$(\mathrm{P}i\mathrm{Pr}_3)\overline{\mathrm{RhOC(Ph)NC}}(=\mathrm{CH}_2)$,[14] which, like 5, also contain a five-membered metallaheterocycle with an exocyclic $=\mathrm{CH}_2$ group.

Acknowledgment. We thank the ministry of education of the People's Republic of China for a stipend (to L.X.) and the Volkswagen-Stiftung for generous financial support. We are also grateful to the Fonds der Chemischen Industrie for a Doktorandenstipendium (to O.N.). Finally, we acknowledge support by Dr. G. Lange and Mr. F. Dadrich (mass spectra), Mrs. R. Schedl, Mrs. U. Neumann, and Mr. C. P. Kneis (elemental analysis), and Mr. Th. Rappert (NMR measurements).

Supplementary Material Available: Additional drawings and tables of all bond distances and angles, positional and thermal parameters, and least-squares planes and deviations for compounds 5 and 6 (18 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Oxidation of *syn*-Dirhodium Complexes of Cyclohepta- and Cyclooctatriene: Influence of C–H Bond Activation in Multiple Electron-Transfer Reactions

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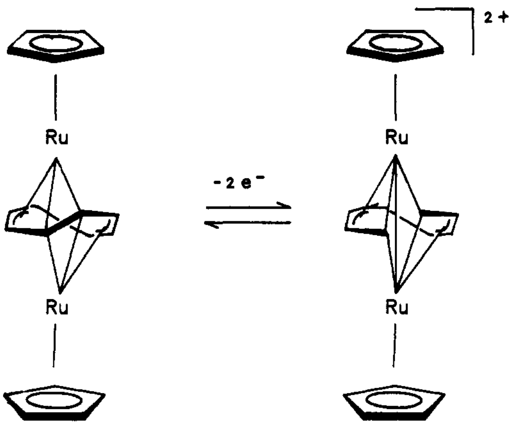
The oxidation of dinuclear complexes $\mathrm{Cp_2Rh_2}(\mu\text{-}\mathrm{C_7H_8})$ (**3**) and $\mathrm{Cp_2Rh_2}(\mu\text{-}\mathrm{C_8H_{10}})$ (**6**) has been examined in dichloromethane and acetone solutions. Complex **3** undergoes one-electron oxidation to $\mathbf{3}^+$ ($E° = -0.04$ V vs SCE), which is further oxidized to highly unstable $\mathbf{3}^{2+}$ at $E_p = +0.34$ V ($\mathrm{CH_2Cl_2}$). Bulk electrolysis of **3** gave a mixture of the tropylium complex $[\mathrm{Cp_2Rh_2}(\mu\text{-}\mathrm{C_7H_7})]^+$ (**4**) and the μ-hydrido complex $[\mathrm{Cp_2Rh_2}(\mu\text{-H})(\mu\text{-}\mathrm{C_7H_8})]^+$ (**5**), the relative amounts depending on the electrolysis potential. Complex **6** gave the persistent cation radical $\mathbf{6}^+$ ($E° = +0.14$ V) and underwent oxidation to a transient dication ($E° = +0.45$ V). Both $\mathbf{6}^+$ and $\mathbf{6}^{2+}$ eventually form complex **7**, characterized in situ by NMR spectroscopy as $[\mathrm{Cp_2Rh_2}\{\mu\text{-}(1,2,5,6\text{-}\eta{:}2\text{-}\sigma,3,4\text{-}\eta)\text{-}\mathrm{C_8H_9}\}]^+$, in which one of the sp^2 ring carbons has lost an H atom and become σ bonded to a Rh atom. Complex **7** was reduced back to **6** electrochemically. The *one*-electron processes seen for these syn-dinuclear complexes, in contrast with the *two*-electron processes observed for anti analogues, and the differences are rationalized in terms of the type of structural rearrangements available to the one-electron intermediates in the two cases. The one-electron intermediates with syn-dinuclear metals enjoy greater thermodynamic stability compared to their anti counterparts since C–H bond cleavage is required to produce multielectron processes in the former.

Introduction

We report the electrochemical oxidation of two complexes in which two CpRh (Cp = η^5-cyclopentadienyl) moieties are bonded to the same face of an unsaturated $\mathrm{C_7}$ or $\mathrm{C_8}$ polyolefin and joined by a metal–metal bond. Interest in these systems derives from two viewpoints. First, dinuclear Rh and Ru complexes in which the metals are aligned on the *opposite* sides of a bridging $\mathrm{C_8H_8}$ ligand (an anti arrangement) have been shown to undergo novel structural rearrangements when oxidized by two electrons,[1–6] leading ultimately to efficient reversible insertion of metals into the C–C framework of the hydrocarbon. The anti-dinuclear pseudo-triple-decker complex $\mathrm{Cp_2Ru_2}(\eta^5,\eta'^5\text{-}\mathrm{C_8H_8})$ (**1**) forms the flyover complex **2** in an overall 2e⁻ process via an ECE mechanism.[3,6] An important structural feature of **2** is its M–M bond, which allows each metal to achieve an 18e⁻ configuration. Metal–metal bonds are a common feature of syn-dinuclear complexes of bridging cyclic polyolefins.[7] This stands in contrast to their anti analogues, raising the question of how metal–metal bonding might influence insertion of electron-deficient metals into the C–C bonds of oxidized syn com-



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[7] See, for example: (a) Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: London, **1979**. (b) Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W. *J. Organomet. Chem.* **1981**, *221*, 339. (c) Jonas, K.; Wiskamp, V.; Tsay, Y.-H.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480. (d) Reference 4. (e) Edelman, F.; Takats, J. *J. Organomet. Chem.* **1988**, *344*, 351.

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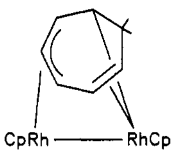
plexes. This question has increased relevance since the complexes may be viewed as crude models of hydrocarbons chemisorbed onto metal surfaces.

A second aspect of this redox chemistry, one that did not become obvious until preliminary results were obtained, is the activation of polyolefin C–H bonds which occurs upon oxidation. This has relevance to C–H cleavage reactions and to the transfer of H^m (m = 1+, 0, 1–) in both organic and organometallic systems.

The present report shows that the complexes $Cp_2Rh_2(\mu\text{-}C_7H_8)$ (**3**) and $Cp_2Rh_2(\mu\text{-}C_8H_{10})$ (**6**) each undergo reversible one-electron oxidations to detectable cation radicals. The radical derived from **6** is quite persistent.



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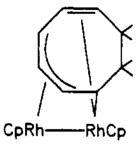

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Further oxidation gives transient dications, and all oxidized complexes ultimately lead to structures *in which the Rh–Rh bond is retained* and a formal 18e⁻ count is maintained for each metal. The inert-gas configuration is achieved by rearrangement following cleavage of a C–H bond and transfer of an H^+ or H atom. This mechanism stands in contrast to those previously investigated involving anti-dinuclear complexes, in which M–C or C–C bond cleavage is the initial step following electron transfer.[5,6] The implications of these different mechanisms in determining whether or not a dinuclear complex will exhibit two-electron voltammetric waves is discussed.

Experimental Section

Electrochemical and preparative procedures were conducted under an atmosphere of dinitrogen using drybox or Schlenk techniques. Solvents were dried and distilled by conventional procedures.

Chemicals. The dinuclear complexes $Cp_2Rh_2(\mu\text{-}C_7H_8)$[8] (**3**) and $Cp_2Rh_2(\mu\text{-}C_8H_{10})$[8] (**6**), their protonation products,[8] and $[Cp_2Rh_2(\mu\text{-}C_7H_7)]Cl$[9] (**4**) were prepared by literature methods. $Cp_2Rh_2(\eta^6\text{-}C_8H_8)$ was kindly donated by Dr. A. Salzer. $[C_7H_7][BF_4]$ (Aldrich) and $[Ph_3C][BF_4]$ (Aldrich) were used as purchased, trifluoroacetic acid (Aldrich) was freshly distilled prior to use, and ferrocenium hexafluorophosphate, $[Cp_2Fe][PF_6]$, was prepared by oxidation of Cp_2Fe with equimolar $AgPF_6$ (Ozark-Mahoning) in CH_2Cl_2.

NMR spectra were obtained on Bruker 250- and 270-MHz instruments and calibrated against TMS. ESR spectra were obtained using a modified Varian E-4 spectrometer.

Electrochemistry. Electrochemical procedures were similar to those reported in previous studies.[10] A Ag/AgCl electrode was used as a reference for low-temperature voltammetry, and an aqueous saturated calomel electrode (SCE) was employed in room-temperature experiments. Potentials were related by use of a ferrocene internal standard and are reported vs the room-temperature SCE potential. These potentials may be converted to the Cp_2Fe/Cp_2Fe^+ reference by addition of –0.46 V for CH_2Cl_2 solutions and –0.48 V for acetone solutions. Formal potentials ($E°$ values) are calculated for reversible systems from the average of the E_{pa} and E_{pc} values measured by cyclic voltammetry. $E_{1/2}$ potentials are quoted for scans with a rotating platinum electrode.

Synthesis of $[Cp_2Rh_2\{\mu\text{-}(1,2,5,6\text{-}\eta:2\text{-}\sigma,3,4\text{-}\eta)\text{-}C_8H_9\}][PF_6]$ (7). To a stirred solution of **6** (50 mg, 0.113 mmol) in acetone (10 mL) was added $[Cp_2Fe][PF_6]$ (37.4 mg, 0.113 mmol). After 1 h the red solution was filtered, the solvent partially removed in vacuo, and hexane added to precipitate the cation. After copious washings with hexane, the sample was recrystallized from CH_2Cl_2/hexane as a dark red microcrystalline solid, yield 38 mg (60%). ^1H NMR (DMSO-d_6): δ(Cp) 6.01 (d, J_{Rh-H} = 0.6 Hz, 5 H), 5.77 (d, J_{Rh-H} = 0.6 Hz, 5 H); δ(C*H*) 5.75 (s, br, 1 H), 5.70 (s, br, 1 H), 5.21 (s, br, 1 H), 4.13 (s, br, 2 H), δ(C*H*)$_2$ 2.75 (m, 1 H), 2.10 (m, 1 H), 1.69 (m, 1 H), 1.54 (m, 1 H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ(Cp) 89.3 (d, J_{Rh-C} = 4.2 Hz), 86.5 (d, J_{Rh-C} = 5.7 Hz); δ(CH) 71.5 (d, J_{Rh-C} = 7.3 Hz), 66.2 (d, J_{Rh-C} = 11.8 Hz), 65.9 (d, J_{Rh-C} = 8.0 Hz), 59.6 (d, J_{Rh-C} = 5.0 Hz), 58.3 (d, J_{Rh-C} = 9.7 Hz); δ(CH_2) 42.0 (s), 25.6 (s). Anal. Calcd for $C_{18}H_{19}Rh_2F_6P$: C, 36.86; H, 3.24. Found: C, 37.04; H, 2.36.

Table I. Electrochemical Potentials for Complexes Studied (in V vs SCE)

complex	solvent	oxidn $E°_1$	oxidn $E°_2$	redn E_{pc}
$Cp_2Rh_2(\mu\text{-}C_7H_8)$ (**3**)	acetone	–0.04	+0.29^b	
	CH_2Cl_2	–0.04	+0.34^a	
$[Cp_2Rh_2(\mu\text{-}C_7H_7)]^+$ (**4**)	acetone			–1.30^b
$[Cp_2Rh_2(\mu\text{-}H)(\mu\text{-}C_7H_8)]^+$ (**5**)	acetone			–1.22^b
$Cp_2Rh_2(\mu\text{-}C_8H_{10})$ (**6**)	acetone	+0.17	+0.39^b	
	CH_2Cl_2	+0.14	0.45	
$[Cp_2Rh_2(\mu\text{-}C_8H_9)]^+$ (**7**)	acetone			–1.07^{b,c}
	CH_2Cl_2			–1.13^b
$[Cp_2Rh_2(\mu\text{-}C_8H_9)]^+$ (**8**)	acetone			–1.28^b
$[Cp_2Rh_2(\mu\text{-}H)(\mu\text{-}C_8H_{10})]^+$ (**9**)	acetone			–1.29^b

[a] Chemically reversible at Hg electrode, v = 10 V/s, 276 K. [b] Irreversible wave; peak potential quoted, v = 0.20 V/s. [c] A further irreversible reduction observed at E_p = –1.69 V.

Generation of $[Cp_2Rh_2\{\mu\text{-}(1\text{-}7\text{-}\eta)\text{-}C_8H_9\}][CF_3CO_2]$ (8). $Cp_2Rh_2(\eta^6\text{-}C_8H_8)$ (10 mg, 0.02 mmol) was placed in an NMR tube and dissolved in $CDCl_3$ (0.5 mL). Trifluoroacetic acid (2 μL, >0.02 mmol) was added, the dark orange solution lightened, and the ^1H NMR spectrum indicated complete reaction. ^1H NMR ($CDCl_3$): δ(Cp) 5.65 (d, J_{Rh-H} = 1.5 Hz); $\delta(H_{outer})$ 1.36 (d of t, J_{H-H} = 13.0, 6.1 Hz); $\delta(H_{inner})$ 2.59 (d of t, J_{H-H} = 13.0, 6.0 Hz); $\delta(H_{1,7})$ 3.16 (dddd, J_{H-H} = 8.3, 6.1, 7.8 Hz, J_{Rh-H} 1.6 Hz); $\delta(H_{2,6})$ 3.54 (d of d, J_{H-H} = 7.8, 6.0 Hz); $\delta(H_{3,5})$ 4.16 (t, br); $\delta(H_4)$ 4.95 (t of d, J_{H-H} = 6.1 Hz, J_{Rh-H} = 1.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(Cp) 87.3, 85.5 (d, J_{Rh-C} = 5.7 Hz); $\delta(C_4)$ 73.9 (d, J_{Rh-C} = 6.7 Hz); $\delta(C_{2,3,5,6})$ 53.4 (d, J_{Rh-C} = 8.2 Hz), 51.3 (d, J_{Rh-C} = 9.2 Hz); $\delta(C_{1,7})$ 17.7 (d, J_{Rh-C} = 7.7 Hz); $\delta(C_8)$ 20.0 (s).

Results and Discussion

Oxidation of $Cp_2Rh_2(\mu\text{-}C_7H_8)$ (3). The cyclic voltammetry of **3** (Table I) was similar in acetone and dichloromethane, showing two anodic waves at mild potentials (Figure 1). At both platinum and glassy-carbon electrodes, **3** underwent a diffusion-controlled, chemically reversible[11] oxidation (i_c/i_a = 1, $i_a/v^{1/2}$ = constant at 50 mV/s < v < 500 mV/s, $E°$ = –0.04 V) followed by a second irreversible oxidation at a potential approximately 300 mV more positive (Table I). The second oxidation wave remained irreversible at lower temperatures and fast scan rates (260 K, 10 V/s, Pt bead) but exhibited some reversibility under these conditions at mercury. Coupled to this second oxidation wave was a broad cathodic wave at ca. –1.25 V. Voltammetry at the rotating platinum electrode (RPE) gave approximately equal plateau currents for the first and second waves, indicating that the second wave arose from the one-electron oxidation of 3^+.

Controlled-potential electrolyses (Table II) at E_{appl} = +0.40 V (positive of the second oxidation wave) were carried out in acetone at 298 and 233 K. In both cases 1.4 faradays was released and irreversible cathodic product

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[8] Evans, J.; Johnson, B. F. G.; Lewis, J.; Watt, R. *J. Chem. Soc., Dalton Trans.* **1974**, 2368.

[9] Salzer, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 1145.

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[11] The chemical reversibility of this couple at Pt was very dependent on experimental conditions, in general exhibiting only partial chemical reversibility at slow scan rates. However, chemical reversibility was always observed at a glassy-carbon electrode.

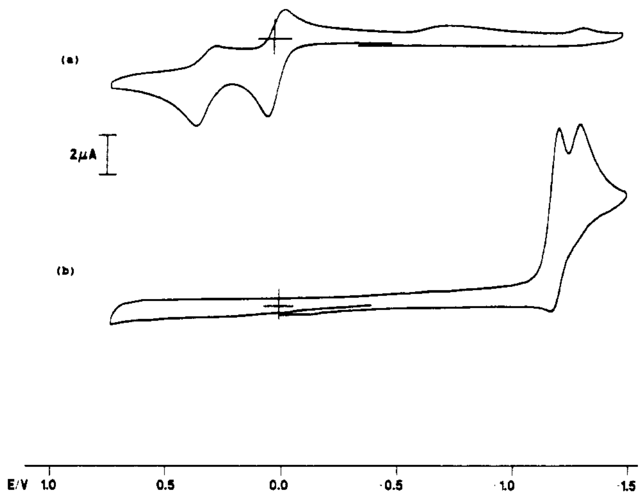


Figure 1. Cyclic voltammograms recorded at a platinum electrode on a dichloromethane solution containing **3** (0.2 mmol dm^{-3}) and [NBu$_4$][PF$_6$] (0.1 mol dm^{-3}): (a) initial solution; (b) solution after controlled-potential electrolysis (E_{appl} = +0.15 V). The scan rate was 0.2 V s^{-1} and the initial scan direction positive.

Table II. Coulometric Data for Oxidation of Complexes 3 and 6 and Reduction of 7[a]

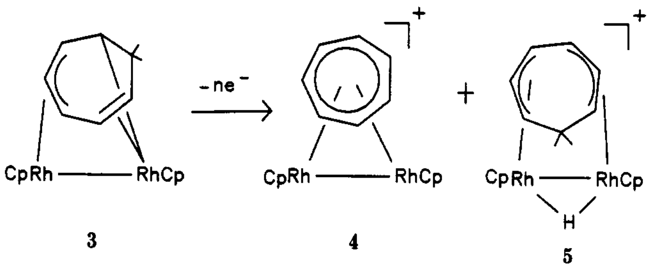
complex	solvent; temp, K	E_{appl}, V	current, faraday	products
3	acetone; 298 or 233	+0.15	0.94	33% **4**, 67% **5**
3	acetone; 298 or 233	+0.40	1.4	75% **4**, 25% **5**
6	acetone; 298	+0.25	2.0	**7**
6	acetone; 298	+0.48	2.0	**7**
6	CH$_2$Cl$_2$; 248	+0.20	0.97	**6**$^+$
7	acetone; 298	−1.40	1.9	**6**

[a] Complex **7** was generated by bulk electrolysis of **6**. The coulometry results assume quantitative conversion of **7** from **6**. The equal plateau currents in RPE scans before and after electrolysis of **6** support this assumption.

waves were observed at −1.31 and −1.22 V in a ratio of 3:1, as judged by their RPE plateau currents. The combined heights of the two product waves were approximately equal to that of the starting material, indicating mass balance in the reaction. These products were later identified (vide infra) as the tropylium complex [Cp$_2$Rh$_2$(μ-C$_7$H$_7$)]$^+$ (**4**; E_p = −1.31 V) and the bridging hydrido complex [Cp$_2$Rh$_2$(μ-H)(μ-C$_7$H$_8$)]$^+$ (**5**; E_p = −1.22 V).

The same product waves were observed following exhaustive electrolyses (298 or 233 K) at +0.15 V (0.94 faraday), the potential of the first oxidation wave, but in a ratio of 1:2 for **4** and **5**. The identities of the electrolysis products were established by NMR spectroscopy. One equivalent of [Cp$_2$Fe][PF$_6$] fully oxidized a CH$_2$Cl$_2$ solution of **3** at 245 K. The ^{13}C{^{1}H} NMR spectrum of the reaction mixture was assigned to two known species, [Cp$_2$Rh$_2$(μ-C$_7$H$_7$)]$^+$ (**4**) and [Cp$_2$Rh$_2$(μ-C$_7$H$_8$)(μ-H)]$^+$ (**5**), in equimolar amounts. Cyclic voltammograms of authentic samples of **4** and **5** confirmed their identities as the electrolysis products, showing irreversible cathodic waves at −1.31 and −1.22 V,[12] respectively.

Therefore, the *overall* oxidation of the cycloheptatriene compound can be written as



A mechanism for the oxidation can be proposed on the basis of Coulombic results and the observed product ratios. The electrode process arising from the double oxidation of **3** is best treated in terms of the EECC mechanism of eqs 1–4.

$$3 \rightleftarrows 3^+ + e^- \qquad (1)$$

$$3^+ \rightleftarrows 3^{2+} + e^- \qquad (2)$$

$$3^{2+} \rightarrow 4 + H^+ \qquad (3)$$

$$3 + H^+ \rightarrow 5 \qquad (4a)$$

$$3^{2+} + 3 \rightarrow 4 + 5 \qquad (4b)$$

Voltammetry establishes that a rapid reaction follows formation of the dication of **3**. Deprotonation of **3**$^{2+}$ is a likely decomposition route and has ample precedence in organic oxidation chemistry[13,14] and limited precedence in organometallic oxidation chemistry.[15–19] The most likely bases in the deprotonation reaction are the solvent and the original complex **3**. Johnson et al.[8] reported that **3** was susceptible to protonation by trifluoroacetic acid, yielding **5**. In the present case, **3** might serve as a base to either solvated H$^+$ released by **3**$^{2+}$ (eq 4a) or to **3**$^{2+}$ itself (eq 4b). Since both eq 4a and eq 4b result in conversion of starting material to a product (**5**) without passage of current, they affect the coulomb count in bulk electrolyses. If eq 4a or 4b were to proceed rapidly and irreversibly to completion, full electrolysis at the second anodic potential of **3** would result in passage of only 1 faraday/mol of **3** and a 1:1 product ratio of **4** and **5** (eq 5).

$$2\,3 \rightleftarrows 4 + 5 + 2e^- \qquad (5)$$

In the absence of eq 4, 2 faradays would be released and **4** would be the exclusive product. Experimentally we observe 1.4 faradays for electrolysis at +0.40 V, close to that predicted (1.5 faradays) for the observed product ratio of 3:1 for **4**:**5**. Therefore, the fact that the *dication* **3**$^{2+}$ *reacts by proton loss* is firmly established, the main product being the tropylium complex **4**, having two 18-electron metals. The minor product **5** is the μ-H complex

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[12] Peak potentials for irreversible couples are those measured with v = 0.20 V/s.

[13] An early example: Geske, D. H. *J. Am. Chem. Soc.* **1959**, *81*, 4145.

[14] Reviews of oxidations of hydrocarbons: (a) Eberson, L.; Utley, J. H. P. In *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; Chapter 13. (b) Perichon, J. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1978; Vol. XI, Chapter 1.

[15] Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208.

[16] Silverthorn, W. E. *J. Am. Chem. Soc.* **1980**, *102*, 842.

[17] (a) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 14. (b) Connelly, N. G.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 16.

[18] Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910.

[19] Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241.

[20] Passage of 1.0 faraday/mol of **3** would arise from the reaction sequence

$$2\,3 \rightarrow 2\,3^+ + 2e^-$$

$$2\,3^+ \rightarrow 5 + 4$$

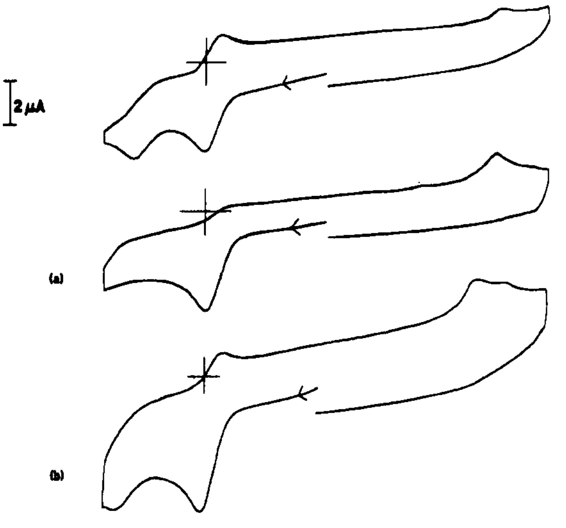

Figure 2. Cyclic voltammograms recorded at a glassy-carbon electrode on a dichloromethane solution containing **3** (0.2 mmol dm^{-3}) and [NBu$_4$][PF$_6$] (0.1 mol dm^{-3}), scan rate 0.2 V s^{-1}: (a) solution in the presence of Bu$_3$SnH (0.3 mmol dm^{-3}), scan rate 0.1 V s^{-1}; (b) as in (a) with scan rate 0.5 V s^{-1}.

derived either from direct reaction of **3** with **3**$^{2+}$ in an H$^+$-transfer comproportionation reaction (eq 4b) or from protonation of **3** by solvated H$^+$ (eq 4a).

The situation at the potential of the first oxidation (E_{appl} = 0.15 V) is more complicated. Although **3**$^+$ is stable on the CV time scale, it reacts over the period of a bulk electrolysis (0.94 faraday) to yield **4** and **5**, but in this case the μ-H complex predominates, the ratio of **4**:**5** being 1:2. H *atom* transfers appear to rationalize the product distribution. The monocationic radical **3**$^+$ may react with any source of H$^\bullet$ to give **5**. Like many organometallic cation radicals,[21-24] however, **3**$^+$ may also be prone to H atom loss, yielding **4**. This reaction is seen more clearly after one-electron oxidation of the cyclooctatriene analogue **6** (vide infra). Thus, the competition between eq 6 and eq 7 likely determines the product ratio. The H atom donors and

$$\mathbf{3}^+ + \text{RH (or SH)} \rightarrow \mathbf{5} + \text{R}^\bullet \text{ (or S}^\bullet) \qquad (6)$$

$$\mathbf{3}^+ \rightarrow \mathbf{4} + \text{H}^\bullet \qquad (7)$$

acceptors are unspecified and might include solvent or adventitious impurities. That **3**$^+$ may react with H atom donors to produce **5** (eq 6) was clearly demonstrated by CV scans of **3** in the presence of HSnBu$_3$, which showed an *irreversible* first oxidation wave at slow sweep rates (Figure 2a). At higher sweep rates the H atom transfer reaction was unimportant (Figure 2b). The H atom disproportionation mechanism of eq 8 should also be considered. Two observations dictate against this being an

$$2\,\mathbf{3}^+ \rightleftarrows \mathbf{4} + \mathbf{5} \qquad (8)$$

important reaction route. One is that the product ratio is predicted to be 1:1,[20] in contrast to the 1:2 ratio found by experiment. A second is that the chemical reversibility of the couple **3**/**3**$^+$ in CV scans was not affected by concentration over the range 0.1–2.0 mM, dictating against a rate-determining reaction second order in **3**$^+$. Therefore, the reaction chemistry of **3**$^+$ appears to be dominated by routes typical of radical reactivity (H atom loss and gain). However, *both mono-* and *di*oxidation of **3** lead ultimately to diamagnetic products in which a metal–metal bond is retained without insertion into the framework of the bridging hydrocarbon.

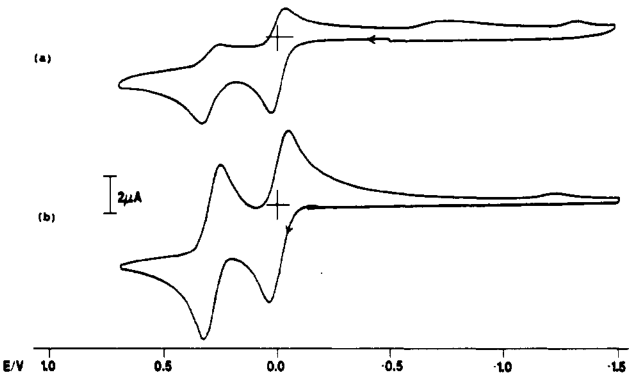

Figure 3. Cyclic voltammograms recorded at a platinum electrode: (a) acetone solution of **6** (0.3 mmol dm^{-3}); (b) dichloromethane solution of **6** (0.4 mmol dm^{-3}). The scan rate was 0.2 V s^{-1}.

Oxidation of Cp$_2$Rh$_2$(μ-C$_8$H$_{10}$) (6). Voltammetric studies of **6** in acetone showed a chemically reversible oxidation to **6**$^+$ ($E°$ = +0.17 V) followed by an irreversible one-electron oxidation (E_p = +0.39 V) similar to the case for the μ-C$_7$H$_8$ analogue **3**. The chemical reversibility of the second wave was greatly enhanced in CH$_2$Cl$_2$, the i_c/i_a value being 0.75 at v = 0.50 V/s (Figure 3). The half-life of the *dication* **6**$^{2+}$ is ca. 1 s at ambient temperature.[25] In both solvents a cathodic product wave is associated with scans through the second anodic wave (E_{pc} = −1.07 V in acetone, −1.13 V in CH$_2$Cl$_2$).

Exhaustive electrolyses were performed in acetone with E_{appl} = +0.25 V (first wave) or +0.48 V (second wave) with identical results, the major features being passage of 2.0 faradays and formation of a single cathodic product wave (E_{pc} = −1.07 V). RPE scans suggest that this product, **7**, is formed in virtually quantitative yield.[26] Reductive electrolysis of **7** with E_{appl} = −1.4 V passed 1.9 faradays and regenerated **6** in quantitative yield. In contrast, oxidation of **6** in CH$_2$Cl$_2$ at E_{appl} = +0.2 V (first wave) resulted in release of only one electron (measured 0.97 faraday) and a forest green solution of the monocation **6**$^+$. Immediate reduction of the green solution gave back the starting material (0.7 faraday, >90% yield), but when **6**$^+$ stood in solution for about 1 h, at 298 K, compound **7** formed in high yield (E_{pc} = −1.13 V). The oxidative decomposition product was identified by NMR studies (vide infra). These experiments establish that **7** may be formed through either the mono- or dication of **6** (eqs 9–11).

$$\mathbf{6} \rightleftarrows \mathbf{6}^+ + \text{e}^- \qquad (9)$$

$$\mathbf{6}^+ \rightleftarrows \mathbf{6}^{2+} + \text{e}^- \qquad (10)$$

$$\mathbf{6}^{+,2+} \rightarrow \mathbf{7} + \text{H}^{0,+} \qquad (11)$$

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[21] (a) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648. (b) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (c) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (d) Asaro, M. F.; Cooper, S. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 5187.

[22] Bodner, G. S.; Gladysz, J. A.; Neilson, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757.

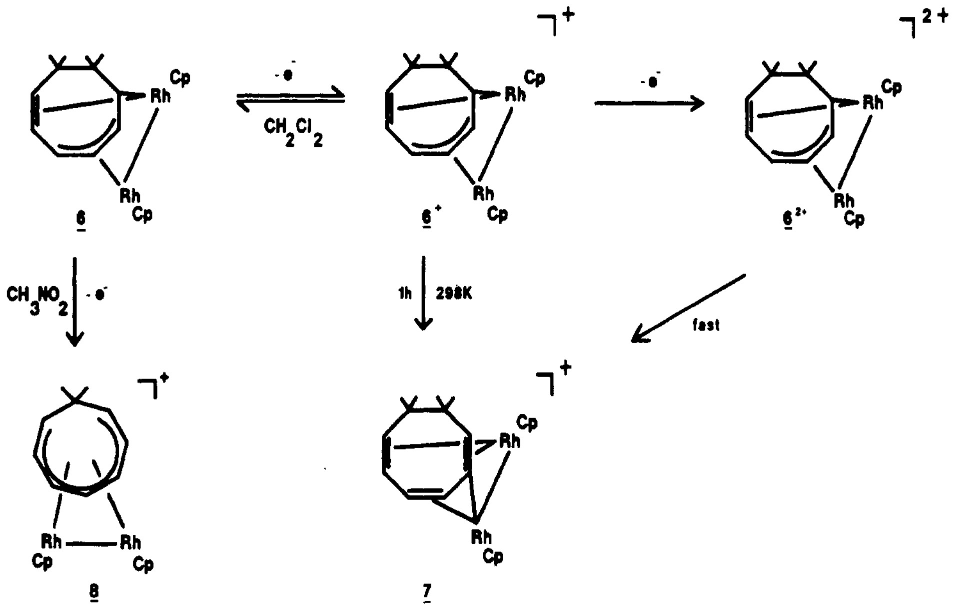
[23] Tilset, M.; Bodner, G. S.; Senn, D. R.; Gladysz, J. A.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7551.

[24] Doherty, N. M.; Howard, J. A. K.; Knox, S. A. R.; Terrill, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 638.

[25] The half-life of **6**$^{2+}$ was calculated from the i_c/i_a values at CV scan rates of 0.50 V/s or lower, using the procedure of Nicholson and Shain (*Anal. Chem.* **1964**, *36*, 706). Owing to the proximity of the two anodic waves, i_{pa} for the second wave was measured from scans originating at a rest potential between the two waves.

[26] The RPE plateau current for **7** was essentially equal to that of **6**. Complex **7** has a second irreversible wave at $E_{1/2}$ = −1.69 V.

Scheme I



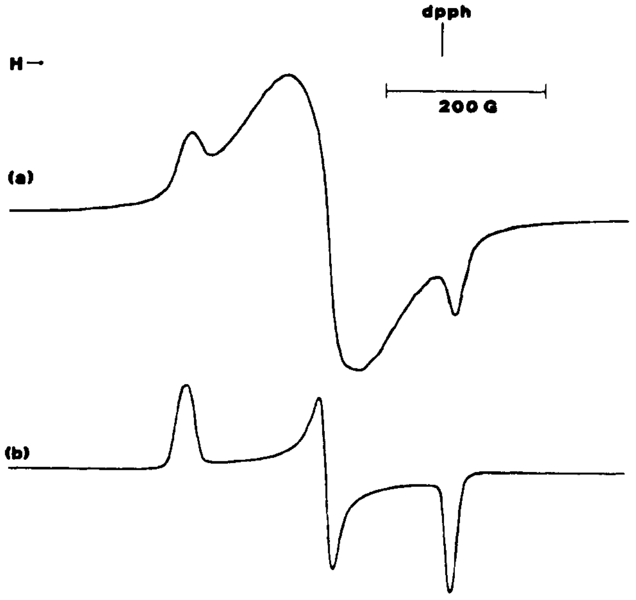
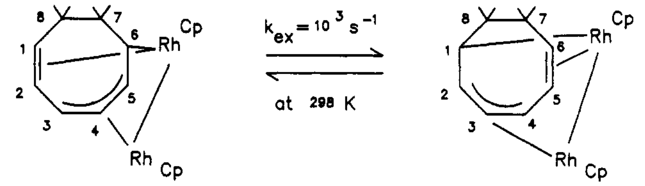
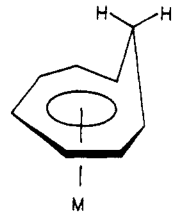


Figure 4. X-Band ESR spectra at 77 K of 6^+, generated chemically at 243 K by addition of 1 equiv of $[Cp_2Fe][PF_6]$ to: (a) a dichloromethane solution containing 6; (b) a 1:1 dichloromethane/dichloroethane solution of 6.

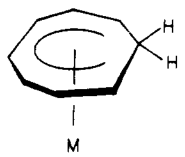
The temperature-independent ^1H and $^{13}C\{^1H\}$ NMR spectra of 7 revealed the presence of four methylene protons and five olefinic ring protons. A $^{13}C\{^1H\}$ DEPT[27] experiment confirmed the presence of two CH_2 groups and five CH groups, the latter all exhibiting Rh–C coupling. The eighth carbon resonance was not observed, although the integrity of the ring is maintained (addition of H^- to 7 regenerated 6). However, all nine protons are accounted for by the seven observed carbon resonances, implying that no protons are bound to the eighth carbon. The position of this carbon atom was ascertained by reacting 7 with $NaBD_4$ in THF at 298 K, which generated the monodeuterated analogue of 6. Evans et al.[8] reported that 6 interconverts between two equivalent enantiomeric forms ($k_{ex} = 10^3\ s^{-1}$ at 303 K):



The fast-exchange ^1H NMR spectrum (DMSO, 343 K) showed that the deuterium was incorporated at the C_2 or C_5 position. This was confirmed by the low-temperature limiting spectrum ($CDCl_3$, 208 K), in which the combined integrated intensity of the H_2 and H_5 resonances was one proton. Further inspection of the $^{13}C\{^1H\}$ NMR spectrum revealed that all five CH resonances fall in the coordinated olefinic region; i.e., the upfield resonance of C_1 in 6 (17.9 ppm) has shifted markedly downfield in 7. Thus, 7 seems to be best represented by the structure shown in Scheme I, $[Cp_2Rh_2\{\mu\text{-}(1,2,5,6\text{-}\eta\text{:}2\text{-}\sigma,3,4\text{-}\eta)\text{-}C_8H_9\}]^+$, in which the C_1–C_2 bond is olefinic. To the best of our knowledge this mode of bonding is unprecedented and represents the third type of coordination of a monocyclic η^7-C_8H_9 ligand. The other known modes of coordination are as homotropylium[28] (A) and cyclooctatrienylium[29] (B) moieties.



A



B

The synthesis of $Cp_2Rh_2(C_8H_9)^+$ was attempted via an alternate route. Protonation of $Cp_2Rh_2(\eta^6\text{-}C_8H_8)$ by CF_3CO_2H in $CDCl_3$ resulted in the quantitative formation of $[Cp_2Rh_2\{\mu\text{-}(1\text{-}7\text{-}\eta)\text{-}C_8H_9\}][CF_3CO_2]$ (8). In contrast to

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[27] DEPT = Distortionless Enhancement by Spin Polarization Transfer.

[28] Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Friedrich, E. C. *J. Am. Chem. Soc.* **1965**, *87*, 3267.

[29] Bau, R.; Chaw-Kuo Chou, B.; Knox, S. A. R.; Riera, V.; Stone, F. G. A. *J. Organomet. Chem.* **1974**, *82*, C43.

the case for 7, the C_8 moiety was coordinated in a cyclooctatrienylium fashion. The most notable feature of the ^1H NMR spectrum was the small difference in shifts between the inner and outer methylene protons (1.24 ppm), much smaller than that reported in homotropylium complexes[30] and characteristic of cyclooctatrienylium moieties. The ^1H and $^{13}C\{^1H\}$ NMR spectra also indicated that a mirror plane bisected the C_8H_9 ligand. CV studies on 8 in acetone showed an irreversible reduction at −1.28 V[12] compared to −1.07 V for 7. When 6 was allowed to react with trityl ion, complex 7 was formed along with the μ-hydrido complex $[Cp_2Rh_2(\mu\text{-}C_8H_{10})(\mu\text{-}H)]^+$ (**9**). Complex **9** was independently generated in situ by protonation of **6** with CF_3CO_2H in acetone and had an irreversible reduction wave at −1.29 V.[12] Interestingly, ferrocenium oxidation (1 equiv) of **6** in nitromethane resulted in the formation of **8** as the dominant product (Scheme I). Therefore, the oxidation of **6** yielded $\mathbf{6}^+$, **7**, or **8**, depending on solvent and the length of the reaction.

At 243 K the electrochemically generated one-electron-oxidation product $\mathbf{6}^+$ was persistent and exhibited an ESR spectrum at 77 and 298 K. In CH_2Cl_2 the low-temperature spectrum (Figure 4a) is a superposition of two signals, a rhombic spectrum ($g_1 = 2.222$, $g_2 = 2.092$, $g_3 = 1.992$; $\langle g \rangle_{av}(\text{calc}) = 2.102$) and a broad featureless peak at $g = 2.10$. A similar ESR spectrum was obtained with 1 equiv of Cp_2Fe^+ at 243 K in CH_2Cl_2 or $C_2H_4Cl_2$. However, in a mixture of $CH_2Cl_2/C_2H_4Cl_2$ (1:1), which forms a good glass when frozen, only the rhombic spectrum was present. The broad peak ($g = 2.10$) arises from crystallites of $\mathbf{6}^+$ not randomly dispersed in the glass matrix and therefore subject to significant broadening. The rhombic signal has a calculated average g value equal to that of the broad signal, consistent with this interpretation. The fluid spectrum of $\mathbf{6}^+$ consisted of a single broad line ($g_{iso} = 2.108$). No ^{103}Rh hyperfine coupling was observed. Addition of a second equivalent of ferrocenium ion to a CH_2Cl_2 solution of the monocation at 243 K resulted in the rapid generation of **7**.

Let us now turn to mechanistic aspects of the oxidation of the cyclooctatriene complex **6**. The conversion of **6** to **7** requires overall loss of H^- from **6** (eq 12). In the second

$$\mathbf{6} \rightleftarrows \mathbf{7} + H^- \qquad (12)$$

oxidation wave of **6** this is most likely to occur via an EEC mechanism (eqs 13–15), involving double oxidation fol-

$$\mathbf{6} \rightleftarrows \mathbf{6}^+ + e^- \qquad (13)$$

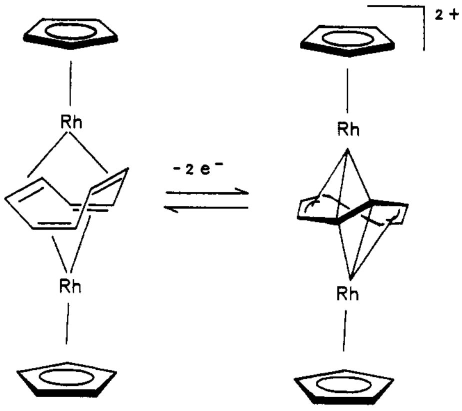
$$\mathbf{6}^+ \rightleftarrows \mathbf{6}^{2+} + e^- \qquad (14)$$

$$\mathbf{6}^{2+} \rightarrow \mathbf{7} + H^+ \qquad (15)$$

lowed by proton loss, analogous to the fate of $\mathbf{3}^{2+}$ (eqs 1–3). However, in this case the proton released in eq 15 is not captured by **6**, which appears to be a weaker base than **3**.[31] This mechanism is given additional weight by the observation that solutions of the monocation $\mathbf{6}^+$ treated with 1 equiv of Cp_2Fe^+ at 243 K rapidly form **7**.

One remarkable feature of the oxidation of **6** to **7** is that the inert-gas configuration is achieved for the two metals in the latter complex by removal of an H atom from an sp^2-rather than sp^3-hybridized carbon in the bridging polyolefin ring. We rationalize this observation by proposing that an agostic Rh–H interaction weakens the $C(sp^2)$–H bond in the radical $\mathbf{6}^+$, facilitating cleavage of that bond. An agostic hydrogen is reasonable in $\mathbf{6}^+$, owing to the electron-deficient Rh atom adjacent to the C–H bond. Agostic interactions are generally restricted to electron-deficient metal centers, although the metals usually have 16- rather than 17-electron configurations.[32,33] However, agostic interactions with paramagnetic metals are hard to diagnose, owing to the lack of NMR data for such systems.

Comparison of Oxidation Pathways of Syn and Anti Dinuclear Complexes. It is of interest to compare the present results with those seen for the oxidation of the anti complexes $Cp_2Rh_2(\eta^4,\eta'^4\text{-}C_8H_8)$ (**11**) and $Cp_2Ru_2(\eta^5,\eta'^5\text{-}C_8H_8)$ (**1**). Both the oxidation of **11** and the coupled reduction of **12** occur in single two-electron waves above 273 K.[2,5] A similar situation occurs for the couple involving the ruthenium analogue $\mathbf{1} \rightleftarrows \mathbf{2} + 2e^-$ (vide ante).[3,6] In contrast, the syn complexes investigated in the present work display discrete one-electron waves with appreciable separation of the formal potentials (e.g. $\Delta E° = 380$ mV for **3** in CH_2Cl_2). Therefore, the paramagnetic intermediates enjoy considerable thermodynamic stabilization in the syn complexes compared to the anti analogues.



11 **12**

The nature of the reaction routes available to the oxidized complexes is key to understanding both the 1e$^-$ vs 2e$^-$ electrochemistry and the identities of the final products. In neither anti complex **11** nor **1** does the bridging C_8H_8 ligand possess saturated carbons unbonded to the metals. Oxidations of *all* these complexes produce reactive, electron-deficient metals which force structural changes in the molecules, resulting in metals having an inert-gas configuration. The route available to **11** is formation of a multicentered bond involving both metals and a bridging C–C bond of the cyclooctatraene ring. This may be thought of as partial insertion into the C–C bond, so that each metal is formally bonded to five carbons in the C_8H_8 ring, resulting in two 18-electron metals in **12**. The ruthenium complex **1** already has maximum coordination (η^5,η'^5) of the C_8H_8 ring, and so oxidation results in full insertion into the C–C bond and concomitant formation of a M–M single bond, once again resulting in two 18-electron metals. The making and breaking of bonds producing these structures is very rapid in either the one-electron stage[6] or two-electron stage,[5] facilitating *transfer of two electrons in a single wave.* The literature can be consulted for more complete arguments.

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[30] Winstein, S. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1971; Vol. 3, Chapter 22.

[31] It is reported[8] that **5**, the protonation product of **3**, was isolated as its PF_6^- salt, whereas **9**, the corresponding protonation product of **6**, was stable only in trifluoroacetic acid solutions.

[32] For a recent review see: Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

[33] (a) Ittel, S. D.; Van-Catledge, F. A.; Tolman, C. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 1317. (b) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905. (c) Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981.

The syn complexes 3 and 6 have a M–M bond in the unoxidized form, therefore requiring donation of only 6 π electrons from the bridging polyolefin to achieve the 18-electron configuration for each metal. When these complexes are oxidized, the ultimate products once again have two 18-electron metals (4 and 5 from 3, 7 from 6). In these cases, however, expansion of hapticity of the bridging polyolefin occurs through *loss of hydrogen* (as an atom or ion) from one of the polyolefin carbons. This is very similar to the hapticity expansions observed in mass spectrometry of metal π complexes.[34,35]

The one-electron intermediates 3^+ and 6^+ display considerably higher thermodynamic and kinetic stabilities than do the corresponding monocations of the anti complexes 11^+ and 1^+. This is not surprising, in view of the need to break relatively strong C–H bonds in 3^+ or 6^+ to produce the ultimate electrolysis products.

Conclusions

The *syn*-dirhodium complexes 3 and 6 oxidize in two discrete one-electron steps, in contrast to the case for the anti-dinuclear complex 11. This difference in behavior arises from greater stability of the one-electron intermediates in the oxidation of the syn complexes, owing to relatively slow cleavage of polyolefin C–H bonds in the radical cations. One-electron processes have also been reported for syn-dinuclear complexes of Cr and V,[36] therefore appearing to be the favored route for complexes in which a bonded pair of metals is coordinated to the same face of a polyolefin. The two-electron reactions noted for 11 and 1 require structural changes which are fast and reversible on the voltammetric time scale, involving at least in part significant changes in the degree of the metal–metal interaction. Such a change is not available to the *syn*-dirhodium complexes upon oxidation.

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Supplementary Material Available: Ambient-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of 7 in DMSO-d_6 (1 page). Ordering information is given on any current masthead page.

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[34] Litzow, M. R.; Spaulding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier: Amsterdam, 1973; Chapter 11, Section 8–12.

[35] For example, $[Cp^*Rh(\eta^4\text{-}C_5Me_5H)]^+ \rightarrow Cp^*{}_2Rh^+$: Cloke, F. G. N.; Day, J. P.; Greenway, A. M.; Seddon, K. R.; Shimran, A. A.; Swain, A. C. *J. Organomet. Chem.* **1989**, *372*, 231.

[36] Bachman, B.; Han, F.; Heck, J.; Wuensch, M. *Organometallics* **1989**, *8*, 2523.

Transition-Metal-Promoted Conversion of Dichlorovinylcyclobutanes to Cyclohexadienes

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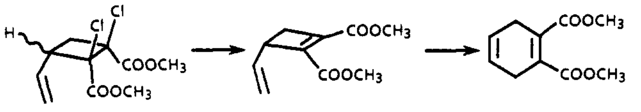
The nickel(0)- and iron(0)-promoted dechlorination of dimethyl 1,2-dichloro-3-vinylcyclobutane-1,2-dicarboxylate (1) to dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (2) occurs faster in the trans isomer. Nickel(0) and nickel(I), but not iron(0), with promote the rearrangement of this vinylcyclobutene to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (3). The effect of methyl substituents on these reactions indicate that the nickel must transfer to the vinyl group before the rearrangement can occur. It also was found that nickel will cleave exclusively the bond between an sp^2- and an sp^3-hybridized carbon.

A number of years ago, we reported[1a,2] that the $Ni(CO)_4$-promoted dechlorination and ring expansion of dimethyl 1,2-dichloro-3-vinylcyclobutane-1,2-dicarboxylate (1) to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (3) occur in two distinct steps with dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (2) as an isolable intermediate.



1 2 3

In addition, we showed by deuterium labeling experiments that this reaction is unimolecular, and it is an sp^2 and not an sp^3 carbon of vinylcyclobutene (2) which migrates to give the product. This reaction represents one of only a few cases in which an sp^2 carbon rather than an sp^3 carbon undergoes a metal-promoted migration.[3]

More recently,[1b] we showed that the transformation of 2 to 3 could be promoted by $(PPh_3)_2Ni(C_2H_4)$ at elevated temperatures, or by $(PPh_3)_2Ni(C_2H_4)$ at room temperature if the nickel(0) is first oxidized to nickel(I). We speculated that the role of the oxidation was to allow transfer of the nickel from the ring double bond to the vinyl group. In this paper, the effect methyl substituents have on this unique isomerization reaction will be studied in order to

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[1] (a) DiFrancesco, D.; Pinhas, A. R. *J. Org. Chem.* **1986**, *51*, 2098. (b) Choi, H.; Hershberger, J. W.; Pinhas, A. R.; Ho, D. M. *Organometallics* **1991**, *10*, 2930.

[2] Also see: Scharf, H.-D.; Korte, F. *Chem. Ber.* **1966**, *99*, 1299, 3925.

[3] See for example: (a) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015 and references cited therein. (b) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

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