the β-naphthalene carbon atoms are C8···C22 at 3.75(1) Å, C7···C22 at 3.80(1) Å, and C19···C28 at 3.45 (1) Å. It is of interest to note that the ferricenium cation is both *staggered* and *highly distorted.* The angle between the Cp ring planes is 9.1°, which is a very large distortion for a ferricenium cation.[14] The staggering and bending of the ferricenium cation occurs presumably to reduce the magnitude of the β-naphthalene–proton to Cp–proton nonbonded contacts. It is surprising, given the likely small barrier to ring rotation, that the staggering phenomenon does not occur in the neutral **1a** and **1b** species. As has been pointed out previously,[15] ferrocene usually occurs in a more nearly eclipsed rather than staggered conformation in properly analyzed structures, while unhindered ferricenium ions occur in the eclipsed conformation.[14,16] It is clear that a number of factors are responsible for the detailed distortions observed in these molecules. Nevertheless, the present results argue strongly that the primary contribution to the larger repulsion of cofacial aromatic rings in **1a** and **1b**, compared with the related phenylated naphthalenes **3**, **4**, and **5**, is the high negative charge on the Cp rings in the metallocenes, which is relieved by oxidation of one of the two metal centers.

The crystal structure of **1a**$^+$ is shown in Figure 4. Note that the cations occur in a distorted *stack* and are related by the symmetry operation (x, $^1/_2 - y$, $^1/_2 + z$) within the stack. The angle between pairs of intermolecular Cp rings in the stack is 26.6 (5)°. Representative C···C distances are C8···C18′ at 3.30 (1) Å and C10···C17′ at 3.47 (1) Å. However, although there are short contacts, no measurable conductivity was observed. It is quite possible that since the b axis is the direction of crystal elongation (this is the axis normal to the page in Figure 4), a remeasurement of conductivity along a more favorable direction is merited. Unfortunately, to date we have been unable to obtain crystals of sufficient size for such a measurement.

Acknowledgment. This research was supported by a grant from the Department of Energy (85ER45193) which is gratefully acknowledged. The investigation was supported (in part) by the National Institutes of Health Research Grant No. RR00317 from the Biotechnology Resources Branch, Division of Research Resources (principal investigator Professor K. Biemann).

Registry No. **1a**, 94161-70-3; **1a**$^+$BF$_4^-$, 94161-72-5; **1b**, 112461-16-2; **3**, 1038-67-1; **4**, 57620-87-8; **5**, 5710-05-4; **7**, 1730-04-7; **8**, 11106-52-8; Pd(dppf)Cl$_2$, 72287-26-4; ruthenocene, 1287-13-4; siler tetrafluoroborate, 14104-20-2.

Supplementary Material Available: Tables SI through SVIII, listing thermal parameters, atomic coordinates for hydrogen atoms, additional bond lengths and angles, and best weighted least-squares planes for each structure (13 pages); tables of observed and calculated structure factors for each structure (17 pages). Ordering information is given on any current masthead page.

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One-Electron Oxidation of (η^4-Cot)RhCp: Rearrangements of the Radical Cation and of the Resulting Dimerization Product[†]

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The complex (η^4-Cot)RhCp (Cot = cyclooctatetraene; **3**) undergoes an irreversible one-electron oxidation to a transient radical cation. Detailed voltammetric studies suggest that the radical rearranges to (η^5-C_8H_8)RhCp$^+$ before dimerizing through the allyl radical section of the C_8 ring. Anodic or chemical oxidation (using [FeCp$_2$]$^+$ or AgPF$_6$) in CH_2Cl_2 gives the C–C bonded dimer [(η^5:η'^5-$C_{16}H_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (**4**) which thermally isomerizes to [(η^2,η^3:η'^2,η'^3-$C_{16}H_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (**2b**) and then to [(η^2,η^3:σ',η'^4-$C_{16}H_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (**5**). The asymmetric species **5** has been fully characterized as the [BPh$_4$]$^-$ salt by single-crystal X-ray diffraction. Crystallographic data: $C_{74}H_{66}B_2Rh_2$, a = 20.421 (5) Å, b = 15.198 (2) Å, c = 19.528 (4) Å, β = 114.10 (2)°, space group $P2_1/c$, R = 0.083, R_w = 0.077. The dication of **5** contains two rhodium atoms, each carrying an η^5-cyclopentadienyl ring bridged [Rh···Rh = 6.514 (2) Å] by a $C_{16}H_{16}$ ligand. The ligand is formally derived from two Cot molecules by formation of three C–C bonds linking the two original C_8 rings. The resultant tetracyclic ligand bonds via σ,η^4- and η^2,η^3-linkages to the two rhodium atoms, acting as a five-electron donor to each.

Introduction

With the exception of the reduction of [(η^4-1,3-C_8H_8)ML][ML = Fe(CO)$_3$[2] or CoCp[1,3]], one-electron oxidation or reduction of η^4-bound cyclooctatetraene (Cot) complexes produces a structural rearrangement of the metal–π-system. When the Cot ligand is bonded in a tub form through nonadjacent double bonds [e.g., as in (1,5-Cot)CoCp], the

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[†] This may be considered as part 17 of the series Structural Consequences of Electron Transfer Reactions (part 16: Edwin, J., et al. *J. Am. Chem. Soc.*, **1987**, *109*, 7893) and as part 28 of the series Reduction–Oxidation Properties of Organotransition-Metal Complexes (part 27: *J. Chem. Soc., Dalton Trans.*, in press).

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[§] University of Vermont.

(1) Abbreviations used in this paper: C, chemical reaction following electron transfer (E); Cot, cyclooctatetraene; Cp, η^5-cyclopentadienyl; CV, cyclic voltammetry; E_{pa}, anodic peak potential; FDMS, field desorption mass spectrum; RSD, relative standard deviation; SCE, saturated calomel electrode; TMS, tetramethylsilane; v, cyclic voltammetry scan rate.

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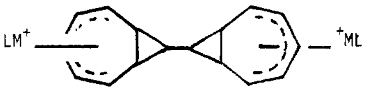
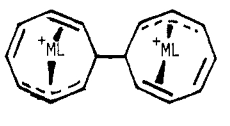
radical anion rearranges within a millisecond to the chair-bonded isomer [(1,3-Cot)CoCp]$^{-}$.[3,4]

The one-electron oxidation of (1,5-Cot)CoCp gives a cation that decomposes too rapidly for structural characterization.[5] However, the oxidation of the chair-bonded complexes (η^4-1,3-Cot)ML leads to rapid formation of the dimeric dications 1, ML = Fe(CO)$_3$,[6] or **2a**, ML = Ru(CO)$_3$.[7] The dications both have 18-electron metals, although they differ in the mode of ring coupling. Details of the stereo- and regioselectivity of the C–C bond formation have been presented.[8]

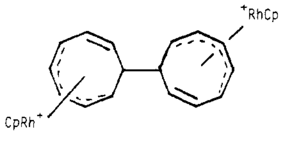


1, ML = Fe(CO)$_3$



2a, ML = Ru(CO)$_3$
2b, ML = RhCp

Since the ring-coupling reactions of cations derived from 1,5-Cot complexes might be expected to be different from their 1,3-Cot counterparts, we decided to study the oxidation of (η^4-1,5-Cot)RhCp (**3**). This has led to the characterization of a third structural form of the $C_{16}H_{16}$ ligand, **4**. Perhaps more importantly, however, **4** undergoes thermal isomerization first to **2b** and then to the asymmetric species **5** which has been characterized by X-ray crystallography. In **5** the $C_{16}H_{16}$ ligand is η^2,η^3-bonded to one rhodium atom and σ,η^4-bonded to the other. The final isomerization involves the spontaneous formation of two C–C bonds through addition of the uncoordinated double bond in half of **2b** to the terminal carbon atoms of the coordinated alkene and allyl groups in the other half of the molecule.



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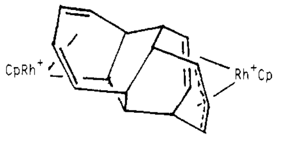

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Experimental Section

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled, and deoxygenated solvents. The compounds [Rh(μ-Cl)(η^4-Cot)]$_2$,[9] (η^4-Cot)RhCp[10] (**3**), and [FeCp$_2$][PF$_6$][11] were prepared by published methods or by modifications thereof as described below. Other chemicals were of commercial origin. Hydrogen (^{1}H) and proton-decoupled carbon (^{13}C) NMR spectra were recorded on a JEOL FX 200 or FX 90Q instrument (Bristol) and on IBM 270 and Bruker 250 instruments (Vermont) and calibrated against TMS as internal reference. Field desorption mass spectra were obtained at the NIH regional facility in Cambridge, MA, through the courtesy of Dr. Catherine Costello. Electrochemical studies were carried out in a Vacuum Atmospheres drylab by using instrumentation described previously.[3] The reference electrode was the SCE.[1] Microanalyses were carried out by the Microanalytical Service of the School of Chemistry, University of Bristol. Satisfactory analytical data (±0.3% for C, H) were obtained for complexes **2b**, **4**, and **5**.

Tetra-*n*-butylammonium Tetraphenylborate ([*n*-Bu$_4$N][BPh$_4$]). A mixture of [*n*-Bu$_4$N]Br (5.0 g, 15.5 mmol) and Na[BPh$_4$] (5.8 g, 17.0 mmol) in 50 mL of acetone was refluxed for 15 min. After filtration, addition of 200 mL of H$_2$O gave a white crystalline precipitate. Recrystallization from acetone–water (twice) and then from acetone–diethyl ether gave the product as white crystals, yield 7.8 g (90%).

(η^4-Cot)RhCp (3). To a suspension of [Rh(μ-Cl)(η^4-Cot)]$_2$ (9.50 g, 19.6 mmol) in toluene (250 mL) was added TlCp (11.0 g, 40.8 mmol). After the mixture was stirred for 5.5 h, it was filtered and the solvent was removed in vacuo to give a yellow residue. Extraction with hexane (3 × 200 mL) and removal of solvent gave **3** as a yellow solid (8.1 g, 77%).

Reaction of 3 with AgPF$_6$. (i) In CH$_3$CN. Solid AgPF$_6$ (0.28 g, 1.1 mmol) was added to a solution of **3** (0.30 g, 1.1 mmol) in CH$_3$CN (20 mL) yielding a red solution. Filtration through Celite to remove precipitated silver, and addition of diethyl ether gave (Cot)[RhCp]$_2$[PF$_6$]$_2$ as a red solid, yield 0.10 g (26%).

(ii) In CH$_2$Cl$_2$. Solid AgPF$_6$ (0.56 g, 2.2 mmol) was added to a stirred solution of **3** (0.6 g, 2.2 mmol) in 100 mL of CH$_2$Cl$_2$. Filtration through Kieselguhr or Celite to remove precipitated silver gave an orange solution. Reduction in volume (to $\simeq$30 mL) and addition of diethyl ether yielded a yellow solid which was found to be a mixture of mononuclear [(η^5-C$_8$H$_9$)RhCp][PF$_6$] (**6**) and dinuclear **4** (yield 0.46 g). The mixture is moderately soluble in CH$_2$Cl$_2$ and acetone giving yellow solutions which decompose over 7–14 days.

[(η^5:η'^5-C$_{16}$H$_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (4). Method a. When the yellow solid (0.35 g, 1.3 mmol) prepared as described above from **3** and AgPF$_6$ in CH$_2$Cl$_2$ was dissolved in acetone (7 mL), yellow crystals of pure **4** were deposited after 1 day; yield 0.085 g (25%).

Method b. A mixture of **3** (0.50 g, 1.84 mmol) and [FeCp$_2$][PF$_6$] (0.60 g, 1.8 mmol) was stirred in 30 mL of CH$_2$Cl$_2$ at 273 K until all the ferrocenium salt had dissolved (ca. 2 h). The resulting yellow precipitate was washed with CH$_2$Cl$_2$ and then purified by dissolution in CH$_3$CN or CH$_3$NO$_2$, followed by filtration and precipitation by diethyl ether; yield 0.61 g (80%). Complex **4** is air-stable and dissolves in CH$_3$CN or CH$_3$NO$_2$ to give yellow solutions which slowly isomerize to **2b** (see below).

[(η^2,η^3:η'^2,η'^3-C$_{16}$H$_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (2b). An acetone solution of **4** was heated under reflux for 2.5 h. The resulting yellow solution was filtered, washed with CH$_2$Cl$_2$, and dried in vacuo; yield ca. 25% of **2b**. Air-stable yellow solutions of **2b** in CH$_3$CN or CH$_3$NO$_2$ isomerize further over 2 months at ambient temperatures to give **5** (see below).

[(η^2,η^3:σ',η'^4-C$_{16}$H$_{16}$)Rh$_2$Cp$_2$][PF$_6$]$_2$ (5). A solution of **2b** (54 mg, 0.06 mmol) in CD$_3$NO$_2$ (0.7 mL) was heated at 333 K for 1 day. Addition of diethyl ether to the orange solution gave **5** as an amber solid (25 mg, 49%). It is soluble in CH$_3$CN or CD$_3$NO$_2$ to give orange-yellow solutions that appear to be indefinitely stable in air.

[(η^2,η^3:σ'^4,η'^4-C$_{16}$H$_{16}$)Rh$_2$Cp$_2$][BPh$_4$]$_2$. A solution of 0.1 g (0.12 mmol) of **5** in 10 mL of CH$_3$CN was refluxed in the presence of 0.25 g (0.45 mmol) of [*n*-Bu$_4$N][BPh$_4$] for 2 h. The bis(tetraphenylborate) salt precipitated from solution. After the solution was cooled, the crystals were separated from the mother liquor and washed with 10 mL of CH$_2$Cl$_2$ and dried under vacuum to give 0.12 g of the desired salt (0.10 mmol, 83%). Crystallographic-quality yellow cuboidal crystals were deposited when a hot concentrated solution of the complex in DMSO was allowed to cool and stand for 48 h at room temperature.

Crystal Structure Analysis of [(η^2,η^3:σ',η'^4-C$_{16}$H$_{16}$)-Rh$_2$Cp$_2$][BPh$_4$]$_2$. Diffracted intensities were measured at 293 K for a crystal, of approximate dimensions 0.35 × 0.25 × 0.08 mm, glued in a thin-walled glass capillary under N$_2$. Of the 7638 independent reflections measured for $4 \leq 2\theta \leq 50°$ on a Nicolet P3m diffractometer, 5254 satisfied the criterion $I \geq 1.5\sigma(I)$ and

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were used in the final refinement of the structure. Three check reflections (41$\bar{2}$, 231, 122) were remeasured every 50 reflections and indicated no significant crystal decay during data collection. Corrections were applied for Lorentz and polarization effects but not for X-ray absorption.

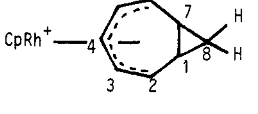
Crystal data for [(η^2,η^3:σ',η'^4-$C_{16}H_{16}$)Rh_2Cp_2][BPh_4]$_2$: $C_{74}H_{66}B_2Rh_2$, M_r 1182.8; monoclinic, space group $P2_1/c$ (No. 14); $a = 20.421$ (5) Å, $b = 15.198$ (2) Å, $c = 19.528$ (4) Å, $\beta = 114.10$ (2)°; $V = 5532$ (2) Å^3; D(calcd) = 1.42 g cm^{-3}, $Z = 4$; $F(000) = 2439.7$; Mo Kα X-radiation (graphite monochromator), $\lambda = 0.71069$ Å; μ(Mo Kα) = 6.30 cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by full-matrix, blocked-cascade least squares. All non-hydrogen atoms except the carbon atoms of the cyclopentadienyl rings were refined with anisotropic displacement parameters. The cyclopentadienyl groups were disordered and were modeled by a pair of rigid C_5H_5 rings of D_{5h} local symmetry (C–C = 1.42 Å, C–H = 0.96 Å) of occupancy 0.667 (8) and 0.333 (8) by refinement. The carbon atoms of these rings were assigned isotropic displacement parameters. Phenyl rings of the [BPh_4]$^-$ anions were constrained to idealized geometry with C–C = 1.395 Å and C–H = 0.96 Å. Hydrogen atoms of the $C_{16}H_{16}$ ligand were assigned idealized positions with C–H = 0.96 Å. All hydrogen atoms were given fixed isotropic displacement parameters ca. 1.2 times those of their attached carbon atoms.

Weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.0007|F_o{}^2|]^{-1}$, and refinement converged to $R = 0.083$, $R_w = 0.077$, and $S = 1.158$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$, and $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_{par})]^{1/2}$. A final electron-density difference synthesis showed no peaks > 0.67 or <−0.79 e Å^{-3}. The moderate values of the final residuals reflect the precision of the intensity data, which is in turn a consequence of size and diffracting power of the crystal. The adequacy of the refined model is indicated by the satisfactory goodness of fit, S. Scattering factors were taken from Ref 12 and all computations were carried out within the laboratory on a Data General Eclipse S230 computer with the SHELXTL system of programs.[13] Selected bond lengths and angles and torsion angles are given in Tables II (supplemental material) and III, respectively. The final non-hydrogen atom coordinates are listed in Table IV (supplementary material). Full tables of bond lengths and angles and hydrogen atomic coordinates and a listing of observed and calculated structure factor have been deposited and are available as supplementary material.

Results and Discussion

A. Chemical Oxidation of (η^4-Cot)RhCp. The chemical oxidation of 3 was carried out with either [$FeCp_2$][PF_6] or $AgPF_6$ in CH_2Cl_2. The reaction with $AgPF_6$ immediately gave a precipitate of metallic silver and a yellow-orange solution from which a yellow solid was deposited on addition of n-hexane. The ^{1}H NMR spectrum of the solid showed a mixture of two major components and a small amount of a third unidentified species. The first of the major species was readily identified as [(η^5-C_8H_9)RhCp][PF_6] (**6**) on the basis of four resonances at δ 1.38 (1 H, m, $H^8{}_{endo}$), 1.76 (1 H, m, $H^8{}_{exo}$), 2.38 (2 H, m, H^1, H^7), and 7.50 (1 H, dd, H^4). These signals correlate well with those previously reported[14] for **6** generated from 3 in CF_3CO_2H (δ 1.36, 1.74, 2.24, and 7.46); signals for protons H^2, H^3, H^5, and H^6 were obscured by those of the second major component of the reaction. The resonances due to **6** slowly disappeared from the ^{1}H NMR spectrum of the mixture, possibly as isomerization occurred to the ring-opened complex **7**; weak signals similar to those reported[14] for **7** were observed but could not be assigned unambiguously.



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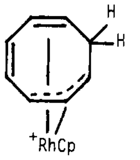

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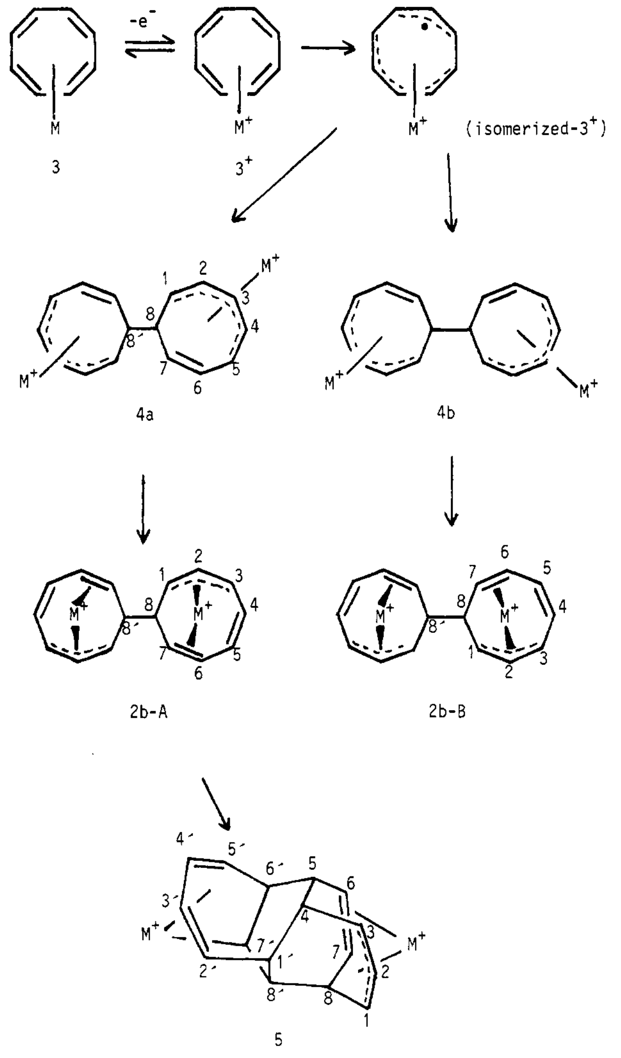
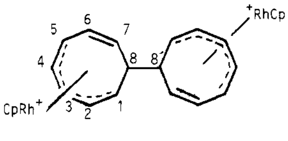
Scheme I



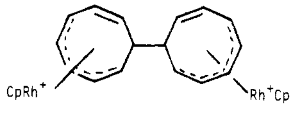
ᵃM = RhCp.

Pure yellow crystals of the second major component could be isolated after the mixture had been dissolved in acetone at room temperature for 24 h. However, this complex, 4, was better prepared by reacting 3 with rigorously dried [$FeCp_2$]$^+$ in CH_2Cl_2 at 273 K; after 2 h the product had formed in near quantitative yield as a yellow crystalline precipitate.

The ^{1}H NMR spectrum of 4 (Table I) can be fully assigned to a mixture of two diastereoisomeric dimers (**4a**,**b**;



4a



4b

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Table I. ^1H and ^{13}C NMR Spectroscopic Data[a]

complex	^1H $(\delta)^b$	^{13}C (ppm)^c
$[(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})Rh_2Cp_2]^{2+}$ (**4**)	3.51 (1 H, m br, H^8), 3.55 (1 H, m br, H^{8*}), 4.59 [1 H, dd, $J(H^{7*}H^{6*}) = 5$, $J(H^{7*}H^{8*}) = 2$, H^{7*}], 5.12 (4 H, m, H^1, H^{1*}, H^5, H^{5*}), 5.52 (3 H, m, H^6, H^{6*}, H^7), 5.75 [4H, m, $J(H^2H^1) = 9$, $J(H^4H^5) = 9$, H^2, H^{2*}, H^4, H^{4*}], 5.98 [5 H, d, $J(RhH) = 1$, $C_5H_5{}^*$], 6.00 [5 H, d, $J(RhH) = 1$, C_5H_5], 6.99 [1 H, dd, $J(H^3H^2) = 7$, $J(H^3H^4) = 7$, H^3], 7.12 [1 H, dd, $J(H^3H^{2*}) = 7$, $J(H^{3*}H^{4*}) = 7$, H^{3*}]	
$[(\eta^2,\eta^3{:}\eta'^2,\eta'^3\text{-}C_{16}H_{16})Rh_2Cp_2]^{2+}$ (**2b**)	3.68 (1 H, m, H^8), 4.04 (3 H, m, H^7, H^{7*}, H^{8*}), 4.86 [2 H, m, $J(H^2H^1) = 8$, $J(H^{2*}H^{1*}) = 8$, $J(H^{2*}H^{1*}) = 8$, H^2, H^{2*}], 5.13 [1 H, dd, $J(H^{1*}H^{2*}) = 8$, $J(H^{1*}H^{8*}) = 8$, H^{1*}], 5.31 [1 H, dd, $J(H^1H^2) = 8$, $J(H^1H^8) = 8$, H^1], 5.52 (2 H, m, H^5,H^{5*}), 5.70 [1 H, d br, $J(H^6H^7) = 8$, H^6], 5.87 [10 H, d, $J(RhH) = 1$, C_5H_5, $C_5H_5{}^*$], 5.8–6.1 [5 H, m, H^3, H^{3*}, H^4, H^{4*}, H^{6*}]	41.7 (C^8), 49.4 [d, $J(C^7Rh) = 6$, C^7], 54.7 [d, $J(C^1Rh) = 4.5$, C^1], 80.8 [d, $J(C^3Rh) = 10$, C^3], 87.3 [d, $J(C^2Rh) = 6$, C^2], 92.2 [d, $J(C_5H_5Rh) = 4.5$, C_5H_5], 92.6 [d, $J(C^6Rh) = 9$, C^6], 133.7, 134.0 (C^4, C^5)
$[(\eta^2,\eta^3{:}\sigma',\eta'^4\text{-}C_{16}H_{16})Rh_2Cp_2]^{2+}$ (**5**)	2.50 [2 H, m, $J(H^{1'}H^4) = 9$, $H^{1'}$,H^4], 2.86 [1 H, dd br, $J(H^5H^{6'}) = 0.5$, $J(H^5H^4) = 10$, $J(H^5H^6) = 6.5$, H^5], 3.24 [1 H, m, $J(H^{8'}H^{7'}) = 3$, $J(H^{8'}H^8) = 8$, $H^{8'}$], 3.29 [1 H, m, $J(H^{6'}H^{5'}) = 9$, $J(H^{6'}H^{7'}) = 10$, $J(H^{6'}H^5) = 0.5$, $H^{6'}$], 3.44 [1 H, m, $J(H^{7'}H^{6'}) = 10$, $J(H^{7'}H^{8'}) = 3$, $J(H^{7'}H^{1'}) = 4$, $J(H^{7'}Rh) = 3$, H^6], 3.44 [1 H, m, $J(H^{7'}H^{6'}) = 10$, $J(H^{7'}H^{8'}) = 3$, $J(H^{7'}H^{1'}) = 4$, $J(H^{7'}Rh) = 3$, $H^{7'}$], 3.62 [1 H, td, $J(H^7H^6) = 7$, $J(H^7H^8) = 8$, $J(H^7Rh) = 1$, H^7], 3.76 [1 H, q br, $J(H^8H^{8'}) = 8$, $J(H^8H^7) = 8$, $J(H^8H^1) = 8$, H^8], 4.58 [1 H, t, $J(H^{5'}H^{6'}) = 9$, $J(H^{5'}H^{4'}) = 8$, H^5], 4.80 [1 H, td, $J(H^2H^1) = 7$, $J(H_2H^3) = 6$, $J(H_2Rh) = 1.5$, H^2], 5.10 [1 H, tt, $J(H^1H^8) = 7.5$, $J(H^1H^2) = 7$, $J(H^1H^3) = 1$, $J(H^1Rh) = 1$, H^1], 5.49 [1 H, t br, $J(H^6H^5) = 6.5$, $J(H^6H^7) = 7$, H^6], 5.87–6.22 [4 H, m, $J(H^{2'}H^{3'}) = 8$, $J(H^{3'}H^{4'}) = 8$, $J(H^{2'}Rh) = 1.5$, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^3], 5.82 [5 H, d, $J(C_5H_5Rh) = 0.7$, C_5H_5], 5.95 [5 H, d, $J(C_5H_5Rh) = 0.7$, C_5H_5]	4.42 [d, $J(CRh) = 14$], 47.8, 54.5 [d, $J(CRh) = 4$], 54.9 [d, $J(CRh) = 4$], 57.5, 81.4 [d, $J(CRh) = 4$], 91.6 [d, $J(CRh) = 5$, C_5H_5], 93.6 [d, $J(CRh) = 5$], 93.9, 94.2 [d, $J(CRh) = 5$, C_5H_5], 104.6 [d, $J(CRh) = 5$]^d

[a] Complex numbering is as in Scheme I. J values in Hz. [b] 200-MHz spectra, in CD_3NO_2. The asterisk (*) refers to the less abundant diastereoisomer. [c] 50-MHz spectra, in CD_3NO_2 unless otherwise stated. [d] In CD_3CN.

see also Scheme I) with η^5-dienyl-bonded C_8 rings. The assignment of two diastereoisomers is based on the observation of pairs of signals throughout the spectrum, corresponding to analogous protons on each isomer. These are in an approximate 6:5 ratio in each case, although the assignment of a set of signals to a particular diastereomer was not possible. The diastereomerism arises from the asymmetric bonding of the two rhodium fragments to the rings, creating two chiral centers at C(8) and C(8′). Once formed, complex **4** slowly isomerizes further in CH_3CN or CH_3NO_2 as described below. However, if the initial reaction between **3** and $AgPF_6$ is carried out in acetonitrile, little or no **4** is formed. Instead, the reaction mixture is red, and $[(\eta^5{:}\eta'^5\text{-}C_8H_8)Rh_2Cp_2][PF_6]_2$ (**8**) is isolable in low yield as a red solid; this species has previously been prepared by the oxidation of the pseudo-triple-decker species $[(\eta^4{:}\eta'^4\text{-}C_8H_8)Rh_2Cp_2]$.[15]

When complex **4** is dissolved in CD_3NO_2, the ^1H NMR spectrum changes as slow thermal isomerization occurs.[16] At room temperature, the first new species shows one cyclopentadienyl resonance and is the symmetric dimer **2b** (see below); after 6 weeks the final product shows two cyclopentadienyl signals and has the asymmetric bimetallic structure **5**. Each of these two species has been isolated substantially free of any other isomer and has been fully characterized.

Complex **2b** was readily prepared from the original mixture of **4** and **6** by heating under reflux in acetone for 4 h, to give a yellow precipitate, or by allowing yellow plates to crystallize from the acetone solution at room temperature over 3 days.

The ^1H and ^{13}C NMR spectra of **2b** are identical with those of the crystals formed by anodic oxidation of **3** in CH_2Cl_2 (see below). Note however that **2b** was isolated from the electrolysis instead of **4** only because of the time scale of the experiment; there is no fundamental difference between the chemical and electrochemical oxidation reactions.

A comparison of the ^1H and ^{13}C NMR spectra of **2b** with those of $[(\eta^2,\eta^3{:}\eta'^2,\eta'^3\text{-}C_{16}H_{16})Ru_2(CO)_4(PPh_3)_2]^{2+}$, the bis(triphenylphosphine) derivative of **2a**, together with ^1H-$\{^1H\}$-decoupling experiments, shows that the former has the structure shown in Scheme I. The ^1H NMR spectrum again revealed the presence of two diastereomers of **2b**, with the protons closest to the chiral centers [C(8) and C(8′)] showing the greatest shift differences between the two [e.g., H^1 (δ 5.31) and H^{1*} (δ 5.13); H^8 (δ 3.68) and H^{8*} (δ 4.04); the asterisk refers to atoms of the second diastereoisomer]. Analogous protons distant from C(8) and C(8′) have indistinguishable shifts. For example, the C_5H_5 hydrogens give rise to a single 10 H doublet at δ 5.87 [$J(RhH) = 1$ Hz].

The initial spectrum of **26** shows an approximate ratio of 3:1 for the diastereomers, but with time the minor component disappears. Since the final isomerization product **5**, described below, can only form from **2b-A** (see

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[15] Edwin, J.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 3052.

[16] It is a feature of the NMR spectra of all the dinuclear complexes reported herein that one isomer is never entirely free of the next until the final step in the sequence (formation of **5**) is complete. It should be noted, however, that the spectra given in Table I are those of samples which were substantially isomerically pure.

Table III. Selected Torsion Angles (deg)[a]

C(8)–C(1)–C(2)–C(3)	−22.7 (18)	C(2)–C(1)–C(8)–C(7)	86.9 (15)
C(2)–C(1)–C(8)–C(8′)	−47.6 (19)	C(1)–C(2)–C(3)–C(4)	41.8 (17)
C(2)–C(3)–C(4)–C(5)	−96.6 (14)	C(2)–C(3)–C(4)–C(1′)	26.6 (12)
C(3)–C(4)–C(5)–C(6)	30.2 (16)	C(3)–C(4)–C(5)–C(6′)	150.5 (12)
C(1′)–C(4)–C(5)–C(6)	−89.1 (15)	C(1′)–C(4)–C(5)–C(6′)	31.2 (17)
C(3)–C(4)–C(1′)–C(2′)	145.2 (9)	C(3)–C(4)–C(1′)–C(8′)	−94.2 (11)
C(5)–C(4)–C(1′)–C(2′)	−93.4 (13)	C(5)–C(4)–C(1′)–C(8′)	27.2 (17)
C(4)–C(5)–C(6)–C(7)	−53.9 (16)	C(6′)–C(5)–C(6)–C(7)	−64.2 (14)
C(4)–C(5)–C(6′)–C(5′)	75.2 (15)	C(4)–C(5)–C(6′)–C(7′)	−53.9 (16)
C(6)–C(5)–C(6′)–C(5′)	−159.4 (11)	C(6)C(5)–C(6′)–C(7′)	71.6 (12)
C(5)–C(6)–C(7)–C(8)	−14.5 (19)	C(6)–C(7)–C(8)–C(1)	−95.9 (15)
C(6)–C(7)–C(8)–C(8′)	38.9 (18)	C(1)–C(8)–C(8′)–C(1′)	33.0 (18)
C(1)–C(8)–C(8′)–C(7′)	153.5 (13)	C(7)–C(8)–C(8′)–C(1′)	89.8 (14)
C(7)–C(8)–C(8′)–C(7′)	30.7 (18)	C(4)–C(1′)–C(2′)–C(3′)	11.7 (16)
C(8′)–C(1′)–C(2′)–C(3′)	−110.7 (14)	C(4)–C(1′)–C(8′)–C(8)	53.2 (14)
C(4)–C(1′)–C(8′)–C(7′)	−71.5 (13)	C(2′)–C(1′)–C(8′)–C(8)	179.1 (11)
C(2′)–C(1′)–C(8′)–C(7′)	54.4 (12)	C(1′)–C(2′)–C(3′)–C(4′)	53.2 (20)
C(2′)–C(3′)–C(4′)–C(5′)	2.2 (23)	C(3′)–C(4′)–C(5′)–C(6′)	−33.0 (22)
C(4′)–C(5′)–C(6′)–C(5)	−54.0 (19)	C(4′)–C(5′)–C(6′)–C(7′)	80.2 (17)
C(5)–C(6′)–C(7′)–C(8′)	12.2 (15)	C(5′)–C(6′)–C(7′)–C(8′)	−124.8 (11)
C(6′)–C(7′)–C(8′)–C(8)	−72.6 (14)	C(6′)–C(7′)–C(8′)–C(1′)	49.8 (12)

[a] Estimated standard deviations in the least significant digit in parentheses, here and throughout this paper.

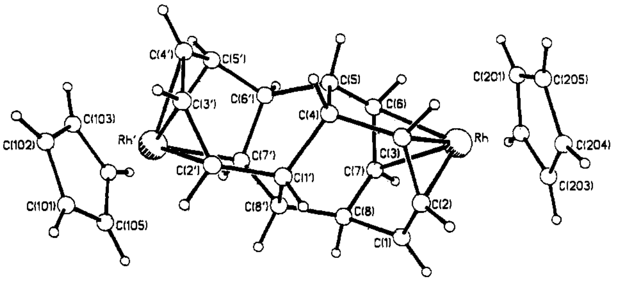


Figure 1. Molecular structure of the dication of **5**, $[(C_{16}H_{16})Rh_2Cp_2]^{2+}$, showing the atom-labeling scheme.

Scheme I), we assume that **2b-B** is slowly converted to **2b-A**.

The final species in the thermal isomerization sequence is easily prepared by heating a concentrated solution of **2b** or **4** in CH_3NO_2 or CH_3CN to 60 °C for 24 h; addition of diethyl ether gave **5** as an air-stable solid.

The ^1H and ^{13}C NMR spectra of **5** (Table I) are complex, each showing two C_5H_5 resonances and 16 other C or H signals consistent with a totally asymmetric structure. The ^1H NMR spectrum was only assigned after the molecular structure of **5** had been determined by X-ray crystallography and then only with the aid of $^1H\{^1H\}$ decoupling of both the 200- and 270-MHz spectra.

B. Identification of 5 by X-ray Crystallography. X-ray diffraction data were collected from crystals of the bis(hexafluorophosphate) salt of **5**, but the structure proved to be disordered. Thus, the bis(tetraphenylborate) complex was prepared by metathesis with $[n\text{-}Bu_4N][BPh_4]$ in acetonitrile, and yellow cubes were crystallized from hot DMSO.

The X-ray diffraction study, full details of which are given in the Experimental Section, revealed the structure of the dication of **5** to be as shown in Figure 1; the atom labeling scheme for the carbon atoms is given in that figure and the attached hydrogen atoms (labels omitted for clarity) are numbered accordingly. Selected bond lengths and angles are given in Table II (supplementary material) and important torsion angles are listed in Table III.

The crystal structure consists of isolated dications $[(C_{16}H_{16})Rh_2Cp_2]^{2+}$ and $[BPh_4]^-$ anions. The rhodium atoms of the dication bridged by the $C_{16}H_{16}$ ligand are well-separated [Rh···Rh′ = 6.514 (2) Å]. Each rhodium carries an η^5-bound cyclopentadienyl ligand. The $C_{16}H_{16}$ ligand bonds to Rh by η^2 and η^3 interactions [C(6), C(7) and C(1),C(2),C(3), respectively] and to Rh′ by σ- and η^4-interactions [C(7′), and C(2′),C(3′),C(4′),C(5′), respectively]. The tetracyclic sttructure of the $C_{16}H_{16}$ ligand in **5** illustrated in Figure 2 is formally derived from that of the $C_{16}H_{16}$ ligand in **2b-A** (see Scheme I) by addition of the free alkene function [C(4)–C(5)] in a 1,4 fashion to the second ring [i.e., at C(1′) and C(6′)]. The additional C–C bonds formed are therefore C(4)–C(1′) and C(5)–C(6′). The ring system contains one six-membered ring [C(1′),C(4),C(5),C(6′),C(7′),C(8′)], three seven-membered rings [C(5),C(6),C(7),C(8),C(8′),C(7′),C(6′); C(5),C(6),C(7),C(8),C(8′),C(1′),C(4); and C(1),C(2),C(3),C(4),C(1′),C(8′),C(8)], three eight-membered rings [C(1–8); C(1′–8′); and C(1′),C(2′),C(3′),C(4′),C(5′),C(6′),C(5),C(4)], as well as larger rings. The largest ring is 14-membered (see Figure 2). The $C_{16}H_{16}$ ligand may therefore be regarded as a derivative of tetracyclo[8.3.3.$0^{2,9}$.$0^{4,11}$]hexdecane.

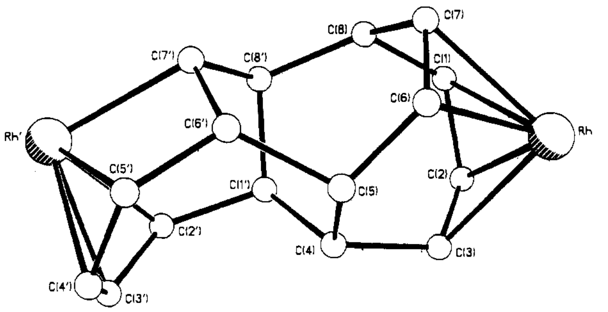


Figure 2. An alternative view of the $C_{16}H_{16}$ core of the dication of **5** with hydrogen atoms omitted for clarity.

As indicated by the torsion angles listed in Table III, the conformation of the six-membered ring is a twisted boat [e.g., C(8′)–C(7′)–C(6′)–C(5) = 12.2 (15)°; C(5)–C(4)–C(1′)–C(8′) = 27.2 (17)°]. The seven-membered rings show conformations loosely describable as tubs with rather approximate mirror symmetry about planes through C(7) and the midpoint of C(6′), C(7′); C(7) and the midpoint of C(1′), C(4); and C(8) and the midpoint of C(3)–C(4), respectively. The complex twistings in these conformations are quantified in Table III. The eight-membered rings derived from the original Cot ligands [C(1–8) and C(1′–8′)] show different conformations, being tublike and twist-chair-like, respectively. The other eight-membered ring has a slightly distorted tub conformation [e.g. C(1′)–C(4)–C(5)–C(6′) = 31.2 (17)°]. The most significant bond angle distortions within the ligand are those at the carbon atoms between the metal bonding sites. Thus at C(8), between the η^2- and η^3-functions, C(1)–C(8)–C(7) equals 95.3 (11)° and at C(6′), between the σ- and η^4-functions, C(5′)–C(6′)–C(7′) equals 104.1(11)°.

C. Electrochemical Oxidation of (η^4-Cot)RhCp. CV scans of **3** in CH_2Cl_2 at a platinum electrode revealed a diffusion-controlled but chemically irreversible oxidation wave with an anodic peak potential of ca. +0.55 V. No reverse cathodic wave for the simple cation radical **3**$^+$ was seen by using maximum CV scan rates of several volts per second. This wave was of approximately the same height as that of decamethylferrocene, which undergoes a one-electron oxidation.

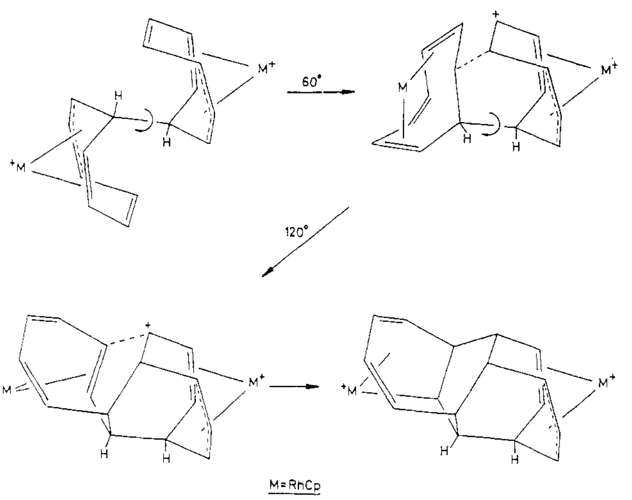
Controlled potential coulometry with E_{app} = +0.8 V confirmed the one-electron oxidation of **3** (n_{app} = 1.03 e). If the concentration of **3** was originally less than 10 mM, the electrolysis produced clear yellow-orange solutions that slowly deposited golden yellow crystals of the dinuclear complex **2b** when kept at 295 K for 48 h. These crystals were originally formulated as a dimeric dication based on their FDMS[1] which showed an intense peak at *m/e* 545.

Since the stable electrolysis products and the chemical oxidation studies detailed above indicated that a dimerization of the radical cation **3**$^+$ had taken place, CV measurements were undertaken to confirm that the reaction following electron transfer (i.e., the reaction of **3**$^+$) was second-order in complex. Surprisingly, it was found that the rate of disappearance of **3**$^+$ is *independent* of the concentration of **3**. This implies that a rapid first-order reaction precedes the dimerization of the radical cation and suggests strongly that **3**$^+$ isomerizes to a new structure prior to the ring-coupling reaction. The mechanistic implications are discussed in more detail below. We concentrate here on details of the electrochemical experiments.

Voltammetry in CH_2Cl_2 is subject to appreciable resistive errors under normal circumstances. To monitor shifts in anodic potentials, E_{p_a}, as a function of CV scan rate, v, we therefore employed an internal standard, decamethylferrocene, which displays Nernstian redox behavior.[17] The E_{p_a} value of **3** was referenced to that of the standard. The concentration of decamethylferrocene was adjusted so that its anodic peak height was equal to that observed for **3** at a particular scan rate and concentration.

With use of a concentration of **3** of 0.35 mM, E_{p_a} (corrected) shifted positive by an average of 29.8 mV per tenfold increase in v in two separate experiments. This is consistent with the oxidation of **3** being a EC mechanism[18] in which a rapid chemical reaction or isomerization follows a one-electron transfer (predicted 30-mV shift). The shape of the anodic wave establishes that the initial heterogeneous electron transfer is rapid (Nernstian), the value of $E_{p_a} - E_{p_a}/2$ being 56 ± 2 (RSD[1]) mV, close to the value of 57 mV predicted for a Nernstian one-electron process.[18] The corrected E_{p_a} was independent of the concentration of **3** (±4 mV, RSD) over the concentration range 0.23–1.36 mM at 10 separate scan rates from v = 0.04 to v = 0.40 V/s. The electrochemical data therefore suggest that the initial charge transfer to form the one-electron oxidized product is rapid (diagnostic: $E_{p_a} - E_{p_{a/2}}$), that the radical cation undergoes a very rapid first-order reaction (diagnostics: E_{p_a} shifts with v but not with concentration of **3**), and that the dimerization of the rearranged **3**$^+$ is still so rapid that no wave for the rearranged **3**$^+$ is seen in CV experiments. The following sequence is consistent with these observations:

Scheme II



$$3 \rightleftarrows 3^+ + e^- \quad \text{fast} \tag{1}$$

$$3^+ \rightarrow \text{isomerized-}3^+ \quad \text{very fast} \tag{2}$$

$$\text{isomerized-}3^+ \rightarrow 4 \quad \text{fast} \tag{3}$$

$$4 \rightarrow 2 \quad \text{slow} \tag{4}$$

D. Mechanistic Considerations. (i) Dimerization of the Radical Cation. Voltammetric data are consistent with release of one electron from **3** to give a transient radical, **3**$^+$, which rapidly isomerizes before dimerization. Given the fact that the initially detected dimer **4** contains two η^5-bound Cot rings, it is likely that the isomerization of **3**$^+$ is as shown in the first line of Scheme I. The initially formed 17-electron radical **3**$^+$ is proposed to rearrange to a (η^5-C_8H_8)RhCp$^+$ complex which has an 18-electron metal and an allyl-like radical structure in the C_8 ligand. Dimerization would be expected to occur rapidly by coupling of the allyl portions of two such radicals, producing **4**.

(ii) Isomerization Reactions of 4 and 2. The formation of the diastereomers **4a** and **4b** results from the two ways in which the allyl radical can couple, assuming that the new C–C bond is always exo with regard to the two RhCp moieties.

The oxidations of (η^4-Cot)M(CO)$_3$ are also likely to proceed in the above manner, though analogues of **4** are not observed; rather, dications **2a** and **1** are the only products isolated and diastereoisomers are not observed. The isomerization of **4** to **2b** most likely occurs via a route similar to that by which (η^5-C_8H_9)RhCp$^+$, the product of protonation[14] of **3**, is converted to (η^2,η^3-C_8H_9)RhCp$^+$; a full discussion of the protonation of coordinated cyclooctatetrene and of the isomerization of the resulting C_8H_9 ligand can be found in ref 19. Thus, it is likely that diastereoisomer **4a** is the precursor to **2b-A** and **4b** is likewise converted to **2b-B**.

The mechanism of the formation of **5** from **2b** might appear complex, but the X-ray structural study on the asymmetric product allows us to provide a reasonable postulate. In this mechanism it is apparent that only **2b-A** can give **5**. The first step in the reaction requires a rotation about the C(8)–C(8′) of **2b-A** (Scheme II) so that C(4), one of the carbon atoms of the uncoordinated double bond of one ring, comes close to C(1′), one of the terminal carbon

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(17) Gennett, T.; Weaver, M. *J. Electroanal. Chem.* **1985**, *186*, 179. Under our conditions, the anodic peak current for decamethylferrocene shifted positive by about 12 mV when v increased from 0.04 to 0.40 V/s.

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

(19) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* 1981, *20*, 2353.

atoms of the coordinated allyl group of the other ring. Electrophilic attack of the latter on the former then generates bond C(4)–C(1′), leaving a residual positive charge on C(5). A second electrophilic attack then occurs, of C(5) on C(5′), one of the coordinated alkenes of the second ring. Once bond C(5)–C(6′) is formed, Rh′ is σ-bonded to C(7′) and η^4-bonded to the butadiene fragment C(2′)–C(5′).

As noted above, this reaction sequence can only occur with diastereoisomer **2b-A**. In this case, the formation of the two C–C bonds, C(4)–C(1′) and C(5)–C(6′), results in two new seven-membered rings, C(1)C(2)C(3)C(4)C(1′)C(8′)C(8) and C(5)C(6)C(7)C(8)C(8′)C(7′)C(6′). A similar sequence beginning with **2b-B** would generate new six- and eight-membered rings in a more strained polycyclic structure. We conclude, therefore, that diastereoisomer **2b-B** (the minor component, shown by ^{1}H NMR spectroscopy) is slowly converted to **2a-A** and then to **5**.

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Registry No. **2b**, 113706-13-1; **3**, 55480-71-2; **4**, 113706-11-9; **5**, 113725-95-4; **6**, 55480-76-7; **8**, 89958-69-0; [Rh(μ-Cl)(η^4-Cot)]$_2$, 12308-49-5; TlCp, 34822-90-7; [#-Bu$_4$N][BPh$_4$], 15522-59-5; [*n*-Bu$_4$N]Br, 1643-19-2; Na[BPh$_4$], 143-66-8; [FeCp$_2$][PF$_6$], 11077-24-0; [(η^2,η^3:σ',η^4–C$_{16}$H$_{16}$)Rh$_2$Cp$_2$][BPh$_4$]$_2$, 113747-48-1.

Supplementary Material Available: Full tables of bond lengths and angles (Table II), atomic coordinates (Table IV), and atomic displacement parameters for compound **5** (9 pages); a listing of structure factors for compound **5** (31 pages). Ordering information is given on any current masthead page.

Cycloaddition Reactions of Tetrafluorodisilacyclobutene with Conjugated Dienes Mediated by Metal Carbonyls. 4. Stereoselective 1,4-Addition and Conformations of 1,4-Disilacycloocta-2,6-dienes

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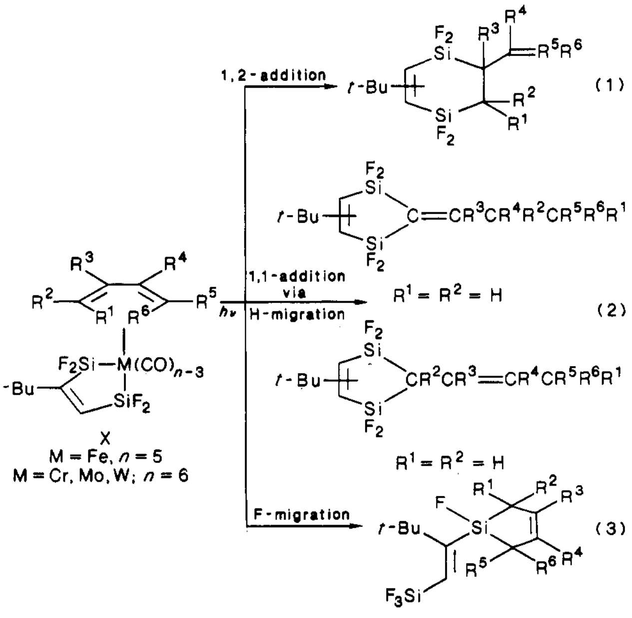
Cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and various conjugated dienes mediated by Ni(CO)$_4$ have been studied. The reactions proceed via a (η^4-diene)disilametallacycle intermediate that decomposes to result in the stereoselective 1,4-addition products, 1,4-disilacycloocta-2,6-dienes. Variable-temperature ^{19}F NMR study of one derivative of the 1,4-disilacycloocta-2,6-dienes (**2i**) shows that it exists in a chair form in solution. Compound **2i** undergoes chair to chair interconversion, with free energy of activation, $\Delta G^\ddagger = 10.5 \pm 0.1$ kcal/mol.

We recently reported in a series of papers the transition-metal carbonyl mediated cycloaddition reactions between disilacyclobutenes and conjugated dienes, carried out under photochemical conditions.[1-5] With use of different metal carbonyls (M = Fe, Cr, Mo, W) and substituted dienes, the reaction intermediate X was shown to proceed via different reaction pathways, eq 1–3.

Since the reaction pathways can be controlled by the geometry of X,[1] the electronic properties of the central metal,[3] and the steric effects of the substituents,[2] a model of "fine-tuning" can be demonstrated. For example, in the reaction of cyclohexadiene, the geometry of the intermediate $\overline{\mathrm{F_2Si}(t\text{-Bu})\mathrm{C{=}CHSiF_2M}}(\eta^4\text{-C}_6\text{H}_8)(\text{CO})_{n-3}$ allows both SiF$_2$ groups to make the initial attack in the case of M = Fe but allows only one SiF$_2$ group to make the initial attack in the case of M = W.[1] Also, under the same reaction conditions, F-migration is the preferred reaction pathway when hard metals are used (i.e., M = Cr), whereas H-migration goes with softer metals such as W and Fe.[1,3]



Interestingly, the most commonly observed reaction pathway, namely, 1,4-addition to the conjugated dienes was not observed in these reactions. The Pd- and Pt-mediated cycloaddition reactions between disilabutenes and conju-

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