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Electrochemical Reduction Pathways of the Rhodocenium Ion. Dimerization and Reduction of Rhodocene

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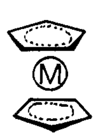
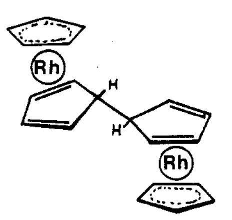
The electrochemical reduction of the rhodocenium ion, Cp_2Rh^+, and its dicarbollide analogue, $[(B_9C_2H_{11})_2Rh]^-$, has been studied in nonaqueous solvents by dc and ac polarography, cyclic voltammetry, and controlled potential coulometry. The starting Rh(III) complexes can both be reduced in two separate one-electron processes to Rh(II) and Rh(I) compounds which are very reactive. Cp_2Rh has a lifetime of about 2 s at room temperature but can be stabilized by performing the electrolysis at low temperatures. Rhodocene decomposes by dimerizing to form $[Cp_2Rh]_2$, which can be isolated in good yield by electrolysis of Cp_2Rh^+ solutions. Evidence is presented for the transient existence of the rhodocene anion, and comparison to the reduction of Cp_2Co^+ is made.

Introduction

One interesting aspect of metallocene chemistry is the contrasting stabilities often found between a first-row transition-metal complex and its second- or third-row congener. For example, cobaltocene (**1**), Cp_2Co, is an air-sensitive but otherwise stable compound which can be oxidized or reduced by one electron to the very stable d^6 cobaltocenium ion, Cp_2Co^+, or the reactive cobaltocene anion, Cp_2Co^-, respectively.[1,2] However, the heavier analogues of cobaltocene, namely, rhodocene, Cp_2Rh (**2**), and iridocene, Cp_2Ir (**3**), are highly unstable, and no evidence of anions of these species has been reported.



2, M = Rh



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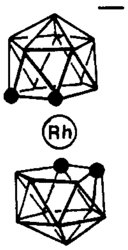

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The neutral compounds **2** and **3** can be trapped at dry ice temperatures on a cold finger after reduction of $(\mathbf{2})^+$ or $(\mathbf{3})^+$ with molten sodium, but warming to room temperature produced a dimer with the postulated structure **4**,[3] shown for Rh. This dimer could be isolated only in low yields (ca. 8%).[3]

Because very little is known about the redox reactions of second- and third-row metal sandwich compounds, we have investigated the electrochemical reduction of Cp_2Rh^+ and its isoelectronic[4] carborane analogue $[(1,2\text{-}B_9C_2H_{11})_2Rh]^-$.[5]

The results confirm that Rh(II) is a highly reactive oxidation state for rhodium π complexes. Cp_2Rh is stable only for several seconds in solution and, under appropriate conditions, can be reduced to a (very reactive) anion, Cp_2Rh^-. The dimer **4** is isolated in high yield from electrolyzed solutions of Cp_2Rh^+.

Experimental Section

Electrochemical experiments were performed under an atmosphere of prepurified nitrogen by using solvents prepared by standard methods. The supporting electrolyte was Bu_4NPF_6, 0.1 M in each case. $Cp_2Rh^+PF_6^-$ was prepared by a method to be published.[17] The tetraethylammonium salt of $[(B_9C_2H_{11})_2Rh]^-$ was obtained from Dr. J. N. Francis and Professor M. F. Hawthorne. All potentials are reported vs. the aqueous saturated calomel electrode (SCE). The dimer $[Cp_2Rh]_2$ isolated from the electrolysis solutions melted (with decomposition) at 174 °C and gave an elemental analysis consistent with the dimeric structure. Anal. Calcd: C, 51.53; H, 4.32; Rh, 44.15. Found: C, 51.56; H, 4.34; Rh, 44.34. The infrared spectrum of this

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Table I. Dc Polarographic Data for Some Rhodium and Cobalt π Complexes in Acetonitrile

compd	$E_{1/2}$[a]	I_d[b]	D_0[c]
Cp_2Rh^+	−1.41	3.68	2.6×10^{-5}
	−2.18	*d*	
Cp_2Co^+	−0.94	3.60	2.5×10^{-5}
	−1.88		
$[(B_9C_2H_{11})_2Rh]^-$	−1.82	4.60	4.2×10^{-5}
	−2.48	*d*	

[a] Half-wave potential in volts vs. SCE. [b] Diffusion current constant (equal to $i_d/C_0m^{2/3}t^{1/6}$). [c] Diffusion coefficient calculated from Ilkovič equation. [d] Drop time dependent.

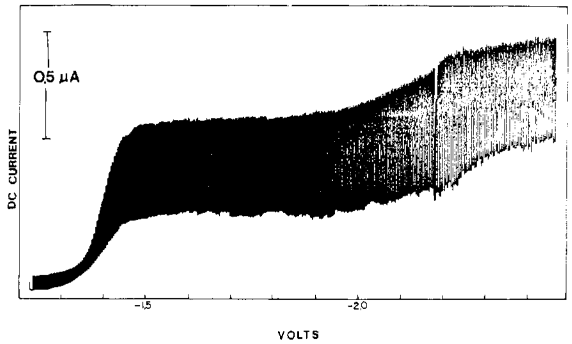

Figure 1. Dc polarogram of 5.0×10^{-4} M $Cp_2Rh^+PF_6^-$ in CH_3CN/0.1 M Bu_4NPF_6. Drop time 2 s.

material (in KBr) was identical with that reported previously.[3] An electron-impact mass spectrum of the dimer has a base peak at *m/e* 233, corresponding to Cp_2Rh^+.

Results and Discussion

Voltammetry of Cp_2Rh^+. In their original report of the synthesis of Cp_2Rh^+, Cotton, Whipple, and Wilkinson reported that this compound gave a single polarographic wave in aqueous solution.[6] We find that two reductions are possible in nonaqueous media (THF, DMF, CH_3CN). Representative half-wave potentials are given in Table I. The first wave, in the vicinity of −1.4 V, was diffusion controlled, but the wave at −2.2 V exhibits kinetic control (Figure 1). The latter reduction will be discussed in detail later in the paper.

The first reduction is a highly reversible one-electron process, resulting in Cp_2Rh, which is not completely stable on the cyclic voltammetry (CV) time scale. These conclusions are established by dc and ac polarography and by CV scans in acetonitrile. The diffusion current constant, I_d, for the reduction (3.6) is the same as that measured for Cp_2Co^+/Cp_2Co in the same electrolyte medium, showing that one electron is consumed.

The high degree of reversibility (in the kinetic sense) of the Cp_2Rh^+/Cp_2Rh couple is shown by phase-selective ac polarography. A well-developed ac polarogram is obtained (Figure 2) having a width at half-height of 88 mV, within experimental error of the 90 mV expected for a reversible one-electron process.[7] The peak current was proportional to the square root of the ac frequency from 17 to 400 Hz, and the cotangent of the phase-shift angle was proportional to the same quantity (Figure 3).

The cotangent data can be used to calculate the standard apparent rate constant k_s for the heterogeneous electron-transfer step. If an α value of 0.5 is assumed,[8,9] the relationship between cot ϕ and k_s is given by eq 1, in which D_0 is the

$$\cot \phi = 1 + (2\omega D_0)^{1/2}/k_s \qquad (1)$$

diffusion coefficient of Cp_2Rh^+ in this medium and ω is the angular ac frequency. $D_0^{1/2}$ was calculated as 5.2×10^{-3} from the measured value of I_d used in the Ilkovič equation. A k_s value of 0.73 cm/s was obtained. This value is diagnostic of very rapid electron transfer and may be compared with 0.86 cm/s reported for Cp_2Co^+/Cp_2Co.[9]

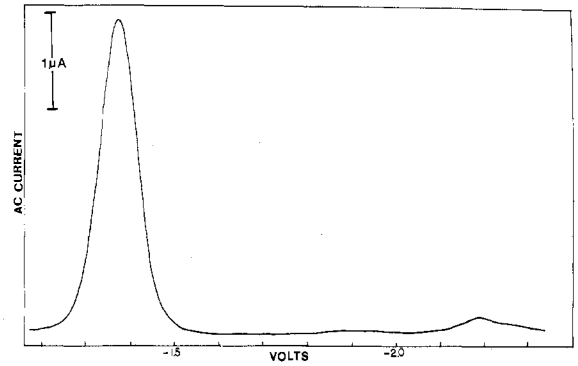

Figure 2. Ac polarogram of Cp_2Rh^+ (same solution as that of Figure 1) (300 Hz, in-phase component detected).

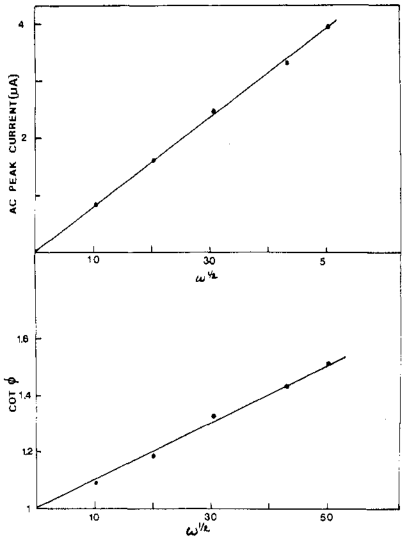

Figure 3. Plots of ac peak currents for in-phase component (upper) and cot ϕ values (lower) vs. $\omega^{1/2}$ for Cp_2Rh^+/Cp_2Rh.

Table II. Cyclic Voltammetry Data for Rhodium Compounds at a Hanging Mercury Drop Electrode in CH_3CN

compd	scan rate[a]	i_a/i_c[b]	$i_{pc}/v^{1/2}$[c]	i_2/i_1[d]
Cp_2Rh^+/Cp_2Rh	0.050	0.51	1.06	
	0.100	0.59	1.04	
	0.200	0.71	1.02	
	0.500	0.84	1.00	
	5.00	1.00	1.00	
Cp_2Rh/Cp_2Rh^-	0.050	irrev	0.24	0.23
	0.100		0.26	0.25
	0.200		0.33	0.32
	0.500		0.44	0.44
	5.00		1.00	1.00
$(B_9C_2H_{11})_2Rh^{-/2-}$	0.200	0.60		
	2.00	0.97		
	5.00	1.00		

[a] In V/s. [b] Ratio of anodic to cathodic currents for a particular redox couple. [c] Current function [(cathodic peak current)/(square root of scan rate)] normalized to value of Cp_2Rh^+ at fast scan rates. [d] Ratio of peak currents of second vs. first Cp_2Rh^+ reduction.

Cyclic voltammetry scans show that neutral Cp_2Rh, produced at the first wave, is not very stable. At scan rates below 1 V/s, i_a/i_c ratios of less than unity were obtained (Table II). Another important observation was that the second reduction peak at −2.2 V was smaller than the first at slow scan rates. As the scan rate was increased, the height of wave 2 relative

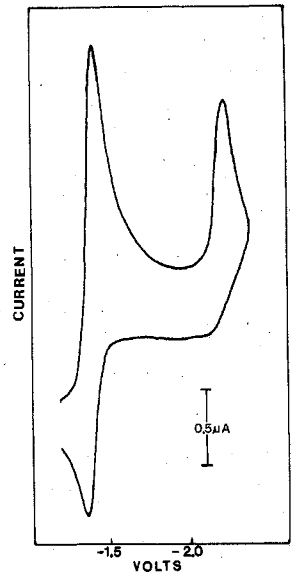

Figure 4. Cyclic voltammetry scan of Cp_2Rh^+ (same solution as that of Figure 1) at a hanging mercury drop electrode. Scan rate 0.50 V/s.

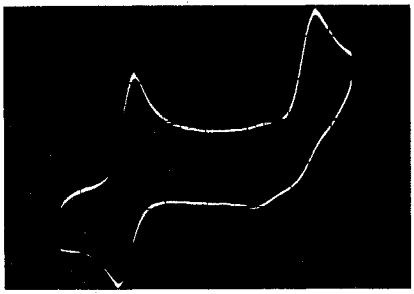

Figure 5. Same as Figure 4, except at a higher scan rate (5.0 V/s), from −1.10 to −2.41 V. Cathodic peak current (first wave) 7.3 μA.

Table III. Variation of Relative Height of Second Cp_2Rh^+ Wave to That of First as a Function of Dc Polarographic Drop Time

drop time, s	2nd/1st ratio[a]	drop time, s	2nd/1st ratio[a]
0.5	1.64	2.0	1.44
1.0	1.49	5.0	1.39

[a] Ratio of second to first waves.

to wave 1 increased (Table II) until the two waves became equal in the fast-scan limit (see Figures 4 and 5). The trends in current function ($i_{pc}/v^{1/2}$) (Table II) establish that the first wave is diffusion controlled whereas the second has kinetic character,[10] the second wave being favored at shorter experiment times.

The CV data are consistent with a scheme wherein the two waves represent the two one-electron reductions of Cp_2Rh^+, mediated by a chemical reaction following the first electron transfer (an ece process). Confirming this, a CV scan back to 0 V from negative of the first wave (Figure 6) shows the oxidation wave at −0.5 V arising from the product of the chemical reaction of Cp_2Rh. This product has been shown to be due to the dimer **4** (see below).

Dc polarographic data are also consistent with the ece scheme, for the height of the second plateau current compared to the first is drop-time dependent (Table III). As expected, the contribution of wave 2 increases at shorter drop times, as time available for the dimerization of Cp_2Rh diminishes.

Reduction of Cp_2Rh. Using the approach of Nicholson and Shain[10] with our measured i_a/i_c values, we estimate a half-life of about 2 s for Cp_2Rh in CH_3CN at 25 °C. Consequently, at fast scans and/or at lower temperatures, the reduction of rhodocene can be studied. Unlike the situation found for the cobaltocene anion,[1,2] Cp_2Rh^- is so unstable in CH_3CN that CV scans at up to 100 V/s fail to reveal any reversibility of the second wave. However, experiments in other solvents were more successful, and reversibility is found for the Cp_2Rh/Cp_2Rh^- wave in THF at high scan rates (100 V/s) or in DMF at slow scans but at low temperatures. Figure 7 shows a slow (0.2 V/s) scan at −50 °C in DMF indicating that Cp_2Rh^- has a definite, albeit transient, existence under these conditions.

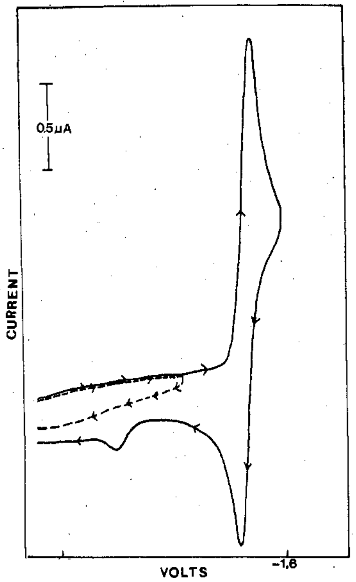

Figure 6. Cyclic scan of the Cp_2Rh^+/Cp_2Rh reduction showing the peak at −0.5 V arising from $[Cp_2Rh]_2$. Note that this oxidation wave is not present unless the scan goes negative of the first Cp_2Rh^+ reduction.

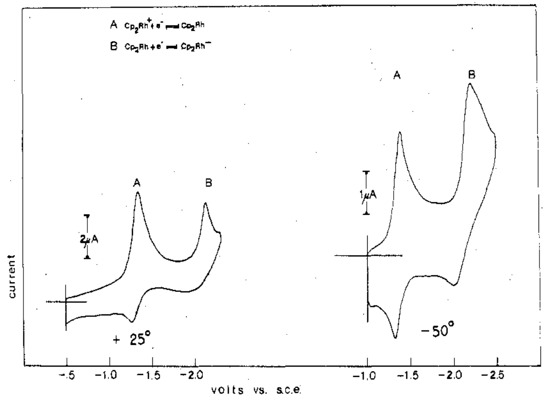

Figure 7. Cyclic scans of Cp_2Rh^+ in DMF, at a Pt electrode at room temperature and at −50 °C. Scan rate 0.10 V/s.

Bulk Electrolysis: Preparation of the Rhodocene Dimer. If solutions containing Cp_2Rh^+ are electrolyzed at the first plateau potential, one electron is consumed and a yellow solution having an oxidation wave at −0.4 to −0.5 V is obtained. If the original Cp_2Rh^+ solution is sufficiently concentrated, a yellow powder precipitates. This material was identified as **4**, $[Cp_2Rh]_2$, according to the physical properties listed in the Experimental Section.

The yellow solutions can be reoxidized back to Cp_2Rh^+. This behavior was found for both CH_2Cl_2 and DMF solutions of the dimer. For example, a 8 × 10^{-4} M solution of $Cp_2Rh^+PF_6^-$ was electrolyzed at −1.6 V in dichloromethane. A total of 1.1 electrons was passed and the resulting yellow solution gave a polarographic oxidation wave at $E_{1/2}$ = −0.4 V of the same height as the original reduction wave. A cyclic voltammogram of this solution shows the oxidation wave to

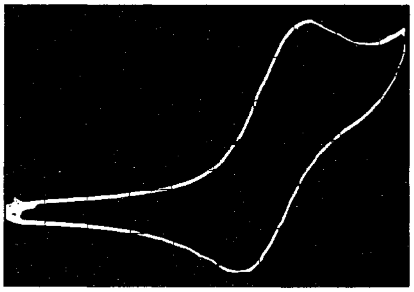

Figure 8. Cyclic scan of a 3.4×10^{-4} M solution of $[(1,2\text{-}B_9C_2H_{11})_2Rh]^-$ in CH_3CN/0.1 M Bu_4NPF_6 at a mercury electrode. Scan rate 2 V/s, range −1.50 to −2.00 V; cathodic peak current 3.2 μA.

be irreversible, generating the Cp_2Rh^+ wave on the reverse cycle. A bulk reoxidation (passing 1.0 electron) at a potential positive of +0.4 V resulted in quantitative regeneration of the original Cp_2Rh^+ solution.

Thus the complete reduction mechanism for Cp_2Rh^+ can be given as

$$Cp_2Rh^+ + e^- \rightleftharpoons Cp_2Rh \qquad -1.4\ V \tag{2}$$

$$Cp_2Rh \rightarrow {}^1/_2[Cp_2Rh]_2 \tag{3}$$

$$Cp_2Rh + e^- \rightleftharpoons Cp_2Rh^- \qquad -2.2\ V \tag{4}$$

$$Cp_2Rh^- \rightarrow \text{products} \tag{5}$$

and the oxidation of the dimer proceeds by eq 6.

$${}^1/_2[Cp_2Rh]_2 \rightarrow Cp_2Rh^+ + e^- \qquad -0.4\ V \tag{6}$$

Thus, when the time scale of the experiment is short compared to the rate of the chemical reactions, a simple ee system (eq 2 and 4) is found, but at longer times an ece mechanism (eq 2–4) is operative.

If the electrolysis solutions are made more concentrated, good yields of the dimer are obtained. Bulk electrolysis of 500 mg of Cp_2Rh^+ in 150 mL of CH_2Cl_2, followed by evaporation of the solvent and removal of supporting electrolyte by acetone washings, gave 240 mg of the dimer (80% yield). This yield is an order of magnitude better than that previously reported for the dimer by metal reduction.[3]

The isolated dimer could also be oxidized back to Cp_2Rh^+ (quantitatively) by $(C_6H_5)_3C^+BF_4^-$ in CH_2Cl_2. The progress of the oxidation was monitored by polarography.

Reduction of $[(1,2\text{-}B_9C_2H_{11})_2Rh]^-$. Several years ago, Hawthorne and Wegner pointed out[4] the potential similarities between metallocenes and dicarbollide complexes of the type **5** due to the fact that the bonding molecular orbitals of the $B_9C_2H_{11}^{2-}$ ligand and the $C_5H_5^-$ ligand are similar. The isoelectronic nature of these compounds has been established through a variety of studies,[11-15] and a very recent molecular orbital calculation has discussed the usefulness of the *qualitative* aspects of this analogy.[16]

As with Cp_2Rh^+, two reduction waves were observed for $[(B_9C_2H_{11})_2Rh]^-$. Again, the first wave was a diffusion-controlled one-electron wave (I_d = 4.6 in CH_3CN) and the second polarographic wave was only a fraction of the height of the first. CV scans show that the first reduction is reversible at rapid scan rates (Figure 8), leading to the Rh(II) species $(B_9C_2H_{11})_2Rh^{2-}$. But, like Cp_2Rh, this Rh(II) product is unstable, and at 0.2 V/s, an i_a/i_c value of 0.60 was measured, far below the value of 1.0 which would be obtained if the Rh(II) complex were stable over the lifetime of the CV experiment.

The wave at −2.5 V was completely irreversible. Detailed mechanistic work was not purused because after several minutes in solution (either CH_3CN or 1,2-dimethoxyethane), an irreversible wave grew in with a cathodic peak potential of −2.05 V. Apparently the Rh(III) complex undergoes some decomposition in these solutions.

Summary

From strictly an electron-transfer point of view, the reductions of Cp_2Co^+ and Cp_2Rh^+ are very similar. Each proceeds by two discrete one-electron processes, the first of which has a very rapid electron-transfer rate (with k_s ca. 0.8 cm/s). The electron-transfer step cannot therefore involve any large structural changes in the molecules. The $E_{1/2}$ values for the two waves are separated by a similar amount for each complex (0.94 V for Co vs. 0.78 V for Rh) implying there is a similar charge distribution (metal vs. ligand) in the complexes. Neither compound is oxidized within the potential range available on a Pt electrode (CV scans to +2.2 V in either CH_3CN or CH_2Cl_2 fail to reveal any oxidation waves), demonstrating the high stability of the d^6 electron configuration for metallocenes. The electron-transfer properties of the bis(dicarbollyl)rhodium complex parallel those of rhodocenium, with $\Delta E_{1/2}$ = 0.66 V for $(B_9C_2H_{11})_2Rh^{-/2-/3-}$. The more negative $E_{1/2}$ potentials reflect the greater negative charge on the dicarbollyl anion (2−) compared to that on the cyclopentadienide ion (1−).

However, the Rh(II) and Rh(I) compounds arising from the reductions are much less stable than their Co(II) and Co(I) counterparts.

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Registry No. Cp_2Rh^+, 37205-11-1; $[(B_9C_2H_{11})_2Rh]^-$, 69855-41-0; Cp_2Rh, 37205-11-1; Cp_2Rh^-, 69847-30-9; $[(B_9C_2H_{11})_2Rh]^{2-}$, 69855-42-1; $[Cp_2Rh]_2$, 1298-74-4.

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