Stereoselective Rhodium-Promoted Ring Closure of an η^4-1,3-Pentadienediyl Ligand to an η^4-1,3-Cyclopentadiene, with Subsequent Regiospecific *endo*-H Migration: Molecular Structure of $[Rh(\eta^5\text{-}C_5H_5)((1\text{–}4\text{-}\eta)\text{-}C_5H_3\text{-}1,2,exo\text{-}5\text{-}^tBu_3)]$

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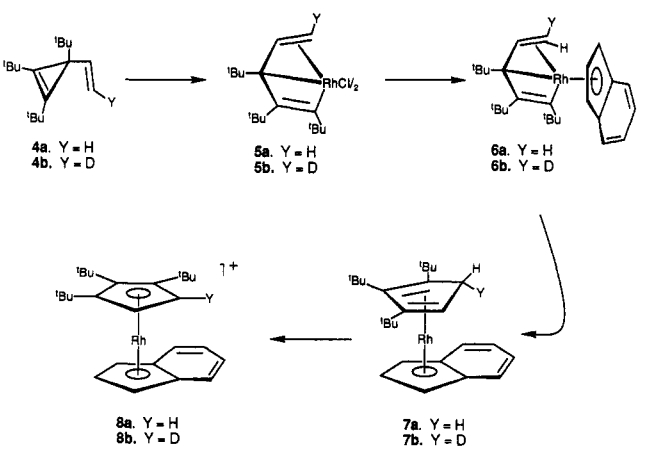
In contrast to its indenyl derivative, which undergoes ring closure to a 1,2,3-tri-*tert*-butylcyclopentadiene complex, dimeric bis[(μ-chloro)((1,3–5-η)-1,2,3-tri-*tert*-butylpentadienediyl)rhodium] (**5a**) undergoes ring closure accompanied by rearrangement to give 1,4,5-tri-*tert*-butylcyclopentadiene dimer **9a** on heating or prolonged standing in solution. Studies using syn-deuterated **5b** have shown that the majority of the deuterium resides in the endo position of **9b**, although some scrambling into both the α- and β-positions was observed. The rearrangement and scrambling can both be explained by a combination of [1,5]-*exo*-hydride shifts around the cyclopentadiene ring and *endo*-hydride migrations to the metal and back to the ring. Similarly, in the presence of ethylene, scrambling of the deuterium into the ethylene occurs and may be explained by hydride migrations between the metal and coordinated ethylene. To verify the structure of **9a**, its cyclopentadienyl derivative **10a** was prepared and subjected to crystallographic study: $C_{22}H_{35}Rh$, triclinic, $P\bar{1}$, a = 8.705(3) Å, b = 9.481(4) Å, c = 13.722(6) Å, α = 71.77(3)°, β = 86.43(3)°, γ = 71.95(3)°, V = 1022.0(7) Å^3, Z = 2.

Introduction

3-Vinyl-1-cyclopropenes are known to undergo thermal and photochemical ring expansion to cyclopentadienes and indenes.[2] Transition metals have also effected this ring expansion both catalytically and stoichiometrically, giving cyclopentadienes, cyclopentadiene complexes, and cyclopentadienyl complexes:[3] on treatment with carbonyl-bearing metal complexes, cyclohexadienones, cyclohexadienone complexes, and phenols have been prepared.[3,4] In several of these closures, pentadienediyl intermediates resulting from ring opening of the vinylcyclopropenes are observed.[3,5,6] These ring-closure reactions, with and without incorporation of CO, are models for the key ring-formation steps in the synthetically useful Dötz reaction, in which metal–carbene ligands are linked with alkynes to give five-membered rings such as **1** or, after CO incorporation, six-membered rings such as **2** (Scheme I).[7] In a proposed mechanism of the Dötz reaction, the ring-closure step to give a cyclopentadiene ring is usually written as proceeding via reductive elimination from the putative metallacyclohexadiene intermediate **3**. We have already provided evidence in the literature that such metallacyclohexadiene species can be synthesized directly from metal-promoted ring-opening reactions of a prefabricated five-carbon vinylcyclopropene precursor[3] but that metallacyclohexadienes may be mechanistic red herrings with respect to the actual ring-closure step.[6]

Specifically, the ring opening of 1,2,3-tri-*tert*-butyl-3-vinyl-1-cyclopropene (**4a**) on reaction with $[Rh(C_2H_4)_2Cl]_2$ was recently shown to give ring-opened dimer **5a**,[5] whose indenyl derivative **6a** underwent ring closure to **7a**.[6] The analogous reaction sequence involving selectively



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(2) (a) Padwa, A. *Org. Photochem.* **1979**, *4*, 261–326 and references therein. (b) Breslow, R. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley: New York, 1963; Part 1, p 236. (c) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (d) Zimmerman, H. E.; Kreil, K. J. *J. Org. Chem.* **1982**, *47*, 2060–2075. (e) Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539–2551.

(3) (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694–1695. (b) Egan, J. W.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578–1581. (c) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015–1019.

(4) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 4397–4399. Cho, S. H.; Liebeskind, L. S. *J. Org. Chem.* **1987**, *52*, 2631–2634.

(5) Donovan, B. T.; Egan, J. W., Jr.; Hughes, R. P.; Spara, P. P.; Trujillo, H. A.; Rheingold, A. L. *Isr. J. Chem.* **1990**, *30*, 351–360.

(6) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7076–7077.

(7) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608. For a recent detailed mechanistic discussion, see: Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293–9319.

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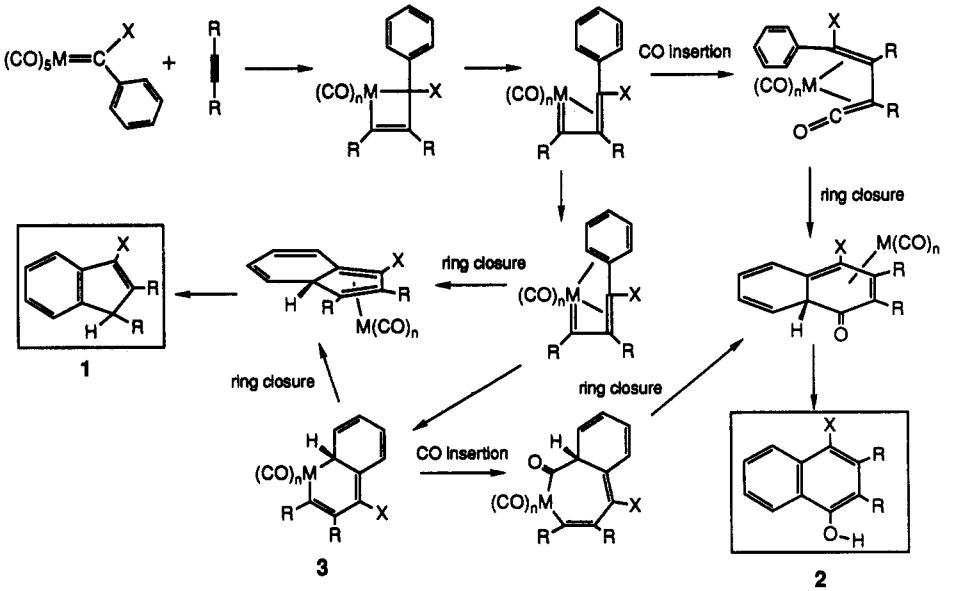
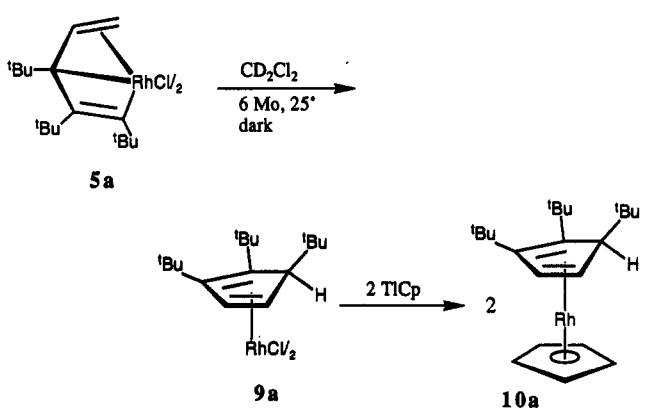
Scheme I



deuterated compounds **4b** → **5b** → **6b** → **7b** demonstrated the stereochemistry of both the ring-opening and -closure reactions and eliminated the possibility of an intermediate metallacyclohexadiene species, in which a plane of symmetry would bisect the vinylic CHD group and scramble the isotopic label.[5,6] A ring-closure mechanism consistent with the observed stereochemistry invokes a direct coupling of the vinyl and allyl termini of the dienediyl ligand in **6**.[6] Ring-closed product **7a** was shown to undergo facile oxidation to sterically congested 1,2,3-tri-*tert*-butylrhodocenium cation **8a**; the corresponding reactions of labeled **7b** showed this reaction to involve a net stereoselective *exo*-hydride abstraction.[8] In this paper we report the ring closure and subsequent rearrangement of the dimeric parent compounds **5**.

Results and Discussion

Unlike its indenyl derivative **6a**,[6] dimeric **5a** survived chromatography unchanged. On prolonged standing in methylene chloride for several months, however, **5a** underwent reactions to give **9a**, whose ^{1}H NMR spectrum showed rather broad featureless peaks. The long reaction



time is necessary, as heating leads to partial decomposition (see below). Conversion of **9a** to its mononuclear cyclopentadienyl derivative **10a** resulted in a product exhibiting much sharper ^{1}H NMR peaks. The NMR spectrum of **9a**

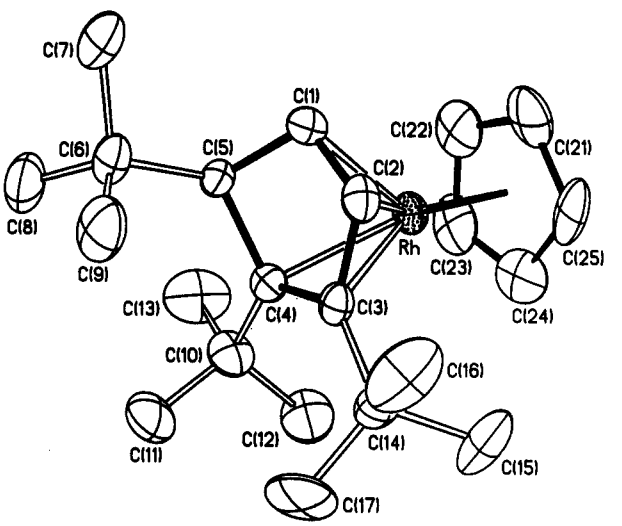


Figure 1. ORTEP representation of **10a**.

and **10a** indicated that the ring-closure product did not contain the AB quartet pattern expected for the exo- and endo-geminal protons of the methylene group in a cyclopentadiene ligand analogous to that observed in **7**. Instead, three *tert*-butyl resonances were observed, together with three weakly coupled resonances for the three ring protons. The poorly resolved peaks observed in the NMR spectrum of the chloride-bridged dimer **9a** may be due to the fact that the resultant cyclopentadiene ligand is asymmetric, leading to the possibility of slightly different chemical shifts due to *RR*/*SS* and *RS*/*SR* diastereomers in solutions of **9a**. Conversion to the mononuclear complex **10a** removes this possibility and affords sharp, well-resolved spectra.

The identity of the rearranged product was unambiguously defined by a single-crystal X-ray diffraction study of the cyclopentadienyl derivative **10a**. An ORTEP representation of the structure is given in Figure 1; crystallographic and data collection parameters are listed in Table I and atomic coordinates, in Table II. Bond lengths and angles for the tri-*tert*-butylcyclopentadiene portion of the compound are depicted in Figure 2; a complete listing is available as supplementary material. The structure shows that the complex contains an η^4-cyclopentadiene ligand, with the three *tert*-butyl groups

(8) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1992**, *11*, 64–69.

Table I. Crystallographic Data for $C_{22}H_{35}Rh$ (10a)

(a) Crystal Parameters

formula	$C_{22}H_{35}Rh$	γ, deg	71.95(3)
fw	402.41	V, Å^3	1022.0(7)
cryst syst	triclinic	Z	2
space group	$P\bar{1}$	cryst dimens, mm	0.28 × 0.32 × 0.41
a, Å	8.705(3)	cryst color	yellow
b, Å	9.481(4)	D(calc), g cm^3	1.308
c, Å	13.722(6)	μ(Mo Kα), cm^{-1}	8.06
α, deg	71.77(3)	temp, K	296
β, deg	86.43(3)		

(b) Data Collection

diffractometer	Nicolet R3m
monochromator	graphite
radiation	Mo Kα (λ = 0.710 73 Å)
2θ scan range, deg	4–60
data collected (hkl)	±13, ±14, ±20
no. of rflns collected	5992
no. of indpt rflns	5655
no. of indpt obs rflns $F_o \geq n\sigma(F_o)$	4493 (n = 4)
std rflns	3 std/197 rflns
var in stds, %	12

(c) Refinement

$R(F)$, %	5.06	$\Delta(\rho)$, e Å^{-3}	1.18
$R(wF)$, %	5.93	N_o/N_v	16.4
Δ/σ (max)	0.13	GOF	1.274

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_{22}H_{35}Rh$ (10a)

	x	y	z	U^a
Rh	1335.4(4)	2101.7(4)	3306.0(3)	43.3(1)
C(1)	3417(6)	236(5)	3930(3)	46(2)
C(2)	3813(5)	1511(5)	3236(4)	43(2)
C(3)	3165(4)	1768(4)	2236(3)	37(1)
C(4)	2380(4)	561(5)	2392(3)	36(1)
C(5)	3205(5)	−790(4)	3358(3)	39(1)
C(6)	4805(6)	−2172(5)	3340(4)	54(2)
C(7)	5589(8)	−2908(7)	4406(5)	84(3)
C(8)	4399(9)	−3471(7)	3061(6)	81(3)
C(9)	6017(7)	−1568(7)	2597(5)	75(3)
C(10)	1306(6)	329(7)	1623(4)	58(2)
C(11)	2244(9)	−336(8)	847(5)	79(3)
C(12)	22(8)	1842(8)	1053(5)	85(3)
C(13)	368(9)	−780(10)	2222(6)	96(4)
C(14)	3560(6)	3004(6)	1297(4)	53(2)
C(15)	2318(15)	4640(12)	1079(11)	89(5)
C(16)	5176(14)	3223(16)	1610(11)	95(6)
C(17)	3877(20)	2544(17)	357(8)	116(8)
C(15′)	3599(54)	4346(30)	1664(26)	244(20)
C(16′)	5231(25)	2286(25)	928(16)	122(10)
C(17′)	2178(29)	3777(30)	435(18)	135(12)
C(21)	131(15)	3187(17)	4508(10)	83(8)
C(22)	−667	2138	4407	81(8)
C(23)	−1387	2718	3402	79(8)
C(24)	−1035	4126	2882	87(7)
C(25)	−97	4416	3565	85(7)
C(21′)	−140(30)	2607(30)	4623(13)	104(15)
C(22′)	−1162	2351	3972	122(17)
C(23′)	−1307	3504	2999	112(16)
C(24′)	−375	4474	3048	98(12)
C(25′)	346	3920	4052	89(12)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

occupying adjacent positions, two on one of the ligated double bonds, and the third on the saturated ring carbon atom, in a position exo to the rhodium. Comparison with related cyclopentadiene[9] and cyclohexadienyl[10] complexes shows **10a** to have a structure typical of such complexes:[11] the bond lengths to the methylene group (C(1)–C(5) = 1.484(7) Å and C(4)–C(5) = 1.549(5) Å for **10a**) are normal for sp^3–sp^2 C–C bonds (commonly ~1.51 Å),[12] although the intra-ring bond angle at C(5) is significantly less than the ideal 109° 28′ (∠C(3)–C(4)–C(5) = 95.2(3)°). As in

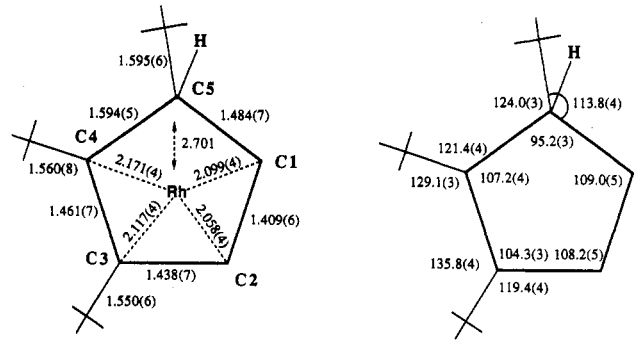


Figure 2. Bond lengths (Å) and angles (deg) for the tri-*tert*-butylcyclopentadiene ligand in **10a**.

related compounds,[9,10] the ligated cyclopentadiene ring atoms C(1)–C(4) are coplanar (±0.002 Å) while C(5) lies 0.614 Å above the C_1–C_4 plane and 2.701 Å from the rhodium. The C(1)–C(4) plane forms an 8.9° dihedral angle with the plane of the C_5H_5 ligand and a 52.3° dihedral angle with the C(1)–C(5)–C(4) plane. This fold angle is more akin to the angles found in cyclohexadienyl ligands (42–50°)[10] than to those of cyclopentadiene ligands (26–36°);[9] the greater puckering is undoubtedly due to the steric bulk of the *tert*-butyl groups. Also typical of cyclopentadiene and cyclohexadienyl compounds, the Rh–(Cp centroid) distance (1.917 Å) is slightly greater than the Rh–(diene centroid) distance (1.748 Å). The steric butterssing of the adjacent *tert*-butyl groups is evident in the structure: as in rhodocenium cation **8a**,[8] the bonds between the *tert*-butyl-bearing ring carbons (C(3), C(4), C(5)) are elongated whereas the remaining ring bonds are compressed. Similarly, the *tert*-butyl groups splay apart, as evidenced by the exocyclic bond angles at C(3), C(4), and C(5) (Figure 2).

When the ring-closure reaction was repeated with selectively deuterated **5b**, roughly 80% of the deuterium was found in the endo position of the product, **9b**. Substantial scrambling into the α- and β-positions, however, had also occurred during the 6-month course of the reaction, as evidenced by ^{2}H NMR. Traces of an uncharacterized side product, possibly a cyclopentadienyl complex arising from oxidation of **5b**, appeared early in the reaction[13] but remained unchanged over its course. In a separate experiment, the rearranged product, **9a**, was shown to be stable for several months in chloroform, a solvent more oxidizing than methylene chloride. This stands in contrast to cyclopentadiene complexes containing

(9) Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1989**, *28*, 2837–2845. Bruce, M. I.; Humphrey, P. A.; Walton, J. K.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1987**, *333*, 393–401. Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222–7227. Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951–953. See also ref 15a and: O'Connor, J. M.; Pu, L.; Rheingold, A. L.; Uhrhammer, R.; Johnson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1889–1891.

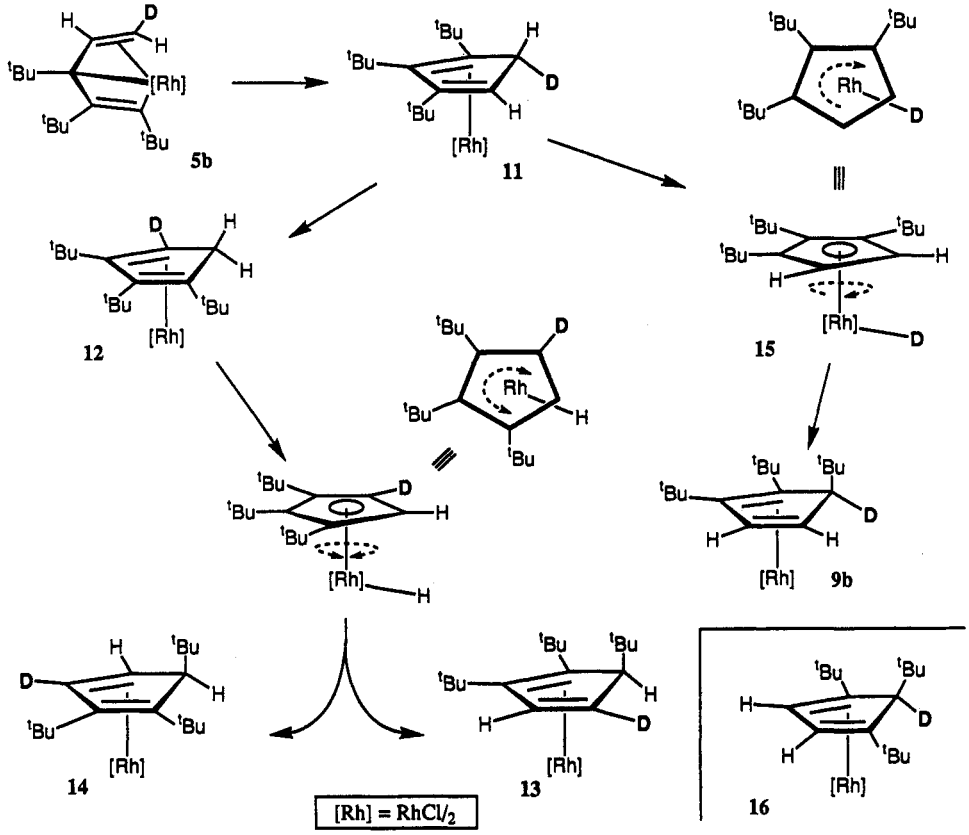
(10) Bruce, M. I.; Catlow, M. P.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1990**, *397*, 187–202. Bailey, N. A.; Blunt, E. H.; Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1980**, 829–836. Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950–1955. Bird, P. H.; Churchill, M. R. *J. Chem. Soc., Chem. Commun.* **1967**, 777–778.

(11) Bond distances and angles not included in Figure 2, the supplementary material, or the literature were calculated using the CHEMX suite of programs (Chemical Design, Ltd., Oxford, U.K.).

(12) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 108.

(13) Similar oxidations to give cyclopentadienyl compounds were observed when deuteriochloroform solutions of cyclopentadiene complexes **7a**[8] and [Rh(C$_5$Me$_5$)(*endo*-C$_5$Me$_5$H)][14] stood for several days.

Scheme II



H in the exo position of the methylene group, in which oxidation of the *exo*-H by $CHCl_3$ is known to be facile.[8,14]

A possible mechanism to explain the formation of these rearrangement products involves both hydride shifts to the metal and [1,5]-sigmatropic shifts on the cyclopentadienyl ring (Scheme II). Initial ring closure by intraligand migratory insertion, with the identical stereochemistry already described for the conversion of indenyl compounds **6** → **7**,[6] would give intermediate **11**, in which all three of the *tert*-butyl groups are held in the plane of the sp^2 carbons and the deuterium is in the endo position. In the indenyl system, complexes **7** are coordinatively saturated, and no further reaction occurs. However, intermediate **11** is a 16-electron species, capable of activating the endo deuteron. Deuterium migration first to the metal and then to a carbon bearing a *tert*-butyl group would form the observed major product, **9b**. Similar hydride migration in a cyclopentadiene complex have been noted by Green.[15] The scrambling of the deuterium into the α- and β-positions may be explained by postulating a [1,5]-sigmatropic hydrogen shift on the exo face of the ring,[16] giving **12**. With the deuterium now in the olefinic position, the metal-based hydride transfers would lead to the two vinylically deuterated products as shown. Rotation of the cyclopentadienyl ring in one sense during the course of the hydride transfer would give α-deuterated product **13**; rotation in the opposite sense would give β-deuterated product **14**.

The driving force for this rearrangement most likely comes from relief of the steric strain. In the rearranged product **9**, the *tert*-butyl groups are considerably more able to bend out of each other's way than they are in either in initial ring-closed product **11** or the required intermediate cyclopentadienyl hydrido species **15**; in these latter cases, they are held nearly coplanar. However, this reasoning predicts the symmetric compound, **16**, to be the thermodynamic product of these rearrangements: with its central *tert*-butyl group riding the crest of the sp^3 carbon, **16** should exhibit even less steric buttressing among its side groups. Compound **16** is not observed, however. Presumably the great relief of steric strain in the **15** → **9b** hydride transfer greatly increases the energy barrier for the transfer back to the metal, by the Hammond postulate.[17] Thus, hydride transfer from Rh to the ring must be sufficiently rapid to occur before the bulky cyclopentadienyl ligand in **15** is able to rotate sufficiently to form the symmetric compound, **16**. Once **9b** forms, cyclopentadienyl intermediate **15** would become energetically inaccessible, precluding eventual conversion to the most thermodynamically stable product, **16**.

The long reaction times required for conversion of **5** to **9** under ambient conditions led to attempts to accelerate the rate by heating. When it was heated in benzene or toluene, **5a** gave a product mixture containing primarily **9a**, the same product formed in the 6-month reaction, but significant decomposition also occurred. Curiously, the thermal reaction gives a significantly cleaner product when

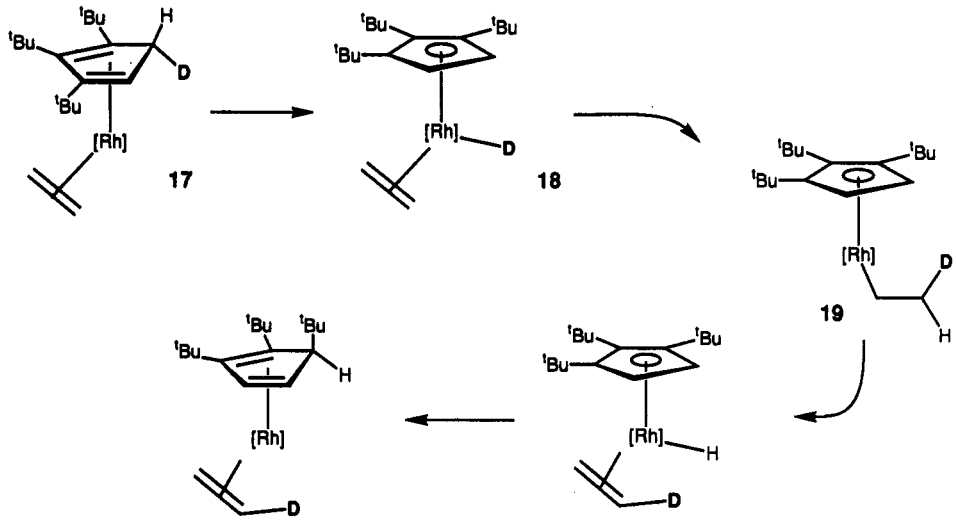
(14) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875–2883.

(15) (a) Feher, F.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 291–293. See also refs 16a and 14 and: Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577–1586. Paneque, M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1989**, 105–106. (b) Williams has concluded that a similar rearrangement, in which an acyl group "migration" takes place from an sp^3 carbon onto an sp^2 carbon occurs by an *inter*molecular proton transfer: Williams, G. M.; Pino, M. J. *Organometallics* **1992**, *11*, 345–349.

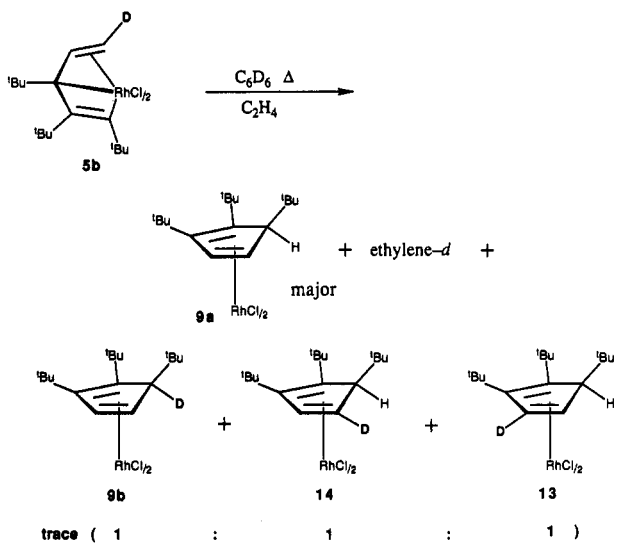
(16) Such shifts have been postulated elsewhere in the literature. See, for example: (a) Cunningham, A. F. Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864–4870. (b) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 5811–5813.

(17) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338. Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 212–214.

Scheme III



performed in the presence of ethylene,[18] although why this is so is not understood. When deuterated **5b** was heated as an NMR sample saturated with ethylene, however, the majority of the deuterium label was lost to the ethylene (Scheme III). What traces of deuterium remained in the complex were found scrambled into all three ring positions, as shown:



The rearrangement mechanism postulated in Scheme II accounts for both this scrambling and the deuterium loss to the ethylene. Migration of deuterium to the metal in intermediate **17** (Scheme III), in which an ethylene is coordinated to the rhodium, would give **18**. The deuteride may now migrate onto the ethylene, to form **19**. Both an isotope effect and a statistical edge favor hydride migration back to the metal over deuteride migration. Once the hydride is on the metal, its migration back to the cyclopentadienyl ligand produces the deuterium-depleted cyclopentadiene. Accordingly, NMR spectra of the ethylene after the reaction showed it to be enriched in deuterium.

(18) Kurosawa has recently reported a coupling reaction on Ni(II) which also is cleaner in the presence of ancillary olefins or acetylenes: Kurosawa, H.; Ohnishi, H.; Emoto, M.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Organometallics* **1990**, *9*, 3038–3042.

As a check on this explanation, the converse experiment was performed. When unlabeled **5a** was heated in the presence of C_2D_4, deuterium washed into the product, to give **9b**. As expected, the majority of the deuterium was found in the endo position. An unidentified impurity peak in the ^2H NMR spectrum obscured the chemical shift region characteristic of deuterium in the β-position, but the spectrum showed conclusively that no deuterium enrichment was present in the α-position. The H/D exchange and the lack of symmetrical product **16** underscore the contrast in rates between the rapid hydride shuttling between the cyclopentadiene ring and the coordinated ethylene by way of the metal and the relatively sluggish rotation of the bulky tri-*tert*-butylcyclopentadienyl ligand. Finally, the ^1H and ^2H NMR spectra of this sample did not change over the course of 4 weeks more at room temperature, confirming that **9b** is formed irreversibly under these conditions and does not rearrange subsequently to give **13** and/or **14**. The irreversible formation of **9** was also confirmed by treating a sample of **9a** with C_2D_4 under the same conditions; washing of deuterium into the cyclopentadiene ring was not observed.

Conclusions

In conclusion, dimeric η^4-pentadienediyl compounds **5** undergo a stereoselective ring closure followed by stereo- and regiospecific rearrangement to give the coordinated cyclopentadiene complexes **9**; relief of steric strain coupled with the availability of a vacant coordination site at rhodium presumably drives this rearrangement. The structure of the product was confirmed by X-ray crystallography of its cyclopentadienyl derivative, **10a**. Ring closure of the deuterated dimer complex **5b**, resulted in partial scrambling of the deuterium, which may be explained by a combination of *endo*-hydride migrations and [1,5]-*exo*-hydride shifts.

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb. Hydrocarbon reaction solvents were distilled under nitrogen from benzophenone ketyl; halo-

genated solvents, from CaH_2, 4-Å molecular sieves, or 10% Na/Pb alloy. Aromatic and unsaturated components of 35–65 °C petroleum ether were removed before distillation by prolonged standing over H_2SO_4 (concentrated) followed by washing with Na_2CO_3 (10% aqueous). ^1H (300 MHz), $^2H\{^1H\}$ (46.1 MHz), and $^{13}C\{^1H\}$ (75.4 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS, referenced to the solvent. Coupling constants are reported in Hz. Elemental analysis was performed by Spang (Eagle Harbor, MI).

Cyclopentadienylthallium was purchased from Aldrich and sublimed before use. Ethylene was purchased from Airco; ethylene-d_4, from Cambridge Isotope Laboratories. Tri-*tert*-butylvinylcyclopropene **4a** and its deuterium-labeled isotopomer **4b**,[5] $[Rh(C_2H_4)_2Cl]_2$,[19] bis[(μ-chloro)((1,3-5-η)-1,2,3-tri-*tert*-butyl-1,3-pentadienediyl)rhodium(III)] (**5a**),[5] and deuterated **5b**[5] were prepared as described in the literature.

Rearranged Dimer 9a and Deuterated Isotopomers. (a) Unlabeled Compound. $[Rh(C_2H_4)_2Cl]_2$ (102 mg, 0.524 mmol of Rh) and tri-*tert*-butylvinylcyclopropene **4a** (167 μL, 0.597 mmol, 1.1 equiv) were dissolved in toluene (10 mL) under nitrogen. The resulting red-orange solution was held at reflux for 1.5 h, during which time it darkened slightly and traces of a fine black precipitate formed. Filtration of the mixture and evaporation gave **9a** as an orange oil which could be purified by elution through Florisil with ether at −40 °C. Subsequent crystallization from CH_2Cl_2/hexanes afforded a 60% yield of **9a** as an orange powder: mp 140 °C dec; ^1H NMR (C_6D_6) δ 4.92 (br, 1H, H_β), 3.53 (br, 1H, H_α), 2.86 (br, 1H, H_{endo}), 1.53 (s, 9H, ^{t}Bu), 1.48 (s, 9H, ^{t}Bu), 0.53 (s, 9H, ^{t}Bu). Anal. Calcd for $[C_{17}H_{30}RhCl]_2$: C, 54.77; H, 8.11. Found: C, 54.60; H, 8.02. The cyclopentadienyl derivative of **9a** was crystallographically characterized. This compound may also be prepared by heating **5a** overnight in ethylene-saturated toluene or as described for the deuterated material below.

(b) Product from Deuterated 5b in the Absence of Ethylene: Deuterium Scrambling. A sealed NMR sample containing **5b** (7.5 mg, 20 μmol of Rh, ~2% α-deuterated material) in CD_2Cl_2 (0.5 mL) and an identical sample in CH_2Cl_2 were allowed to stand for 6 months at 30 °C in the dark. During this period, **5b** converted to **9b** containing ~80% endo deuteration; the isotopomeric complexes **14** and **13** showed ~10% each α- and β-deuteration, respectively. The ^1H NMR spectrum of the product was identical with that of the protic material, with an attenuation of the H_{endo} signal. $^2H\{^1H\}$ NMR (CH_2Cl_2): δ 5.2 (trace, D_β), 3.6 (trace, D_α), 2.9 (1D, D_{endo}). Traces of a complex showing a δ 5.72 resonance by both ^1H and ^2H NMR were detected early in the reaction but remained constant throughout the conversion.

(c) Product from Deuterated 5b in the Presence of Ethylene: Loss of Deuterium. Ethylene was bubbled through a deuteriobenzene (0.7 mL) solution of trans-deuterated dimer **5b** (25 mg) containing traces of the centrally deuterated isotopomer. The NMR sample was then frozen (77 K), evacuated, and sealed. A similar sample in benzene was prepared. These samples were heated for 40 h at 65 °C, until all the starting material had been consumed. The volatiles were removed under vacuum; their ^2H NMR spectra showed that deuterium had been transferred to the ethylene (δ 5.4 s). ^1H NMR spectra of the residue showed the product to be nearly purged of deuterium; the remaining traces were scrambled among the ring positions. Solvent removal afforded **9a** as an orange powder: ^1H NMR, identical with that of the product from the protic reaction above; $^2H\{^1H\}$ NMR (C_6H_6) δ 4.9 (br, D_β), 3.5 (br, D_α), 2.9 (br, D_{endo}).

(d) Product from Unlabeled 5a, under Ethylene-d_4: Incorporation of Deuterium. Ethylene-d_4 (12.5 mL at 25 °C/530 mmHg, 0.39 mmol, 15 equiv, dried by passage through a −78 °C trap) was condensed into an NMR tube (5 mm) containing **5a** (10 mg, 27 μmol of Rh) in C_6D_6 (0.5 mL). A similar sample was prepared using C_6H_6. Both samples were frozen (77 K) and sealed under vacuum. When they were heated at 70 °C (*Caution*! pressure generation), the samples liberated much vinylcyclopropene, which was slowly reconsumed as the conversion to endo-deuterated **9b** proceeded over 60 h. After the volatiles were removed, ^2H NMR showed much deuterium incorporation into the endo position of **9b**. No deuterium incorporation α to the sp^3 carbon was observed; a poor base line made it impossible to discern whether traces had been incorporated into the β-position. ^1H NMR (C_6D_6): δ 4.92 (br, 1H, H_β), 3.53 (br, 1H, H_α), 2.86* (br, H_{endo}), 1.56 (s, 9H, ^{t}Bu), 1.53 (s, 9H, ^{t}Bu), 0.53 (s, 9H, ^{t}Bu). $^2H\{^1H\}$ NMR (C_6H_6): δ 5.0* (v br, D_β), 2.9 (br, D_{endo}). The peaks marked with an asterisk were significantly attenuated by isotopic dilution. When this sample stood for 4 weeks at room temperature, the ^1H and ^2H NMR spectra showed no change, indicating that, once formed, **9b** does not rearrange to **13** and/or **14**. A sample of **9a**, prepared as above, was treated with C_2D_4 under the same conditions and showed no incorporation of deuterium into the cyclopentadiene ring of **9a**, confirming that transfer of the *endo*-H of **9a** to the metal does not occur at any significant rate under these conditions.

Inertness of 9a toward $CDCl_3$ Oxidation. A solution of **9a** (8.8 mg, 24 μmol of Rh) in $CDCl_3$ (0.6 mL) was sealed in an NMR tube under vacuum. After this mixture stood overnight, a small new peak at δ 5.7 appeared in the NMR spectrum due to an unidentified product. After 6 months at 25 °C in ambient light, the δ 5.7 peak did not grow, nor were any other changes observed by NMR.

Cyclopentadienyl Compound 10a. Rearranged dimer **9a** (49 mg, 0.13 mmol) and $[Tl(C_5H_5)]$ (0.04 g, 0.14 mmol, 1 equiv) were stirred in methylene chloride (8 mL) for 40 h at room temperature under nitrogen. The orange mixture was allowed to settle; then, the liquor was filtered and evaporated to give **10a** as a yellow-orange solid (90%): mp 170 °C dec; ^1H NMR ($CDCl_3$) δ 5.16 (d, 5H, J_{RhH} = 0.9, C_5H_5), 4.90 (ddd, 1H, J_{HH} = 3.1, 0.6, J_{RhH} = 1.8, H_β), 3.12 (ddd, 1H, J_{HH} = 3.1, 2.6, J_{RhH} = 1.5, H_α), 2.92 (ddd, 1H, J_{HH} = 2.6, 0.7, J_{RhH} = 0.7, H_{endo}), 1.38 (s, 9H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 0.68 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$): δ 83.55 (dm, J_{CH} = 171, C_5H_5), 74.66 (dd, J_{CH} = 280, J_{RhC} = 11, $C_{\alpha \text{ or } \beta}$), 74.49 (dd, J_{CH} = 174, J_{RhC} = 10.4, $C_{\alpha \text{ or } \beta}$), 68.61 (dd, J_{CH} = 133, J_{RhC} = 4, CH^tBu), 35.14 (qm, J_{CH} = 123, ^{t}Bu), 28.05 (qm, J_{CH} = 125, ^{t}Bu). The remaining resonances could not be unambiguously assigned. A crystal suitable for diffraction was grown from petroleum ether after passage through silica with petroleum ether.

Crystallographic Structure Determination of 10a. A yellow specimen was mounted on a glass fiber and found to belong to the triclinic crystal system. Cell reduction programs failed to find higher symmetry. Azimuthal scans revealed intensity variations of less than 10%. No correction for absorption was applied to the data. A linear decay of ~12% was observed for reflections with 2θ values near 20°, and corrections were applied.

The Rh was obtained from a Patterson map. Rotational disorder occurs in two organic groups: the C_5H_5 ring and the C(14) *tert*-butyl group. Since refinement resulted in statistically identical occupanices (60/40), the positions of the two groups are likely disordered in concert. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed in idealized locations.

All software is contained in the SHELXTL program library (A. Sheldrick, Nicolet Corp., Madison, WI).

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Supplementary Material Available: For complex **10a**, tables of bond lengths (Table 1S), bond angles (Table 2S), anisotropic thermal parameters (Table 3S), and H atom coordinates and isotropic thermal parameters (Table 4S) (5 pages). Ordering information is given on any current masthead page.

(19) Cramer, R. *Inorg. Synth.* **1973**, *15*, 14–16. See also ref 5.

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