Structural Changes Coupled to Two-Electron-Transfer Reactions: Oxidation Mechanism of Pseudo-Triple-Decker Complexes of Co and Rh[†]

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Abstract: A series of four pseudo-triple-decker complexes $(\eta^5\text{-}C_5R_5)_2M_2(\mu\text{-}C_8H_8)$, M = Co or Rh, R = H or Me, undergoes a chemically reversible two-electron oxidation. The neutral complexes have the two metals on either side of a tub-shaped cyclooctatetraene bridging ligand, whereas the dications have a twisted bridging C_8 ring which has two planar C_4 fragments. The two dicobalt complexes $Cp_2Co_2(\mu\text{-}C_8H_8)$, **1**, and $Cp^*_2Co_2(\mu\text{-}C_8H_8)$, **2**, display quasi-reversible couples with $E° = +0.10$ V vs SCE, $k_s > 2 \times 10^{-2}$ cm/s and $E° = -0.22$ V, $k_s = 4.6 \times 10^{-3}$ cm/s, respectively, in CH_2Cl_2. This conclusion is based on data from cyclic voltammetry, controlled potential coulometry, dc polarography, and rotating ring-disc voltammetry experiments. Similar experiments on the dirhodium complex **3**, $Cp_2Rh_2(\mu\text{-}C_8H_8)$, show more complex voltammetric behavior. The oxidation wave for $\mathbf{3}/\mathbf{3}^{2+}$ is over 500 mV positive of the reduction wave for $\mathbf{3}^{2+}/\mathbf{3}$, with CV peak potentials of ca. +0.43 V for the former and −0.11 V for the latter. This couple is described by a square scheme in which the electron-transfer reactions are experimentally separable from the tub ⇌ twist isomerizations. A rate of ca. 2 s^{-1} was measured for the twist → tub isomerization of **3** by cyclic voltammetry, double potential step chronoamperometry, and ring-disc voltammetry. The slower isomerizations of the Rh complex are consistent with larger rearrangement energies for Rh–olefin bonds as compared with Co–olefin bonds. The two-electron oxidation wave of **3** separated into two one-electron waves, the first being reversible, in low-temperature CV experiments in CH_2Cl_2. When combined with fast-scan CV on the reduction of $\mathbf{3}^{2+}$, these experiments show that the chemically reversible couple for *tub*-**3** − 2e⁻ ⇌ *twist*-$\mathbf{3}^{2+}$ proceeds in both directions via EEC mechanisms. This result is compared to other two-electron transfers with associated geometric changes.

Introduction

Dinuclear complexes of cyclooctatetraene interface two areas of organometallic chemistry. They are part of an array of metal–cyclooctatetraene complexes which display fascinating variations in structure, owing to the coordinative and conformational flexibility of the C_8H_8 ligand.[1-5] In addition, the members of this series with metals in the trans (or anti) configuration are viewed as "near miss" triple-decker complexes.[6]

Genuine triple deckers have attracted a great deal of experimental and theoretical attention.[6,7] On the supposition that the geometric distortion of the central ring which separates near misses from true triple deckers (structures I and II in Scheme I, respectively) arises from an improper electron count,[6] the redox chemistry of *trans*-$(ML)_2(\mu$-cyclooctatetraene) complexes has been investigated.[8-11] In earlier communications on pseudo-triple-decker complexes of Co or Rh,[9,10] we showed that oxidation of the 36-electron complexes I (Scheme I, ML = CpM, where Cp = η^5-cyclopentadienyl and M = Co or Rh) failed to produce a structure (II) having a planar middle ring. Rather, the "slipped" triple-decker III was produced. In III, the cyclooctatetraene ring has two planar four-carbon fragments connected by a slight twist (34.8° in the case of the CpRh complex[10]), the metals moving toward one edge so that they are bridged by a C–C bond of the central eight-membered ring. Structure III is also found with the isoelectronic complex $(CpRu)_2(\mu$-cyclooctatetraene) and will be discussed in the following paper in this issue.

The two-electron process involving structures I and III (eq 1)

$$\mathrm{I} \rightleftharpoons \mathrm{III} + 2e^- \qquad (1)$$

is rich in complexity, since a minimum of two one-electron transfers and one structural change are involved. Progress in understanding the relationship between electron transfer and structural changes has been recently reviewed,[12,13] and a growing number of examples have been reported in which profound structural changes are coupled to an overall two-electron transfer.[14] The pseudo-triple-decker complexes $Cp_2Co_2(\mu\text{-}C_8H_8)$, **1**, $Cp^*_2Co_2(\mu\text{-}C_8H_8)$, **2**, and $Cp_2Rh_2(\mu\text{-}C_8H_8)$, **3**, provide an unusual opportunity to investigate details of fast structural changes coupled to multiple electron-transfer reactions. All three complexes un-

Scheme I

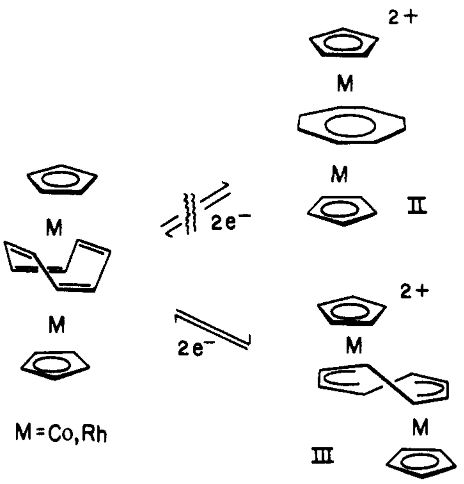
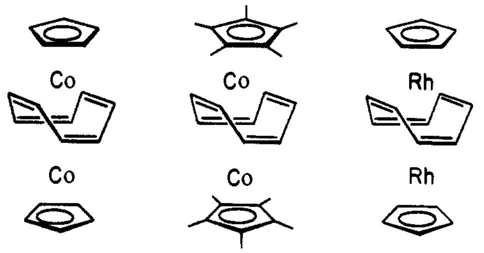


Chart I



1 **2**, — = Me **3**

[†] Part 21 of the series *Structural Consequences of Electron-Transfer Reactions*. Part 20: Pierce, D.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7636.

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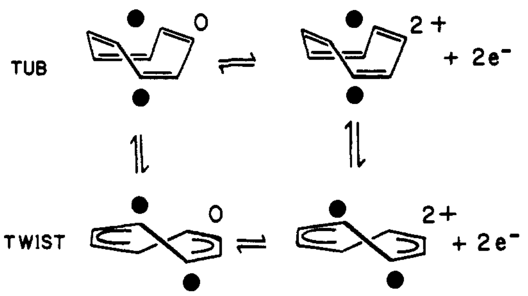
Scheme II



dergo the chemically reversible reaction of eq 1. However, they differ in voltammetric behavior. For example, slow scan rate cyclic voltammetric (CV) peak separations vary from essentially Nernstian (30 mV for a two-electron transfer) for **1** to over 500 mV for **3**. This paper explores details of the two-electron transfer of eq 1 by using a variety of electrochemical methods.

Two isomeric forms are identified in these studies, and we name them according to the conformation of the cyclooctatetraene ring, tub in the case of **I** and twist in **III** (Scheme I). It will be shown that eq 1 is inadequate to describe the electrodic details of the electron transfer and that a square scheme (Scheme II, solid circles represent CpM) is preferable.

Furthermore, in at least one case (**3**), the one-electron components of the overall two-electron transfer are individually detected, and the relative timing of the tub ⇌ twist isomerization and the one-electron transfers is diagnosed.

Experimental Section

All synthetic and electrochemical operations were conducted with the exclusion of oxygen and water. Standard Schlenck procedures were employed in preparative work. The dirhodium complex **3** and its dication appeared to be more stable under Ar than N_2. Most voltammetric work was done in a Vacuum Atmospheres glovebox, but low-temperature experiments on **3** were performed in a vacuum electrochemical cell. Most of these procedures were as previously described.[14,15] A saturated calomel reference electrode was employed. The potential of the ferrocene/ferrocenium couple was +0.46 V in CH_2Cl_2 and +0.48 V in acetone vs the SCE. The supporting electrolyte was 0.1 M Bu_4NPF_6 in all experiments.

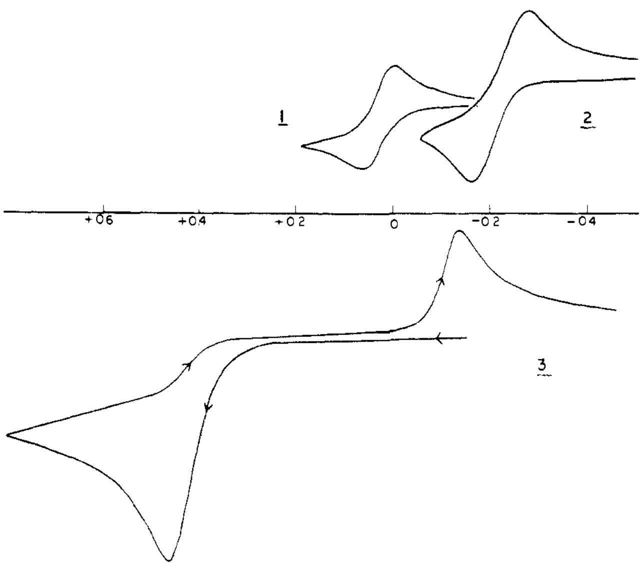


Figure 1. Cyclic voltammograms of $\mathrm{Cp_2Co_2(\mu\text{-}C_8H_8)}$, **1**, $\mathrm{Cp^*{}_2Co_2(\mu\text{-}C_8H_8)}$, **2**, and $\mathrm{Cp_2Rh_2(\mu\text{-}C_8H_8)}$, **3**, in CH_2Cl_2 at Pt electrode, for qualitative comparison. The scan rates were 0.17 V/s for **1**, 0.12 V/s for **2**, and 0.10 V/s for **3**.

Compounds. The preparation of the neutral complexes **1**–**3** was described in the older literature.[16–18] The dications **2**$^{2+}$ and **3**$^{2+}$ were prepared by oxidation of the appropriate neutral complex with silver hexafluorophosphate (Ozark-Mahoning), as previously described.[19] The nickel complex employed as a one-electron standard in low-temperature experiments on **3**, $\mathrm{[CpNi(\eta^4\text{-}C_8H_{12})][PF_6]}$, was also prepared in the literature fashion.[20] Satisfactory elemental and spectral analyses were obtained for each compound. The mixed-metal pseudo-triple-decker complex $\mathrm{CpCo(\mu\text{-}C_8H_8)RhCp}$, **4**, was prepared by the reaction of $\mathrm{CpCo(\eta^4\text{-}C_8H_8)}$[16b] with $\mathrm{[(C_2H_4)_2RhCl]_2}$[21] followed by treatment with [Cp][Tl].[2]

Electrochemistry. Most procedures and equipment were as reported earlier.[14] The rapid sweep, charging current-subtracted CV experiments were performed by David Pierce with a PARC Model 173 potentiostat and a Nicolet Model 4094 digital oscilloscope. A Pt disc of 250 μm diameter served as the working electrode. Rotating disc and rotating ring-disc studies employed a dual potentiostat and ring-disc electrodes of Pt and Au purchased from Pine Instruments Co. The area of the disc electrodes was nominally 0.459 cm^2 (manufacturer's specifications).

Results and Discussion

Each of the three complexes **1**–**3** undergoes a two-electron oxidation to the corresponding dication. Moraczewski found that **1**$^{2+}$ was too unstable in solution to be crystallized,[9] but **2**$^{2+}$ and **3**$^{2+}$ were isolated as crystalline materials.[19] Whereas each of the couples **1**/**1**$^{2+}$, **2**/**2**$^{2+}$, and **3**/**3**$^{2+}$ are chemically reversible, they differ markedly in their *apparent* electrochemical reversibility[22] as manifested in their cyclic voltammograms (Figure 1). It will be shown below that these qualitative changes in voltammetry arise from differences in the rate of the tub ⇌ twist isomerization coupled to the electron-transfer reactions.

The two Co complexes **1** and **2** tended to lose a $(C_5R_5)Co$ "deck" in strong donor solvents, and **1**$^{2+}$ was labile in all solvents except CH_2Cl_2, in which it had a lifetime of about 10 s at room

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(9) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 7431. When CH_2Cl_2 solutions of **1** were treated with two equiv of $AgPF_6$, a black precipitate was collected which gave an analysis close to that expected for $\mathrm{[1][PF_6]_2\cdot 2Ag}$: Anal. Calcd: C, 25.2; H, 2.1; Ag, 25.2; Co, 13.8. Found: C, 23.9; H, 2.0; Ag, 26.0; Co, 10.5. The salt was slightly soluble in CH_2Cl_2, giving a reversible reduction wave at $E°$ = +0.08 V vs SCE. Evidence is therefore strong that the black powder contained at least some of the desired dication $\mathrm{[1]PF_6]_2}$, but all attempts to recrystallize the sample led only to decomposition.

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(22) The distinction between chemical and electrochemical reversibility in a redox couple is fundamental to electrodic considerations. See, for example: Bond, A. M. *Modern Polarographic Methods in Analytical Chemistry*; Marcel Dekker: New York, 1980; p 15. An introductory treatment is also given: Geiger, W. E. in *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; p 88.

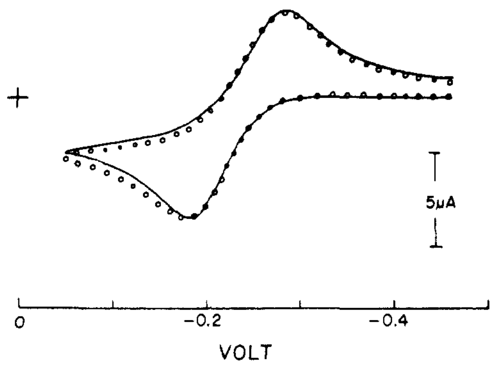

Figure 2. Comparison of experimental (circles) and theoretical (line) cyclic voltammograms for $Cp^*_2Co_2(\mu\text{-}C_8H_8)$, **2**, in CH_2Cl_2 at a hanging Hg drop electrode. Conditions were as follows. Experiment: Concentration 5×10^{-4} M, scan rate 0.50 V/s. Theory: $\alpha(\text{app}) = 0.5$, $k_s(\text{app}) = 5 \times 10^{-3}$ cm/s, $D_o = 1.10 \times 10^{-5}$ cm/s, $n(\text{app}) = 2$.

temperature. The dication 3^{2+} was stable for only brief periods in strong donor solvents like CH_3CN.

I. Oxidation of $Cp_2Co_2(\mu\text{-}C_8H_8)$ (1). This complex oxidizes in a quasi-reversible two-electron couple in CH_2Cl_2. Direct current (dc) polarography shows a single diffusion-controlled wave at $E_{1/2} = +0.09$ V vs SCE with a log slope[23] of 38 mV. The departure of the slope from the value of 29.5 mV predicted for a Nernstian couple is probably due to a combination of solution resistance and sluggish heterogeneous charge-transfer kinetics of eq 2.

$$Cp_2Co_2(\mu\text{-}C_8H_8) \rightleftharpoons Cp_2Co_2(\mu\text{-}C_8H_8)^{2+} + 2e^- \qquad (2)$$

CV experiments on this complex gave ΔE_p values for $\mathbf{1}/\mathbf{1}^{2+}$ as low as 32 mV when the CV scan rate was very low ($v = 0.02$ V/s). The peak separation increased at higher scan rates in approximately the same way as did reversible one-electron standards such as Cp_2M/Cp_2M^+, M = Fe, Co, implying that the ΔE_p values are affected by solution resistance. Use of CH_2Cl_2 severely limits the ability to measure moderately fast charge-transfer rates.[24] A lower limit for the $k_s(\text{app})$ of $\mathbf{1}/\mathbf{1}^{2+}$ of 2×10^{-2} cm/s is indicated by our data (Table IV).

The dication $\mathbf{1}^{2+}$ produced by electrolysis of **1** in CH_2Cl_2 was confirmed by coulometry. After a few minutes a brown precipitate formed in the cell, signaling decomposition of $\mathbf{1}^{2+}$. Since the dication of the pentamethylcyclopentadienyl analogue promised to be more stable, efforts to isolate $\mathbf{1}^{2+}$ were discontinued.[9]

II. The Couple $Cp^*_2Co_2(\mu\text{-}C_8H_8)/[Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{2+}$. Permethylation of the cyclopentadienyl group led to both thermodynamic and kinetic stabilization of the dication. The formal potential of the couple $\mathbf{2}/\mathbf{2}^{2+}$ ($E° = -0.22$ V vs SCE, Table I) is 320 mV negative of that of $\mathbf{1}/\mathbf{1}^{2+}$. More importantly, the dication of **2** was thermally and solvolytically stable in CH_2Cl_2 and acetone, allowing NMR determination of its structure as having the twisted bridging cyclooctatetraene conformation of III.[10] Voltammetry showed that the couple is quasi-reversible, having slower apparent charge-transfer kinetics than its cyclopentadienyl analogue.

CV scans of **2** in CH_2Cl_2 or acetone gave well-shaped waves at either Pt or Hg electrodes with $i_c/i_a = 1.0$ at scan rates from $v = 0.04\text{–}1.0$ V/s. The peak potential separations, ΔE_p, were higher than those of reversible standards, indicative of quasi-reversible charge-transfer kinetics for $\mathbf{2}/\mathbf{2}^{2+}$. The average of E_{pa} and E_{pc}, −0.22 V vs SCE, was taken as the formal potential. The method of Nicholson[25] was used to calculate the ratio $k_s/D_o^{1/2}$, an average of 1.40 $s^{-1/2}$ being calculated from three CV experiments. By using $D_o = 1.10 \times 10^{-5}$ cm²/s, the average of the measured diffusion coefficients for **2** and $\mathbf{2}^{2+}$ (vide infra), a standard *apparent* charge-transfer rate, $k_s(\text{app})$, of 4.6×10^{-3} cm/s is calculated (Table IV).

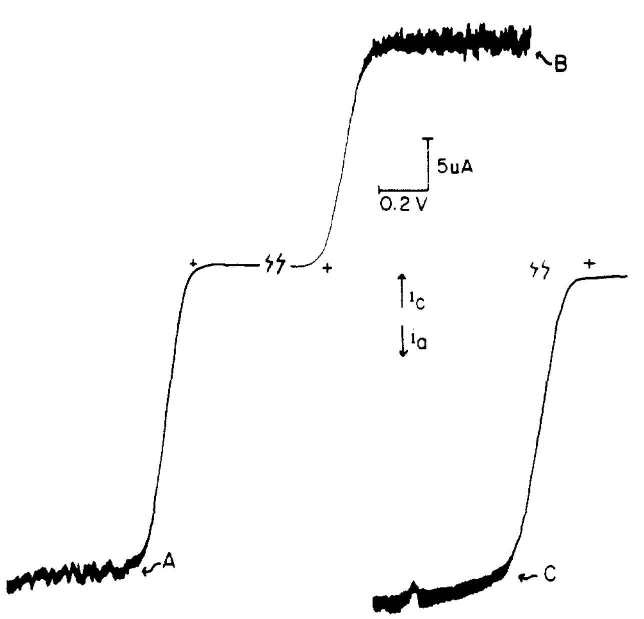

Figure 3. Rotating platinum electrode voltammograms at different points in the bulk electrolysis of a solution originally 6×10^{-4} M in $Cp^*_2Co_2(\mu\text{-}C_8H_8)$, **2**, in CH_2Cl_2 at 263 K. Anodic curve A is that before electrolysis. Cathodic curve B arises from $[Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{2+}$ formed in the electrolysis. Curve C was present after $[Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{2+}$ was back-electrolyzed to the original neutral complex, $Cp^*_2Co_2(\mu\text{-}C_8H_8)$. The cross marks the position of zero volt and zero current in each scan.

Wave shape analysis confirmed that **2** is oxidized in a quasi-reversible two-electron process. Figure 2 shows excellent agreement between the experimental CV trace at $v = 0.05$ V/s and a digital simulation using $k_s(\text{app}) = 5 \times 10^{-3}$ cm/s. Therefore eq 3 *appears* adequate to describe the couple $\mathbf{2}/\mathbf{2}^{2+}$:

$$Cp^*_2Co_2(\mu\text{-}C_8H_8) \rightleftharpoons [Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \qquad (3)$$

However, it is important to realize that eq 3 oversimplifies the reaction $\mathbf{2}/\mathbf{2}^{2+}$ by treating it as an apparent two-electron transfer. Undoubtedly, the sequential one-electron processes of eqs 4 and 5 are a more appropriate description, but direct evidence of the individual one-electron steps was not observed. Such evidence was obtained for **3** (vide infra). The measured $E°$ of −0.22 V is the average of $E°_1$ and $E°_2$.[26] Similarly, the $k_s(\text{app})$ and $\alpha(\text{app})$ values are overall (apparent) parameters, composites of the individual values of $k_s(1)$, $k_s(2)$, α_1, and α_2.[14,27] This result also demonstrates that the tube $\rightleftharpoons$ twist isomerizations for **2** and $\mathbf{2}^{2+}$ are fast on the time scale of the CV experiments.

$$Cp^*_2Co_2(\mu\text{-}C_8H_8) \rightleftharpoons [Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{+} + e^- \quad E°_1 \qquad (4)$$

$$[Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{+} \rightleftharpoons [Cp^*_2Co_2(\mu\text{-}C_8H_8)]^{2+} + e^- \quad E°_2 \qquad (5)$$

Bulk electrolysis of 0.6 mM $Cp^*_2Co_2(\mu\text{-}C_8H_8)$ at 263 K in CH_2Cl_2 with $E_{appl} = +0.5$ V released 2.10 faradays (F) as the solution went from red to the brown of the dication. Back-electrolysis of $\mathbf{2}^{2+}$ at $E_{appl} = -0.6$ V consumed 1.94 F and regenerated neutral **2** in quantitative yield. Exhaustive reduction of solutions of isolated $\mathbf{2}^{2+}$ gave complementary results. Thus, 0.11 mM $\mathbf{2}^{2+}$ in CH_2Cl_2 was electrolyzed at $E_{appl} = -0.6$ V with 1.9 F, yielding a red solution of **2**. Back-electrolysis at 0.5 V regenerated $\mathbf{2}^{2+}$. There is complete chemical reversibility between the two oxidation states.

Interestingly, these electrolysis experiments indicated that the voltammetric currents for the dication are measurably less than those of equivalent concentrations of the neutral complex (Figure 3). Plateau currents with a rotating platinum electrode (RPE) were about 25% lower for the dication, diagnostic of a lower diffusion coefficient (D_o) for $\mathbf{2}^{2+}$ as compared to **2**. This was

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[23] A plot of $-E_{appl}$ vs log $[i/(i_d - i)]$, where i_d is the diffusion controlled limiting current. This slope is 59/n mV for a Nernstian charge transfer.

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Table I. Potentials of Pseudo-Triple-Decker Complexes[a]

complex or couple		potential vs SCE	method
$[Cp_2Co_2(\mu\text{-}C_8H_8)]^{0/2+}$	$\mathbf{1}^{0/2+}$	$E° = +0.10$ V	CV[b]
$[Cp^*{}_2Co_2(\mu\text{-}C_8H_8)]^{0/2+}$	$\mathbf{2}^{0/2+}$	$E° = -0.22$ V	CV[b]
tub-$Cp_2Rh_2(\mu\text{-}C_8H_8)^0$	**3**	$E_p = +0.43$ V	CV[c]
twist-$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+/0}$	$\mathbf{3}^{2+/0}$	$E° = -0.11$ V	CV[b,d]
$[Cp_2CoRh(\mu\text{-}C_8H_8)]^{0/2+}$	$\mathbf{4}^{0/2+}$	$E° = +0.23$ V[e]	CV

[a] In CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$ as supporting electrolyte. [b] Cyclic voltammetry, average of E_{pc} and E_{pa}. [c] Cyclic voltammetry, scan rate 0.1 V/s. [d] In acetone. [e] Tentative assignment. See text.

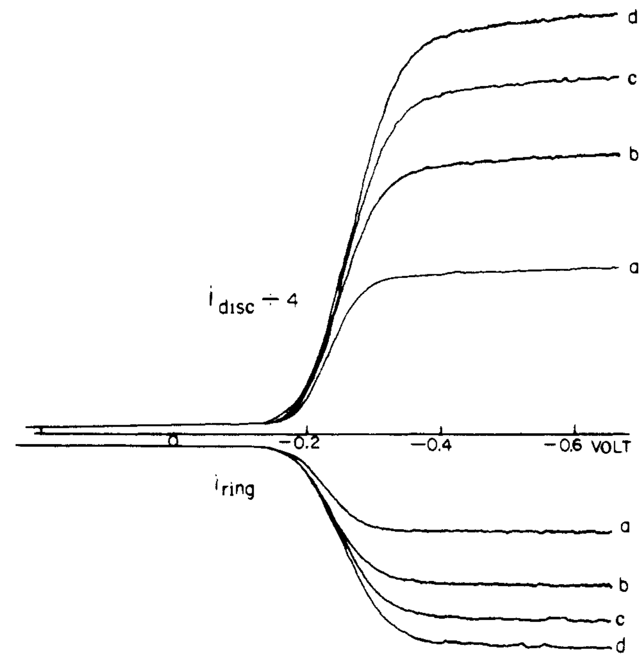

Figure 4. Ring-disc voltammograms of $[Cp^*{}_2Co_2(\mu\text{-}C_8H_8)]^{2+}$, $\mathbf{2}^{2+}$, 1.5 × 10^{-4} M in CH_2Cl_2. Rotation rates in rpm: a, 400; b, 1200; c, 2000; and d, 2800. The plateau current for 2800 rpm was 121 μA.

quantified by dc polarographic experiments in which the D_0 values of the two oxidation states were measured (Table III).[28] Diffusion coefficients calculated from the Lingane–Loveridge equation[29] were $D_0 = 1.57 \times 10^{-5}$ cm²/s for **2** and 6.38×10^{-6} cm²/s for $\mathbf{2}^{2+}$.

Quasi-reversible couples are expected to show different polarographic $E_{1/2}$ values for the two forms of the redox couple, the half-wave potential of the oxidized form being negative of that of the reduced form.[30] By using $k_s(\text{app}) = 5 \times 10^{-3}$ cm/s, a drop time of 1 s, and the quoted diffusion coefficients, we calculate an expected difference of 11 mV in $E_{1/2}$ values, just on the edge of experimental verification. Our measured $E_{1/2}$ values (Table III) are consistent with the theoretical $\Delta E_{1/2}$.[31] Qualitative verification of the $E_{1/2}$ shift was seen in RPE curves before and after electrolyses which consistently showed that the $E_{1/2}$ values of $\mathbf{2}^{2+}$ were 20–30 mV negative of those of **2**.

Finally, the reduction of $\mathbf{2}^{2+}$ was studied at rotating Pt or Au disc electrodes (RDE's) and rotating Pt ring-disc electrodes (RRDE's) in acetone.

Plots of the RDE limiting currents vs square root of rotation rate were linear over the range $\omega = 42\text{–}335$ rad/s. The Levich equation[32] was used to determine the diffusion coefficient of $\mathbf{2}^{2+}$ as 5.90×10^{-6} cm²/s, in reasonable agreement with the value of 6.38×10^{-6} cm²/s determined by polarography.

Table II. Representative Cyclic Voltammetry Data for Pseudo-Triple-Decker Complexes, $v = 0.1$ V/s[a]

complex	$E°$, V	ΔE_p, mV	δE_p,[b] mV	i_{rev}/i_{fd}[c]
$Cp_2Co_2(\mu\text{-}C_8H_8)$	+0.10	75	44	1.0
$Cp^*{}_2Co_2(\mu\text{-}C_8H_8)$	−0.22	100	56	1.0
$[Cp^*{}_2Co_2(\mu\text{-}C_8H_8)]^{2+}$	−0.24	100	54	1.0[d]
$Cp_2Rh_2(\mu\text{-}C_8H_8)$	+0.43[e]	irrev	70	irrev
$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$	−0.11	45	58	0.6
$Cp_2CoRh(\mu\text{-}C_8H_8)$	+0.23[f]	140[g]	55[g]	1.0[g]

[a] In CH_2Cl_2, $T = 298$ K, Pt bead electrode, potentials vs SCE. [b] $E_p - E_{p/2}$. [c] i_c/i_a for oxidation processes, i_a/i_c for reductions. [d] In acetone. [e] E_{pa}. [f] Tentative assignment. See text. [g] Data at scan rate of 10 V/s.

In an RRDE, the disc is surrounded first by a thin insulator and then by a metal ring, the potential of which is independent of the disc.[33,34] The ring may be held at a potential sufficient to detect electrolysis products thrown out from the disc, and the amount of ring current is diagnostic of the chemical reversibility of the couple. In the present case, the ring was held at $E_{appl} = +0.2$ V, while the potential of the disc was scanned in a solution of $\mathbf{2}^{2+}$. Therefore the ring reoxidized any neutral **2** formed while scanning negative at the disc. As expected, the ring current increased as a scaled mirror image of the disc current (Figure 4). The ratio of the limiting ring current to limiting disc current, $i_{R,lim}/i_{D,lim}$, the collection efficiency, N_k, was measured as 0.14 for the couple $\mathbf{2}/\mathbf{2}^{2+}$, close to the value of 0.16 obtained for the standard Cp_2Fe/Cp_2Fe^+.

III. The Couple $Cp_2Rh_2(\mu\text{-}C_8H_8)/[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$. A. Oxidation of *tub*-$Cp_2Rh_2(\mu\text{-}C_8H_8)$ (3). Neutral **3** and its dication also form an electron-transfer pair. Unlike the cobalt complexes **1** and **2**, there is a very large separation (>500 mV) in the peak potentials of the oxidation of **3** and the rereduction of $\mathbf{3}^{2+}$ (Figure 1). The isomerizations (tub ⇌ twist) are apparently much slower for the Rh_2 complexes, allowing separation of the electron-transfer steps from those of the coupled structural changes. In this situation, Scheme II rather than eq 1 is used to describe the mechanism.[12,13,43c]

Positive-going scans of $Cp_2Rh_2(\mu\text{-}C_8H_8)$ in CH_2Cl_2[35] gave an irreversible wave at $E_{pa} = +0.43$ V (Table II) twice the height of 1e⁻ standards. The reduction of the dication $\mathbf{3}^{2+}$, $[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$, occurs on the back scan at about $E_{pc} = -0.1$ V. Together, **3** and $\mathbf{3}^{2+}$ form a chemically reversible couple in which the *neutral* complex has the *tub* structure I and the *dication* has the *twist* structure III.[10]

Coulometric oxidation of a 1 mM solution of **3** in CH_2Cl_2 (298 K, $E_{appl} = +0.8$ V vs SCE) released 2.02 F and resulted in precipitation of the red dication. The Pt basket working electrode became passivated by the precipitate and was periodically removed and washed with cold CH_3CN[36] to remove $\mathbf{3}^{2+}$. Coulometry in 4:3 CH_2Cl_2/acetone of a 0.84 mM suspension of **3**, avoided electrode passivation, 1.8 F being released in formation of the now-soluble dication. Back-electrolysis gave >90% yield of **3**.

CV experiments on the oxidation of **3** were informative about the mechanism of the double electron-transfer reaction. The breadth of the oxidation wave ($E_p - E_{p/2}$, δE_p) was 58–62 mV, apparently interpretable either in terms of a fast (Nernstian) charge transfer with $n = 1$ in the rate-determining step or a slow charge transfer with $\alpha n = 0.8$. However, the response of the anodic peak potential with increasing v showed that another explanation was required.[37]

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(28) Voltammetry at a rotating electrode having a bead shape does not yield precise values for diffusion coefficients, since the relationship between limiting current and D_0 is known only for electrodes with well-defined geometries. See: Sawyer, D. T.; Roberts, J. L., Jr.; *Experimental Electrochemistry for Chemists*; John Wiley and Sons: New York, 1974; p 91.

(29) Lingane, J. J.; Loveridge, B. A. *J. Am. Chem. Soc.* **1950**, *72*, 438. We ascribe the lower D_0 value for $\mathbf{3}^{2+}$ to an increase in solvation or ion pairing.

(30) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1965; p 213.

(31) The precision of these $E_{1/2}$ measurements was ±4 mV.

(32) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 288.

(33) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 96.

(34) Albery, W. J.; Hitchman, M. L. *Ring-Disc Electrodes*; Clarendon Press: Oxford, 1971.

(35) Neutral **3** is soluble and stable in only a few solvents, CH_2Cl_2 being the best choice. It dissolves very slowly in acetone, saturation being observed at about 0.5 mM. The dication $\mathbf{3}^{2+}$ displays converse behavior. It is quite soluble in acetone and nitromethane but poorly soluble in CH_2Cl_2.

(36) Rapid evaporation of the acetonitrile washings was necessary to avoid decomposition of $\mathbf{3}^{2+}$.

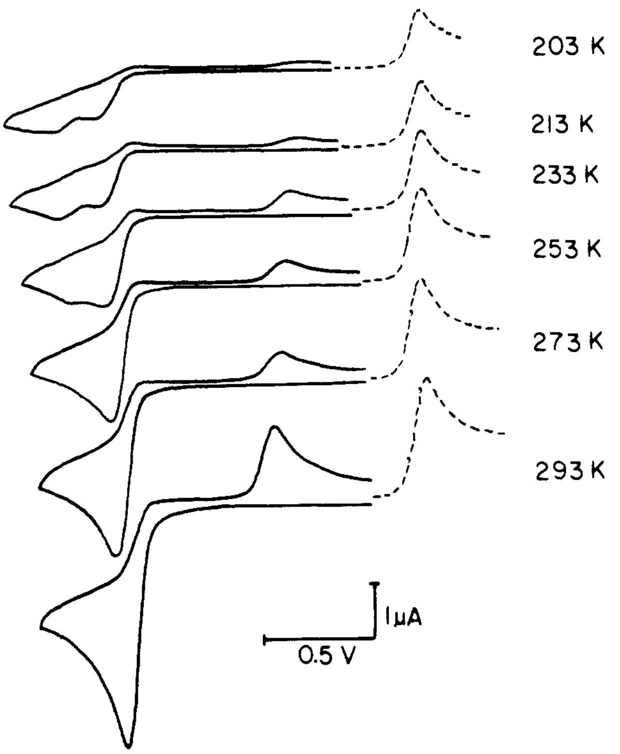

Figure 5. Cyclic voltammograms of $Cp_2Rh_2(\mu\text{-}C_8H_8)$, **3**, in CH_2Cl_2 at subambient tempertures. The dotted line gives the one-electron wave height of the internal standard $Cp^*Ni(\eta^4\text{-}C_8H_{12})^{0/+}$, which was equal in concentration to **3** (6×10^{-4} M). Scan rate = 0.2 V/s. The $E°$ of the nickel complex is −0.82 V vs SCE at 298 K.

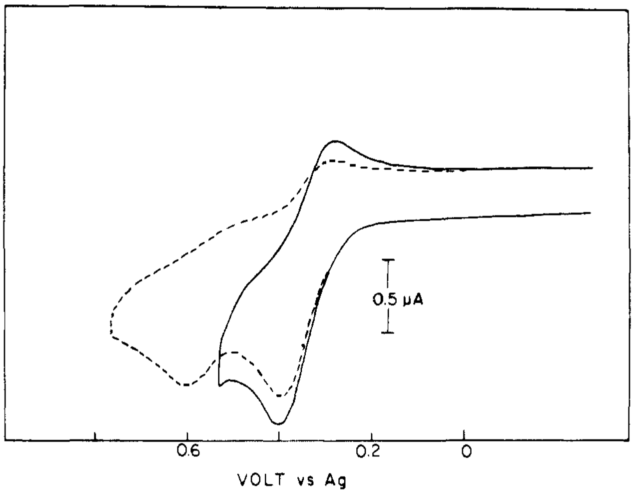

Figure 6. Cyclic voltammograms of $Cp_2Rh_2(\mu\text{-}C_8H_8)$, **3**, in CH_2Cl_2 at 217 K, scan rate = 0.20 V/s, concentration = 6×10^{-4} M. A silver wire was used as a pseudoreference electrode in this experiment, the potential of the internal Ni complex standard being −1.06 V vs it at this temperature.

Table III. dc Polarographic Data for Pseudo-Triple-Decker Complexes[a]

complex	$E_{1/2}$, V	I^b	slope,[c] mV	$D_0{}^d$
$Cp_2Co_2(\mu\text{-}C_8H_8)$	+0.09	5.83	38	1.54×10^{-5}
$Cp^*{}_2Co_2(\mu\text{-}C_8H_8)$	−0.217	5.89	39	1.57×10^{-5}
$[Cp^*{}_2Co_2(\mu\text{-}C_8H_8)]^{2+}$	−0.226	3.77	40	6.38×10^{-6}
$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$	−0.01	4.75[e]	41	1.01×10^{-5}

[a] In CH_2Cl_2 except last entry; 298 K; potentials in volt vs SCE; drop times 1–2 s. [b] Diffusion current constant in units μA mM^{-1} $mg^{-2/3}$ $s^{1/2}$. [c] Slope of plot of $-E_{app}$ vs log $i/(i_d - i)$. [d] Diffusion coefficient in units of cm/s. [e] In acetone.

Table IV. Some Rate Constants Measured in This Study

reaction	k	value	method and ref
1 − $2e^- \rightleftharpoons$ $\mathbf{1}^{2+}$	k_s(app)	$>2 \times 10^{-2}$ cm/s	CV; ΔE_p method[25]
2 − $2e^- \rightleftharpoons$ $\mathbf{2}^{2+}$	k_s(app)	4.6×10^{-3} cm/s	CV; ΔE_p method[25]
2 − $2e^- \rightleftharpoons$ $\mathbf{2}^{2+}$	k_s(app)	5.0×10^{-3} cm/s	CV; dig. sim.[62]
twist-$\mathbf{3}^{2+}$ + $2e^- \rightleftharpoons$ **3**	k_s(app)	0.3 cm/s	CV; ΔE_p method[25]
twist-**3** → *tub*-**3**	k_{isom}	1.5 s^{-1}	CV; from i_a/i_c[40]
twist-**3** → *tub*-**3**	k_{isom}	1.7 s^{-1}	dps chronoamp[41]
twist-**3** → *tub*-**3**	k_{isom}	3 s^{-1}	ring-disc[42]

Low-temperture CV's demonstrated that the anodic wave was a combination of reversible and irreversible one-electron waves. At room temperature in CH_2Cl_2 the anodic wave for **3** at +0.4 V is twice the height of the internal one-electron standard, $Cp^*Ni(C_8H_{12})^{0/+}$. Lowering the temperature resulted in broadening of the anodic wave and separation into two waves below about 233 K. At 203 K, two anodic waves are clearly observed (Figure 5), the first being the same height as the one-electron standard. Switching the scan prior to onset of the second anodic wave shows that the first one is reversible (Figure 6). The cathodic wave for reduction of $\mathbf{3}^{2+}$ is produced upon scanning through the second wave.[38]

These data indicate that the couple $\mathbf{3}/\mathbf{3}^{2+}$ proceeds in two one-electron steps and argue strongly that the isomerization tub ⇌ twist occurs after removal of the *second* electron, in an EEC sequence (Scheme III, eqs 6–8).

Scheme III

$$tub\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \rightleftharpoons tub\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+ + e^- \quad (6)$$

$$tub\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+ \rightleftharpoons tub\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} + e^- \quad (7)$$

$$tub\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} \rightleftharpoons twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} \quad (8)$$

Two possible explanations may be offered for the separation of the two waves at low temperatures. One (a) is that the oxidation $\mathbf{3}^+/\mathbf{3}^{2+}$ has very slow inherent charge-transfer kinetics compared to $\mathbf{3}/\mathbf{3}^+$, leading to increasingly larger overpotentials for the former at lower temperatures. A second (b) assumes that both heterogeneous electron-transfer rates are high but that the rapid isomerization reaction coupled to $\mathbf{3}^+/\mathbf{3}^{2+}$ allows the second electron transfer to proceed at the potential of the first.[39] As the temperature is lowered and the isomerization rate decreases, the second wave shifts positively in the direction of its formal potential. We favor explanation (b), since we know that the isomerization of the tub dication is rapid, and there is no particular reason to expect inherently slow charge-transfer kinetics for the couple $\mathbf{3}^+/\mathbf{3}^{2+}$. It should be noted that when the isomerization rate becomes so rapid that it can be viewed as occurring concomitant with the charge transfer, cases (b) and (a) become phenomenologically equivalent.[12]

B. Reduction of *twist*-$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$ ($\mathbf{3}^{2+}$). The twist dication shows a two-electron CV cathodic wave in the vicinity of −0.1 V vs SCE. Coulometry of a suspension of the dication in 1:1 CH_3NO_2/CH_2Cl_2 at 273 K consumed 1.92 F as the red solution of $\mathbf{3}^{2+}$ was converted to the yellow neutral compound. Confirmation of *tub*-**3** as the electrolysis product came from CV peak matching and by NMR spectroscopy of the yellow crystals isolated by evaporation of the solution and removal of the supporting electrolyte by washing with acetone.

CV scans of $\mathbf{3}^{2+}$ at low sweep rates showed that there are two anodic waves on the reverse scan (Figure 7). The peak at ca. +0.4 V falls at the potential of original **3**, i.e., the tub form of $Cp_2Rh_2(\mu\text{-}C_8H_8)$. The peak at ca. −0.1 V apparently arises from *twist*-**3**, before it isomerizes to *tub*-**3**.

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(37) If the electron-transfer step is rapid, the anodic peak potential is independent of scan rate, whereas an irreversible electron transfer with αn = 0.8 should give a shift of E_p of 37.5 mV per decade increase in v. The experimentally measured shift, corrected for resistance errors, was 15 and 20 mV in two separate experiments over the range v = 0.02–0.60 V/s.

(38) This class of complex has a highly reversible Ni(II)/Ni(I) couple: see ref 20 and Koelle, U.; Werner, H. *J. Organomet. Chem.* **1981**, *221*, 367. The Cp* analogue was used because it was soluble in CH_2Cl_2 over the temperature range employed.

(39) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

Table V. Rotating Ring-Disc Electrode Data for 1.5×10^{-4} M $[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$ in 1:1 CH_2Cl_2/Acetone

rotation rate, RPM	$w^{1/2}$, rad/s	N_k[a]	
		E_r = +0.1 V	E_r = +0.6 V
400	6.5	0.041	0.150
800	9.2	0.062	0.158
1200	11.2	0.070	0.159
1600	12.9	0.083	0.161
2000	14.5	0.090	0.163
2400	15.9	0.099	0.162
2800	17.1	0.107	0.161
3200	18.3	0.109	0.162

[a] Collection efficiency. See ref 34. N_k was found to be 0.16 for this electrode with a reversible system, namely $Cp_2Fe^{0/+}$.

Rotating ring-disc and high-speed CV studies give strong support to this interpretation. As the CV scan rate increased, the relative height of the +0.4 V peak decreased, until at $v > 20$ V/s it virtually disappeared (Figure 7), meaning that the fast experiment outran the rate of the isomerization reaction (eq 9):

$$twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)] \xrightarrow{k_{isom}} tub\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)] \quad (9)$$

From the CV data at lower sweep rates a rate constant of 1.5 ± 0.5 s^{-1} was calculated by using the literature method for an EC mechanism with a first-order reaction[40] (Table IV).

The couple at $E° = -0.11$ V vs SCE behaves like a quasi-reversible two-electron process. The cathodic current function was independent of scan rate over the range v = 0.1–50 V/s, showing no change in n value as the relative amounts of the two product peaks varied. The breadth of the cathodic wave, $E_p - E_{+/2}$, was ca. 38 mV (compared to 63 mV for $Cp_2Co^{0/+}$), and a ΔE_p value of 33 mV was measured when v = 0.04 V/s. The cathodic peak potential moved negatively at 10 mV/decade of v (referenced to $Cp_2Co^{0/+}$), and the ΔE_p value increased markedly at higher scan rates (e.g., ΔE_p was 100 mV at v = 20 V/s). A k_s(app) value of 0.3 cm/s was calculated for the reaction of eq 10.

$$twist\text{-}3^{2+} + 2e^- \rightleftharpoons twist\text{-}3 \quad (10)$$

At high sweep rates the reverse (anodic) branch is considerably broader and lower than the forward (cathodic) branch (Figure 7), diagnostic of a two-electron transfer in which the second charge-transfer step is slower than the first.[14,27a] At v = 50 V/s (peak at +0.4 V absent), the ratio i_a/i_c is only 0.74, rather than the value of 1.0 which would occur for a Nernstian couple with $\alpha n = 1$.

Recognizing that eq 10 is composed of two one-electron steps and that the twist-to-tub isomerization occurs after the second of these steps, the EEC mechanism of Scheme IV describes the reduction of 3^{2+}.

Scheme IV

$$twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} + e^- \rightleftharpoons twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+ \quad (11)$$

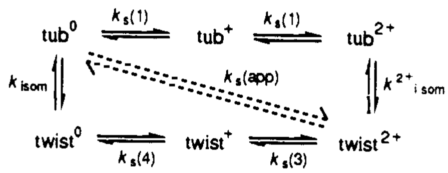
$$twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+ + e^- \rightleftharpoons twist\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \quad (12)$$

$$twist\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \xrightarrow{i_{isom}} tub\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \quad (13)$$

The rate of the isomerization reaction of eq 9 (and 13) was also measured by using double potential step chronoamperometry, employing the method of Shain.[41] The potential of a Pt disc was pulsed from 0 to −0.4 V (reducing *twist*-3^{2+}) and back to 0 V (oxidizing *twist*-**3**), by using step times of 100–500 ms. An average of 1.7 s^{-1} was obtained for k_{isom} (Table IV). A third measure of the isomerization rate was obtained from RRDE experiments (vide infra).

RRDE studies of 3^{2+} were informative. The potential of the disc was scanned negative, and the potential of the ring was held at either +0.1 V (sufficient to reoxidize *twist*-**3**, Figure 8) or +0.6 V (sufficient to reoxidize both *twist*-**3** and *tub*-**3**, Figure 9).

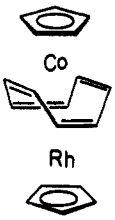
Scheme V



The collection efficiency was quite small at slow rotation rates when the ring potential was +0.1 V. For example, N_k was 0.04 in CH_2Cl_2/acetone at a rotation rate of 400 rpm (Table V). This value increased at higher rotation rates, consistent with less of the twist-to-tub isomerization at shorter experiment times. From similar data in pure acetone and working curves available in the literature[42] a twist-to-tube isomerization rate of ca. 3 s^{-1} was obtained (Table IV).

When the ring was held at +0.6 V, N_k was independent of rotation rate and equal to that of a chemically reversible standard, $Cp_2Fe^{+/0}$, 0.16. This demonstrates again that the two anodic peaks of Figure 7 account quantitatively for the cathodic products of 3^{2+} and that no isomers except the twist and tub isomers are detected after reduction of the dication.

IV. The Couple $CpCo(\mu\text{-}C_8H_8)RhCp/[CpCo(\mu\text{-}C_8H_8)RhCp]^{2+}$. Oxidation of the mixed-metal complex $CpCo(\mu\text{-}C_8H_8)RhCp$, **4**, was also investigated, but with somewhat uncertain results owing to the instability of the dication 4^{2+}.



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CV scans in CH_2Cl_2 at slow sweep rates showed one anodic wave of approximately two-electron height and one cathodic return wave (Figure 10, peak A). The peak separation varied with scan rate, and the voltammetric shapes were not indicative of a simple quasi-reversible charge transfer. At scan rates above 10 V/s, a cathodic return wave grew in coupled to the original anodic wave (Figure 10, peak B), at the expense of peak A. The question is whether the dication 4^{2+} is responsible for peak A or peak B in Figure 10. Bulk coulometry was unsuccessful in answering this question since exhaustive electrolysis of **4** at 298 K (1.55 F) gave evidence only of decomposition. We believe it likely that the pair of peaks with $E° = +0.23$ V vs SCE is due to the couple $4/4^{2+}$ (therefore assigning peak B to 4^{2+}). If correct, this would mean that the CoRh complex oxidizes at approximately the average of the potentials of the Co_2 and Rh_2 analogues **1** and **3**.

V. Mechanistic Aspects: EEC Reactions. We rewrite eq 1 with explicit isomeric designations as eq 14, summarizing the redox couple in simplest terms:

$$tub\text{-}Cp_2M_2(\mu\text{-}C_8H_8) \rightleftharpoons twist\text{-}[Cp_2M_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \quad (14)$$

However, since the isomerization may occur in any of the three oxidation states of the complexes, a more general way of writing this reaction is that of Scheme V, an expanded version of the square scheme, which also recognizes the role of individual one-electron processes in the net two-electron reactions.

The thermodynamically favored isomers for the neutral and dicationic complexes are the tub and twist forms, respectively. However, our data do not allow us to establish the more stable isomer for the monocation. The reversible one-electron oxidation of **3** at low temperatures in CH_2Cl_2 implies detection of *tub*-

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(40) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

(41) Schwarz, W. M.; Shain, I. *J. Phys. Chem.* **1965**, *69*, 30.

(42) Albery, W. J.; Hitchman, M. L.; Ulstrup, J. *Trans. Faraday Soc.* **1968**, *64*, 2831.

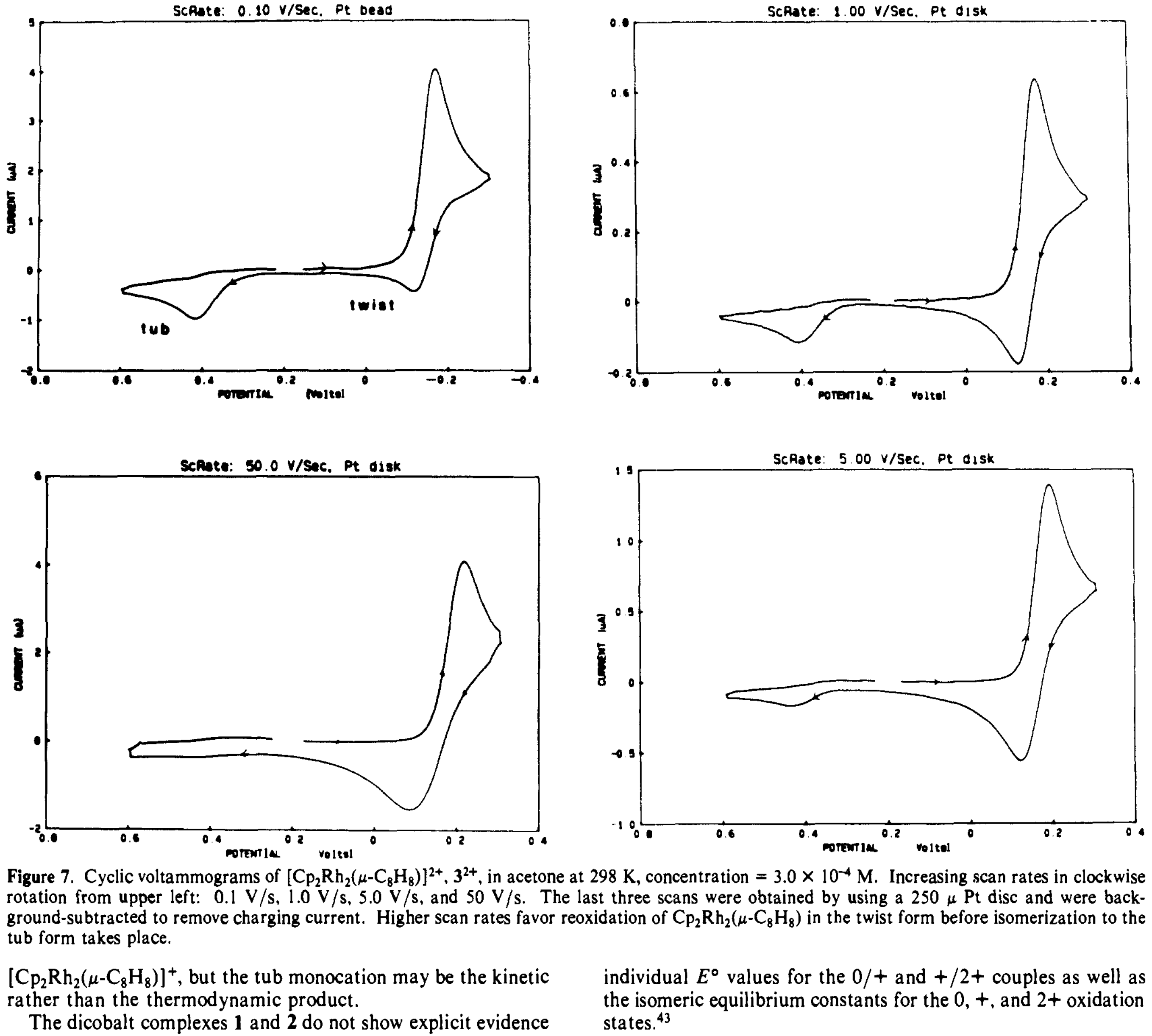

Figure 7. Cyclic voltammograms of $[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$, 3^{2+}, in acetone at 298 K, concentration = 3.0×10^{-4} M. Increasing scan rates in clockwise rotation from upper left: 0.1 V/s, 1.0 V/s, 5.0 V/s, and 50 V/s. The last three scans were obtained by using a 250 μ Pt disc and were background-subtracted to remove charging current. Higher scan rates favor reoxidation of $Cp_2Rh_2(\mu\text{-}C_8H_8)$ in the twist form before isomerization to the tub form takes place.

$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+$, but the tub monocation may be the kinetic rather than the thermodynamic product.

The dicobalt complexes **1** and **2** do not show explicit evidence for separate electron transfer and isomerization steps. Their reactions are therefore adequately described by eq 14, which essentially links the diagonal terms of Scheme V by the dashed lines. On the other hand, the Rh complex **3** clearly follows the perimeter of Scheme V, with two one-electron transfers followed by an isomerization step in both the 2+ → 0 and 0 → 2+ directions. Thus, $Cp_2Rh_2(\mu\text{-}C_8H_8)$ oxidizes and reduces in two EEC mechanisms, the isomerizations providing linkage of the two processes into an overall chemically reversible reaction.

Given the findings concerning **3**, it is very likely that complexes **1** and **2** also follow EEC pathways. The EEC–EEC format of Scheme IV reduces to the quasi-reversible couple of eq 14 only if the isomerization reactions are rapid and reversible on the voltammetric time scale. A number of theoretical studies have addressed this point.[43] We can therefore conclude that the isomerization reactions of eqs 15 and 16 are very rapid. The

$$twist\text{-}(C_5R_5)_2Co_2(\mu\text{-}C_8H_8) \rightleftharpoons tub\text{-}(C_5R_5)_2Co_2(\mu\text{-}C_8H_8) \quad (15)$$

$$tub\text{-}[(C_5R_5)_2Co_2(\mu\text{-}C_8H_8)]^{2+} \rightleftharpoons twist\text{-}[(C_5R_5)_2Co_2(\mu\text{-}C_8H_8)]^{2+} \quad (16)$$

formal potentials of the dicobalt couples are determined by the individual $E°$ values for the 0/+ and +/2+ couples as well as the isomeric equilibrium constants for the 0, +, and 2+ oxidation states.[43]

VI. Why Multielectron Transfers? The origin of two-electron waves is easily understood when the second electron transfer is coupled to a very fast isomerization reaction, since the structural change facilitates the second electron transfer, thereby allowing it to occur with less applied potential than the first. In equivalent language, an EC reaction with a very rapid chemical step moves a voltammetric wave negatively (for an oxidation) compared to the formal potential of the electron transfer alone.[44] In an EEC oxidation, if the isomerization is sufficiently fast to move the potential of the second process negative of the first, an overall two-electron wave results. An equivalent argument can be made for cathodic processes. This situation applies to five of the six reactions, counting the forward and backward two-electron transfers, for compounds **1**–**3**, rewritten as eqs 17–19.

$$tub\text{-}(C_5R_5)_2Co_2(\mu\text{-}C_8H_8) \rightleftharpoons twist\text{-}[(C_5R_5)_2Co_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \quad (17)$$

$$twist\text{-}[(C_5R_5)_2Co_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \rightleftharpoons tub\text{-}(C_5R_5)_2Co_2(\mu\text{-}C_8H_8) \quad (18)$$

$$tub\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \rightleftharpoons twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \quad (19)$$

$$twist\text{-}[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+} + 2e^- \rightleftharpoons twist\text{-}Cp_2Rh_2(\mu\text{-}C_8H_8) \quad (20)$$

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[43] (a) Jacq, J. *J. Electroanal. Chem.* **1971**, *29*, 149. (b) Laviron, E.; Roullier, L. *J. Electroanal. Chem.* **1985**, *186*, 1. (c) Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1983**, *87*, 2492. (d) Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1985**, *89*, 3739.

[44] Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113.

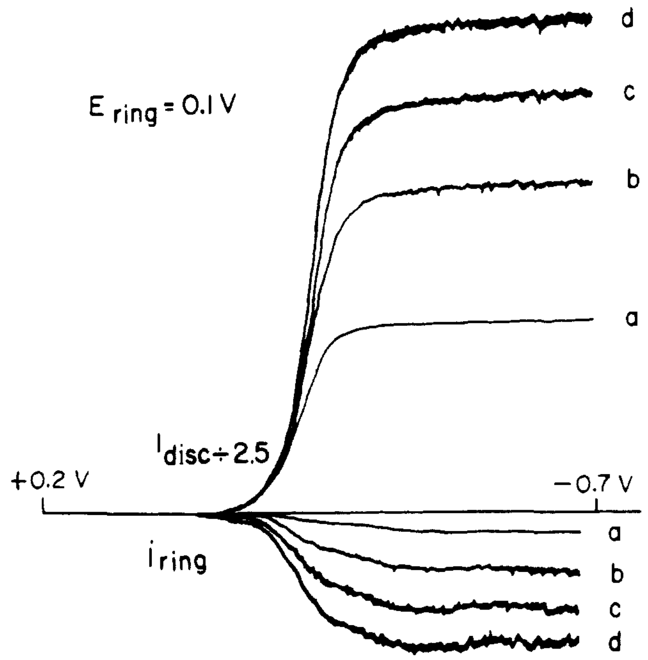

Figure 8. Ring-disc voltammograms of $[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$, 3^{2+}, in 1:1 CH_2Cl_2/acetone at 298 K, concentration = 1.3×10^{-4} M. Rotation rates in rpm: a, 400, b, 1200, c, 2000, and d, 2800. The ring potential was +0.1 V, sufficient to reoxidize *twist*-**3** but insufficient to reoxidize *tub*-**3**.

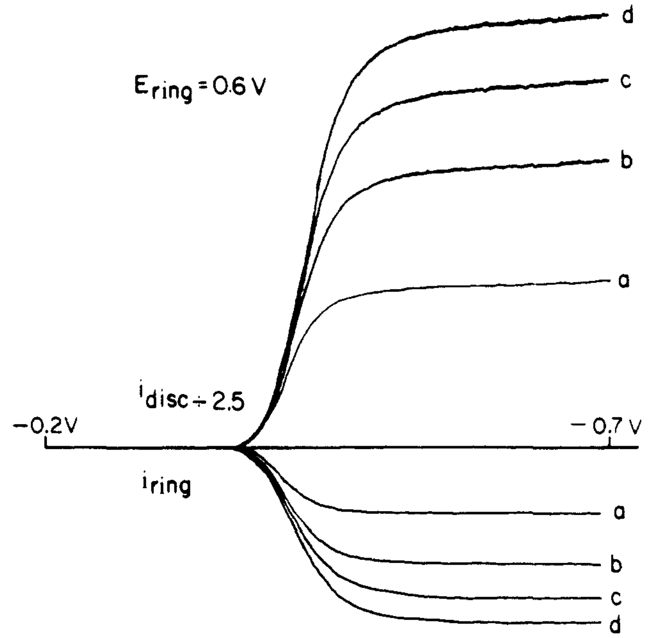

Figure 9. Ring-disc voltammograms of 3^{2+} under conditions identical with Figure 8, except that the ring potential was equal to 0.6 V, sufficient to reoxidize both *twist*-**3** and *tub*-**3**.

However, this does not explain why eq 20 is a two-electron process, since isomerization to *tub*-$Cp_2Rh_2(\mu\text{-}C_8H_8)$ occurs only slowly after formation of *twist*-$Cp_2Rh_2(\mu\text{-}C_8H_8)$. The reversibility of eq 20 does not prove that the complex retains the twist structure during the reduction but only that it does not form the tub structure until the later isomerization. It is quite likely that a more subtle structural change occurs during the first electron transfer to *twist*-3^{2+} which allows the second $E°$ to be more positive of the first, resulting in a net two-electron transfer.[45]

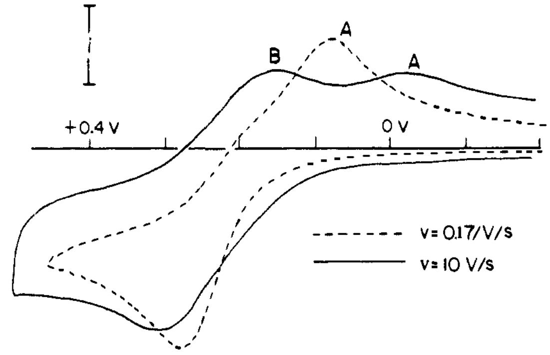

Figure 10. Cyclic voltammograms of 1.6×10^{-4} M **4** in CH_2Cl_2, 298 K, Pt bead electrode, at v = 0.17 V/s (dotted line) and 10 V/s (continuous line). Peak A moved sharply positive as v increased, and a new peak (**B**) gew in that is assigned to the reduction of the dication $\mathbf{4}^{2+}$. The current marker represents 5 μA (v = 0.17 V/s) or 37.5 μA (10 V/s).

VII. Comparison with Other Two-Electron Processes. An increasing number of examples have been studied in which chemically reversible gross structural changes are coupled to two-electron transfer reactions, involving both metal complexes and organic compounds.[46-57] Comparison of our mechanistic results to those of other investigators is therefore warranted.

The most detailed studies show that multielectron transfers with coupled isomerizations generally proceed through an ECE process in one direction and an EEC process in reverse.[53-56] This behavior can be understood with reference to eqs 21–27. Consider the overall reaction to be that of eq 21, in which A and B denote

$$A + 2e^- \rightleftharpoons B^{2-} \tag{21}$$

different isomers. If the intermediate monoanion has the structure B^-, then the reduction would go by an ECE mechanism, eqs 22–24,

$$A + e^- \rightleftharpoons A^- \qquad E°_1 \tag{22}$$

$$A^- \rightarrow B^- \qquad C \tag{23}$$

$$B^- + e^- \rightleftharpoons B^{2-} \qquad E°_2 \tag{24}$$

where C is the isomerization reaction and $E°_2 > E°_1$. The oxidation of B^{2-} back to A proceeds by an EEC mechanism, eqs 25–27. Conversely, if the intermediate has the structure A^-, the reduction/reoxidation cycle would proceed by an EEC–ECE mechanism.

$$B^{2-} \rightleftharpoons B^- + e^- \qquad E°_2 \tag{25}$$

$$B^- \rightleftharpoons B + e^- \qquad E°_1 \tag{26}$$

$$B \rightarrow A \qquad C \tag{27}$$

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(45) A referee has suggested that if a structural change occurs in-between the two one-electron transfers of eq 20, then eq 20 may be viewed as an ECE process. This would make the overall reduction of 3^{2+} to **3** an ECEC process. The present data do not allow differentiation between the ECE and EE models for eq 20.

(46) Leading references may be found in refs 12–14. More recent examples are refs 47–54.

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As implied above, fast ECE processes cannot be ruled out for the two dicobalt complexes, because mechanistic information contained in their quasireversible CV curves is deficient. However, the dirhodium complex has been clearly shown to undergo an EEC–EEC cycle via eqs 6–8 and 11–13. The difference between this result and those of refs 53–56 arises from the relatively slow isomerization of the monocation intermediate **3**$^+$. This eliminates isomerization after a single electron transfer, at least on the CV time scale, and means that in one direction of the reaction an EEC mechanism occurs because of kinetic, rather than thermodynamic, observation of the unisomerized intermediate. Since our observation of *tub*-$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^+$ in CV experiments is not under equilibrated conditions, we cannot with certainty attribute its detection to thermodynamic stability, and we assign it tentatively as the favored structure of the monocation.

VIII. Relevance of Results to Triple-Decker Structures. A small number of complexes have been reported in which two metals are disposed trans across a bridging cyclooctatetraene group. They include complexes such as those discussed in this paper,[1,2] $(\eta^8\text{-}C_8H_8)_2Ti_2(\mu$-cyclooctatetraene),[58] $[(CO)_3M]_2(\mu$-cyclooctatetraene),[59] where M = Fe, Ru, $[Cp^*(CO)Ru]_2(\mu$-cyclooctatetraene),[60] and $CpCo(\mu$-cyclooctatetraene)ML,[61] where ML = $Mo(CO)_4$ or Pd(allyl). Of these, **1**–**3** and the aforementioned titanium complex would appear to offer the best chances to achieve a true delocalized triple-decker structure with a planar bridging ligand. The data on the Ti compound[8] are ambiguous. For **1**–**3**, the logic was that oxidation to 34-electron dications (the maximum electron count for triple deckers[6]) would result in a planar bridging cyclooctatetraene ring. Instead, the dication has a twisted C_8H_8 bridge, with one of the cyclooctatetraene C–C bonds shared by both metals. This arrangement allows each metal to regain the 18-electron configuration that it had in the original neutral tub complex.

It has been recently postulated that Co and Rh atoms are too small to sit over the center of a planar cyclooctatetraene ring.[2,19] A theoretical study of the electronic structure of triple deckers with bridging ligands of different ring sizes has raised another difficulty with a structure like II of Scheme I.

It was shown that if there are to be reasonable Co–C(C_8H_8) distances (2.19 Å in the calculations) then the Co–Co distance would have to decrease to within bonding range (2.41 Å),[7b] a short distance without precedence in triple-decker complexes. It appears unlikely that triple-decker complexes of the later transition metals will be found in which the size of the bridging ring is larger than C_6.

Conclusions

1. The 36-electron pseudo-triple-decker complexes $Cp_2M_2(\mu\text{-}C_8H_8)$, M = Co, Rh, oxidize and reduce in chemically reversible two-electron processes. The dications have structures in which the bridging cyclooctatetraene ligand has two planar four-carbon halves connected by a slight twist. The nominally 34-electron dications actually have two 18-electron metals because the bridging hydrocarbon bonds in a formally pentahapto fashion to each metal. The most profound effect of the 2e$^-$ oxidation is to change the ligation of C_8H_8 from η^4,η'^4 in the neutral complexes to η^5,η'^5 in the dications.

2. The Co complexes display voltammetry consistent with a quasi-reversible two-electron transfer. This can only occur if the tub–twist isomerizations are reasonably rapid and reversible on the voltammetric time scale.

3. The isomerizations coupled to the electron-transfer processes of the Rh complex **3** are slower than those of the Co analogues, allowing experimental verification of the separateness of the electron-transfer reactions from the isomerizations. The slower isomerization rates for the Rh complex are consistent with higher activation barriers to rearrangement as compared to the Co analogues. Greater back-bonding associated with the heavier transition metal rationalizes the observed differences.

4. The two-electron process for *tub*-$Cp_2Rh_2(\mu\text{-}C_8H_8)$/*twist*-$[Cp_2Rh_2(\mu\text{-}C_8H_8)]^{2+}$ follows an EEC–EEC mechanism because the monocation intermediate does not equilibrate to its thermodynamically favored isomer in both directions of the electron-transfer reaction.

Acknowledgment. We thank the National Science Foundation for generous support under Grant CHE86-03728. We also thank David Pierce for the high-speed CV data on the reduction of **3**$^{2+}$ and acknowledge helpful conversations with Dr. Albrecht Salzer. We are also grateful to the Johnson Matthey Co. for a generous loan of Rh starting materials. Results on the oxidation of $Cp_2Co_2(\mu\text{-}C_8H_8)$ were taken from the Ph.D. Thesis of Dr. Jerry Moraczewski, University of Vermont, 1981. We thank Dr. Moraczewski for permission to include these results.

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