first wave in THF. Reduction at −0.6 V of Cp_2VCl_2 ($n_{app} = 1.0$ e^-) gave a solution having a polarogram (Figure 2) exactly like that of the starting solution except that the wave at $E_{1/2} = -0.29$ V was an oxidation. This $Cp_2VCl_2^-$ solution was stable enough to allow complete regeneration of the Cp_2VCl_2 by electrolysis at −0.1 V.

Electrolysis at the second wave gave a solution showing polarographic waves at −0.75 (oxidation) and −2.74 V (reduction). Again, the wave at −2.74 V confirms that vanadocene is the product of the second Cp_2VCl_2 reduction. The oxidation of Cp_2V is shifted to the more negative potential by the presence of chloride ions. Since the oxidation is facilitated by the chloride ion, the equation

$$Cp_2V + nCl^- \rightarrow Cp_2VCl_n^{\,1-n} + e^- \qquad (5)$$

in which the coordination of chloride is concerted with the electron transfer, describes the oxidation mechanism in this medium. Most likely, $n = 2$. Finally, reoxidation of the solution at −0.10 V completely regenerated the original Cp_2VCl_2 polarogram. Our data is consistent with the following mechanism for the reduction of Cp_2VCl_2.

$$Cp_2VCl_2 + e^- \rightleftharpoons Cp_2VCl_2^- \qquad \text{first wave} \qquad (6)$$

$$\left.\begin{aligned} &Cp_2VCl_2^- + e^- \rightleftharpoons Cp_2VCl_2^{2-} &(7)\\ &Cp_2VCl_2^{2-} \rightarrow Cp_2V + 2Cl^- &(8)\end{aligned}\right\}\ \text{second wave}$$

$$Cp_2V + e^- \rightleftharpoons Cp_2V^- \qquad \text{third wave} \qquad (9)$$

Chromocene. Our data shows that Cp_2Cr is the central member of the three-member electron transfer series:

$$Cp_2Cr^+ \xrightleftharpoons{e^-} Cp_2Cr \xrightleftharpoons{e^-} Cp_2Cr^- \qquad (10)$$

In THF both the oxidation and reduction are reversible, but in acetonitrile the reduction is subject to a followup reaction. A variety of criteria involving polarography, cyclic voltammetry, and controlled-potential coulometry established that

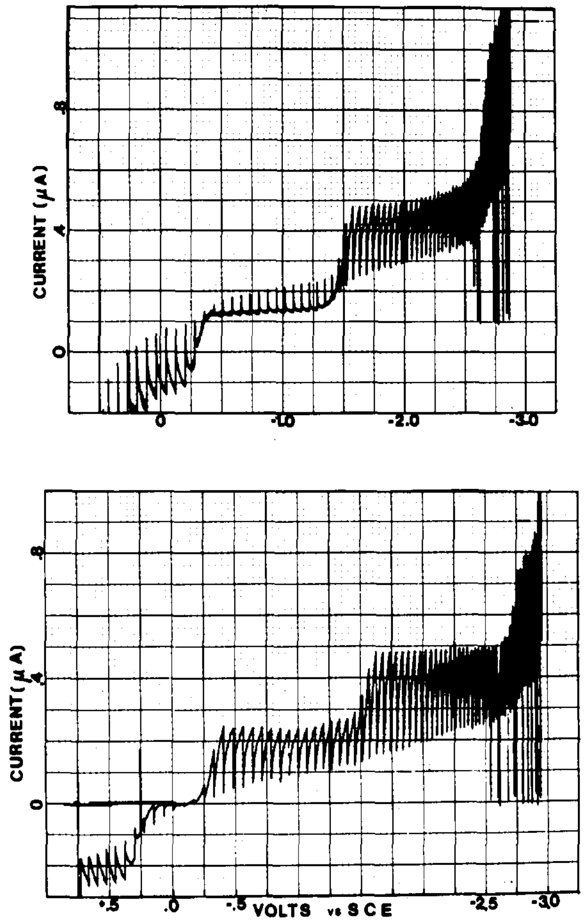


Figure 2. Polarograms of a solution of Cp_2VCl_2 in THF/Bu_4NPF_6 before (bottom) and after (top) bulk electrolysis at −0.6 V. The top polarogram is that of $Cp_2VCl_2^-$.

the oxidation is both electrochemically and chemically reversible, resulting in formation of Cp_2Cr^+. Details are given elsewhere in a paper describing procedures involved in using the vacuum electrochemical cell.[22] Stable solutions of Cp_2Cr^+ PF_6^- may be prepared in this fashion.

The reduction of Cp_2Cr (at −2.30 V in THF) is electrochemically reversible and results in formation of Cp_2Cr^-, a highly reactive anion. In THF the polarographic plateau height for the reduction was only 8% greater than that of the one-electron oxidation and the linear scan peak heights were equal for the oxidation and reduction.[21] CV measurements on the reduction reveal that the anion is not completely stable at slow scan rates. A value of i_a/i_c of 0.75 was observed in THF at a scan rate of 0.10 V s^{-1}, considerably below the 1.0 value of a chemically reversible process to a stable product.

Acetonitrile reacts with the chromocene anion. In this solvent, CV scan rates above 5 V s^{-1} must be employed to completely outrun the rate of the chemical reaction, and the cathodic current function ($i_p/v^{1/2}$) increased at slow scan rates. These data and the bulk coulometry data (n_{app} = 2.2 e^-) suggest that the product of the follow-up reaction is reduced by one electron at a more positive E^0, in an ECE mechanism,[33,34] in this solvent. The cobaltocene anion, Cp_2Co^-, also reacts with acetonitrile in an ECE process.[17]

Bulk reduction of Cp_2Cr in THF (n_{app} = 1.5 e^-) did not give a stable solution of Cp_2Cr^-, a result anticipated by the slow CV measurements. Instead, a product of unknown composition having a well-defined oxidation wave at −0.56 V was formed.

Nickelocene. In spite of being the most electron-rich metallocene known (20 valence electrons), Cp_2Ni is the easiest

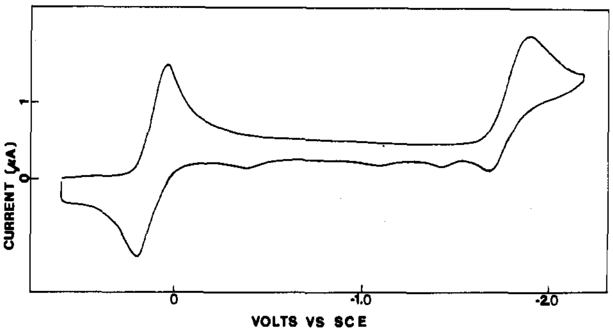


Figure 3. Cyclic voltammogram of the oxidation (ca. 0 V) and reduction of nickelocene in THF at v = 200 mV s^{-1} at a Pt electrode.

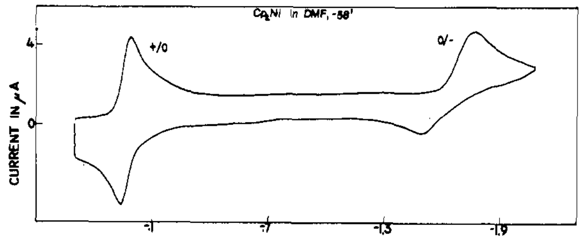
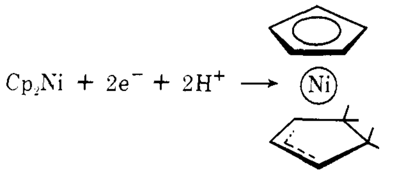


Figure 4. Cyclic voltammogram of Cp_2Ni in DMF at −58 °C, v = 100 mV s^{-1}. Both the cation and anion of nickelocene are stable at this temperature.

of the metallocenes to reduce. The reduction wave, at ca. −1.7 V, reaches a larger plateau height than does the one-electron oxidation wave at −0.1 V already characterized by several groups.[6,10,13] This behavior had been noticed by Gubin et al.,[10] who postulated the formation of $CpNiC_5H_7$ to account for the



(11)

increase over the one-electron height in reaction 11. In acetonitrile this wave gave an apparent n value of 1.4 e^-. If phenol was added to the solution, the authors stated that the wave went to a two-electron height. Thus the reduction of Cp_2Ni was characterized as a two-electron, irreversible process.[10]

Our results show that the reduction of nickelocene is mechanistically very complex. The initial reduction proceeds by one electron to the nickelocene anion. The anion is short lived at ambient temperatures, but clear evidence for it is obtained from cyclic voltammograms in either THF or DMF. A room temperature CV (Figure 3) of the oxidation and reduction of Cp_2Ni in THF shows two waves of equal height with some evidence for reversibility of the reduction. Two major points should be noted. First, the peak spread of the reduction process is greater than that of the oxidation. Second, several oxidation waves due to products of the reaction(s) of Cp_2Ni^- are present at ca. −0.4, −1.1, and −1.4 V (the last being very minor). The product waves are present in either THF, DMF, or CH_3CN, and *none* are due to $CpNiC_5N_7$. We will show, however, that $CpNiC_5H_7$ is a minor product in bulk electrolysis (vide infra).

That the reduction of nickelocene proceeds by slow electron transfer to the nickelocene anion is best demonstrated by low-temperature cyclic voltammetry. At −58 °C in DMF, follow-up reactions of the anion are quenched, as can be seen by the absence of the three product waves (Figure 4). The value of i_a/i_c of 1.0 measured[35] for the reduction shows that Cp_2Ni^- is stable at that temperature. However, the reduction couple

Table II. Effect of Drop Time and Concentration of Trimethylphenol on Height of Cp_2Ni Reduction Wave

i_{red}/i_{ox} [a]	drop time [b]	$[phenol]/[Cp_2Ni]$ [c]
1.16	0.5	0
1.20	1.0	0
1.34	2.0	0
1.48	7.0	0
1.79	0.5	1.1
1.96	1.0	1.1
2.11	0.5	12.3

[a] Ratio of plateau heights of Cp_2Ni reduction and oxidation waves. [b] Capillary drop time in seconds. [c] Ratio of concentration of trimethylphenol to that of nickelocene.

shows a very large peak spread (260 mV) compared to the oxidation couple (56 mV), showing that the heterogeneous electron transfer process is slow for the reduction. According to the Marcus theory,[36] the slow electron transfer must be due either to a major structural change or change in solvation during the electron transfer step. These possibilities are addressed in the Discussion.

Because the overall reduction mechanism did not appear to be solvent dependent, most of our work was carried out in THF, which can be rigorously dried (to minimize protonation reactions) and easily handled in vacuum procedures. DC polarograms again show that the ratio of the (drop-time corrected) reduction wave to that of the one-electron oxidation wave was larger than unity, and that the ratio increased at longer drop times. This behavior is characteristic of a one-electron reduction to an anion which undergoes a follow-up reaction (or reactions) to give a more easily reduced product (an ECE process).

The ratio of the reduction-to-oxidation waves also increased in the presence of an acid, 2,4,6-trimethylphenol, added to the solution (Table II). CV scans confirmed that Cp_2Ni^- reacts rapidly with the phenol, for the anodic current coupled to the reduction decreased after adding the phenol (at $v = 0.5$ V s^{-1}, $i_a/i_c = 0.8$ in absence of phenol, but the wave was completely irreversible in presence of phenol).

Exhaustive electrolytic reduction of Cp_2Ni in THF at a mercury pool passed 1.5 ± 0.1 electrons (four trials). A polarogram of the resulting solution showed three waves, two of them oxidations ($E_{1/2} = +0.6$ and -0.70 V) and one a reduction ($E_{1/2} = -2.5$ V). The waves at +0.6 and −2.5 V are apparently due to a single product, $CpNiC_5H_7$. A sample of this complex prepared independently[37] gave waves within experimental error of these potentials (Table I).[38]

The height of the reduction wave of $CpNiC_5H_7$ was used to calculate the yield of this compound in the bulk reduction of Cp_2Ni. The height of the Cp_2Ni oxidation wave, prior to electrolysis, was used as an internal standard, and in a separate experiment it was found that $i_d/Ct^{1/6}$ for the $CpNiC_5H_7$ reduction[39] was 1.5 times the value for the Cp_2Ni oxidation. This data allowed us to use polarographic currents to measure solution concentrations, and a yield of 30% $CpNiC_5H_7$ was calculated for electrolysis of Cp_2Ni at −1.9 V in THF.

The "missing" 70% of the electrolysis products can be accounted for by the oxidation wave at −0.70 V mentioned previously. Indeed, the plateau height of this product wave is about three-fourths that of the original Cp_2Ni oxidation wave. A reoxidation of the solution by electrolysis at −0.60 V regenerated some nickelocene. The height of the regenerated Cp_2Ni oxidation wave was just half the height of the −0.70 V product wave. These experiments show that (a) the wave at −0.70 V corresponds to the major reduction product, and (b) 0.5 mol of Cp_2Ni is regenerated per mol of product when the latter is oxidized.

Table III. First-Row Metallocenes Known,[a-c] Classified by Electronic Configuration

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
"V^{2+}"	V^+	Cr^+	Cr	Fe^+	Ni^{2+}	Ni^+	Ni	Ni^-
		V	V^-	Mn	Co^+	Co	Co^-	
			Mn^+	Cr^-	Fe			
					Mn^-			

[a] Restricted to metallocenes Cp_2M^n which have been observed to have measurable lifetimes in solution. The d^1 system V^{2+} is formed in the oxidation of V^+ but is too unstable at ambient temperature to observe by cyclic voltammetry. [b] Using the nomenclature $M = Cp_2M$; i.e., V^+ stands for Cp_2V^+. [c] Mn is actually decamethylmanganocene.[41] Mn^+ and Mn^- are listed because the authors of ref 41 report that Mn undergoes a reversible one-electron oxidation and reduction.

Surprisingly, bulk reduction of Cp_2Ni in THF with trimethylphenol added did not result in a significant enhancement of the yield of $CpNiC_5H_7$. Instead, in addition to the three previously discussed waves, a new oxidation wave at $E_{1/2} = -0.45$ V was found.

Discussion

Metallocene Electron-Transfer Series. A fairly clear understanding of the electrochemical behavior of metallocenes is now possible. In general, an electron-transfer series

$$Cp_2M^{2+} \rightleftharpoons Cp_2M^+ \rightleftharpoons Cp_2M \rightleftharpoons Cp_2M^- \qquad (12)$$

encompassing four or less members is possible in which the metal undergoes stepwise reduction from M^{IV} to M^I. However, only in the cases of M = Ni and V is the series complete, and the outlying members of those series (Cp_2V^{2+} and Cp_2Ni^-) are very reactive. Table III lists the ions now known for first-row metallocenes. Cp_2V^{2+} is included in the table but CV studies on its formation show it to be very unstable (vide ante). The anion of unsubstituted manganocene has not been detected,[40] but that of bis(η^5-pentamethylcyclopentadienyl)manganese has been.[47] The general shape of Table III is triangular, peaking at the d^6 configuration known to be so stable in metal π compounds.

$E_{1/2}$ values for the $M^{II} \rightleftharpoons M^I$ reductions were shown[21] to correlate with the second metal ionization potentials for M = Cr, V, Co, and Ni. There are only two possible $M^{II} \rightleftharpoons M^I$ redox processes which involve the d^6 electron configuration and neither of these (M = Fe, Mn) fit this correlation. The reduction of ferrocene is predicted to be at ca. −2.3 V but it is *not* observed out to the electrolyte discharge (−2.9 V). $(C_5Me_5)_2Mn$ is reported[41] to reduce to the d^6 anion at −0.56 V, about 2 V positive of the predicted value. This again demonstrates the extraordinary stability of the d^6 metallocenes.

With the exception of vanadocene, the $E_{1/2}$ potentials of the $Cp_2M^{III} \rightleftharpoons Cp_2M^{II}$ couple correlate well with the gas-phase ionization potentials of the metallocenes. Data taken from the UV photoelectron spectroscopy data of Orchard and coworkers[42] are plotted in Figure 5 against the potential of the $Cp_2M^+ \rightleftharpoons Cp_2M$ couple. The energy of the lowest ionization process was taken. Vanadocene (point 4) is a striking exception to the correlation, being about 750 mV *easier* to oxidize than predicted by the UV-PES data. There would seem to be two factors which could account for the abnormal ease of the vanadocene oxidation. Either the ionization potential of dissolved (solvated) vanadocene is quite a bit different (by ca. 0.8 eV) than the free compound, or else there is an abnormally large change in solvation energies of Cp_2V and Cp_2V^+, compared to other metallocenes.

Relationship of Oxidation State to Structure. Metallocenes of early transition metals in high oxidation states generally assume bent structures like **2** or **3** in which one or two (or even

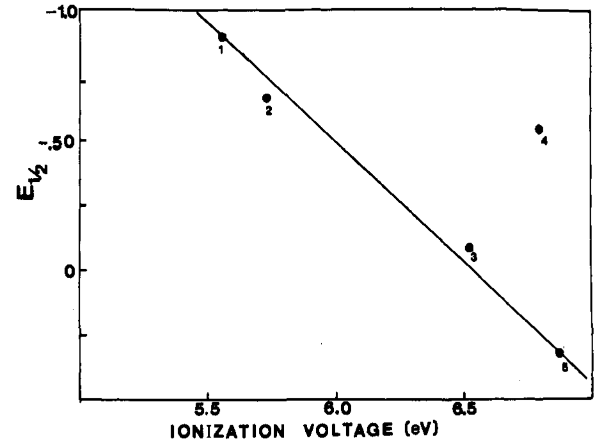


Figure 5. Plot of $E_{1/2}$ for the oxidation of Cp_2M vs. lowest ionization voltage for neutral metallocenes (IV taken from ref 42). Legend: 1 = Cp_2Co, 2 = Cp_2Cr, 3 = Cp_2Ni, 4 = Cp_2V, 5 = Cp_2Fe.

three) ligands are added to the metal coordination sphere[4,30,43,44] in an apparent effort to increase the electron density at the metal. d^1 and d^2 metals form bent structures, in compounds like $Cp_2Ti(C_6H_5)$,[45] $(C_5H_4Me)_2TiCl_2$,[46] Cp_2VCl,[47] and $Cp_2Ti(CO)_2$.[48] d^3 and d^4 compounds, like Cp_2V and $Cp_2Cr^{0/+}$, are assumed to have the coplanar structure (**1**).[49,50] The theoretical treatment of Lauher and Hoffmann[4] shows that the bent structure is destabilized for d^3 compounds in the absence of added ligands because of the increased energy of the metal b_2 orbital that occurs in the bending process. The situation is less clear for low-spin d^2 compounds in which the electron pair would reside in an a_1 orbital largely unaffected by the structure difference.

Our electrochemical data, specifically the reversibility of the oxidations of Cp_2Cr and Cp_2V, are consistent with there being no gross structural *change* in going from d^4 to d^3 or d^3 to d^2 compounds. This would seem to imply that vanadocene cation, isoelectronic with the elusive d^2 titanocene, has the ferrocene-like structure (**1**). But a cautionary note must be injected, since the structure assumed by neutral vanadocene in THF is not known. In fact, the observation that Cp_2V lies so far outside the correlation of $E_{1/2}$ vs. gas-phase ionization potentials (Figure 5) makes one suspicious about whether neutral Cp_2V retains the ferrocene-like structure in these solutions. It is our opinion that this point deserves further experimental attention.

One last point to be made on this topic is that the structural preferences of various oxidation states of Cp_2VX_2 compounds are clear from the data on the Cp_2VCl_2 reduction. Cp_2VCl_2 apparently remains bent as the d^2 monoanion, since the redox couple is highly reversible. The d^2 complex Cp_2VCl has also been found to have the bent structure.[47] But reduction of Cp_2VCl_2 to the d^3 dianion immediately results in loss of both chloride ions and in formation of the vanadocene sandwich.

Models for structural changes in electron-transfer reactions of electron-rich metallocenes have far less precedent. A definitive crystal structure of the d^8 nickelocene has not appeared, but the compound is known to have the ferrocene-like sandwich structure.[49,51-53] No d^9 metallocenes have been reported. Distortions are common, however, in electron-rich (above 18 electron) metals of other classes of compounds. Typical examples are the slipped-sandwich structures of the d^8 and d^9 metallocarboranes[54,55] $Ni(7,8\text{-}B_9C_2H_{11})_2^{2-}$ and $Cu(7,8\text{-}B_9C_2H_{11})_2^{2-}$ with 20 and 21 electrons, respectively, and the ring-distorted structure of $(C_5H_5)_2Mo(NO)R$, a formally 20-electron species.[56] Given the close analogies between cyclopentadienyl and metallocarborane complexes,[57,58] the former is especially attractive as a model for electron-rich molecular distortions, and the reader is referred to the review by Wade[58] for a discussion of this topic. Most recently, the 20-electron species $(C_5H_5)_2W(CO)_2$ has been studied by X-ray crystallography.[59] It was shown that one of the C_5H_5 rings deviates grossly from planarity to take on the characteristics of a three-electron, rather than a five-electron, donor.

As mentioned previously, a major change in structure or solvation during an electron-transfer reaction will lead to slowing down of the reaction.[36] Slow electron transfer is very evident in the case of the nickelocene d^8 to d^9 reduction from the cyclic voltammogram (Figure 4), whereas the d^8 to d^7 oxidation is highly reversible (same figure). From the CV peak spread observed in DMF at room temperature, we calculate an apparent k_s value of about 3×10^{-3} cm s^{-1}.[60] This value is two to three orders of magnitude lower than those reported for other metal sandwich compounds.[68] In fact, it is very similar to that reported for the reduction of cyclooctatetraene, in which the molecule undergoes a profound structural change, i.e., from a tub to a planar system.[61,62] At the present time, however, we cannot say that the electron-transfer rate is not solvent controlled, owing to the difficulty of finding solvents which are conductive enough to lend themselves to reliable rate-constant studies, and yet do not react with Cp_2Ni^-.[63] This point is still being investigated.

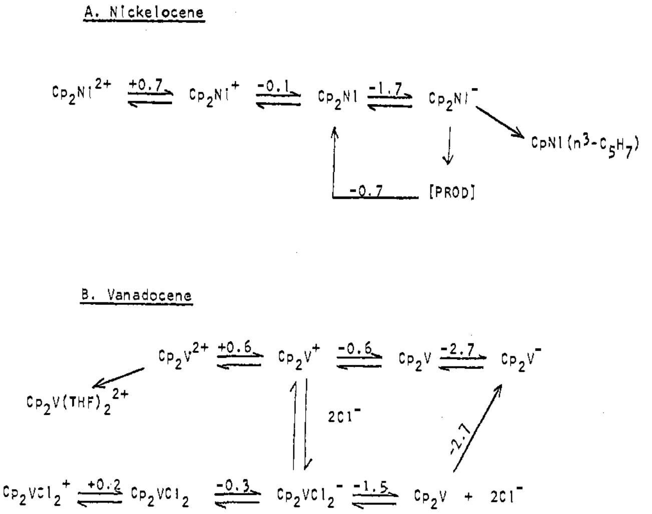


Figure 6. Proposed reaction pathways for oxidation and reduction of biscyclopentadienyls of nickel and vanadium.

Overall Redox Pathways. The electron-transfer and associated reactions of Cp_2V and Cp_2Ni are shown in Figure 6 for summary purposes. The major nickelocene reduction product is still not identified. Since nickelocene can be regenerated in part from oxidation of the product, we favor a structure having two or more nickel-cyclopentadienyl groups, such as a cluster compound or one analogous to the "palladocene" or "platinocene" dimers.[64-67]

Conclusions

A sequence of reversible electron-transfer reactions is a general property of metallocenes. Nickelocene is the only metallocene for which four separate ions have been detected ($Cp_2Ni^{2+/+/0/-}$). Vanadocene also undergoes three electron-transfer steps, but the vanadocene dication was too reactive to detect by cyclic voltammetry. It is noteworthy that only in the latest (Ni) and earliest (V) metallocenes is there a four-member electron-transfer series. In these complexes the necessity of reducing or oxidizing the stable d^6 configuration is avoided.

The electron-transfer reactions are rapid and reversible if confined to d^3 to d^8 compounds and ions. Reduction of d^8

Cp_2Ni to d^9 Cp_2Ni^- is electrochemically slow and must be accompanied by a structural deformation of the compound. Oxidation of d^3 Cp_2V to the d^2 cation is not accompanied by gross distortions (in THF), although there may be significant changes in solvation accompanying the electron-transfer step. The most highly oxidized and reduced metallocenes (d^1 Cp_2V^{2+} and d^9 Cp_2Ni^-, respectively) are highly reactive and undergo rapid chemical transformations to a variety of products.

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