16-Electron through 19-Electron Complexes of the 1,5-COD and 1,3-COD Isomers of $(\eta^5\text{-}C_5Ph_5)Rh(\eta^4\text{-}C_8H_{12})$: Electrochemical Evidence for an Oxidatively Induced Agostic Interaction[†]

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The redox properties of Cp‡Rh (1,5-COD) (**1**) and Cp‡Rh (1,3-COD) (**2**) (Cp‡ = η^5-C$_5$Ph$_5$, COD = η^4-cyclooctadiene) have been investigated by cyclic voltammetry and bulk coulometry. Both compounds display a four-membered electron-transfer series involving complexes of overall 2+, 1+, 0, and 1− charges. The 19-electron complexes [Cp‡Rh(COD)]$^-$ are short-lived, rapidly releasing [C$_5$Ph$_5$]$^-$. The persistent 17-electron complexes [Cp‡Rh(COD)]$^+$ have been characterized by ESR and optical spectroscopies. Complex **1**$^+$ displays an axially symmetric *g*-tensor, demonstrating that the 17-electon system retains the approximate C_{2v} symmetry of its 18-electron precursor. The oxidized forms of **2**$^{n+}$ (n = 1 or 2) undergo slow isomerization to those of **1**$^{n+}$; that is, isomerization of the diolefin ligand from the 1,3- to the 1,5-isomer occurs in the higher oxidation states of [Cp‡Rh(COD)]$^{n+}$. The 1,3-COD ligand imparts an unexpected thermodynamic stabilization of the higher Rh oxidation states. Formation of the 17-electron and 16-electron complexes occurs at potentials ca 0.25 and 0.62 V, respectively, lower than expected. The increasing stabilization of the Rh(II) and Rh(III) complexes is ascribed to progressive formation of an agostic interaction between the metal atom and the hydrogen on carbon 5 of the 1,3-cyclooctadiene ring.

Introduction

A number of metals are known to promote the isomerization of cyclic and acyclic olefins and polyolefins.[1] The fact that various types of organometallic reactions are accelerated in odd-electron complexes[2] suggests the possibility that metal−olefin isomerization processes may be profitably enhanced by oxidation or reduction of 18-electron complexes. Electron-transfer-induced isomerizations have been studied in depth for cyclooctatetraene (COT) complexes of Co[3,4] and, to a lesser extent, Ni and Pd.[4] Cyclooctadiene (COD) complexes of the later transition metals have also received some attention,[5,6] but the metal−1,5-COD bond has generally been found to be unisomerized in the electron-transfer products. A possible exception is the 19-electron anion [CpCo(1,5-COD)]$^-$, which has been reported to isomerize to the 1,3-isomer.[5] In a recent review[7] one of us emphasized that the evidence for formation of the 1,3-COD isomer in the Co complex was indirect, the strongest corroboration being identification of free 1,3-C$_8$H$_{12}$ after degradative oxidation of the 19-electron metal complex. There are, thus far, no reports of comparative redox potentials for metal complexes containing 1,5-bonded vs 1,3-bonded COD ligands, making $E_{1/2}$ values unreliable in identifying isomeric complexes that resist isolation.

The recent report[8] of 1,5-COD and 1,3-COD complexes of (C$_5$Ph$_5$)Rh has finally made it possible to compare the reduction and oxidation potentials of the two relevant metal−cyclooctadiene isomers. We therefore report our studies of the redox properties of [Cp‡Rh(1,5-COD)], **1**, and Cp‡Rh(1,3-COD), **2** (Cp‡ = η^5-C$_5$Ph$_5$). These complexes are found to exist in a string of four oxidation states [Rh(III)/(II)/(I)/(0)] possessing from 16 to 19 valence electrons. We have been able to identify an inefficient isomerization process of the 1,3-isomer to the 1,5-isomer which takes place in higher oxidation states and have found oxidation potential shifts that may be ascribed to agostic interactions involving an aliphatic hydrogen of the 1,3-cyclooctadiene ligand. Reduction of either isomer to the 19-electron Rh(0) complex results in rapid loss of the pentaphenylcyclopentadienyl anion without evidence for prior isomerization.

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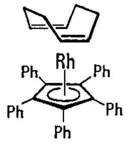

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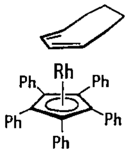

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Experimental Section

Chemicals and Spectral Measurements. Compounds **1** and **2** have been previously reported,[8] but full synthetic details are included here for the first time.

$(C_5Ph_5)Rh(1,5\text{-}COD)$. C_5Ph_5H (0.910 g, 2.00 mmol) was heated in 50 mL of xylene to 120 °C. A 1.4 mL sample of a 1.4 M solution of MeLi in hexanes (2.0 mmol) was added over 5 min, during which time the solution changed from clear yellow to cloudy yellow-orange. After heating the mixture for 2 h at 120 °C, $[RhCl(COD)]_2$ (0.500 g, 1.01 mmol) was added and the resulting solution heated for an additional 1 h. After cooling, the solution was filtered through "Hiflo" and the solvent removed under vacuum to leave a deep red residue. Column chromatography on neutral alumina with 4:1 diethyl ether/petroleum ether gave the product as a brown-yellow solid (0.110 g, 8.5% yield). Recrystallization from dichloromethane/petroleum ether (bp 60−80 °C) gave orange-yellow cubic crystals of $(C_5Ph_5)Rh(1,5\text{-}COD)$ (found C, 78.9; H, 5.80; $C_{43}H_{37}Rh$ requires C, 78.7; H, 5.70). ^1H at 250 MHz in $CDCl_3$: δ 2.00 (4 H, q, J_{HH} 6.0 Hz, CH_2), 2.40 (4 H, q, J_{HH} 4.0 Hz, CH_2), 3.70 (4 H, s, CH═CH), 6.91, 7.03, 7.08 (25 H, m, C_5Ph_5). ^{13}C in CD_2Cl_2: δ 134.8 (5 C), 132.6 (10 C), 127.7 (10 C), 126.4 (5 C) (all s, $C_5\mathit{Ph}_5$), 105.8 (5 C, d, J_{RhC} 3.7 Hz C_5Ph_5), 78.4 (4 C, d, J_{RhC} 14.4 Hz, CH═CH), 32.5 (4 C, s, CH_2). *m*/**z** (positive FAB): 656 (M^+, 100), 548 ($M^+ - C_8H_{12}$, 70), 446 ($C_5Ph_5^+$, 60).

$(C_5Ph_5)Rh(1,3\text{-}COD)$. $[RhBr_2\ (C_5Ph_5)]_2$ (0.800 g, 0.560 mmol), sodium carbonate (0.800 g, 7.55 mmol), and 1,5-cyclooctadiene (8 mL, 65.3 mmol) in 150 mL of ethanol were stirred at room temperature for 24 h, during which time the color changed from red to green and a green solid formed. The latter was filtered off and extracted with diethyl ether until the washings were colorless (5 × 100 mL). Removal of the solvent in vacuo gave a bright yellow solid, which, after vacuum-drying, was found to be a mixture (85:15) of the 1,3- and 1,5-COD isomeric complexes, respectively (0.530 g, 71%). Recrystallization was carried out by slow diffusion of hexane into dichloromethane at −20 °C to give pure $(C_5Ph_5)Rh(1,3\text{-}COD)$ as orange crystals (found C, 77.9; H, 5.70; $RhC_{43}H_{37}$ requires C, 78.7; H, 5.70). ^1H in $CDCl_3$: δ 1.20 (2 H, m, CH_2), 1.35 (2 H, m, CH_2), 1.80 (2 H, m, CH_2), 2.00 (2 H, m, CH_2), 3.55 (2 H, s, CH═CH), 4.65 (2 H, d, J_{HH} 5.0 Hz, CH═CH), 6.90, 7.01, 7.06 (25 H, m, C_5Ph_5). ^{13}C in CD_2Cl_2: δ 134.9 (5 C), 132.5 (10 C), 127.6 (10 C), 126.4 (5 C) (all s, $C_5\mathit{Ph}_5$), 104.3 (5 C, d, J_{RhC} 5.1 Hz, C_5Ph_5), 84.5 (2 C, d, J_{RhC} 5.8 Hz, CH═CH), 61.7 (2 C, d, J_{RhC} 17.8 Hz, CH═CH), 28.7 (2 C, s, CH_2), 25.4 (2 C, m, CH_2). *m*/*z* (positive FAB): 656 (M^+, 100), 548 ($M^+ - C_8H_{12}$, 50), 446 ($C_5Ph_5^+$, 70). This complex was also prepared using the above method, but substituting 1,3-COD for 1,5-COD.

The solvents used for electrochemistry were reagent grade chemicals distilled in vacuo from drying agents: CH_2Cl_2 and $1,2\text{-}C_2H_4Cl_2$ from CaH_2 and THF from potassium. $[NBu_4][PF_6]$ was recrystallized from 95% ethanol and dried in vacuo at 373 K. [PPN]Cl {PPN = bis(triphenylphosphine)imminium chloride} was purchased from Strem Chemicals. Ferrocenium hexafluorophosphate and acetylferrocenium hexafluorophosphate were prepared by oxidation of the corresponding ferrocenes with $Ag[PF_6]$.[9] The complex $[(COD)Rh(THF)_x]^+$ was generated in situ:[10] $[(COD)RhCl]_2$[8a] (7.9 mg, 1.6 μmol) was dissolved in 10 mL of THF and treated with $Ag[PF_6]$ (8.3 mg, 3.3 μmol). The pale yellow solution was stirred for 10 min and then filtered through a plug of glass wool into an electrochemical cell containing 0.50 g of $[NBu_4][PF_6]$ for voltammetric characterization. ^1H NMR spectra were run on a 250 MHz Bruker instrument, and UV−vis spectra were recorded using a Perkin-Elmer Lambda 6 spectrometer. Chemical oxidation of **2** was carried out as follows. Ferrocenium hexafluorophosphate (25 mg, 76 μmol) was added to a solution of $Cp^{\ddagger}Rh(1,3\text{-}COD)$ (50 mg, 76 μmol) in 10 mL of CH_2Cl_2 at 233 K. The solution was stirred for 30 min and then evaporated under reduced pressure. The residue was dissolved in $CDCl_3$ for ^1H NMR analysis: (δ values) free 1,3-COD, 1.5, 2.2, 5.6, 5.8; **1**, 1.95, 2.37, 3.66 plus phenyl region. No free 1,5-COD was observed.

Table 1. $E_{1/2}$ Potentials of Metal−Cyclooctadiene Complexes (Volt vs Ferrocene) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$

complex	2+/1+	1+/0	1−/0	remarks
$Cp^{\ddagger}Rh(1,5\text{-}COD)$, **1**	0.72	0.09		stable 1+, 2+ ions
1 in THF			−3.17	ECE mechanism, loss of $[C_5Ph_5]^-$
$Cp^{\ddagger}Rh(1,3\text{-}COD)$, **2**	0.25	−0.01		cation(s) eventually form **1**
2 in THF			−3.08[a]	anion loses $[C_5Ph_5]^-$
CpRh(1,5-COD)		0.05		irrev if $\nu < 2$ V/s[b]
$(\eta^5\text{-}C_9H_7)Rh(1,5\text{-}COD)$ in THF			−2.19	anion loses $[C_9H_7]^-$ [c]
CpCo(1,5-COD)	0.90[d]	−0.22		refs 18 and *e*
CpCo(1,5-COD) in THF			−3.01	ref 5

[a] Chemically irreversible, peak potential at $\nu = 0.05$ V/s given. [b] Chin, T. T. Unpublished data, University of Vermont. [c] Reference 26. [d] $T = 233$ K. [e] Moraczewski, J.; Geiger, W. E. *Organometallics* **1982**, *1*, 1385.

Electrochemistry. Except for experiments with the optically transparent thin layer (OTTLE) cell, all electrochemical operations were conducted inside a Vacuum Atmospheres drybox under N_2. Details of the electrochemical methodologies have been publshed.[11] The supporting electrolyte {$[NBu_4][PF_6]$ in all cases} concentration was 0.1 M except for OTTLE cell experiments (1.0 M). Rotating Pt electrode (RPE) scans were obtained with a synchronous rotator operating at 1800 rpm. Bulk electrolyses were carried out at a Pt gauze cylinder in a cell in which the anodic and cathodic compartments were separated by a fine glass frit. In this paper all potentials are reported vs the ferrocene/ferrocenium couple (Fc), as recommended by IUPAC.[12] Conversion to the aqueous SCE scale requires addition of 0.46 V for solutions of the chlorinated hydrocarbons or 0.56 V for THF. Evaluation of voltammetric diagnostics for diffusion control and chemical and electrochemical reversibility followed procedures summarized elsewhere.[13]

Results and Discussion

Oxidation of 1 and 2: Production of 17e and 16e Complexes. Complex **1** undergoes two reversible one-electron oxidations with $E_{1/2}{}^1 = 0.09$ V, $E_{1/2}{}^2 = 0.72$ V vs Fc (Table 1), supporting the existence of the three-membered electron-transfer series:

$$\mathbf{1} \rightleftharpoons \mathbf{1}^+ \rightleftharpoons \mathbf{1}^{2+}$$

Cyclic voltammetric (CV) measurements (Figure 1) with 0.05 V/s < ν < 0.3 V/s established that both couples were diffusion controlled and reversible at 278 K in CH2-

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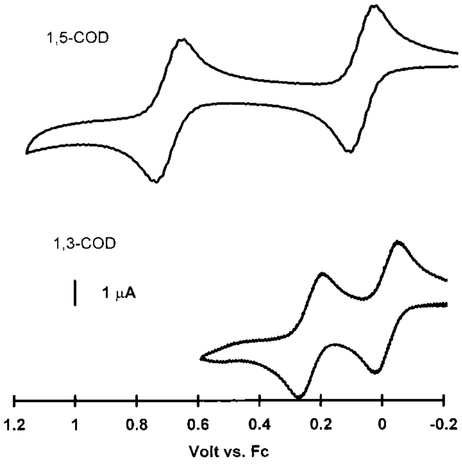

Figure 1. Cyclic voltammograms at 233 K of the oxidations of 1.2 mM **1** (top) and 0.95 mM **2** (bottom) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$, 0.25 mm Pt disk, $\nu = 0.20$ V/s.

Cl_2. CV peak separations were essentially equal to those of Cp_2Fe, suggesting that the redox reactions are approximately Nernstian. Plots of E vs $\log(i_{\mathrm{lim}} - i)/i$ taken from rotating Pt electrode (RPE) scans confirmed this conclusion, slopes of 55 and 62 mV being observed for the first and second waves, respectively, close to the theoretical value of 56 mV at 278 K.

The oxidation product $\mathbf{1}^+$ was sensitive to nucleophiles. After addition of equimolar chloride as [PPN]Cl the first oxidation wave of **1** was no longer reversible.[14] Full chemical reversibility of this anodic process and, even more so, that of the 1,3-COD isomer **2** required pure electrolyte solutions of minimal water content.

The robustness of $\mathbf{1}^+$ was established by bulk electrolysis. When a 1 mM solution of **1** was oxidized ($E_{\mathrm{appl}} = 0.3$ V) at a Pt basket at room temperature ($n_{\mathrm{app}} = 0.9$e), the solution changed from yellow to purple and RPE scans indicated complete conversion to the 17e complex $\mathbf{1}^+$. Samples of this solution removed for ESR analysis retained their purple color for several hours at room temperature. The neutral complex **1** was quantitatively regenerated by exhaustive re-reduction ($E_{\mathrm{appl}} = -0.4$ V). The optical spectrum of $\mathbf{1}^+$ was obtained by spectro-electrochemistry using a gold minigrid electrode sandwiched between two quartz windows (an OTTLE cell).[15] A 5 mM solution of **1** ($\lambda_{\mathrm{max}} = 485$ nm, $\epsilon = 380$) was electrolyzed at the potential of the first oxidation, giving a spectrum attributed to $\mathbf{1}^+$ ($\lambda_{\mathrm{max}} = 554$ nm, $\epsilon = 2300$ assuming complete conversion). Re-reduction of the cation yielded the original spectrum of **1**. The intensity of the transition for $\mathbf{1}^+$ suggests an assignment as a charge-transfer band,[16] most likely $L(\pi) \rightarrow M$.

Table 2. ESR Results for 17-Electron Metal−Cyclooctadiene Complexes in CH_2Cl_2/CH_4Cl_2 Media

radical	temp (K)	g_1	g_2	g_3	$\langle g \rangle$
$[Cp^{\ddagger}Rh(1,5\text{-}COD)]^+$	77	2.181	2.181	1.997 ($g_\perp$)	
	ambient				2.064
$[Cp^{\ddagger}Rh(1,3\text{-}COD)]^+$	77	2.114	2.053	1.989	
	ambient				2.055
$[CpCo(1,5\text{-}COD)]^+$	77	2.329	2.120	2.003	(ref 18)

Solutions of the 16e dication $\mathbf{1}^{2+}$ were produced by bulk electrolysis at $E_{\mathrm{appl}} = 0.9$ V. CV and RPE scans of the resulting green solution indicated formation of $\mathbf{1}^{2+}$, but significant decomposition occurred (voltammetric evidence) even at 233 K over 10 min. Exhaustive re-reduction at $E_{\mathrm{appl}} = -0.4$ V produced only about 10% of the starting material, **1**.

The 1,3-isomer **2** likewise undergoes two one-electron oxidations (Figure 1); in this case $E_{1/2}{}^1 = -0.01$ V, $E_{1/2}{}^2 = +0.25$ V (Table 1):

$$\mathbf{2} \rightleftharpoons \mathbf{2}^+ \rightleftharpoons \mathbf{2}^{2+}$$

The first of these processes is Nernstian and uncomplicated. The reversibility of the second varied, in apparent response to solution conditions (especially, we believe, dryness). In most experiments the second oxidation was also Nernstian, but in some replicates the reversibility of this process (both chemical and electrochemical) was reduced. Decreased chemical reversibility was accompanied by the appearance of small waves at potentials appropriate for **1**. This observation is supported by bulk electrolysis experiments (vide infra) which give evidence of the 1,5-isomer when the 1,3-isomer is oxidized to the dication.

Electrolysis of 1.6 mM **2** at the first oxidation wave ($E_{\mathrm{appl}} = 0.15$ V) at 218 K gave $n_{\mathrm{app}} = 1.0$e as the solution changed from yellow to green. RPE scans of the electrolyzed solution showed that 75% of the complex was in the oxidized form $\mathbf{2}^+$. Re-reduction ($E_{\mathrm{appl}} = -0.5$ V) of $\mathbf{2}^+$ gave back the original amount of **2**.

The dication $\mathbf{2}^{2+}$ formed when bulk electrolysis was carried out at the second wave ($E_{\mathrm{appl}} = 0.5$ V) decomposed slowly at 218 K, as evidenced by voltammetric currents (CV and RPE of $\mathbf{2}^{2+}$) that decreased with time. Exhaustive re-reduction at −0.5 V resulted in waves for both **1** and **2**. Anodic electrolysis at a slightly higher temperature (240 K) gave a brown solution, which turned orange when raised to ambient temperature and showed waves for **1** but not **2**. The decomposition product(s) of $\mathbf{2}^{2+}$ include **1** in one or more of its oxidation states, but there is little that can be said about the mechanism of the process.

Evidence for **1** was also obtained when **2** was chemically oxidized by equimolar $[Cp_2Fe][PF_6]$ in CH_2Cl_2. After 10 min at 298 K, NMR spectra of the evaporated and redissolved (in $CDCl_3$) residue showed that isomer **2** had completely reacted. The only signals observed (see Experimental Section) were those of free 1,3-COD (80% yield) and the 1,5-isomer **1** (20% yield). No free 1,5-COD was detected.

ESR Spectra of 17-Electron Complexes $\mathbf{1}^+$ and $\mathbf{2}^+$. ESR-active samples of $\mathbf{1}^+$ were generated either by bulk electrolysis (vide ante) or by oxidation with equimolar acetylferrocenium ion. Room-temperature solutions of $\mathbf{1}^+$ have a symmetric single peak at $\langle g \rangle = 2.064$ (Table 2). At 77 K in 1:1 CH_2Cl_2/$C_2H_4Cl_2$ a strong spectrum was observed which apparently has axial symmetry ($g_\parallel = 2.181$ and $g_\perp = 1.997$ (Figure 2). An extra nuance was noted near $g = 2.0$, which makes the low-field side of the $g_\perp$ peak appear to be split. Simulations show that

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[14] A product wave appears at $E_{1/2} = -0.85$ V. A likely product of the reaction of $\mathbf{1}^+$ with Cl^- is the chloro-bridged dinuclear complex $[Cp^{\ddagger}Rh(Cl)]_2$.

[15] (a) Murray, R. W.; Heineman, W. R.; O'Dom, G. W. *Anal. Chem.* **1979**, *39*, 1666. (b) Hawkridge, F. M.; Kissinger, P. T. In ref 13, Chapter 9.

[16] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

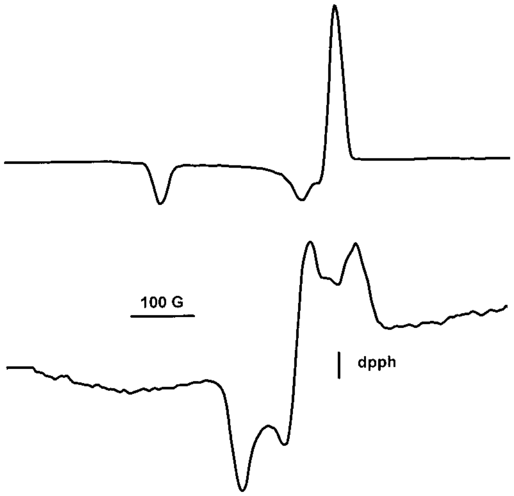

Figure 2. ESR spectra of frozen solutions (T = 77 K) of 17-electron radicals produced by chemical oxidation of neutral complexes. Top: $\mathbf{1}^+$ in $CH_2Cl_2/C_2H_4Cl_2$ (oxidant: acetylferrocenium tetrafluoroborate). Bottom: $\mathbf{2}^+$ in CH_2Cl_2 (oxidant: ferrocenium tetrafluoroborate).

this shape cannot arise from a small deviation from axial symmetry nor from a Rh hyperfine interaction. There may be a small amount of the pentaphenylcyclopentadienyl radical present, or there may be differences in radical environments in the frozen solution. Frozen solutions of $\mathbf{1}^+$ in pure CH_2Cl_2, a nonglassy matrix, have the signals in Figure 2 in addition to a broad line at $g \approx 2.06$. The latter evidently arises from crystallites of $\mathbf{1}^+$ rather than the randomly oriented radicals favored in $CH_2Cl_2/C_2H_4Cl_2$, which forms a better glass.[17] Lacking hyperfine splittings, the spectra of $\mathbf{1}^+$ cannot delineate the precise orbital makeup of the SOMO (semioccupied MO), but they do indicate that the radical retains the approximate C_{2v} symmetry of **1**, since lower symmetry would lead to a splitting of the $g_\perp$ components into a rhombic g-tensor (as seen below for $\mathbf{2}^+$).

Spectra of $\mathbf{2}^+$ were similarly generated, in this case a rhombic g-tensor being observed: $g_1 = 2.114$, $g_2 = 2.053$, $g_3 = 1.989$ (Table 2). The average of the three values, 2.052, is in good agreement with the observed isotropic spectrum, $\langle g \rangle = 2.055$, measured for fluid solutions of $\mathbf{2}^+$ at 233 K.

Both isomers display much smaller g-value anisotropies than their cobalt analogue [CpCo(1,5-COD)]$^+$ (Table 2),[18] mostly notably because of the value of g_1, which is 2.329 in the Co complex, 2.18 in $\mathbf{1}^+$, and 2.11 in $\mathbf{2}^+$. Since the spin−orbit coupling constant of Rh is considerably larger than that of Co, one would expect the opposite trend in g-values, all other bonding factors remaining equal. The fact that g_1 (almost surely g_y, using the coordinate system of ref 18) is so much closer to the free spin value in the Rh analogues must arise from either (i) less metal character in the SOMOs of the Rh complexes and/or (ii) greater separation of the $3d_{xz}$-containing ground state from the first excited state containing a $3d_{z^2}$ contribution. The former is almost certainly operative, given the increased metal−ligand covalency normally associated with Rh π-complexes compared to their Co congeners.[20,21]

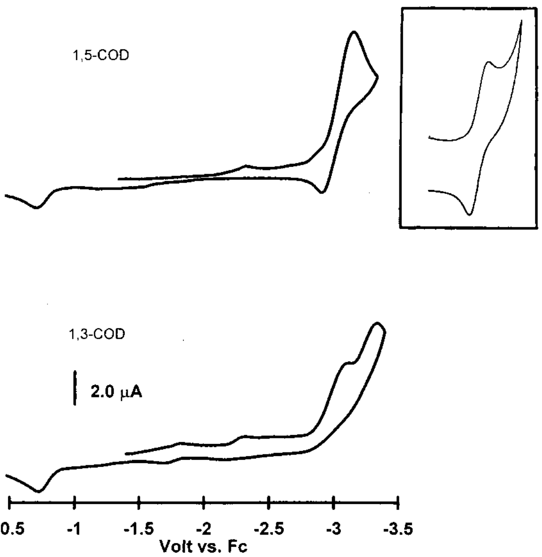

Figure 3. Cyclic voltammograms at ambient temperatures of the reductions of **1** (top) and **2** (bottom) in THF/0.1 M $[NBu_4][PF_6]$, 0.8 mm Pt disk, $\nu = 0.80$ V/s, concentrations = 1.2 mM. Inset gives result (unscaled) at $\nu = 100$ V/s for **1**.

Kinetic Stabilization Imparted by the (C_5Ph_5) Ligand. Kinetic stabilization of the 17-electron species by the pentaphenylcyclopentadienyl ligand is apparent in the contrasting lifetimes of $\mathbf{1}^+$ and [CpRh(1,5-COD)]$^+$. The latter has only brief existence under the same conditions that give long-lived $\mathbf{1}^+$. Unpublished work by T. T. Chin at the University of Vermont showed that the oxidation of CpRh(1,5-COD) ($E_{1/2} = 0.05$ V vs Fc) is chemically reversible only at CV scan rates over 20 V/s in CH_2Cl_2. In contrast, even the 16-electron *di*cations of **1** and **2** are detectable on the voltammetric time scale.

The increased lifetimes of the C_5Ph_5 complexes most likely arise from steric hindrance of reactions at the metal center or the five-membered ring that are commonly encountered with 17-electron complexes of this general type.[22]

Reduction of 1 and 2 in THF. The reductions of both isomers give unstable anions. At a scan rate of $\nu = 0.1$ V/s, **1** displays a cathodic wave ($E_{pc} = -3.23$ V) that is 2.6 times the height of the one-electron oxidation wave ($\mathbf{1}/\mathbf{1}^+$) previously detailed. As the scan rate is increased to 0.8 V/s, the ratio of current functions falls to 2.0 and a coupled anodic wave appears, suggesting the onset of chemical reversibility for the $\mathbf{1}/\mathbf{1}^-$ couple (Figure 3), $E_{1/2} = -3.17$ V. At scan rates above about 10 V/s the wave is chemically reversible (Figure 3, inset: CV at 100 V/s). The evidence is consistent with

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an ECE mechanism for the reduction of **1**, with the 19-electron complex $\mathbf{1}^-$ (apparent half-life 0.1 s) undergoing decomposition to electroactive product(s) **Z**:

$$\mathbf{1} + e^- \rightleftarrows \mathbf{1}^- \rightarrow \mathbf{Z}\,(+\,ne^-) \rightarrow \mathbf{Z}^{n-}$$

One of these products is the pentaphenylcyclopentadienyl anion, detected on reverse sweeps as a reversible couple with $E_{1/2} = -0.84$ V.[23,24]

The reduction of **2** occurs at a potential 150 mV positive of that of **1** ($E_{pc} = -3.08$ V at $\nu = 0.095$ V/s). In this case the wave is of one-electron height and is chemically irreversible, independent of ν. As with the 1,5-isomer, the reduction of **2** releases $[C_5Ph_5]^-$ (CV product wave at $E_{1/2} = -0.84$ V). A point of difference in the reductions of **1** and **2** is that a second cathodic wave, also irreversible, is seen when **2** is scanned to more negative potentials (Figure 3).

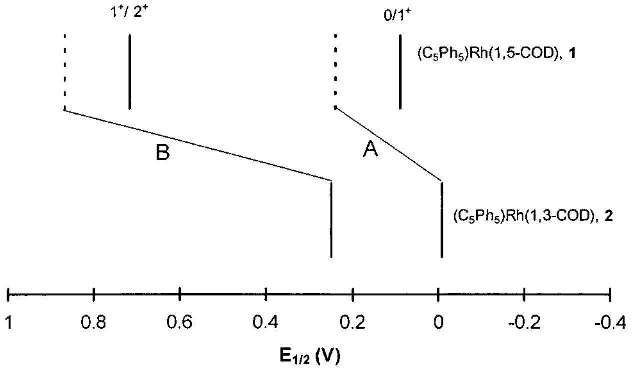
Since release of $[C_5Ph_5]^-$ leaves the formal fragment (COD)Rh, which would undoubtedly be solvated if formed, we generated the complex $[(1,5\text{-COD})Rh(THF)_x]^+$ for comparison of its redox potentials to those of the product waves of **2**. Two irreversible waves were observed for $[(1,5\text{-COD})Rh(THF)_x]^+$ at $E_{pc} = -2.09$ and -2.54 V, neither of which coincides with the product wave at -3.3 V for the reduction product of **2**.

None of the electrochemical data suggest that either of the 19-electron anions isomerizes to the other form.

19-Electron Species: Fate of $[\text{Cp}^{\ddagger}\text{Rh(COD)}]^-$. Both 19-electron species generated in this study, namely, $\mathbf{1}^-$ and $\mathbf{2}^-$, are subject to rapid loss of the C_5Ph_5 ring, most likely as the anion $[C_5Ph_5]^-$, the longer-lived species $\mathbf{1}^-$ having a half-life of ≈0.1 s at room temperature. Cleavage of $[C_5R_5]^-$ from analogous 19e rhodium complexes has been observed previously. The parent system CpRh(1,5-COD) does not show a reduction prior to electrolyte breakdown,[25] but $\text{Cp}^{\ddagger}\text{Rh(CO)}_2$ is reduced with loss of $[C_5Ph_5]^-$.[23] More direct precedent comes from the studies of Amatore et al.[26] on the reduction of (indenyl)Rh(1,5-COD) (indenyl = η^5-C_9H_7). In spite of the general ability of the indenyl ligand to stabilize hypervalent metals (most likely through hapticity lowering[27]), the anion $[(\text{indenyl})\text{Rh(COD)}]^-$ decomposes with a half-life of about 1 s at room temperature.[26] The increased kinetic and thermodynamic stabilities of 19-electron species containing the C_5Ph_5 ring as compared to the C_5H_5 ring have been previously noted, as has been the propensity of such systems to decompose by loss of $[C_5Ph_5]^-$.[23,24]

The ring-cleavage reactions of $\mathbf{1}^-$, $\mathbf{2}^-$, and perhaps $[(\text{indenyl})\text{Rh(COD)}]^-$ [26] are most simply explicable in terms of dissociation of the 19-electron radical without slip-fold distortion of the five-membered ring. The SOMO orbitals of the Rh complexes $\mathbf{1}^-$ and $\mathbf{2}^-$ are expected to be predominantly Rh $4d_{yz}$, having significant antibonding character between the metal and the five-membered ring.[21,22] It is therefore not surprising that the 19e system loses $[C_5Ph_5]^-$, especially when one considers that, contrary to loss of the diolefin, loss of the C_5-hydrocarbon provides a mechanism for carrying off the negative charge.

Scheme 1. Representation of agostic stabilization eneries of the oxidized forms of 2. The shift of A is 0.25 V; that of B is 0.62 V. The dotted lines represent the expected $E_{1/2}$ values in the absence of agostic interactions, assuming a raising of the HOMO by 0.15 eV in the neutral 1,3-isomer.



Comparison of the Potentials of the 1,5-COD and 1,3-COD Isomers. The one-electron oxidation of **1** ($E_{1/2} = +0.09$ V) occurs 100 mV positive of the corresponding oxidation of **2**. The converse is true for the one-electron reductions of the two isomers, the potential of **1** being about the same amount *negative* of that of **2**. That is, the 1,3-isomer is both easier to oxidize and easier to reduce than its 1,5-analogue. The more facile reduction is explicable in the simple notion of increased metal–ligand delocalization in the LUMO of the 1,3-isomer.

The more facile oxidation of **2** requires more consideration, since this contrasts with expectations based on reported ionization potentials of CpRh (η^4-diolefin) complexes. Green and co-workers[20] showed that the first ionization potentials of complexes of two conjugated diolefins (viz., butadiene and 1,3-cyclohexadiene) were *higher* (by an average of 0.15 eV) than those of complexes of either 1,5-COD or bis-ethylene. On this basis one would predict an ordering of the first oxidation potentials for **1** and **2**, namely, $E_{1/2}(\mathbf{2}) > E_{1/2}(\mathbf{1})$, opposite of that observed. Taking into account that the measured value of $E_{1/2}(\mathbf{2})$ is 0.1 V less than $E_{1/2}(\mathbf{1})$, there is an unaccounted-for stabilization of about 0.25 V (=0.15 V + 0.10 V) in the formation of $\mathbf{2}^+$.

An even larger negative shift of the oxidation potential of the 1,3-isomer is seen for the *second* oxidation of **2** compared to **1** (0.47 V). The separation of the two $E_{1/2}$ values for the stepwise oxidation of **2** is therefore quite small, 0.26 V [cf. 0.63 for **1** and 1.12 V for CpCo(1,5-COD)]. These shifts are depicted graphically in Scheme 1, in which the dotted lines are the relative oxidation potentials expected from the photoelectron spectroscopy data of Green.[20]

Because solvation energies should be very similar for the various redox states of **1** compared to **2**, the progressive stabilization of higher oxidation states of **2** must have its origin in electronic and molecular structural differences between the two compounds. ESR spectra of the monocations do not suggests major differences in the metal–ligand delocalization (vide ante), and there is no evidence for isomeric interconversions on the voltammetric time scale. The $E_{1/2}$ shifts

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[23] Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219.

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[26] Amatore, C.; Ceccon, A.; Santi, S.; Verpaux, J.-N. *Chem.-Eur. J.* **1997**, *3*, 279.

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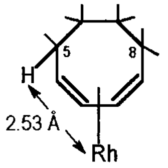
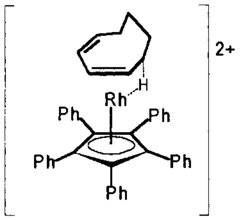
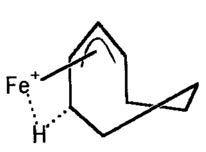
may be accounted for, however, in terms of increasingly strong interactions between an aliphatic hydrogen of the cyclooctadiene ring and the metal atom as the oxidation state of the complex increases.

The geometry of the 1,3-COD ligand in **2** places a C-5 hydrogen (below, left) about 2.53 Å from the rhodium atom (in contrast, that of the C-8 carbon is 3.03 Å away).[8,28] The former already places the ring hydrogen within the M−H distance suitable for an agostic interaction.[29] The empty metal orbital necessary to fully "turn on" the agostic interaction is achieved when the metal center is doubly oxidized (above, right), creating a three-center, two-electron situation. The 17-electron monocation is expected to have a smaller agostic interaction owing to its three-center, *three*-electron local electronic structure. This model predicts a progressively larger negative shift of the oxidation potentials arising from the increasingly greater agostic stabilization of the higher oxidation states. The flexibility of the aliphatic backbone of the 1,3-COD ligand allows for a shortening of the Rh−H distance without introducing undue strain into the C_8 ring. The same cannot be said for the 1,5-COD ligand, which has no aliphatic hydrogens at suitable distances in **1** and whose relatively rigid structure will not allow for such interactions in higher oxidations states.





Spectroscopic (NMR) confirmation of the proposed agostic interaction has thus far failed owing to the paramagnetic nature of $\mathbf{2}^+$ and the short lifetime of $\mathbf{2}^{2+}$. Diagnosis of agostic interactions in odd-electron species is, indeed, rare. Precedent for this model exists, however, in the impressive structural studies of Ittel et al., on cyclooctenyl iron complexes.[30] These workers isolated the complexes $\{[P(OMe)_3]_3Fe(\eta^3\text{-}C_8H_{13})\}^m$ in the oxidation states $m = -1, 0, +1$. The orientation of the C_8 ring (shown below) in the formally 16-electron monocation allows the coordination of an aliphatic-H with an Fe−H distance of 1.95 Å. The neutral (17e) complex has a weak agostic interaction, $d_{FeH} = 2.77$ Å. The 18e anion was not structurally characterized, but the isoelectronic cobalt complex has no significant M−H interactions. In proceeding from the 18e anion to the "16e" cation, the C_8 ring becomes more asymmetric to allow the interacting C−H group to swing in closer to the metal. A similar set of geometric changes is very likely operative in the sequence $\mathbf{2} \rightarrow \mathbf{2}^+ \rightarrow \mathbf{2}^{2+}$.



Mechanism of Formation of 2. The fact that Cp‡-Rh(1,3-COD) is the only known complex in which the cyclooctadiene ligand has been confirmed as being bonded in a 1,3-fashion to rhodium raises the question of the reason(s) for its formation and stability. It had been previously[8] suggested that the isomerization of cyclooctadiene occurs through a 19e intermediate formed under the reducing conditions (namely, base and alcohol) used in the preparation of **2**. The present results indicate that this is not the case.

A more reasonable alternative is the formation of a cyclooctenyl intermediate, Cp‡Rh(1,3-C_8H_{13})Br, in the reaction of [Cp‡$RhBr_2$]$_2$ with 1,5-COD. An analogous complex, (C_5Me_5)Rh(C_8H_{13})Cl, has been isolated from the reaction of [(C_5Me_5)$RhCl_2$]$_2$ with 1,5-COD under similar conditions (Na_2CO_3 in ethanol), which ultimately lead to (C_5Me_5)Rh(1,5-COD).[31] Whereas the stronger donor C_5Me_5 stabilizes the Rh(III) intermediate, the C_5Ph_5 ligand does not, leading to ready elimination of HBr. This elimination would be promoted by the steric effect of the pentaphenylcyclopentadienyl ligand[32] and by the undoubted stability of complex **2**.

Summary

(1) Both the 1,5- and 1,3-isomers of Cp‡Rh(COD) oxidize to persistent 17-electron monocations, the lifetime of the 1,5-isomer being enormously increased over that (≈1 s) of the unsubstituted cyclopentadienyl analogue [CpRh(1,5-COD)]$^+$. The 16-electron dications are detected voltammetrically for both the 1,5- and 1,3-isomers.

(2) ESR spectra of both 17-electron complexes, $\mathbf{1}^+$ and $\mathbf{2}^+$, are explicable in terms of a SOMO having a smaller metal d_{xz} contribution than seen previously for the cobalt analogue [CpCo(1,5-COD)]$^+$. The axially symmetric g-tensor of $\mathbf{1}^+$ suggests that this radical retains approximate C_{2v} symmetry.

(3) The $E_{1/2}$ values of **2** demonstrate that the higher oxidation states of the 1,3-isomer are significantly stabilized (cf. 1,5-isomer) and that the energy of stabilization increases with increasing oxidation state. A progressively stronger agostic interaction between the Rh atom and the C_5 aliphatic hydrogen of the cyclooctadiene ring is proposed to account for this thermodynamic stabilization, estimated as 0.62 eV (14 kcal/mol) in the dication $\mathbf{2}^{2+}$.

(4) The reduction potential of the 1,3-isomer is ca 0.1 V positive of that of the 1,5-isomer. Both 19e complexes, $\mathbf{1}^-$ and $\mathbf{2}^-$, expel [C_5Ph_5]$^-$ quite rapidly.

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[28] H atoms were not located in the structure of **2** in ref 8. H-positions were calculated assuming a C−H bond length of 0.96 Å.

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