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Ligand-Based Reduction and Electron-Transfer-Induced Tub-to-Chair Isomerization of Cyclooctatetraene Ligand in Rh(η^5-C_5Ph_5)(η^4-C_8H_8)

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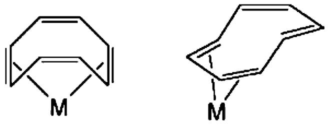
Summary: The electrochemical reduction of Rh(η^5-C_5Ph_5)(η^4-C_8H_8), ***1****, has been studied in THF/0.1 M [NBu_4]A, where A = [PF_6]$^-$ or [CF_3SO_3]$^-$. Cyclic, differential pulse, and square-wave voltammetry establish that* ***1*** *exists as two isomers having tub-shaped (1,5-bonded) or chair-shaped (1,3-bonded) cyclooctatetraene (COT) ligands. The former is the major isomer at room temperature. One-electron reduction of 1,5-**1** ($E_{pc} \approx -2.7$ V vs ferrocene) results in rapid isomerization to the chair isomer. Electrolysis produces [1,3-**1**]$^-$ ($E_{1/2} = -2.37$ V), which has ESR spectra consistent with a SOMO that is largely (COT) ligand-based. Equilibrium and rate constants are estimated for a square scheme describing the combined electron-transfer/isomerization sequence. The tub isomer is more highly favored at room temperature for Rh(η^5-C_5Ph_5)(COT) than for the previously studied Co(η^5-C_5H_5)(COT). Because the redox behavior of* ***1*** *closely parallels that of the cobalt analogues, the present result strengthens evidence for the decidedly different electronic structures of nominally isoelectronic Co-group versus Ni-group η^4-COT compounds. Formally d^9 complexes of the former are classified as highly delocalized "18 + δ" complexes, whereas the latter are more traditional 19-electron systems.*

Introduction

The cyclooctatetraene (COT) ligand has been shown to have a number of possible coordination modes for π-bonding to a transition metal.[1,2] In the two most common coordination geometries for *tetrahapto*-bonding to a single metal, the COT ligand adopts either a tub- or chairlike shape,[2] where the latter (1,3) isomer involves butadiene-like coordination of adjacent double bonds. Isomerization between the 1,5- and 1,3-isomers is well-known for a number of cobalt-COT compounds and is greatly facilitated by one-electron reduction of complexes of the type Co(η^5-C_5R_5)(COT), R = H or Me.[2−7] The 1,5-isomer, which is favored in the 18-electron neutral compounds, converts rapidly and quantitatively to the 1,3-isomer in the radical anion. To date only cobalt compounds have been shown to produce such interconversions. By way of contrast, isoelectronic nickel-group analogues retain their 1,5-COT geometry in both the 18- and 19-electron forms of the complexes [M(η^5-C_5R_5)(COT)]^z, M = Ni, R= H, Me; M = Pd, R = Ph; $z = +1, 0$.[2] Extended Hückel calculations[4] and ESR measurements[2,3] showed that the contrasting redox behavior originates in electronic structure differences of the Co-group versus Ni-group compounds. The SOMO of the former is highly delocalized, with at least half of the orbital residing in the COT ring, whereas that of the latter is essentially metal-based (mostly d_{yz}).



M(1,5-COT) M(1,3-COT)

A point of inquiry is whether Co-group COT compounds of the second or third row exhibit tub/chair ligand isomerization processes in the 18-electron or 19-electron systems. With this in mind, we chose to study the reduction of Rh(η^5-C_5Ph_5)(COT), **1**. There is ample precedence for significantly different reductive electron-transfer behavior of 18 e$^-$ sandwich or half-sandwich compounds involving either first- or second-row metals in general,[8,9] or Co and Rh in particular.[9] In the present case, however, although there are quantitative differences in the tub/chair equilibrium constants for the neutral compounds of the two metals, their overall behavior is quite similar. As will be shown below, the favored tub bonding of the cyclooctatetraene ligand in Rh(η^5-C_5Ph_5)(1,5-COT) is replaced by chair bonding in the mononanion [Rh(η^5-C_5Ph_5)(1,3-COT)]$^-$. The behavior of the Co- and Rh-COT anion radicals appears to be

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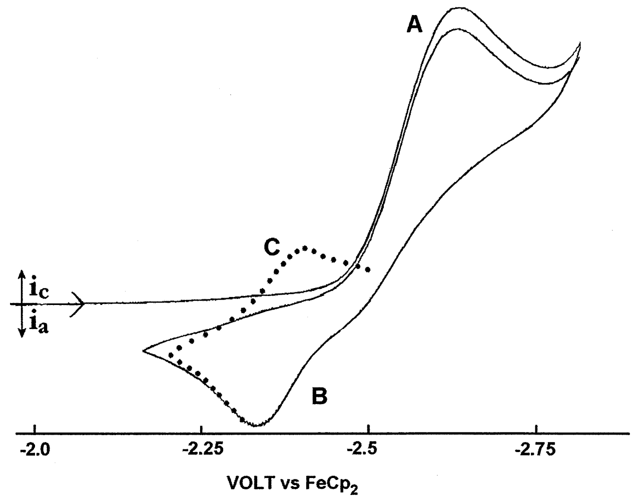
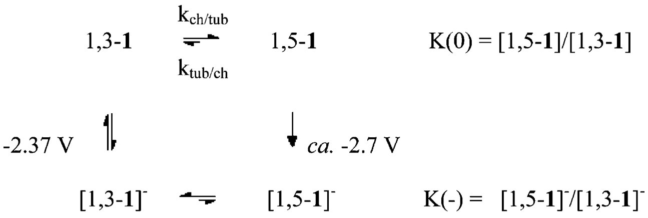


Figure 1. Cyclic voltammogram of 0.9 mM **1** in THF/0.1 M [NBu$_4$][PF$_6$] at ambient temperature. Changing the scan rate from 0.05 V s^{-1} (line) to 1.6 V s^{-1} (dots) increases the chemical reversibility of the [1,3-**1**]$^{-/0}$ couple, here shown as peak B for the oxidation of [1,3-**1**]$^-$ to neutral 1,3-**1** and peak C for the reduction of 1,3-**1** formed in the diffusion layer. The peak current for the 0.05 V s^{-1} scan is approximately 0.3 μA, and the relative currents of the two scans have been corrected for scan rate.

Scheme 1

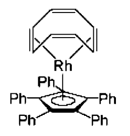


dominated by the highly ligand-based nature of the LUMO in M(η^5-C$_5$R$_5$)(COT). The pentaphenyl-cyclopentadienyl derivative was used in order to take advantage of the generally increased stabilities observed for 19-electron species compared to their cyclopentadienyl counterparts.[10]

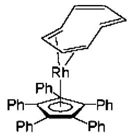
Results and Discussion

NMR spectra of the neutral title compound reveal the presence of only the tub isomer. In THF/0.1 M [NBu$_4$][PF$_6$],[11] 1,5-**1** undergoes a chemically irreversible one-electron reduction at ca. -2.7 V vs ferrocene (E_{pc}, ν = 0.2 V s^{-1}, wave A in Figure 1) and gives a product having anodic wave B. The latter is part of a B/C redox couple ($E_{1/2} = -2.37$ V), which is chemically reversible at higher scan rates (dotted line in Figure 1). Careful inspection of the original negative-going scan (arrow in Figure 1) discloses a small sigmoidally shaped section near -2.35 V. This feature, which is better observed by differential pulse voltammetry (DPV) or square-wave (SW) voltammetry (vide infra), is suggestive of a reduction mechanism involving major (A) and minor (C) isomers, both of which give the anion B when reduced.

These characteristics are strongly reminiscent of the voltammetric behavior of the analogous cobalt complex CoCp(COT) (Cp = η^5-C$_5$H$_5$) and support a square-scheme mechanism (Scheme 1) favoring the 1,5-isomer in **1** and the 1,3-isomer in **1**$^-$.



(1,5-**1**)



(1,3-**1**)

Bulk electrolysis of **1** in THF at room temperature ($E_{appl} = -2.9$ V) passed 1.02 F/eq and resulted in [1,3-**1**]$^-$ as the major product. The ESR signals of samples from this solution were very broad in fluid solutions (and undetectable at room temperature) but well-behaved when frozen. A rhombic g-tensor having g_1 = 2.064, g_2 = 2.014, g_3 = 1.892 is observed, with the only resolved rhodium hyperfine splitting (^{103}Rh, 100%, I = 1/2) being ca. 7 G at g_2 (Figure 2). Of the reported 19-electron metal-(η^4-C$_8$H$_8$) complexes, only 1,3-COT isomers have been shown to have g-value components less than 2.0.[2] The low g-value is consistent with mixing of the ligand-favored SOMO with a close-lying LUMO (most likely the metal d$_{yz}$). In contrast, the SOMO of a 1,5-COT isomer would be largely metal d$_{yz}$ and considerably lower in energy than the next highest orbital. On this basis, the spectrum of **1**$^-$ is assigned to the chair isomer [Rh(η^5-C$_5$Ph$_5$)(η^4-1,3-C$_8$H$_8$)]$^-$.

The voltammetry data hold information about the thermodynamic and kinetic aspects of the interconversions in Scheme 1. The analogous mechanism for the cobalt congeners has been the subject of a number of papers using different spectroscopic and voltammetric approaches.[2-7] Included in the earlier studies was a finding that the homogeneous electron-transfer cross-reaction of eq 1

$$[1,3]^- + 1,5 \rightleftharpoons 1,3 + [1,5]^- \qquad (1)$$

played a significant role in the voltammetric behavior, and detailed simulations at different temperatures, concentrations, and scan rates were necessary to quantify the equilibrium and rate constants of the square scheme.[7] In the present case we offer a less stringent analysis, which, nevertheless, results in useful estimates of the rate and equilibrium constants of the square scheme for **1**.

A qualitative analysis of the CV data for **1** suggests that $K(0) \gg 1$, $K(-) \ll 1$, and that the tub isomer [1,5-**1**]$^-$ converts quickly to the chair isomer [1,3-**1**]$^-$ in the 19-electron species (scans up to 20 V s^{-1} at 228 K failed to show any reversibility for the couple 1,5-**1**/[1,5-**1**]$^-$). Quantitative voltammetric analysis was carried out by a sequence of three procedures. First, the approximate value of $k_{ch/tub}$ was obtained from the reversibility of the B/C couple (Figure 1) using a standard approach.[12] Next, square-wave voltammetry[13] was used to obtain both the

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[10] Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1987**, 467. The cyclopentadienyl parent complex RhCp(COT) undergoes reduction at $E_{pc} = -3.05$ V vs ferrocene in THF/0.1 M [NBu$_4$][PF$_6$]. Bulk cathodic reduction of RhCp(COT) did not give products that were readily identified (Moraczeski, J.; Edwin, J., unpublished data, University of Vermont).

[11] The supporting electrolyte in subambient temperature experiments was 0.1 M [NBu$_4$][CF$_3$SO$_3$].

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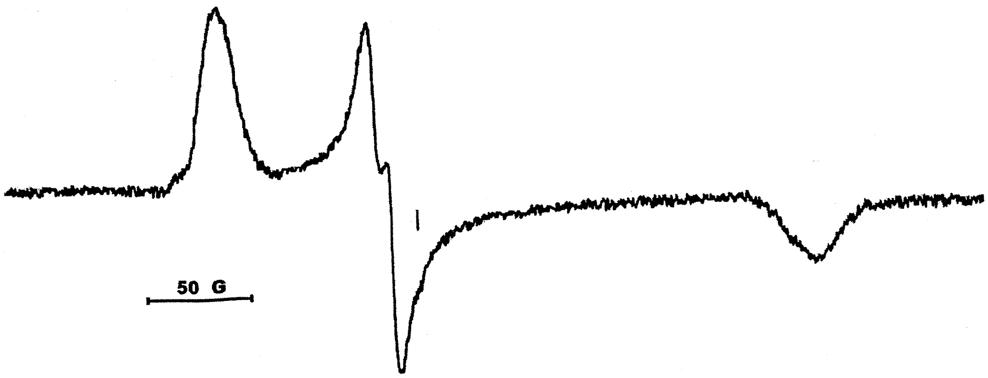

Figure 2. ESR spectrum of $[1,3\text{-}\mathbf{1}]^-$ obtained from a frozen (77 K) sample taken from a cathodic electrolysis solution of 2 mM **1** in THF/0.1 M $[NBu_4][PF_6]$. The resonance position of a dpph standard is shown.

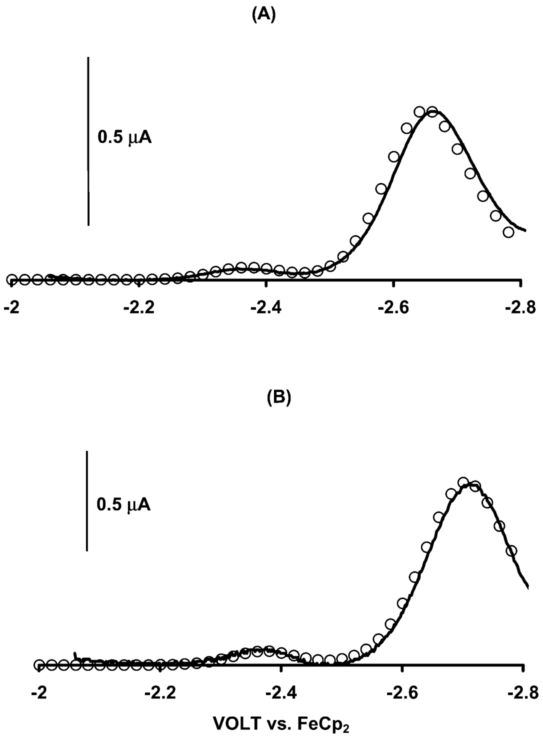

Figure 3. Square-wave voltammetry data for 0.72 mM **1** in THF/0.1 M $[NBu_4][CF_3SO_3]$ at 296 K at a 2 mm glassy carbon electrode. Pulse height is 50 mV; pulse width is 2 mV. Experimental data are shown as solid lines; simulated, as open circles using parameters in Table 1. Frequency is 10 Hz (A); 100 Hz (B).

value of $K(0)$ (from the relative heights of the two peaks) and the standard heterogeneous electron-transfer rate (k_s) of the 1,5-**1** reduction (from its peak width). These values were then used in both CV simulations[14] and SW simulations,[15] which afforded good fits with experiment (Figures 3 and 4). SW voltammetry was particularly valuable here owing to its superiority over cyclic voltammetry for the measurement of small concentrations,[16] of relevance to the determination of 1,3-**1**. The final values are given in Table 1.

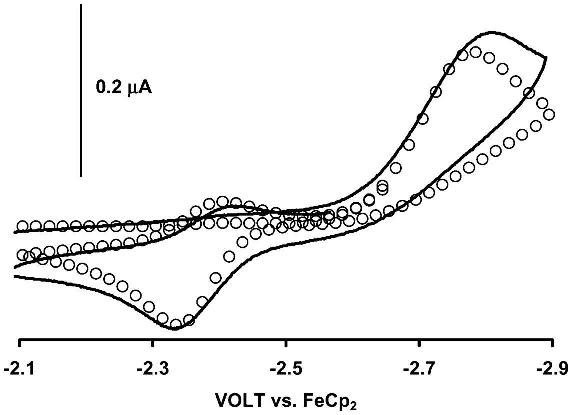

Figure 4. CV data for 0.72 mM **1** in THF/0.1 M $[NBu_4][CF_3SO_3]$ at 296 K at a 2 mm glassy carbon electrode. Scan rate is 0.8 V s^{-1}. Experimental data are shown as solid lines; simulated, as open circles using parameters in Table 1.

Table 1. Values Used in Simulations of Cyclic Voltammetry and Square-Wave Voltammetry Experimental Data

parameter	1,3-isomer	1,5-isomer	isomerizations
$E_{1/2}$ (V vs $FeCp_2$)	−2.370	−2.765	
k_s (cm s^{-1})	0.05	0.02	
α (chg transfer coeff)	0.5	0.5	
$K(0)$ (= $k_{ch/tub}/k_{tub/ch}$)			65
$K(-)$ (= $[1,5\text{-}\mathbf{1}]^-/[1,3\text{-}\mathbf{1}]^-$)[a]			1.2×10^{-5}
$k_{ch/tub}$ (s^{-1})			2.0
$k_{tub/ch}$ (s^{-1})[a]			0.031

[a] Fixed by other values in the simulation.

Notable is the $K(0)$ value of 65, indicating the strong dominance of the 1,5-isomer in the neutral compounds and rationalizing the lack of an observable NMR signal for the 1,3-isomer. A value of approximately 2 s^{-1} is found for the isomerization rate of 1,3-**1** to 1,5-**1**. The $K(-)$ value of 1.2×10^{-5} is similar to that reported for CoCp(COT).[7] Only the lower limit of the isomerization rate for the tub radical anion can be determined from these data. The lifetime of $[1,5\text{-}\mathbf{1}]^-$ is too short to be determined by cyclic voltammetry.[17]

When the CV scan of $Rh(\eta^5\text{-}C_5Ph_5)(COT)$ is taken to more negative potentials, a second cathodic peak of one-electron height is observed ($E_{pc} = -3.04$ V at $\nu = 0.2$ V/s), which must arise from the one-electron reduction of $[1,3\text{-}\mathbf{1}]^-$. A new product wave is seen at $E_{pa} = -1.62$

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(14) CV simulations were performed using Digisim 3.1 (Bioanalytical Systems).

(15) SW simulations were performed using ESP version 2.4 (written by Carlo Nervi), available at http://lem.ch.unito.it/.

(16) Osteryoung, J.; O'Dea, J. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 14, pp 209 ff.

(17) The value used in these simulations for the rate of $[1,5\text{-}\mathbf{1}]^-$ to $[1,3\text{-}\mathbf{1}]^-$ was 10^5 s^{-1}. Decreasing this value to 10^3 s^{-1} had no discernible effect.

V (Supporting Information Figure SM1). Because these features are again very similar to those of the CoCp analogue,[3b] we ascribe these processes to the formation of [1,3-**1**]$^{2-}$ followed by rapid adventitious protonation to give the cyclooctatriene complex [Rh(η^5-C_5Ph_5)(η^3-C_8H_9)]$^-$ or another protonation product.

In summary, the one-electron reduction of Rh(η^5-C_5Ph_5)(η^4-C_8H_8) is structurally and mechanistically very similar to that of the intensively studied cobalt analogues. The thermodynamically favored form of the 18-electron compound is the tub-shaped 1,5-COT isomer, whereas that of the radical anion is the chair-shaped 1,3-COT isomer. The latter is formed rapidly from electrogenerated [1,5-**1**]$^-$. The chair form comprises significantly less of the isomer makeup of the neutral Rh complex (ca. 2% at room temperature) than found in the Co analogue CoCp(C_8H_8) (ca. 20% 1,3-isomer).[7] Given the convergent physical properties of the Co and Rh systems and the highly COT-based radical structure of the former, the anions [M(η^5-C_5Ph_5)(1,3-COT)]$^-$, M = Co or Rh, may both be classified as having an "18 + δ" electronic structure, using the Tyler notation.[18]

Experimental Section

Synthesis of Rh(η^5-C_5Ph_5)(η^4-C_8H_8). A mixture of [Rh(η^5-C_5Ph_5)Br_2]$_2$ (0.500 g, 0.353 mmol), sodium carbonate (0.500 g, 4.71 mmol), and cyclooctatetraene (1.80 cm^3, 15.9 mmol) in ethanol (100 cm^3) was heated under reflux for 4 h. During this time the solution changed from deep red to orange and an orange solid precipitated. The solvent was removed in vacuo, and the residue was washed with hexane (3 × 5 cm^3) and then extracted into diethyl ether (3 × 50 cm^3); removal of the ether in vacuo left a fine orange solid. This was then chromatographed on neutral alumina; an orange fraction eluted with hexane/diethyl ether (1:1), and removal of the solvent in vacuo gave the product as an orange crystalline solid (found C, 78.20; H, 5.00; $RhC_{43}H_{33}$ requires C, 79.14; H, 5.10). ^{1}H NMR at 250 MHz in $CDCl_3$: δ 3.85 (4 H, "t", $J_{HH} = J_{RhH}$ 1.0 Hz, coord. CH=CH), 5.80 (4 H, br s, uncoord. CH=CH), 6.98 (10 H, m, C_5Ph_5), 7.04 (10 H, m, C_5Ph_5), 7.10 (5 H, m, C_5Ph_5). ^{13}C NMR in $CDCl_3$: δ 135.3 (4 C, s, uncoord. CH=CH) 133.4 (5C), 131.8 (10C), 127.4 (10C), 126.3 (5C) (all s, C_5Ph_5), 105.7 (5C, d, J_{RhC} 3.7 Hz, C_5Ph_5), 79.1 (4C, d, J_{RhC} 12.8 Hz, coord. CH=CH). *m*/*z* (positive FAB): 652 (M$^+$, 100), 548 (M$^+$ − C_8H_8, 50).

Electrochemistry and Spectroscopy. THF was purified first by distillation from potassium, then treated with sodium/benzophenone until the solution was deep purple. The solvent was then transferred under static vacuum to a flask that was opened in the drybox. Electrochemical glassware was heated overnight at 120 °C and transferred quickly to a Vacuum Atmospheres drybox antechamber. All electrochemical experiments were carried out in the drybox under nitrogen.

The voltammetry scans were carried out using a glassy carbon electrode of 1 or 2 mm diameter that was polished with diamond paste on a Buehler microcloth. After the polishing, the electrode was rinsed with Nanopure water and dried under vacuum. The working electrode for the bulk electrolysis was a platinum gauze basket. The functional reference electrode was a Ag/AgCl electrode prepared by anodizing a silver wire in HCl solution. It was separated from the working electrode solution by a fine glass frit. The potentials in this paper are referred to the ferrocene/ferrocenium couple, as recommended elsewhere.[19] Ferrocene served as an internal reference and was added to the solution at an appropriate time in the experiment. The potentials in this paper can be changed to SCE reference values by addition of 0.56 V. The supporting electrolyte was 0.1 M [NBu_4][PF_6] unless otherwise noted. Electrochemistry was performed using a PARC model 273 potentiostat interfaced to a personal computer with homemade software. ESR spectra were obtained with a Bruker spectrometer.

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Supporting Information Available: Three figures: (i) CV data for **1** scanning to −3.2 V, (ii) plot of reversibility measurables as a function of scan rate (CV) or frequency (SWV) for EC mechanism, and (iii) table giving SWV values used to construct (ii). This material is available free of charge via the Internet at http://pubs.acs.org.

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