The above results suggest the following conclusions: (a) The carboxylate of Asp-99 is able to carry out its function without forming H bonds to Tyr-52 and Tyr-73. (b) The phenolic hydroxyl of neither Tyr-52 nor Tyr-73 is catalytically essential even though they are absolutely conserved in groups I and II PLA2 sequences. (c) The aromatic rings of both residues are required, possibly for structural reasons. (d) If the H-bonding network shown in Figure 1 is really important in interfacial catalysis,[13a,17d] it should not involve Tyr-52 or Tyr-73.

Mechanism of Rhodium-Promoted Conversion of 3-Vinyl-1-cyclopropenes to 1,3-Cyclopentadienes. Stereochemistry of the Carbon–Carbon Bond-Forming Step

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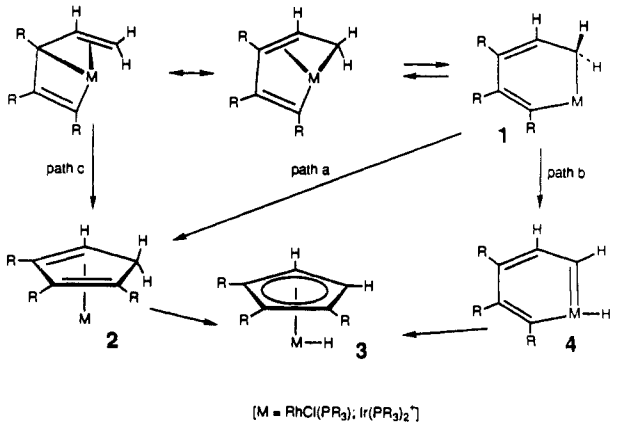
The transition-metal-promoted reactions of cyclopropenes are of great synthetic utility and mechanistic interest.[1] We have demonstrated that 1,2,3-triphenyl-3-vinyl-1-cyclopropene undergoes a facile C–C cleavage reaction promoted by Pt(0), Rh(I), and Ir(I) complexes to give 1,2,3,5-η- or 1,5-η-pentadienediyl (metallacyclohexadiene) complexes of Pt(II),[2] Rh(III),[3] and Ir(III).[3,4] Subsequent ring closure occurs under variable conditions to afford free 1,2,3-triphenyl-1,3-cyclopentadiene,[2] η^4-complexes of this diene,[2] or η^5-cyclopentadienyl(hydrido) complexes presumably derived from the latter.[3,5] It has been suggested that formation of the cyclopentadiene or (cyclopentadienyl)hydrido complexes may occur by either of two mechanisms, in both of which a metallacyclohexadiene intermediate **1** plays a key role (Scheme I).[3,5,6] Reductive elimination and C–C bond formation from **1** (path a) would give a coordinated cyclopentadiene complex **2**; subsequent addition of the *endo*-C–H bond to the metal would yield the (cyclopentadienyl)hydrido complex **3**. Alternatively, α-H elimination from **1** (path b) would afford (metallabenzene)hydrido intermediate **4**, which could then undergo C–C coupling to afford **3**. Here we report that closure to give an η^4-cyclopentadiene ligand can occur stereospecifically from the 1,2,3,5-η-ligand (path c) under conditions where the absence of any metallacyclic intermediates can be demonstrated unambiguously.

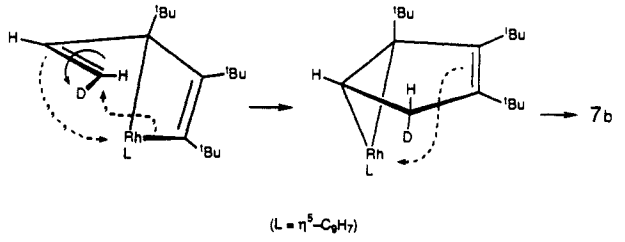
Syntheses of the sterically crowded complex **5a** and its D-labeled isotopomer **5b** have been reported; the half-life for scrambling of D between the syn and anti positions in **5b** is ca. 45 days at 110 °C,[7] indicating a high activation barrier for formation of metallacyclohexadiene **6** from **5**. No ring closures of **5a,b** to give a cyclopentadiene ligand were observed under these conditions.[7]

Scheme I



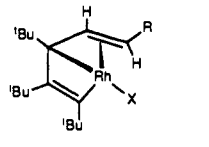
[M = RhCl(PR$_3$); Ir(PR$_3$)$_2^+$]

Scheme II

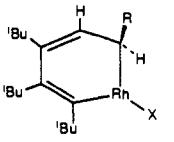


(L = η^5-C$_9$H$_7$)

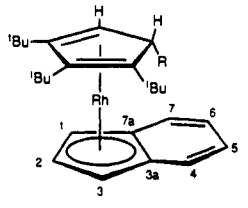
Chart I



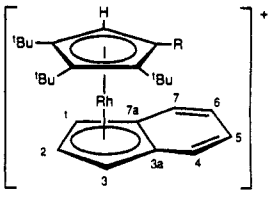
5 a. X = η^5-C$_5$H$_5$; R = H
5 b. X = η^5-C$_5$H$_5$; R = D
5 c. X = η^5-C$_9$H$_7$; R = H
5 d. X = η^5-C$_9$H$_7$; R = D



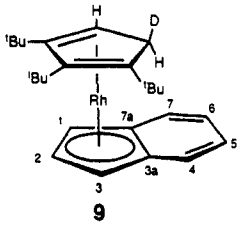
6 (X = η^5-C$_5$H$_5$; R = H, D)



7 a. R = H
7 b. R = D



8 a. R = H
8 b. R = D



9

In contrast, the indenyl analogues **5c,d**[8] undergo ring closure in refluxing benzene to give (at <50% conversion) their cyclopentadiene isomers **7a,b**; **7b** is formed as a single *endo*-D isoto-

(1) For a review of the transition-metal chemistry of cyclopropenes, see: Binger, P.; Büch, H. M. In *Topics in Current Chemistry*; Meijere, A., Ed.; Springer-Verlag: Berlin, GDR, 1987; pp 77–151.

(2) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

(3) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578.

(4) 1,2,3,5-η- and 1,5-η-pentadienediyl complexes of Ir(III) have been made by a different route and can be transformed into (cyclopentadienyl)-hydrido[5] or metallabenzene complexes.[5b,6]

(5) (a) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

(6) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. Y. *J. Am. Chem. Soc.* **1989**, *111*, 4118.

(7) Donovan, B. T.; Egan, J. W. Jr.; Hughes, R. P.; Spara, P. P.; Trujillo, H. A.; Rheingold, A. L. *Isr. J. Chem.* In press.

(8) Prepared from the chloride-bridged dimer[7] and indenylpotassium. **5c**: orange crystals, mp 58–60 °C; ^{1}H NMR ($CDCl_3$) δ 7.17 (m, 2 H, $H_{4,7}$), 6.88 (m, 2 H, $H_{5,6}$), 6.09 (br, 1 H, $H_{1/3}$), 5.96 (br, 1 H, $H_{1/3}$), 5.72 (br, 1 H, H_2), 4.01 (ddd, 1 H, J_{HH} = 10.6, 6.3, J_{RhH} = 2.0, $H_{central}$), 2.77 (dd, 1 H, J_{HH} = 6.6, J_{RhH} = 1.5, H_{syn}), 1.35 (s, 9 H, ^{t}Bu), 1.34 (dd, 1 H, J_{HH} = 10.6, J_{RhH} = 2.2, H_{anti}), 0.94 (s, 9 H, ^{t}Bu), 0.88 (s, 9 H, ^{t}Bu). **5d**: ^{1}H NMR ($CDCl_3$) identical except for δ 4.01 (dd, 1 H, J_{HH} = 10.6, J_{RhH} = 2.0, $H_{central}$), 1.34 (dd, 1 H, J_{HH} = 10.6, J_{RhH} = 2.2, H_{anti}); ^{2}H{^{1}H} NMR ($CHCl_3$) δ 2.77 (s, 1 D, D_{syn}). Satisfactory microanalysis data (C, H) were obtained for all compounds reported here.

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pomer.[9] This transformation can also be accomplished quantitatively by chromatography of **5c,d** on Florisil at -50 °C.[10] The mechanism of the Florisil-promoted closure is unclear, but its stereochemistry is identical with that observed in the thermal closure. Assignment of the *endo*-D configuration to **7b** is supported by spectroscopy and chemical reactivity studies. η^4-Cyclopentadiene complexes of Rh(I) containing *exo*-H atoms have been shown to exhibit an anomalously low C-H stretching frequency (<2850 cm^{-1}) in their IR spectra;[11] this low-frequency band is observed for **7a** and **7b**.[9] Reaction of **7b** with $Ph_3C^+BF_4^-$ affords the rhodicinium cation **8b** in which D is retained;[12] this type of reaction is known to proceed by a net abstraction of the *exo*-H^-.[14-16] Finally, reaction of cation **8a**[12] with BD_4^- affords exclusively the *exo*-D isotopomer **9**,[9] which does not exhibit a low-frequency C-H stretch in its IR spectrum and which reacts with $Ph_3C^+BF_4^-$ to regenerate **8a** with quantitative loss of deuterium.[17]

These data unambiguously define the stereochemistry of ring closure of **5d** to give **7b**. Closure cannot proceed by any pathway in which a plane of symmetry bisects the CHD group, thus excluding metallacyclohexadiene or metallabenzene intermediates. Accordingly, ring closure of **5c,d** must involve direct C-C bond formation from the puckered ligand and may best be viewed as the intraligand migratory insertion reaction shown in Scheme II. Addition of the Rh-C bond to the underside of the coordinated olefin requires that the CHD terminus rotate as shown to give *endo*-D isotopomer **7b**. This insertion mechanism also maintains bonding interaction between the Rh and the organic ligand, and presumably it has a lower activation barrier than a direct reductive elimination of two Rh-C bonds.

The demonstrable absence of a metallacyclohexadiene intermediate and the implicit inaccessibility of a metallabenzene species in this reaction suggest that such species may be mechanistic red herrings[18] en route to cyclopentadiene or (cyclopentadienyl)hydrido complexes in related systems.[3,5]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for generous support of our research. A generous loan of rhodium salts from Matthey-Bishop Inc. is also gratefully acknowledged.

General Strategy for the Systematic Synthesis of Oligosiloxanes. Silicone Dendrimers

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In view of the widespread use of silicones (polysiloxanes),[1] it is rather surprising that the literature documents virtually no *systematic* approaches to the synthesis of structurally defined oligosiloxanes. The availability of many of these compounds is necessitated in an ongoing project of our laboratories, and for this reason we have selected and modified a set of reactions to formulate a reliable general synthetic strategy as summarized in this paper. The validity of this strategy has been proven by the synthesis of a variety of oligosiloxanes and even silicone dendrimers (see later text) with discrete molecular weights of >10000. Several different modes of linear and branched elongation are delineated in the following text to illustrate this development. Most of the reactions proceed in high yield (>60%), unless otherwise specified.

1. Linear (Stepwise) Homologation of α-Hydropermethyloligosiloxane, $(MD_nM^H)^2$ (1). Scheme I illustrates the use of two basic reactions, hydroxylation of **1**[3] and coupling with chlorodimethylsilane, and this homologation (**1** → **3**) is conveniently carried out without the isolation of **2**.[4] Reiterate application to MM^H (**4**) leads to homologous MD_nM^H (n = 1-8), many of which were isolated earlier from a mixture of several MD_nM^H components obtained by the transition-metal-catalyzed redistribution of **4**.[4]

2. Branched Elongation. Replacement of $ClSiMe_2H$ (used in the above linear coupling) by Cl_2SiMeH, Cl_2SiH_2, and Cl_3SiH in the reaction with MM^{OH} (**5**) leads to the synthesis of **6-8** (Scheme II), which can be transformed into the branched-chain compounds **9-11**, respectively.[4] In addition to **9-11**, which are symmetrically branched, unsymmetrically branched hydrooligosiloxanes can be prepared. Thus, for example, the two chlorine functionalities of Cl_2SiMeH react stepwise with **12** to afford **13**,

(9) **7a**: yellow crystals, mp 109-110 °C; ^1H NMR (C_6D_6) δ 7.11 (m, 2 H, $H_{4,7}$), 6.85 (m, 2 H, $H_{5,6}$), 6.13 (dt, $J_{HH} = J_{RhH} = 2.6$, H_2), 5.76 (br, 1 H, $H_{1/3}$), 5.63 (br, 1 H, $H_{1/3}$), 3.69 (ddd, 1 H, $J_{HH} = 2.7$, 1.4, $J_{RhH} = 1.5$, $H_{olefinic}$), 2.49 (ddd, 1 H, $J_{HH} = 12.4$, 1.3, $J_{RhH} = 4.6$, H_{exo}), 2.38 (ddd, 1 H, $J_{HH} = 12.4$, 2.6, $J_{RhH} = 2.6$, H_{endo}), 1.35 (s, 9 H, ^{t}Bu), 1.32 (s, 9 H, ^{t}Bu), 1.14 (s, 9 H, ^{t}Bu). **7b**: ^1H NMR (C_6D_6) identical except for δ 3.69 (dd, 1 H, $J_{HH} = J_{RhH} = 1.5$, $H_{olefinic}$), 2.49 (ddt, 1 H, $J_{HH} = J_{HD} = 1.5$, $J_{RhH} = 4.8$, H_{exo}); $^2H\{^1H\}$ NMR (C_6H_6) δ 2.30 (s, 1 D, D_{endo}); IR (KBr) 2770 (m) cm^{-1}; νCH_{exo}. **9**: ^1H NMR (C_6D_6) identical except for δ 3.68 (dd, 1 H, $J_{HH} = 2.9$, $J_{RhH} = 1.8$, $H_{olefinic}$), 2.36 (ddt, 1 H, $J_{HH} = J_{RhH} = J_{HD} = 2.4$, H_{endo}); $^2H\{^1H\}$ NMR (C_6H_6) δ 2.50 (s, 1 D, D_{exo}).

(10) Chromatography on silica gel or alumina under identical conditions effects <5% ring closure.

(11) (a) *exo*- and *endo*-[Rh(η^5-C_5H_5)(η^4-C_5Me_5H)]: Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875-2883. (b) Related exampled: refs 14, 17, and 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. Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339-2343.

(12) **8a**: PF_6^- salt, orange crystals, mp 234-235 °C, structure confirmed by X-ray crystallography;[13] ^1H NMR (CD_3CN) δ 7.65 (m, 2 H, $H_{4,7}$), 7.44 (m, 2 H, $H_{5,6}$), 6.45 (dd, 2 H, $J_{HH} = 2.7$, $J_{RhH} = 0.7$, $H_{1,3}$), 5.81 (dt, 1 H, $J_{HH} = 2.7$, $J_{RhH} = 1.3$, H_2), 5.50 (d, 2 H, $J_{RhH} = 0.9$, C*H*C^{t}Bu) 1.43 (s, 18 H, ^{t}Bu), 1.40 (s, 9 H, ^{t}Bu). **8b**: ^1H NMR (CD_3CN) identical except δ 5.50 resonance half the intensity of that in **8a**; $^2H\{^1H\}$ NMR (CH_3CN) δ 5.50 (s, 1 D, C*D*C^{t}Bu).

(13) Rheingold, A. L. Private communication.

(14) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024-2030. Efraty, A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1967**, *89*, 3744-3750.

(15) **7a,b** can be oxidized to **8a,b** with *N*-bromosuccinimide or $CDCl_3$. Similar oxidation of *exo*-[Rh(η^5-C_5H_5)(η^4-C_5Me_5H)] is facile, but the *endo*-H isomer is not oxidized.[11a] Analogous oxidation of cyclopentadiene-cobalt complexes is less selective, depending on the oxidant.[16]

(16) O'Connor, J. M.; Johnson, J. A. *Synlett* **1989**, *1*, 57-59 and references therein.

(17) See ref 11a, and: White, C.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3322-3326. Bailey, N. A.; Blunt, E. H.; Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1980**, 829-836. Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857-2859. Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296-5298. Johnson, F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084-2089.

(18) We disagree with a reviewer's suggestion that use of the term "red herring" is inappropriate in this context. It seems to be a useful expression to describe a mechanistic side-trail that is irrelevant to the pathway of interest. See: Sayers, D. L. *The Five Red Herrings*; Harper & Row: New York.

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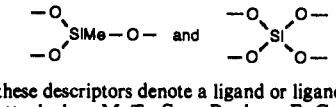
(1) For reviews of silicone, see for instance: (a) Stark, F. O.; Falender, J. R.; Wright, A. P. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 2, Chapter 9.3. (b) Kendrick, T. C.; Parbhoo, B.; White, J. W. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, S., Eds.; John Wiley and Sons Ltd.: Chichester, 1989; Part 2, Chapter 21.

(2) Descriptors M, D, T, and Q are conventionally used in silicone chemistry to denote Me_3Si-O-, -O-$SiMe_2$-O-



Superscripts on these descriptors denote a ligand or ligands substituting a Me or Me_2 ligands attached on M-T. See: Rochow, E. G. *An Introduction to the Chemistry of the Silicones*, 2nd ed.; Wiley: New York, 1951. Wilcock, D. F. *J. Am. Chem. Soc.* **1946**, *68*, 691.

(3) Barnes, G. H., Jr.; Daughenbaugh, N. E. *J. Org. Chem.* **1966**, *31*, 885.

(4) Representative experimental procedures, size-exclusive chromatographic results of **22** and **20A-C**, and physical properties of oligosiloxanes with pertinent references are found in the supplementary material.

0002-7863/90/1512-7077$02.50/0