104337-84-0; **9**, 104337-85-1; **10**, 88825-26-7; **11a**, 104419-23-0; **11a**-*d*, 104419-66-1; **11b**, 104419-24-1; **11b**-*d*, 104338-00-3; **12**, 104337-86-2; **13**, 104337-87-3; **14**, 104351-64-6; **15**, 104337-89-5; **15**-*d*, 104338-09-2; **16**, 88825-24-5; $Cp^*(PMe_3)Rh(n\text{-propyl})(H)$, 84624-04-4; $Cp^*(PMe_3)Rh(n\text{-pentyl})(H)$, 104337-90-8; $Cp^*(PMe_3)Rh(n\text{-octyl})(H)$, 104337-91-9; $Cp^*(PMe_3)Rh(cyclobutyl)(H)$, 104267-59-6; $Cp^*(PMe_3)Rh(cyclopropyl)(I)$, 92984-73-1; $Cp^*(PMe_3)Rh(2,2\text{-dimethylcyclopropyl})(I)$, 104267-61-0; $Cp^*(PMe_3)Rh(cyclobutyl)(I)$, 104337-92-0; $Cp^*(PMe_3)Rh(n\text{-hexyl})(I)$, 104337-93-1; $Cp^*(PMe_3)Rh(n\text{-octyl})(I)$, 104337-94-2; $Cp^*(PMe_3)Rh(trimethylsilyl)(I)$, 104337-95-3; $Cp^*(PMe_3)Rh(cyclopentyl)(I)$, 104337-96-4; $Cp^*(PMe_3)Rh(cyclohexyl)(Br)$, 104337-97-5; $Cp^*(PMe_3)Rh(isobutyl)(I)$, 104338-03-6; $Cp^*(PMe_3)Rh(n\text{-pentyl})(I)$, 104338-04-7; $Cp^*(PMe_3)Rh(cyclohexyl)(H)$, 104338-05-8; $Cp^*(PMe_3)Rh((1\text{-}^{13}C)ethyl)(H)$, 104338-07-0; $Cp^*(PMe_3)Rh(methyl\text{-}d_3)(I)$, 104338-11-6; $[Cp^*(PMe_3)Rh(methyl\text{-}d_3)]Li$, 104338-12-7; $Cp^*(PMe_3)Rh(n\text{-butyl})(I)$, 104337-88-4; $Cp^*(PMe_3)Rh(ethyl)(Br)$, 88825-27-8; $Cp^*(PMe_3)RhCl_2$, 80298-79-9; $Cp^*(PMe_3)RhBr_2$, 88704-26-1; $Cp^*(PMe_3)RhI_2$, 88704-27-2; $(\eta^5\text{-}C_5H_5)RhPMe_3(C_2H_4)$, 69178-16-1; $(\eta^5\text{-}C_5H_5)Rh(PMe_3)H_2$, 104337-98-6; $(\eta^5\text{-}C_5H_5)Rh(PMe_3)I_2$, 83614-91-9; $[(\eta^5\text{-}C_5H_5)(PMe_3)RhH]Li$, 104337-99-7; $(\eta^5\text{-}C_5H_5)(PMe_3)Rh((1\text{-}^{13}C)ethyl)(H)$, 104338-02-5; $Cp^*(PMe_3)Rh(methyl)(I)$, 86225-06-1; propane, 74-98-6; *n*-butane, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-octane, 111-65-9; isobutane, 75-28-5; 1,1-dimethylcyclopropane, 1630-94-0; trimethylsilane, 993-07-7; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; ethane, 74-84-0; methyl tosylate, 80-48-8; ethyl tosylate, 80-40-0; butyl tosylate, 778-28-9; *n*-hexyl tosylate, 3839-35-8; (1-methylcyclopropyl)methyl tosylate, 13033-53-9; benzene, 71-43-2; toluene-d_8, 108-88-3; *n*-dodecane, 112-40-3; *n*-decane, 124-18-5; 1,1,1,2,2-pentadeuterioethyl tosylate, 59034-23-0; $(1\text{-}^{13}C)$ethyl tosylate, 83587-73-9; 1-methylcyclopropylcarbinol, 2746-14-7.

C–C Activation of Organic Small Ring Compounds by Rearrangement of Cycloalkylhydridorhodium Complexes to Rhodacycloalkanes. Synthesis of Metallacyclobutanes, Including One with a Tertiary M–C Bond, by Nucleophilic Addition to π-Allyl Complexes

Roy A. Periana and Robert G. Bergman*

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720. *Received March 27, 1986*

Abstract: Generation of the coordinatively unsaturated fragment [Cp*RhL] (Cp* = η^5-C_5Me_5; L = PMe_3) at −60 °C in cyclopropane by both photolysis of $Cp^*(L)RhH_2$ and thermal decomposition of Cp*(L)Rh(neopentyl)(H) results only in C–H bond insertion to yield Cp*(L)Rh(cyclopropyl)(H) (**1**). This complex rearranges at −20 °C in arene solvents to the rhodacyclobutane $Cp^*(L)\overline{Rh\text{–}CH_2\text{–}CH_2\text{–}CH_2}$ in 65% yield. Mechanistic studies of regiospecifically ^{13}C-labeled cyclopropylhydridorhodium complexes indicate that the rearrangement is intramolecular and occurs by migration of the Cp*RhL unit to the α-carbon–carbon bond of the cyclopropyl ring. Similarly, C–C activation of 1,1-dimethylcyclopropane is observed to occur by intramolecular rearrangement of Cp*(L)Rh(2,2-dimethylcyclopropyl)(H) (**2**). This rearrangement occurs with complete regiospecificity, yielding only the β,β-dimethylrhodacyclobutane, $Cp^*(L)\overline{Rh\text{-}CH_2\text{–}CMe_2\text{–}CH_2}$. The possible intermediate formation of the isomeric α,α-dimethyl rhodacyclobutane was ruled out by independent synthesis of this isomer (see below) and the demonstration of its stability under the conditions used for isomerization of the cyclopropylhydridorhodium complex **2**. Reaction of [Cp*RhL] with cyclobutane also initially forms the C–H insertion product Cp*(L)Rh(cyclobutyl)(H). This species rearranges only in poor yields; it is best carried out in dilute solutions of cyclobutane and produces a product which is tentatively assigned as the rhodacyclopentane $Cp^*(L)\overline{Rh(\text{–}CH_2)_3\text{–}CH_2}$ in modest yields (12–30%). Treatment of $Cp^*(L)Rh(\overline{CH\text{–}CR_2\text{–}CH_2})(X)$ (R = H; R = Me; X = I) with $AgBF_4$ results in the formation of the cationic π-allyl complexes $[Cp^*(L)Rh(\eta^3\text{-}CR_2\text{–}CH\text{–}CH_2)]^+BF_4^-$ (R = H, Me). Subsequent treatment of these cations with $LiEt_3BH$ results in the clean formation of neutral rhodacyclobutanes $Cp^*(L)\overline{Rh\text{–}CR_2CH_2\text{–}CH_2}$ (R = H; R = Me). In the case where R = H the use of $LiEt_3BD$ indicates that the addition of hydride is completely regio- as well as stereospecific, the hydride adding to the β-carbon syn to Cp* ligand.

Cleavage of carbon–carbon bonds in alkanes is observed frequently in heterogeneous catalysis. In petroleum refining, alkane skeletal rearrangements and cracking occur easily in catalytic reforming by oxide-supported platinum catalysts; this is one of the largest scale processes in modern industry.[1-5]

In contrast, there is no known case of intermolecular insertion of an organometallic complex into an unstrained alkane C–C bond in a homogeneous reaction. Most of the reported cases of carbon–carbon activation by soluble transition-metal complexes in-

(1) Evidence suggests that C–H activation by the supported platinum metal is the first step.[2] Subsequent C–C activation may actually proceed largely via carbonium ion chemistry catalyzed by acidic sites on the supports.[3]

(2) Anderson, J. H. *Adv. Catal.* **1977**, *23*, 1.

(3) Sinfelt, J. H. In *Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer Verlag: New York, 1981; Vol. 1, p 257.

(4) (a) Clark, J. K. S.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125. (b) Anderson, J. R.; Baker, B. G. In *Chemisorption and Reactions on Metallic Films*; Anderson, J. R., Ed.; Academic Press: New York, 1971; Vol. 2, p 64. (c) Davis, S. C.; Klabunde, K. *J. Chem. Rev.* **1982**, *82*, 153. (d) Gault, F. G. *Adv. Catal.* **1981**, *30*, 1.

(5) (a) Kembal, C. *Proc. Roy. Soc. London, Ser. A.* **1954**, *223*, 377. (b) Carter, J. L.; Cusumano, J. A.; Sinfelt, J. H. *J. Catal.* **1971**, *20*, 223.

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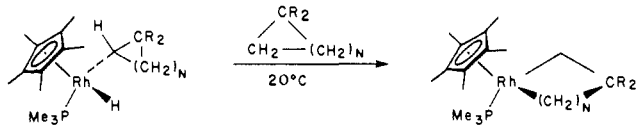
Scheme I



1 (N = 1, R = H)
2 (N = 1, R = Me)
3 (N = 2, R = H)

4 (N = 1, R = H)
5 (N = 1, R = Me)
6 (N = 2, R = H)

volve strained systems such as cyclopropane or cubane,[6] intramolecular ligand activation, or activated systems such as aromatic nitriles and alkyl-substituted cyclopentadienes.[7] In one recent example, Crabtree and co-workers recently reported that 1,1-dimethylcyclopentane was converted to an η^5-methylcyclopentadienyl ligand by reaction with an iridium complex.[8] The reaction was found to proceed by prior C–H cleavage and dehydrogenation, leading to a coordinated 1,1-dimethylcyclopentadiene, which transfers a methyl group to the metal center. Suggs and co-workers have also reported an interesting example of intramolecular C–C activation involving mildly activated bonds.[9] They found that the α-keto carbon–carbon bonds of 8-quinoline alkyl ketones may be cleaved by a rhodium complex to give alkyl–acyl complexes. In this case the reaction presumably proceeds by prior coordination through the nitrogen atom of the quinoline ring. Thermodynamic factors may disfavor C–C activation in systems where extra driving forces such as relief of ring strain, aromatization, or chelation are not possible. By some estimates insertion into C–C bonds is endothermic by 25 kcal/mol,[10] a value just offset by relief of ring strain and the energy gained upon aromatization in the Crabtree example. However by other estimates C–C insertion reactions can be exothermic[11] and most likely the thermodynamics depend strongly on the metal system.[12]

The generation of "naked" metal atoms in alkanes, both in the gas phase and in matrices, leads to C–H and C–C bond activation. In the case of Fe^+ ions, generated in the gas phase, C–C bond cleavage is the preferred mode of activation.[13] This preference for C–C activation correlates with Beauchamp's measurement of the $Fe-CH_3^+$ bond strength as 69 ± 5 kcal mol^{-1} and the smaller value for $Fe-H^+$(58 ± 5 kcal mol^{-1}).[14,15] Thus at least in this case, C–C activation appears to be thermodynamically favored. Analogous organic examples of C–C activation by small reactive species in so-called "super acid" solutions have been known for many years.[16]

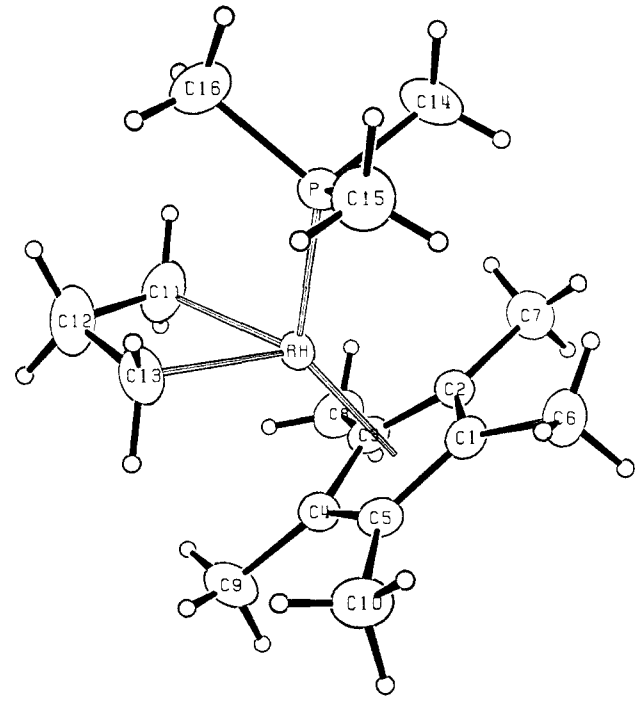


Figure 1. ORTEP diagram illustrating the structure of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(CH_2)_3$ (**4**). Selected bond distances (Å): $Rh-C_{11} = Rh-C_{13} = 2.085$; $C_{11}-C_{12} = 1.512$; $C_{12}-C_{13} = 1.527$. Selected bond angles: $C_{11}C_{12}Rh = 99.55$; $C_{12}C_{13}Rh = 96.59$. Complete structural details are given in the supplementary information provided with ref 18.

The contrast between the reactivity of "naked" metal atoms and that of bulkier ligated transition-metal complexes would seem to suggest that even in thermodynamically favorable systems, direct C–C insertion by soluble organometallic complexes might be kinetically slow processes due to the poor steric accessibility of C–C bonds. Thus in reaction with alkanes, bulky ligated transition-metal complexes capable of C–C activation would most likely be intercepted by the more accessible C–H bonds before any significant C–C bond breaking occurs. However, there may be cases where M–C bonds are comparable in strength to M–H bonds and the C–C insertion product may be comparable in thermodynamic stability to the C–H product. Thus it would seem reasonable to try effecting the rearrangement of C–H to C–C activation products.

In our initial work on C–H activation by the unsaturated fragment $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)]$ we observed, as in the case of the iridium analogue, that generation of this fragment in cyclopropane at −60 °C resulted only in C–H insertion to give the cyclopropyl hydride **1** (Scheme I).[17] Subsequently however, we communicated the observation that **1** rearranges by an intramolecular pathway to the rhodacyclobutane **4** in high yield.[18] This observation presented a unique opportunity to study the direct rearrangement of the initial product of C–H activation, an alkyl hydride, to the C–C insertion product. The following describes a mechanistic study of the rearrangement of **1** to **4** and our limited success in extending the chemistry to cyclobutane. Additionally some related chemistry on the independent synthesis of rhodacyclobutanes is reported.

Results and Discussion

Preparation of the Rhodacycloalkanes. The alkylhydridorhodium complexes, $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(R)(H)$, are unstable

(6) For an excellent review of this area, see: Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.
(7) Kang, J. W.; Mosley, R.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1325. (c) Chong, K. S.; Green, M. L. H. *Chem. Commun.* **1982**, 991. (d) Elbracht, P. *Ber.* **1976**, *109*, 1429 and 3136; **1980**, *113*, 542, 1033, 1420, and 2211. (e) Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4211, 4221, 4229, and 4235. (f) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1200 and 7418. Grubbs, R. H.; Miyashita, A. *Chem. Commun.* **1977**, 864. (g) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (h) Henrici-Olive, G.; Olive, S. *Coordination and Catalysis*, Verlag Chemie: Weinheim, 1977. (i) Muller, E.; Segnitz, A.; Langer, E. *Tetrahedron Lett.* **1969**, 1129. (j) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, 1795. (k) Flood, T. C.; Bittler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (l) Lisko, J. R.; Jones, W. M. *Organometallics.* **1985**, 92.
(8) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260.
(9) (a) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (b) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. Suggs, J. W.; Jun, C.-H. *Chem. Commun.* **1985**, *92*.
(10) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.
(11) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205.
(12) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Patai, S., Ed.; Wiley: New York, 1982.
(13) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *Ibid.* **1982**, *104*, 3565. (c) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 6501.
(14) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.
(15) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.
(16) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.
(17) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508.
(18) Part of the research described here has been reported earlier in preliminary form: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

materials which typically decompose above −20 °C to generate alkanes (R–H) and the reactive unsaturated fragment [(η^5-C_5Me_5)(PMe_3)Rh].[17-19] This unsaturated fragment can be trapped by ligands such as CO or ethylene or alternatively by oxidative addition to arene C–H bonds to produce aryl hydrides which are stable at room temperature. When R = cyclopropyl or cyclobutyl, the complexes also undergo rearrangement. Thus upon warming a 0.15 M solution of cyclopropyl hydride **1** in cyclopropane to −20 °C the complex rearranged in quantitative NMR yield to rhodacyclobutane **4** (Scheme I). Similarly, a 0.15 M solution of 2,2-dimethylcyclopropyl hydride complex **2** afforded only the β,β-dimethylrhodacyclobutane **5** in quantitative yield upon rearrangement in dimethylcyclopropane; none of the α,α-dimethyl rhodacyclobutane was observed, as determined by ^1H and ^{13}C NMR analysis.

We believe the cyclobutyl hydride **3** undergoes an analogous rearrangement in cyclobutane to rhodacyclopentane **6** although assignment of the structure of this product is more tentative than that of **4** or **5**. At 0.15 M it is formed in only 12% yield. Rearrangement of **3** in cyclobutane carried out at 0.021 M concentration resulted in a 30% yield of **6**. Consistent with the lower yields of **6** obtained on rearrangement of **3**, attempts at rearrangement of the analogous cyclopentyl hydride (0.025 M in cyclopentane) resulted in the formation of a mixture of products which was too complex for characterization.

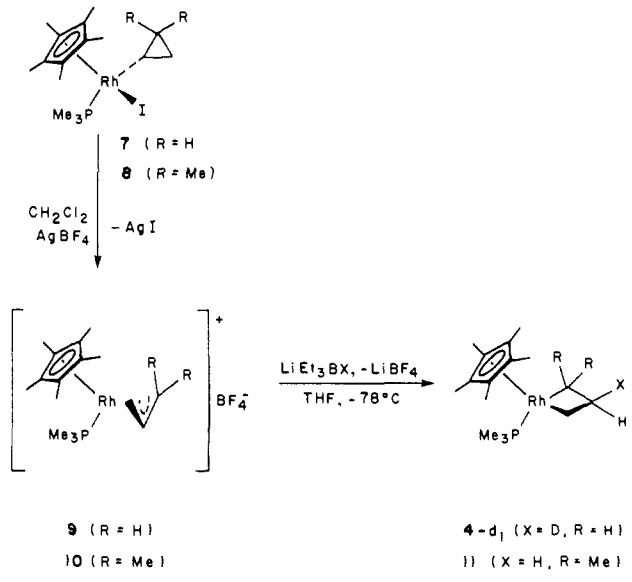
Solutions of the rhodacycloalkane complexes **4**, **5**, and **6** are stable at room temperature and only mildly air sensitive. However, the complexes are quite sensitive to typical chromatographic supports at room temperature and are best purified chromatography on alumina III at −100 °C with 3% Et_2O/pentane as eluant. Following chromatography, the complexes can be obtained in crystalline form by slow recrystallization from pentane allowing complete characterization by analytical and spectroscopic methods. As reported earlier,[18] crystals of **4** were obtained, and its structure was solved by X-ray diffraction. An ORTEP diagram of the structure is reproduced in Figure 1; details of the structure determination were provided as supplementary material with the earlier communication.

The ^1H NMR spectrum of rhodacyclopentane **6** was complex and provided only suggestive evidence for the assigned structure. As in the case of the analogous PPh_3 analogue,[20] treatment with HCl resulted in a mixture of *n*-butane (identified by GC/MS spectral analysis), other hydrocarbons we believe to be butenes, and the dichloride (η^5-C_5Me_5)(PMe_3)$RhCl_2$. Treatment with Br_2 resulted in the formation of the dibromide (η^5-C_5Me_5)(PMe_3)-$RhBr_2$ and mainly 1,4-dibromobutane, identified by GC/MS analysis.

In order to confirm this assignment and obtain the rhodacyclopentane **6** more conveniently, we attempted to synthesize the complex by the reaction of 1,4-dilithiobutane with (η^5-C_5Me_5)(PMe_3)RhX_2 (X = Br and I), following the procedure reported by Diversi for the preparation of the triphenylphosphine analogue.[20] However, although **6** was produced in these reactions (as evidenced by NMR analysis), it was a minor product and could not be separated from impurities by column chromatography at −100 °C or by recrystallization techniques.

In contrast, rhodacyclobutane **4** could be conveniently synthesized independently by treatment of the cationic π-allyl complex **9** with $LiEt_3BH$, as shown in Scheme II. This novel reaction is only the second example of a π-allyl system that adds nucleophiles to the center rather than the end of the three-carbon chain.[22] The π-allyl complex **9** is readily obtained in quantitative yield by

Scheme II



treatment of the iodocyclopropyl complex **7** with $AgBF_4$ in methylene chloride. These reactions were also extended to the iodo(2,2-dimethylcyclopropyl) complex **8**. Treatment of this material with $AgBF_4$ resulted in the formation of the α,α-dimethyl-π-allyl complex **10** which was fully characterized. Subsequent reaction with $LiEt_3BH$ resulted in a high yield of only the α,α-dimethyl rhodacyclobutane **11**. This material is clearly different from **5**, the product of rearrangement of **2**, and is a rare example of a stable transition-metal alkyl complex which contains a tertiary metal–carbon bond.

Solutions of **11** are stable at room temperature, decomposing after days to a complex mixture of products. However the material is sensitive to both air and chromatographic supports and is best purified by chromatography at −100 °C on alumina III with 3% Et_2O/pentane as eluant. It can be obtained as yellow microcrystals by recrystallization of chromatographed material at −78 °C from hexamethyldisiloxane, in which it is very soluble. Evidence for the assigned structure is readily obtained from proton-coupled and decoupled ^{13}C NMR spectra. The two α-carbons bonded to rhodium appear in the ^{13}C NMR spectra, characteristically most upfield, as doublets of doublets due to rhodium and phosphorous coupling. The lower field α-carbon resonance shows no ^1H coupling in the ^1H coupled ^{13}C spectra while the upfield α-carbon resonance is a triple doublet of doublets with J_{CH} = 137 Hz. This demonstrates that the lower field resonance arises from a carbon with no hydrogens attached to it.

Reaction of the cationic π-allyl complex **9** with $LiEt_3BD$ produces **4-*d*$_1$** (Scheme II). Analysis by ^1H NMR confirmed that attack of D^- occurred exclusively at the β-carbon of the π-allyl group of **9**. The use of D^- also indicated that the reaction occurred with complete stereospecificity, placing the incoming nucleophile syn to the pentamethylcyclopentadienyl ligand in the rhodacyclobutane ring. This was determined by ^1H and ^2H NMR analysis of the deuterated complex. The β-hydrogen signals of **4** appear in the ^1H NMR as multiplets at 3.48 and 3.20 ppm (C_6D_6) and are baseline separated. Both the ^1H and ^2H NMR of **4-*d*$_1$** indicated that to greater than 95% accuracy only the hydrogen which resonates in the upfield position has been replaced by deuterium. The X-ray structure of **4** demonstrates that (at least in the solid state) the rhodacyclobutane ring is essentially planar. Dihedral angles of cis substituents on the ring are close to 0°, and trans dihedral angles are 100°. Assuming this structure is maintained in solution, the Karplus relationship predicts that cis H–H through-bond coupling would be greater than trans H–H through-bond coupling.[21] In addition, we observe two through-space nuclear Overhauser (NOE) enhancements: (a) between the pentamethylcyclopentadienyl ligand and only the upfield set of α-hydrogens, which we assign as syn to the Cp* ligand and (b)

(19) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

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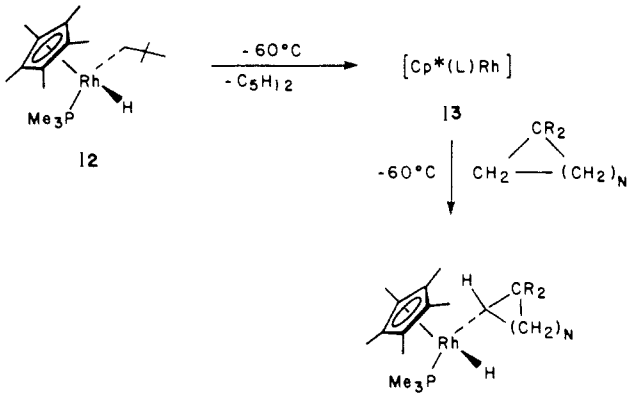
(21) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11. Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

(22) The previously reported example of C-2 attack is (a) Ephretikine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. For an excellent discussion of the factors controlling these reactions, see: (b) Curtis, M. S.; Eisenstein, O. *Organometallics* **1984**, *3*, 1660.

Scheme III

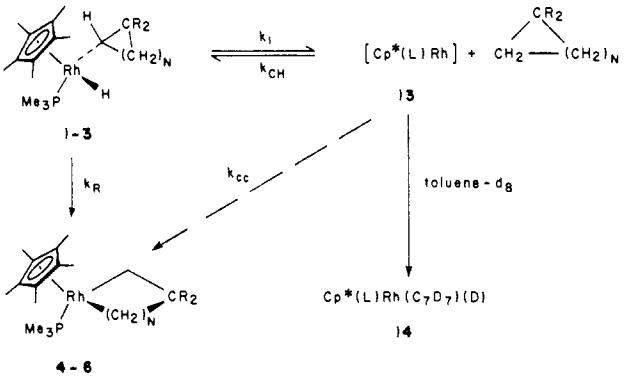


between the PMe_3 ligand and the lower field set of α-hydrogens, which are assigned as anti to the Cp* ligand. Presumably this result is a direct consequence of a preferred orientation of the π-allyl ligand shown in Scheme II, in which the β-carbon of the alkyl group points away from the Cp* ligand. Trans attack of H^- at the β-position with closure to the rhodacyclobutane would result in the observed regio- and stereospecific mode of addition. These results confirm a recent suggestion by Curtis and Eisenstein that the $[(\eta^5\text{-}C_5H_5)(L)M(\pi\text{-allyl})]^+$ (M = Co, Rh) systems should occur with center-carbon addition of nucleophiles to the π-allylic ligand.[22b]

Rate, Solvent, and Ligand Effect Studies of the Cycloalkyl Hydride to Metallacycle Rearrangement. As reported in the accompanying paper,[23] the reactive intermediate $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh$ (**13**) can be generated under very mild, nonphotochemical conditions by preparing $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(H)$(neopentyl) (**12**) at −90 °C and allowing it to undergo reductive elimination of neopentane at −60 °C. When this is done in cyclopropane, 1,1-dimethylcyclopropane, or cyclobutane solvent, we observe insertion of the unsaturated fragment into the C–H bonds of the solvent to produce hydridocycloalkyl complexes **1**, **2**, and **3**, respectively (Scheme III). No C–C insertion reactions leading to rhodacycloalkanes are observed at this temperature. These observations, coupled with the subsequent rearrangement chemistry of the cycloalkyl hydrides, require that the kinetic product of the reaction of the unsaturated fragment **13** with cycloalkanes is formed by insertion into the strong C–H bonds of the organic molecules, whereas the thermodynamic product is formed by insertion into the relatively weaker C–C bonds. The kinetic preference for C–H activation may be due to the greater steric accessibility of the C–H bond to the bulky intermediate Cp*RhL.

The simplest mechanism (mechanism A) which can account for the conversion of the cycloalkyl hydrides **1**, **2**, and **3** to the rhodacycloalkanes **4**, **5**, and **6** in cycloalkane solvent can be discussed with reference to Scheme IV. This suggests that rapid, reversible cycloalkane reductive elimination/C–H insertion occurs initially at −20 °C (k_1 and k_{CH}). Occasionally however, C–C insertion (k_{CC}) might occur, leading irreversibly to the more stable rhodacycloalkanes. This mechanism can be easily tested by carrying out the decomposition in a different solvent. Competition studies carried out by thermal generation of the intermediate **13** at −60 °C in mixtures of hydrocarbons have shown that k_{CH} for reaction of toluene-d_8 with **13** (to give the *m*- and *p*-tolylhydridorhodium complexes **14** described earlier by Jones and Feher[19]) is greater than k_{CH} for reaction with cyclopropane,

Scheme IV



1,1-dimethylcyclopropane, or cyclobutane.[23] This simple mechanism therefore predicts that replacing the cycloalkane solvents with toluene-d_8 should divert the rearrangement entirely to toluene-d_8 insertion products **14**. Accordingly, the complexes **1**, **2**, and **3** were warmed to −20 °C in toluene-d_8. To our surprise in every case significant amounts of rhodacycloalkane were still observed by NMR: 65% of **3** in the case of **1**, 75% of **4** in the case of **2**, and 5–10% of **6** in the case of **3**. These results require that at least these percentages of rhodacycloalkanes cannot arise from free intermediate **13**, as it would have been effectively scavenged by toluene-d_8. Thus the results require that the cycloalkane fragment and the rhodium atom remain associated with one another during the conversion of the cycloalkyl hydrides to the rhodacycloalkanes. That is, the rearrangement is at least partially intramolecular, and a direct route (k_R) must be included in Scheme IV. Since no **4**, **5**, or **6** is formed on generation of **13** at low temperature, $k_{CH} \gg k_{CC}$, and in fact we have no direct evidence requiring that any rhodacycloalkanes are *necessarily* formed by the k_{CC} path.

Consistent with an intramolecular rearrangement independent of the solvent, the cycloalkyl hydrides **1**, **2**, and **3** were also found to rearrange in THF-d_8 and methylcyclohexane-d_{14} to produce in both cases the rhodacycloalkanes **4**, **5**, and **6** in 65%, 75%, and 5–10% yields, respectively, as determined by NMR. Kinetic studies of the rearrangement of **1** in toluene-d_8 and THF-d_8 also support this conclusion. Thus **1** was found to rearrange to **4** at −20 °C in both solvents with clean first-order kinetics over 4 half-lives and similar rate constants: k_R(toluene-d_8) = (2.1 ± 0.2) × 10^{-4} s^{-1}, k_R(THF-d_8) = (2.3 ± 0.2) × 10^{-4} s^{-1}.

Phosphine dissociation was also ruled out as a necessary step for the rearrangement of **1** to **4**: addition of 10 equiv of PMe_3 to a toluene-d_8 solution of **1** did not affect the rate or product ratio for the rearrangement of **1**. Furthermore, added $P(CD_3)_3$ was incorporated into **1** only very slowly compared with the rate of rearrangement of **1** to **4**.

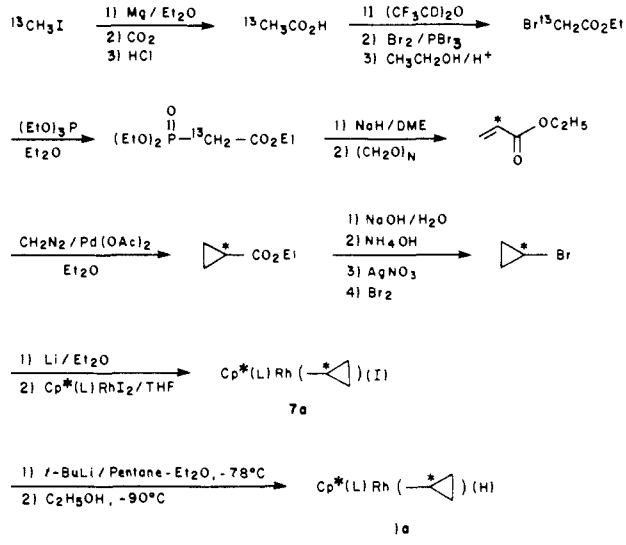
Thermal Rearrangement of [1-^{13}C]Cyclopropyl Hydride. Following the establishment of the cycloalkyl hydride to rhodacycloalkane rearrangement, experiments were carried out designed to determine the mechanistic pathway by which these transformations occur. Initially, it was important to determine whether insertion into the C–C bond of the cycloalkane fragment occurs regiospecifically. In addition, we have investigated the intramolecularity of the process, in hopes of learning whether σ-complex intermediates are involved, as we believe they are in the C–H insertion reactions discussed in the accompanying paper.[23]

We first prepared [1-^{13}C]cyclopropyl hydride **1a**, by using the sequence of known reactions shown in Scheme V. The last step allows the generation of clean pentane/Et_2O solutions of the labeled complex at low temperatures and in high yield (95 ± 5%) from the labeled [1-^{13}C]cyclopropyliodorhodium complex **7a**. The pentane/Et_2O solution was replaced with toluene-d_8 at −78 °C, the complex was warmed to −20 °C, and the rearrangement was monitored periodically by ^{1}H and ^{13}C NMR spectrometry. The results are summarized in Scheme VI.

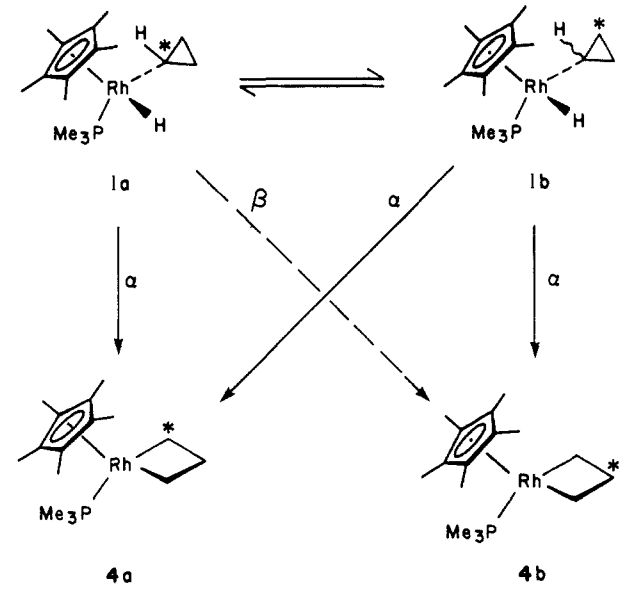
The $^{13}C\{^1H\}$ NMR spectra are most informative; representative examples are shown in Figure 2. At t = 0 the excess ^{13}C provided

(23) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.*, preceding paper in this issue.

Scheme V



Scheme VI



$$[4a]/[4b] = 5.6 \pm 0.1$$

by the label is clearly seen to reside only in the α-position of **1a** and appears as a characteristic doublet of doublets due to rhodium and phosphorus coupling centered at −7.4 ppm. At intermediate times before the rearrangement to metallacycle **4** is complete, **1a** also undergoes a qualitatively slower degenerate rearrangement to place the ^{13}C label into the β-positions of the cyclopropyl ring generating the [2-^{13}C]cyclopropyl hydride complexes **1b**. This is evidenced in the spectra at t = 127 min by the appearance of the resonances due to ^{13}C enriched β-cyclopropyl carbons of **1b** (7.8 and 13.2 ppm) along with the appearance of the resonances due to the ^{13}C enriched α and β carbons of the rhodacyclobutane complexes **4a** and **4b** (−20.5 and 35.2 ppm, respectively). Reductive elimination of cyclopropane from **1a(b)** is competitive with these processes and is evidenced by the appearance of the resonance of free [^{13}C]cyclopropane (−2.2 ppm).

After the rearrangement is complete, the ^{13}C label is found to reside in the α- and β-carbon positions of the rhodacyclobutane and in the ^{13}C-cyclopropane formed on reductive elimination. The ratio of **4a** to **4b** at the end of the reaction was determined to be 5.6 ± 0.5 by the use of $^{13}C\{^1H\}$ NMR pulse sequences which allow quantitative analysis of the resonances of the ^{13}C spectra. The observation that the ^{13}C label resides preferentially in the α-carbon position of the rhodacyclobutane ring (and that [**4a**]/[**4b**] is

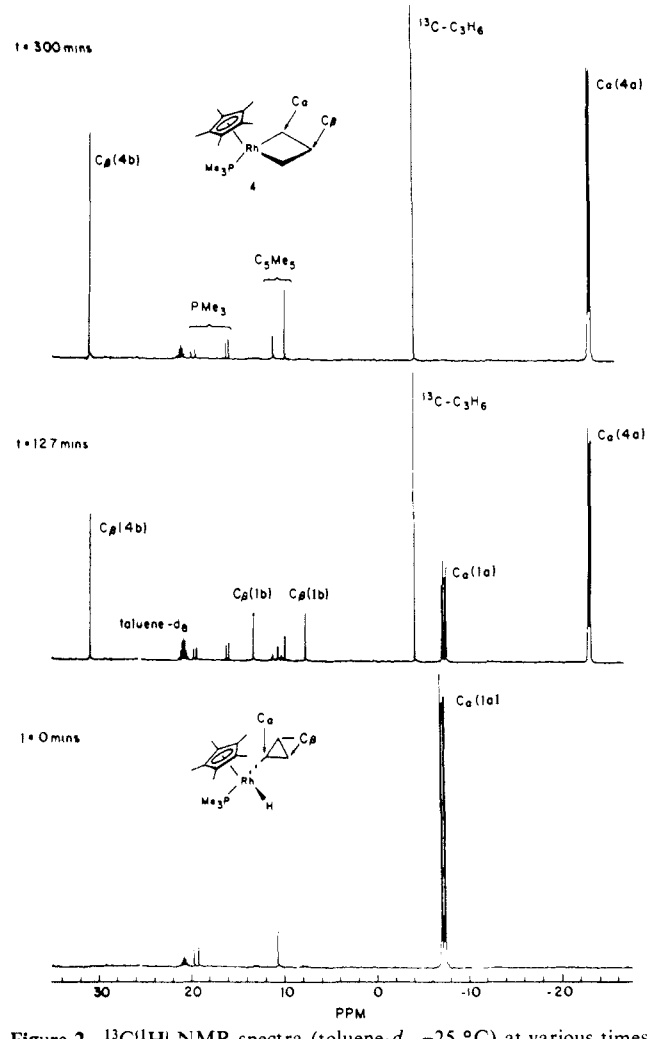
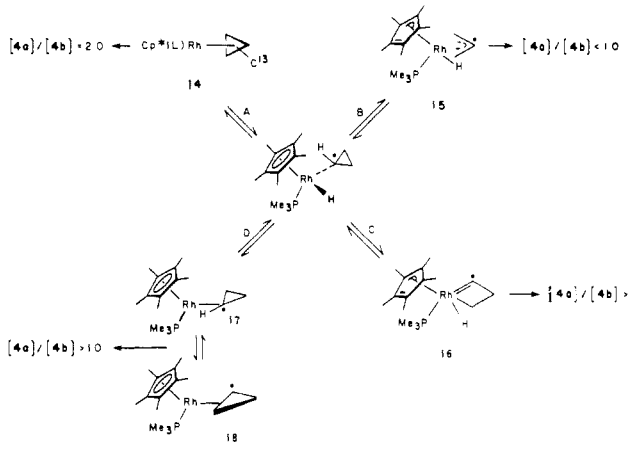


Figure 2. $^{13}C\{^1H\}$ NMR spectra (toluene-d_8, −25 °C) at various times of the thermally induced rearrangement of [1-^{13}C]cyclopropyl hydride (**1a**) to [2-^{13}C]cyclopropyl hydride (**1b**) and the rhodacyclobutanes **4a** and **4b**, ^{13}C-labeled in the α- and β-positions, respectively. Free [^{13}C]-cyclopropane is also generated. Chemical shifts are recorded in ppm downfield from Me_4Si.

greater than the statistical value of 2.0), coupled with observation of slower degenerate isomerization of **1a** to **1b**, suggests that the rearrangement of **1** to **4** occurs by a regiospecific insertion into the cyclopropyl C–C bond α to the rhodium atom (Scheme VI). Neither indiscriminate insertion (which predicts that [**4a**]/[**4b**] = 2.0) nor exclusive insertion into the C–C bond β to the rhodium atom (which predicts that [**4a**]/[**4b**] < 1.0) will account for the results. The observation that the rearrangement of **1** to **4** occurs by regiospecific α-insertion lends credence to the proposal that the hydridocycloalkyl rearrangements are intramolecular processes (Scheme IV).

In light of the facile carbon skeletal rearrangement observed in platinacyclobutane complexes[24] it was important to carry out control studies to determine if such rearrangements could occur in **4**, subsequent to its formation, under the conditions of the rearrangement of **1**. This was accomplished most rigorously by carrying out the rearrangement of **1** in the presence of a pure sample of the [β-^{13}C]rhodacyclobutane **4b**. The regiospecifically labeled complex **4b** was prepared (eq 1) from [1-^{13}C]iodocyclopropyl complex **7a** (Scheme V) by treatment with $AgBF_4$ to produce π-allyl complex **9**, regiospecifically β-^{13}C-labeled. Subsequent reaction with $LiEt_3BH$ resulted in the quantitative formation of **4b**. After purification by cold column chromatography as described earlier for **4**, **4b** was mixed with an equal amount of unlabeled **1** in toluene-d_8 at −60 °C. The mixture was warmed to 20 °C, and the resulting rhodacyclobutane mixture was analyzed by $^{13}C\{^1H\}$ NMR. This indicated that the added

Scheme VII



4b had not undergone any rearrangement and the ^{13}C label remained only in the β-position of the rhodacyclobutane ring. Thus unlike the platinacyclobutanes[24] the rhodacyclobutane **4** is stable to skeletal rearrangements under the conditions of its formation, indicating that the labeling pattern observed on rearrangement of **1a** is diagnostic of the intrinsic mechanism of the rearrangement process.

Insertion into the cyclopropyl C–C bond α to the rhodium atom in the parent complex is consistent with the regiospecific rearrangement of dimethyl complex **2** to the β,β-dimethyl rhodacyclobutane **5** discussed earlier. In this case two differently substituted cyclopropyl α-C–C bonds are available. Insertion into the less highly substituted bond leads to the observed product; insertion into the more substituted bond, if it occurred, would have led to the α,α-dimethyl rhodacyclobutane **11**. The availability of **11** by the independent route shown in Scheme II allowed us to determine whether **11** could have been an intermediate in this reaction. Accordingly, we allowed **2** to rearrange in the presence of a pure sample of the α,α-isomer **11**. This demonstrated that **11**, like ^{13}C-labeled **4b**, is stable to rearrangement under the reaction conditions. Thus formation of **5** from **2** must be occurring by regiospecific intramolecular insertion into the less highly substituted α-C–C bond of the 2,2-dimethylcyclopropyl ligand.

Mechanism of Cycloalkyl Hydride Rearrangement. Several mechanisms can be considered which would be consistent with a true intramolecular rearrangement of the cycloalkyl hydrides to the corresponding rhodacycloalkanes. Those which seem most reasonable to us are summarized as pathways A, B, C, and D in Scheme VII. As with the C–H insertion study discussed in the accompanying article,[23] the most intriguing pathways involve transient σ-complexes formed by weak interactions between the cyclopropane C–H (or even C–C) bonds and the rhodium center. The cyclopropane system has the interesting characteristic of possibly forming highly symmetric σ-complexes, such as intermediate **14** shown in Scheme VII, or analogous intermediates of lower symmetry, such as **17** and **18**. Mechanisms A, B, C, and D and will be discussed for the specific case of rearrangement of [1-^{13}C]cyclopropyl hydride **1a** to the rhodacyclobutanes **4a** and **4b**.

The observed rearrangement occurs to place the ^{13}C label predominantly in the α-position of the rhodacyclobutane ring (Scheme VI; [**4a**]/[**4b**] = 5.6 ± 0.1). This allows some of the possible mechanisms to be ruled out. Mechanism A involves the intermediate formation of a symmetrically coordinated cyclopropane complex **14**, a mode of cyclopropane bonding proposed to occur on metal surfaces.[6] This mechanism can be readily ruled out because subsequent oxidative addition to the C–C bonds of the symmetrically bound cyclopropane would result in the ^{13}C label statistically scrambled between the α- and β-positions of the rhodacyclobutane ring and would predict that [**4a**]/[**4b**] = 2.0.

(24) For an excellent review of platinacyclobutane chemistry, see: Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

Mechanism B involves C–C scission by β-alkyl elimination of the cyclopropyl group and requires either expansion of the rhodium coordination shell to 20 electrons or an $\eta^5 \rightleftharpoons \eta^3$ "slippage" of the C_5Me_5 ring. This pathway would place the ^{13}C label regiospecifically in the β-position of the π-allyl ligand of the proposed intermediate **15**. Subsequent transfer of hydride to the β-carbon would result with the rhodacyclobutane ^{13}C-labeled only in the β-position, predicting that [**4a**]/[**4b**] < 1.0, a result clearly contradictory to our observations.

Interestingly, exactly such a regiospecific β-rearrangement *does* occur on treatment of the [1-^{13}C]cyclopropyliodorhodium complex **7a** with $AgBF_4$ to produce the [β-^{13}C]π-allyl complex **9**. Here the necessary vacant coordination site is generated by abstraction of I^-. A similar regiospecific β-rearrangement of a σ-cyclopropyl to a π-allyl platinum complex has been observed by Puddephatt and co-workers and was proposed to occur by a similar mechanism.[25]

Mechanism C is similar to mechanism B but involves α-allyl elimination and $\eta^5 \rightleftharpoons \eta^3$ "slippage" of the C_5Me_5 ring. The α-alkyl elimination step would place the ^{13}C label regiospecifically in the α-position of the carbene complex **16** as shown in Scheme VII. Subsequent transfer of hydride to this carbon would result in the ^{13}C label residing exclusively in the α-position of the rhodacyclobutane, a result which cannot be rigorously ruled out by the observations. Mechanism D involves the reductive elimination of cyclopropane from **1a** to produce a cyclopropane σ-complex[23] such as **17**. Subsequent rearrangement to the rhodacyclobutane can occur either concertedly or perhaps via an edge cyclopropane complex **18** in which edge-to-edge migrations are slow compared to C–C oxidative addition.

Mechanisms C and D both predict regiospecific insertion into the α-carbon–carbon bond of the cyclopropyl group. As such, they are consistent with the observations made in this study and are the two most difficult mechanisms to distinguish rigorously. However, we feel that mechanism D provides the more reasonable way of interpreting our results. One reason for this is that the type of α-alkyl elimination represented in mechanism C is a very rare occurrence. We are aware of only two such examples. In the more recent, Jones and Lisko reported the photoinduced rearrangement of a σ-cyclopropyl–iron complex into a ferracyclopentenone.[26a] Earlier, Grubbs and co-workers postulated α-elimination, leading to metal–carbene complexes, in the decomposition of nickelacyclohexanes.[27a] Furthermore, in both of these systems a good case can be made that initial formation of 16-electron intermediates are required for the α-elimination to occur. In contrast, although we cannot rule out η^5, η^3-Cp "slippage" as a way of producing such coordinative unsaturation in our systems, despite several attempts we have been unable to obtain positive evidence for such slippage induced by external reagents (e.g., substitution of PMe_3 by $P(CD_3)_3$ is very slow). Finally, in the accompanying paper we reported results implicating σ-complex intermediates in the degenerate isomerizations of alkylhydridorhodium complexes.[23] In view of these considerations, it seems most reasonable at the present time to assume that α-elimination would be slow in our systems, and therefore mechanism D is the more likely (and certainly more economical) hypothesis to use in understanding our results.

The observed regiospecific rearrangement of the 2,2-dimethylcyclopropyl hydride **2** to the β,β-dimethylrhodacyclobutane **4** is consistent with the predictions based on mechanism D. Thus it would be expected that the σ-complex intermediate formed on reductive elimination of **2** would rearrange preferentially into the less highly substituted α-carbon–carbon bond purely on steric grounds to give only the observed isomer **5**.

(25) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1970**, 1733.

(26) (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944. (b) Examples of the reverse reaction are rare also: cf. Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765.

(27) (a) Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1974**, *100*, 7418. (b) Benson, S. W. *Thermochemical Kinetics*, 2nd, ed.; Wiley-Interscience: new York, 1976; p 273. (c) Basolo, F. *Inorg. Chim. Acta.* **1981**, *50*, 65. (d) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054.

Both mechanisms C and D suggest that good interaction between the metal center and the α C–C bond of the cycloalkyl group is an important factor in facilitating these rearrangement reactions. Thus it is not unexpected that cyclopropane with "bent" carbon–carbon bonds which project beyond the carbon framework would participate well in the rhodacyclobutane rearrangement. Cyclobutane, with almost the same total strain energy[27b] and therefore less strain per bond, should have less driving force for rearrangement. Consistent with this trend, cyclopentane with "normal" carbon–carbon bonds and substantially less ring strain energy does not undergo observable carbon–carbon activation.

The rearrangement of **2** to **5** by exclusive insertion into the less highly substituted α-carbon–carbon bond of the cyclopropyl group indicates that steric effects play an important role in these reactions. Consistent with this, the high yields of rearrangement products in neat cyclopropane solvent, compared with the amounts formed in other solvents such as toluene and THF, suggest that dissociation from the complex to form free Cp*RhL and a three-membered ring compound occurs competitively with conversion to rearrangement product. If this occurs, one might ask what effect changes in steric properties might have on the percent of rearranged product observed in these other solvents. It seems likely that decreasing steric bulk might allow C–C insertion in a σ-complex to occur more easily, by slowing dissociation of free cycloalkane from the complex. Conversely, if intramolecularity is enforced only by solvent cages (see discussion in previous paper[23]), an increase in steric bulk might retard the rate of diffusion from the cage, and more C–C insertion product might be observed. Consistent with the σ-complex hypothesis, initial attempts at investigating the rearrangement of the parent complex (η^5-C_5H_5)(PMe_3)Rh(cyclopropyl)(H)[23] indicates that the rearrangement to rhodacyclobutane is more efficient in this unsubstituted cyclopentadienyl complex than in pentamethyl analogue **1**. However, there may also be an electronic effect operating here. Basolo and co-workers have proposed that replacement of Me by H on the Cp ring facilitates bimolecular substitution reaction by allowing more facile $\eta^5 \rightleftharpoons \eta^3$ "slippage" in the C_5H_5 complexes.[27c] Perhaps a certain amount of hapticity change and steric uncrowding combine to facilitate the rearrangement reactions.

As noted by a referee, there is one further important relative rate inference which can be drawn if, in fact, the C–H insertion and cyclopropyl hydride-to-rhodacycloalkane rearrangements proceed via a common σ-complex intermediate or set of intermediates. As mentioned above, the rate of C–C insertion in this complex must be competitive with that for dissociation to free cyclopropane and Cp*RhL. However, when Cp*RhL is generated by H_2 or neopentane elimination at low temperature, and the σ-complex is formed by interaction of this intermediate with cyclopropane, the absence of rhodacycloalkane product requires that the rate of C–H insertion is higher than that for C–C insertion.[23] Therefore, if the σ-complexes are common intermediates (or, more likely, structurally different ones are able to interconvert rapidly), we must conclude that the activation energy barrier associated with insertion of the rhodium center into C–H bonds in the cyclopropane σ-complex is substantially lower than the comparable barriers associated with dissociation of Cp*RhL and with insertion into a C–C bond in the complex. This is consistent with the fact that Cp*(L)Rh(H)(1-methylcyclopropyl)methyl (compound **8** in the previous paper[23]) rearranges to its cyclopropyl C–H inserted isomer Cp*(L)Rh(H)(2,2-dimethylcyclopropyl) essentially quantitatively in toluene-d_8. These considerations also discourage further our consideration of solvent cages[23] as possible alternatives to σ-complexes, because diffusion from a cage containing neutral molecules is normally expected to occur with an activation barrier very close to zero.

Summary and Conclusion

This work provides the first examples of the facile rearrangement of cyclopropyl and cyclobutylhydridorhodium complexes to the corresponding rhodacyclobutane and rhodacyclopentane complexes. Additionally this work has allowed the observation of the second example of a π-allyl complex which adds nucleophiles to the center rather than the end carbon of a π-allyl ligand leading to metallocyclobutanes, and has added one member to the small group of complexes having a tertiary metal–carbon bond.

Cycloalkyl hydrides are the kinetic products of reaction of [Cp*(L)Rh] with cyclopropane and cyclobutane. C–C insertion, the thermodynamically favored process, is found to occur only by subsequent intramolecular rearrangement of the cycloalkyl hydrides by insertion of the metal specifically into the α-carbon–carbon bond of the cycloalkyl group. This supports Suggs' suggestion[27d] that (at least for similar reactive transition-metal species) carbon–carbon activation of more typical alkanes might proceed by prior C–H activation.

Our mechanistic studies suggest that rearrangement of the C–H to C–C insertion products occurs via the intermediacy of alkane C–H σ-complexes. Possibly the conceptually similar η^2-C–C alkane σ-complexes **18** may also be involved as immediate precursors to rhodacycloalkanes **4**, but we have no direct evidence for such species. Very little is known about σ-complexes and further work on understanding and more clearly defining their properties is necessary. Our preliminary observations that the rearrangements occur more efficiently in the η^5-C_5H_5 system is encouraging and suggests that similar C–H to C–C rearrangements may be possible in other systems.

Experimental Section

All manipulations were conducted under a nitrogen atmosphere by using standard or modified Schlenk techniques or in a Vacuum Atmospheres Corp. HE-553 Dri-Lab with attached MO-40-1 Dri-Train. Nuclear magnetic resonance (NMR) spectra were recorded on 250- and 300-MHz highfield Fourier transform instruments consisting of Cryomagnetics, Inc. Magnets, Nicolet 1180 or 1280 data collection systems, and electronics assembled by Rudi Nunlist of the University of California, Berkeley (UCB) and on a Bruker AM 500 highfield Fourier transform spectrometer. Quantitative analysis of the $^{13}C\{^1H\}$ NMR spectra were carried out on the AM 500 NMR spectrometer by use of the Bruker automated program, INVGATE AU, which allows the acquisition of ^1H decoupled ^{13}C NMR spectra with NOE suppression. A relaxation delay time of 3 min was allowed between pulses. Observation of through-space nuclear Overhauser enhancements (NOE) were carried out on the Bruker AM 500 NMR spectrometer with the use of the Bruker automated program, NOEDIFF AU (D1 = 9 s, D2 = 1 s.). The temperature for NMR experiments was regulated by Nicolet and Bruker BVT-1000 temperature control units (±0.1 °C). The temperature control units were calibrated by using standard methanol calibration samples obtained from Wilmad Glass Co. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer by using NaCl solution cells.

Gas-liquid chromatography (GLC) analyses were performed on a Varian 90P chromatograph by using a 10 ft × 0.75 in. glass column packed with 15% Apiezon L on acid washed Chromosorb W at 150 °C (gas flow rate = 20 mL/min). Electron impact mass spectroscopic (MS) analyses were recorded at the UCB mass spectral facility on an AEI MS-12 and a Finnegan 4000 mass spectrometer. Elemental analyses were performed by the UCB microanalytical facility. Mass spectral analyses of volatile gases were carried out by expanding the gases directly into the sampling port of the mass spectrometer. Melting points were taken in glass capillary tubes in a Thomas-Hoover capillary melting point apparatus and are not corrected.

Preparative column chromatography (20 °C) was performed on silica gel that was degassed before being taken into the drybox. Low-temperature (−100 °C) column chromatography was carried out on degassed alumina III in a double-sided column cooled by bubbling N_2 through a Dewar of liquid N_2. All chromatograms were run under air-free conditions. Low temperatures were maintained by liquid N_2 (−196 °C), CH_3OH/liquid N_2 (−95 °C), or acetone/liquid N_2 (−78 °C). Other temperatures were maintained by use of a Neslab Cryocool C-C-100 immersion cooler and a Neslab Endocal ULT-80 refrigerated circulating bath. Kontes k-826510 Teflon stopcocks are referred to as right angle vacuum stopcocks. Cylindrical Pyrex vessels equipped with Kontes k-826510 Teflon stopcocks are referred to as glass bombs.

Tetrahydrofuran and diethyl ether were distilled prior to use from sodium/benzophenone ketyl. Toluene-d_8, benzene-d_6 and -h_6, and tetrahydrofuran-d_8 were vacuum transferred and stored after stirring for 12 h over 1:5 sodium/potassium alloy. Methylcyclohexane-d_{14} and other aliphatic solvents (UV grade) were stirred with concentrated H_2SO_4 for 24 h, washed successively with $KMnO_4$ in 10% H_2SO4, 3 portions of H_2O, and 1 portion of 25% NaOH, dried over $CaCl_2$, and vacuum distilled onto 1:5 sodium/potassium alloy after 3 freeze–pump–thaw cycles. After stirring for 12 h, the solvents were vacuum transferred into a glass

bomb for storage. Cyclopropane and 1,1-dimethylcyclopropane were stirred with a mixture of 2 g of $HgSO_4$, 0.6 mL of concentrated H_2SO_4, and 25 mL of H_2O for 5 h. The mixture was degassed by 3 freeze–pump–thaw cycles and vacuum transferred at −78 °C onto 1:5 sodium/potassium alloy. After stirring for 24 h at room temperature, the hydrocarbons were vacuum transferred into a glass bomb for storage. Cyclobutane was prepared according to the method of D. Connor and E. Wilson from 1,4-dibromobutane and lithium amalgam.[29] The cyclobutane obtained was further purified as described above for cyclopropane. $CDCl_3$ was vacuum transferred from P_2O_5 and degassed by freeze–pump–thaw cycles. Trimethylphosphine was purchased frm the Strem Company, dried over 1:5 sodium/potassium alloy, and always handled by vacuum transfer. $AgBF_4$ was obtained from the Aldrich Chemical Co. and purified by recrystallization from toluene. $LiEt_3BH$ and $LiEt_3BD$ were obtained as 1 M solutions in THF from the Aldrich Chemical Company. [^{13}C]Methyl iodide (99% ^{13}C-enriched) was obtained from Cambridge Isotope Laboratories and diluted to 55% enrichment with [^{12}C]methyl iodide. $Cp^*(PMe_3)RhX_2$ (X = Cl, Br, and I) were prepared according to the cited literature procedures.[30] The preparations of **1**, **2**, and **3** are described in the accompanying paper.[23] $RhCl_3$ was obtained from Johnson Matthey Inc.

[2-^{13}C]Acetic acid, 55% ^{13}C-enriched, was prepared as an aqueous solution in 85% yield from [^{13}C]iodomethane (12.0 g, 84 mmol, 55% ^{13}C enriched) according to the procedure of Calvin et al.[31]

[2-^{13}C]Bromoacetic acid, 55% ^{13}C-enriched (mp 46–49 °C), was isolated in 83% yield (based on $^{13}CH_3I$) after treatment of [1-^{13}C]acetic acid with trifluoromethanesulfonic anhydride $(CF_3CO)_2O$) followed by Br_2 and phosphorous tribromide according to the procedure of Roberts and Poulter.[32]

Ethyl [2-^{13}C]bromoacetate, 55% ^{13}C-enriched (bP 158–159 °C), was obtained in 87% yield by esterfication of [2-^{13}C]bromoacetic acid in ethanol with *p*-toluenesulfonic acid catalyst according to the procedure of Stuetzel et al. for the preparation of the chloro analogue.[33]

Ethyl [2-^{13}C](diethoxyphosphinyl)acetate, 55% ^{13}C-enriched (bp 105–113 °C, 1 torr), was prepared in 97% yield from ethyl [2-^{13}C]-bromoacetate by treatment with triethyl phosphite according to the procedure of Davidson and Kenyon.[34]

Ethyl [2-^{13}C]acrylate, 55% ^{13}C-enriched, was prepared as a dimethoxyethane solution in 73% yield from ethyl [2-^{13}C](diethoxyphosphinyl)acetate by treatment with NaH followed by paraformaldehyde according to the procedure of Davidson and Kenyon.[35]

Ethyl [1-^{13}C]cyclopropanecarboxylate, 55% ^{13}C-enriched, was prepared in 60% yield (based on ethyl [2-^{13}C](diethoxyphosphinyl)acetate) by treatment of ethyl [2-^{13}C]acrylate with diazomethane and catalytic amounts of $Pd(OAc)_2$ according to the method of Vorbruggen for the cyclopropanation of acrylate esters.[35]

Cyclopropanecarboxylic [1-^{13}C]acid, 55% ^{13}C-enriched, was synthesized from ethyl [1-^{13}C]cyclopropanecarboxylate in 83% yield as a crude solid by the following procedure. A mixture of ethyl [1-^{13}C]cyclopropanecarboxylate (3.66 g, 221 mmol) and NaOH (1.23 g, 30.8 mmol) in 10 mL of water was heated to 85 °C for 2 h. The solution was washed with ether and acidified with 1:1 hydrochloric acid, and the cloudy aqueous solution which was produced was extracted with ether (4 × 10 mL). The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was evaporated to yield the crude cyclopropanecarboxylic [1-^{13}C]acid (2.28 g).

Silver [1-^{13}C]cyclopropanecarboxylate, 55% ^{13}C-enriched, was prepared from the crude cyclopropanecarboxylic [1-^{13}C]acid in 76% crude yield (based on ethyl [1-^{13}C]cyclopropanecarboxylate) by neutralization with ammonium hydroxide followed by treatment with silver nitrate according to the procedure of Roberts and Chambers.[36]

[1-^{13}C]Bromocyclopropane, 55% ^{13}C-enriched, was prepared in 51% yield by treatment of silver [1-^{13}C]cyclopropanecarboxylate with Br_2 in dichlorofluoromethane according to the procedure of Roberts and Chambers.[36]

[1-^{13}C]Cyclopropyllithium, 55% ^{13}C enriched, was prepared in 89% yield by treatment of [1-^{13}C]bromocyclopropane with lithium according to the procedure of Seyferth and Cohen.[37]

(η^5-C_5Me_5)(PMe_3)Rh([1-^{13}C]cyclopropyl)(I), 55% ^{13}C-enriched, was prepared as described earlier[23] from [1-^{13}C]cyclopropyllithium and (η^5-C_5Me_5)(PMe_3)RhI_2 in THF in 91% yield.

(η^5-C_5Me_5)(PMe_3)Rh([1-^{13}C]cyclopropyl)(H) (1a), 55% ^{13}C-enriched, was prepared in 93% yield as described earlier[23] by the treatment of (η^5-C_5Me_5)(PMe_3)Rh([1-^{13}C]cyclopropyl)(I) with 2 equiv of *t*-BuLi at −78 °C followed by deuteration with C_2H_5OD at −60 °C: ^{1}H NMR (toluene-d_8, −90 °C) δ 1.73 (d, *J* = 1.8 Hz, 15 H), 1.21 (dd, *J* = 9.7, 0.7 Hz, 9 H), 0.53–0.0 ppm (m, 5 H), 14.73 (dd, *J* = 45.1, 32.4 Hz, 1 H); ^{13}C{^{1}H} NMR (toluene-d_8, −60 °C) δ 97.3 (m, C_5Me_5), 19.5 (d, *J* = 30.2 Hz, PMe_3), 12.5 (m, CH_2), 10.6 (s, C_5Me_5), 9.8 (m, CH_2), 7.4 (dd, *J* = 38.3, 19.5 Hz, RhCH). Integration of the ^{13}C satellites of the β-carbons of the cyclopropyl group (12.5 and 9.8 ppm) indicated that the α-carbon position of cyclopropyl group was 55% ^{13}C-enriched.

Preparation of Rhodacyclobutanes by Thermal Rearrangement of the Cycloalkylhydridorhodium Complexes. **(a) (η^5-C_5Me_5)(PMe_3)Rh–CH_2–CH_2–CH_2 (4).** The cyclopropyl hydride **1** (0.64 mmol) was prepared as described earlier[23] at −60 °C in a glass bomb equipped with vacuum stopcock. The complex was cooled to −196 °C, and cyclopropane (~5 mL) was vacuum transferred into the bomb. The mixture was warmed to −60 °C and agitated to allow **1** to dissolve completely. The solution was then warmed to −15 °C for 1 h. After cooling the solution to −70 °C, the cyclopropane was carefully removed under high vacuum. The resulting pale brown residue was taken up in pentane (2 mL) and chromatographed on alumina III at −100 °C with 2% Et_2O/pentane as elutant. The product eluted in the first fraction; it was collected, concentrated to 2 mL, and cooled to −40 °C to yield the rhodacyclobutane **4** as large yellow-brown crystals. The crystals were removed by filtration and vacuum dried to afford 0.16 g (73%) of the product in analytically pure form: ^{1}H NMR (C_6D_6) δ 3.48 (m, 1 H), 3.20 (m, 1 H), 1.77 (d, *J* = 1.9 Hz, 15 H), 1.04 (dd, *J* = 8.7, 1.0 Hz, 9 H), 0.38 (m, 2 H), 0.20 (m, 2 H); ^{13}C NMR (gated, C_6D_6) δ 96.57 (m, C_5Me_5), 31.33 (dt, *J* = 125, 5.8 Hz, CH_2), 16.30 (qd, *J* = 127.0, 28.0 Hz, PMe_3), 9.89 (q, *J* = 125.5 Hz, C_5Me_5), −22.85 (tdd, *J* = 132.0, 19.1, 9.8 Hz, $RhCH_2$); ^{31}P{^{1}H} NMR (C_6D_6) δ 6.37 (d, *J* = 188.5 Hz); MS, 356 (M^+); mp 185 °C dec. Anal. Calcd for $C_{16}H_{30}PRh$: C, 53.98; H, 8.43. Found: C, 53.83; H, 8.39.

(b) (η^5-C_5Me_5)(PMe_3)Rh–CH_2–CMe_2–CH_2 (5). This complex was prepared exactly as described for **4** from the thermal rearrangement of **2** (0.64 mmol) in 1,1-dimethylcyclopropane (5 mL). The product was obtained as yellow microcyrstals (0.2 g, 83% yield): ^{1}H NMR (C_6D_6) δ 1.76 (d, *J* = 2.1 Hz, 15 H), 1.17 (s, 3 H), 1.13 (s, 3 H), 1.06 (dd, *J* = 8.81, 1.1 Hz, 9 H), 0.32 (m, 2 H), 0.23 (m, 2 H); ^{13}C NMR (gated, C_6D_6) δ 96–98 (m, C_5Me_5), 43.21 (d, *J* = 6.1 Hz, CMe_2), 21.2 (q, *J* = 126.1 Hz, (CMe_2), 16.58 (qd, *J* = 126.8, 28.1 Hz, PMe_3), 11.21 (q, *J* = 125.6 Hz, CMe_2), 9.5 (q, *J* = 1261.1 Hz, C_5Me_5), −23.1 (tdd, *J* = 134.2, 21.2, 9.3 Hz, $RhCH_2$); ^{31}P{^{1}H} NMR (C_6D_6) δ 7.1 (d, *J* = 187.3 Hz); MS, 384 (M^+); mp 187 °C dec. Anal. Calcd for $C_{18}H_{34}PRh$: C, 56.27; H, 8.86. Found: C, 56.02; H, 8.54.

(c) (η^5-C_5Me_5)(PMe_3)Rh–CH_2–$(CH_2)_2$–CH_2 (6). The cyclobutyl hydride **3** (0.64 mmol) was prepared at −60 °C in a glass bomb equipped with a vacuum stopcock.[23] The complex was cooled to −196 °C, and cyclobutane (~30 mL) was vacuum transferred into the bomb. The mixture was warmed to −60 °C and agitated to allow **3** to dissolve completely. The solution was warmed to −25 °C for 3 h and then cooled to −78 °C, and the cyclobutane was carefully removed under high vacuum. The resulting brown residue was dissolved in 2 mL of pentane and purified by chromatography on alumina III at −100 °C with 3% Et_2O/pentane as elutant. The product eluted in the first fraction and was collected, and the solvent was removed in vacuo. The yellow residue was dissolved in hexamethyldisiloxane (~1 mL) and cooled to −78 °C. The resulting yellow/brown crystals of the product were removed by filtration and vacuum dried to yield 0.71 g (30% yield) of **6**: ^{1}H NMR (toluene-d_8) 2.2 (m, 4 H), 1.78 (d, *J* = 1.9 Hz, 15 H), 1.21 (m, 4 H), 0.91 (dd, *J* = 8.7, 0.9 Hz, 9 H); ^{13}C NMR (gated, toluene-d_8) δ 96.31 (m, C_5Me_5), 33.2 (t, *J* = 125.3 Hz, CH_2), 22.3 (tdd, *J* = 128.2, 19.3, 9.6 Hz, $RhCH_2$), 17.1

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(qd, J = 127.1, 28.3 Hz, PMe_3), 9.23 (q, J = 126.3 Hz, C_5Me_5); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 7.3 (d, J = 179.2 Hz); MS, 370 (M^+); mp 176 °C dec. Anal. Calcd for $C_{17}H_{32}PRh$: C, 55.15; H, 8.65. Found: C, 55.31; H, 8.72.

Reactions of the Rhodacyclopentane 6. (a) With HCl. The purified rhodacyclopentane **6** (10 mg, 0.027 mmol) was dissolved in benzene (3 mL) in a glass bomb equipped with a vacuum stopcock. The solution was cooled to −196 °C and evacuated, and excess pure dry HCl was added by vacuum transfer. The reaction mixture was warmed to room temperature and agitated periodically for 30 min. During this time the reaction changed color from a pale yellow to bright orange as (η^5-C_5Me_5)(PMe_3)$RhCl_2$ formed. The bomb was cooled to −78 °C, and the volatile gases were allowed to expand into a flask equipped with a rubber septum; N_2 was then added to bring the system to atmospheric pressure. A sample of the gases was removed and analyzed by GLC/MS spectral techniques. The mixture consisted of 53% n-butane (as identified by comparison to an authentic sample) and other unidentified volatiles, probably butenes. The benzene and HCl were removed in vacuo from the reaction mixture, and the orange residue was taken up in C_6D_6. Subsequent ^1H NMR spectra allowed identification of the material as (η^5-C_5Me_5)(PMe_3)$RhCl_2$ by comparison with an authentic sample.

(b) With Br_2. The purified rhodacyclopentane **6** (10 mg, 0.027 mmol) was dissolved in diethyl ether (~3 mL) in a glass bomb equipped with a vacuum stopcock. The solution was cooled to −196 °C and evacuated, and Br_2 (3 mL, 0.059 mmol) was added via vacuum transfer. The reaction was shielded from light and warmed to −78 °C for 2 h with periodic agitation. The mixture was then allowed to warm to room temperature, and the volatile materials were vacuum transferred to a flask equipped with a rubber septum. GLC/MS spectral analysis of the Et_2O solution revealed the presence of 1,4-dibromobutane (as identified by comparison with an authentic sample) along with minor amounts of unidentified products. The red residue in the glass bomb was dissolved in C_6D_6 (0.6 mL) and analyzed by ^1H NMR. It was found to consist of (η^5-C_5Me_5)(PMe_3)$RhBr_2$ by comparison with an authentic sample.

Preparation of Cationic π-Allyl Complexes 9, 9a, and 10 from Cyclopropyliodo Complexes 7, 7a, and 8, Respectively. (a) [(η^5-C_5Me_5)(PMe_3)Rh(η^3-C_3H_5)]$^+BF_4^-$ (9). Cyclopropyl iodide **7** (0.31 g, 0.64 mmol)[23] was dissolved in CH_2Cl_2 (20 mL). The solution was stirred vigorously, and $AgBF_4$ (0.13 g, 0.67 mmol) dissolved in CH_2Cl_2 (5 mL) was added dropwise at room temperature over a period of 30 min. The color of the reaction mixture changed from dark red to bright orange over the course of the addition along with the formation of a yellow precipitate of insoluble AgI. The solution was allowed to stir for an additional 30 min and was filtered to remove the AgI. The filtered solution was concentrated in vacuo to 3 mL and cooled to −45 °C to yield **9** as bright yellow crystals. The crystals were removed by filtration and vacuum dried at room temperature to afford 0.26 g (91% yield) of product: ^1H NMR (CD_2Cl_2) 3.97 (m, 1 H), 2.96 (br d, J = 7.3 Hz, 2 H), 1.97 (br t, J = 11.5 Hz, 2 H), 1.88 (d, J = 2.8 Hz, 15 H), 1.40 (dd, J = 9.7, 0.6 Hz, 9 H); ^{13}C NMR (gated, CD_2Cl_2) 102.1 (m, C_5Me_5), 89.04 (br d, J = 162.6 Hz, CH), 51.44 (br t, J = 159.1 Hz, $RhCH_2$), 16.4 (qd, J = 130, 22.5 Hz, PMe_3), 9.89 (q, J = 128.0 Hz, C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) −0.21 (d, J = 156.9 Hz); MS, 442 (M^+); mp 230 °C dec. Anal. Calcd for $C_{16}H_{29}BF_4PRh$: C, 43.46; H, 6.61. Found: C, 43.23; H, 6.76.

(b) [(η^5-C_5Me_5)(PMe_3)Rh([2-^{13}C]η^3-C_3H_5)]$^+BF_4^-$, 55% ^{13}C-Enriched (9a). This ^{13}C-labeled complex was prepared exactly as described above for **9** from the reaction of the ^{13}C-labeled complex **7a** (0.063 g, 0.13 mmol) dissolved in CH_2Cl_2 (5 mL) with $AgBF_4$ (0.027 g, 0.14 mmol). The crystalline complex was obtained in 89% yield (0.051 g): ^1H NMR (CD_2Cl_2) 3.97 (br m, 1 H), 2.96 (m, 2 H), 1.97 (m, 2 H), 1.88 (d, J = 2.8 Hz, 15 H), 1.40 (dd, J = 9.7, 0.6 Hz, 9 H); MS, 442 (M^+) 45, 443 (M^+), 55. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 102.0 (m, C_5Me_5), 89.07 (br s, CH), 51.42 (m, $RhCH_2$), 16.4 (d, J = 22.3 Hz, PMe_3), 9.91 (s, C_5Me_5). Integration of the ^{13}C resonances of the α and β carbons of the π-allyl group indicated that only the β-carbon was ^{13}C-enriched.

[(η^5-C_5Me_5)(PMe_3)Rh(η^3-CMe_2-CH-CH_2)]$^+BF_4^-$ (10). This complex was prepared exactly as described above for the preparation **9** from the reaction of 2,2-dimethylcyclopropyl iodide **8** (0.32 g, 0.64 mmol) and $AgBF_4$ (0.13 g, 0.67 mmol) in CH_2Cl_2 (20 mL): ^1H NMR (CD_2Cl_2) 3.77 (m, 1 H), 2.92 (br d, J = 7.1 Hz, 2 H), 2.23 (br t, J = 11.2 Hz, 2 H), 1.78 (d, J = 2.7 Hz, 15 H), 1.52 (s, 3 H), 1.46 (d, J = 9.7 Hz, 9 H), 1.13 (d, J = 3.1 Hz, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 101.60 (m, C_5Me_5), 86.65 (d, J = 5.0 Hz, CH), 81.2 (dd, J = 10.3, 3.9 Hz, $RhCMe_2$) 48.9 (dd, J = 13.6, 3.8 Hz, $RhCH_2$), 28.36 (s, $RhCMe_2$), 24.15 (d, J = 7.9 Hz, $RhCMe_2$), 17.39 (d, J = 30.3 Hz, PMe_3), 9.81 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −0.31 (d, 157.1 Hz); MS, 469.8 (M^+); mp 215 °C dec. Anal. Calcd for $C_{18}H_{33}BF_4PRh$: C, 45.99; H, 7.03. Found: C, 45.71; H, 7.06.

Preparation of the Rhodacyclobutanes 4, 4b, and 11 from the Cationic π-Allyl Complexes 9, 9a, and 10, Respectively. (a) (η^5-C_5Me_5)(PMe_3)-Rh-CH_2-CH_2-CH_2 (4). The π-allyl complex **9** (0.28 g, 0.64 mmol) was slurried in THF (~20 mL). The stirred slurry was cooled to −78 °C, and $LiEt_3BH$ (1.0 M in THF, 0.67 mL, 0.67 mmol) was added dropwise over a period of 30 min. The reaction mixture was stirred for a further 30 min at this temperature, then allowed to warm to room temperature, and stirred for an additional 15 min. The THF was removed in vacuo, and the resulting yellow/brown residue was extracted 3 times with 10 mL each of hexane. The combined hexane extracts were concentrated and chromatographed on alumina III at −100 °C with 3% Et_2O/pentane as elutant. The product eluted in the first fraction; it was collected, concentrated to 2 mL and cooled to −40 °C to yield 0.19 g of the product as large yellow crystals (85% yield). The complex was identical with that obtained by the rearrangement of **1**.

(b) (η^5-C_5Me_5)(PMe_3)Rh-CH_2-$^{13}CH_2$-CH_2, 55% ^{13}C-Enriched (4b). This ^{13}C-labeled complex was prepared exactly as described above from a THF solution (5 mL of **9a** (0.05 g, 0.11 mmol) and $LiEt_3BH$ (1.0 m in THF, 0.12 mL, 0.12 mmol). After low-temperature chromatography the complex was obtained in 83% yield (0.032 g): ^1H NMR (C_6D_6) δ 3.40–3.0 ppm (m, 2 H), 1.77 (d, J = 1.9 Hz, 15 H), 1.04 (dd, J = 8.7, 1.0 Hz, 9 H), 0.38–0.20 (m, 4 H); MS, 356 (M^+) 45, 356 (M^+) 55; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 96.57 (m, C_5Me_5), 31.33 (t, J = 5.8 H_2, CH_2) 16.30 (d, J = 28.0 Hz, PMe_3), 9.89 (s, C_5Me_5), −22.85 (m, $RhCH_2$). Integration of the ^{13}C resonances of the α and β carbons of the rhodacyclobutane ring indicated that only the β-position was ^{13}C enriched.

(c) (η^5-C_5Me_5)(PMe_3)Rh-CMe_2-CH_2-CH_2 (11). This complex was prepared exactly as described above for **4** from the reaction of the π-allyl complex **8** (0.30 g, 0.64 mmol) and $LiEt_3BH$ (1.0 m in THF, 0.67 mL, 0.67 mmol) in THF. The product was obtained as yellow microcrystals in 72% yield (0.17 g): ^1H NMR (C_6D_6) δ 3.41 (m, 1 H), 2.52 (br q, J = 11.2 Hz, 1 H), 1.70 (d, J = 2.1 Hz, 15 H), 1.50 (s, 3 H), 1.20 (dd, J = 3.9, 1.3 Hz, 3 H), 1.10 (dd, J = 8.3, 1.0 Hz, 9 H), 0.81 (m, 1 H), 0.53 (m, 1 H); ^{13}C NMR (gated, toluene-d_8) δ 97.65 (m, C_5Me_5), 47.88 (tdd, J = 124.5, 3.9, 3.9 Hz, CH_2), 37.68 (q, J = 126.5 Hz, $RhCMe_2$), 36.56 (qd, J = 125.2, 11.0 Hz, $RhCMe_2$), 18.78 (qd, J = 128.2, 24.5 Hz, PMe_3), 10.63 (q, J = 125.76 Hz, C_5Me_5), −4.69 (dd, J = 19.68, 6.62 Hz, $RhCMe_2$), −16.81 (tdd, J = 137.1, 19.72, 10.18 Hz, $RhCH_2$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 6.51 (d, J = 182.6 Hz); MS, 384 (M^+); mp 159 °C dec. Anal. Calcd for $C_{18}H_{34}PRh$: C, 56.24; H, 8.86. Found: C, 56.35; H, 8.93.

Attempted preparation of (η^5-C_5Me_5)(PMe_3)Rh-CH_2-$(CH_2)_2$-CH_2 from Cp*(L)RhI_2 and 1,4-dilithiobutane (based on procedure by Diversi et al.[20]). Cp*(L)RhI_2 (1.5 g, 2.64 mmol) was slurried in toluene (50 mL). The slurry was cooled to −20 °C with vigorous stirring, and 1,4-dilithiobutane[38] (0.75 M in Et_2O, 3.87 mL, 2.91 mmol) was added over a period of 10 min. The reaction mixture was stirred for a further 60 min at −20 °C and allowed to warm to room temperature. The reaction mixture changed from a dark red slurry to a pale orange solution along with the precipitation of insoluble LiI. The toluene was removed in vacuo, and the resulting orange residue was extracted 3 times with 10 mL of pentane. The combined extracts were filtered, and the solvent was removed in vacuo. The residue was taken up in 1.5 mL of pentane and chromatographed on alumina III at −100 °C with 2% Et_2O/pentane as elutant. The product, as identified by ^1H NMR, along with several impurities eluted in the first fraction and was collected, and the solvent was removed. Attempts at crystallization from hexamethyldisiloxane failed to afford the product in pure form.

Reaction of [(η^5-C_5Me_5)(PMe_3)Rh(η^3-C_3H_5)]$^+BF_4^-$ (9) with $LiEt_3BD$ (NMR Scale). The π-allyl complex (13.9 mg, 0.032 mmol) was dissolved in 5 mL of THF. The solution was cooled to −78 °C, and $LiEt_3BD$ (1.0 M in THF, 33 mL, 0.033 mmol) was added dropwise with stirring over a period of 10 min at −78 °C. The reaction mixture was allowed to warm to room temperature, and the THF was removed in vacuo. The residue was extracted with 0.6 mL of C_6D_6 and filtered through a plug of glass wool in a Pasteur pipette directly into an NMR tube. The tube was capped, and the contents were analyzed by ^1H NMR. The tube was reopened, the C_6D_6 was removed in vacuo and replaced with C_6H_6 (0.6 mL), and the solution was analyzed by ^2H NMR [^1H NMR (C_6D_6) δ 3.45 (m, 1 H), 1.77 (d, J = 1.9 Hz, 15 H), 1.04 (dd, J = 8.7, 1.0 Hz, 9 H), 0.35 (m, 2 H), 0.18 (m, 2 H)]. Integration of the residual proton region at 3.2 ppm against the C_5Me_5 resonances indicated that the complex was >95% deuterium labeled in this position [$^2H\{^1H\}$ NMR (C_6H_6) δ 3.18 (br s)]. No resonance could be detected at 3.48 ppm, within the sensitivity of the analysis (±10%).

Thermal Rearrangement of the Cycloalkylhydridorhodium Complexes in Various Solvents. NMR Scale. These experiments are exemplified by

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the thermal rearrangement of the cyclopropyl hydride **1** in toluene-d_8. Complex **1** (22.8 mg, 0.064 mmol) was prepared at −60 °C in an NMR tube equipped with a vacuum stopcock. The solution was cooled to −196 °C, and toluene-d_8 (0.6 mL) and tetramethylsilane (Me_4Si, 0.032 mmol) were vacuum transferred into the tube. The tube was flame sealed and warmed to −60 °C, and the contents were analyzed at −60 °C by ^1H NMR in order to precisely determine the amount of **1** present (by integration relative to Me_4Si). The tube was then warmed to 20 °C for 1 h and subsequently analyzed by ^1H NMR. The rhodacyclobutane **4** was found to be produced in 66% yield along with 33% of a mixture of *m*- and *p*-tolyl deuterides **14**, which were identified by comparison with Jones and Feher's data on these complexes:[19b] ^1H NMR of **4** in toluene-d_8 3.35 (m, 1 H), 2.95 (m, 1 H), 1.70 (d, J = 1.9 Hz, 15 H), 0.975 (dd, J = 8.7, 1.0 Hz, 9 H), 0.1 (m, 2 H), −0.05 (m, 2 H).

(b) Thermal Rearrangement of 1 in THF-d_8. The rhodacyclobutane **4** was produced in 62% yield along with several unidentified products: ^1H NMR of **4** in THF-d_8 δ 2.95 (m, 1 H), 2.63 (m, 1 H), 1.75 (d, J = 1.9 Hz, 15 H), 1.11 (dd, J = 8.7, 1.0 Hz, 9 H), −0.13 (m, 4 H).

(c) Thermal Rearrangement of 1 in Methylcyclohexane-d_{14}. The rhodacyclobutane **4** was produced in 65% yield along with several unidentified products: ^1H NMR of **4** methylcyclohexane-d_{14} δ 2.95 (m, 1 H), 2.71 (m, 1 H), 1.71 (d, J = 1.9 Hz, 15 H), 1.27 (dd, J = 8.7, 1.0 Hz, 9 H), −0.05 (m, 2 H), −0.09 (m, 2 H).

(d) Thermal Rearrangement of 2,2-Dimethylcyclopropyl Hydride 2 in Toluene-d_8. The 2,2-dimethyl rhodacyclobutane **5** was found to be produced in 76% yield along with 23% of the meta and para isomers of the tolyl deuterides **14**: ^1H NMR of **5** in toluene-d_8 δ 1.72 (d, J = 2.1 Hz, 15 H), 1.08 (s, 3 H), 1.06 (s, 3 H), 1.06 (dd, J = 8.8, 1.1 Hz, 9 H), 0.2 (m, 2 H), 0.13 (m, 2 H).

Thermal Rearrangement of [1-^{13}C]Cyclopropyl Hydride 1a at −20 °C Toluene-d_8. The ^{13}C-labeled complex **1a** (~0.09 mmol) was prepared as described above in NMR tube equipped with a vacuum stopcock. The complex was cooled to −196 °C, and toluene-d_8 (0.6 mL) was vacuum transferred into the tube. The tube was flame sealed, warmed to −60 °C, and quickly placed in an NMR probe cooled to −60 °C. The solution of **1a** was examined at this temperature by ^1H and ^{13}C NMR. It was then warmed to −20 °C, and ^1H and ^{13}C NMR spectra were obtained periodically until the rearrangement of **1a** was complete (see text). The tube was cooled to −196 °C, cracked open as described in the accompanying paper,[23] and warmed to −78 °C. The volatile materials evolved were examined by mass spectroscopy and found to consist of [^{13}C]-cyclopropane (m/e = 43, 55) and [^{12}C]cyclopropane (m/e = 42, 45) along with minor amounts of toluene-d_8.

Thermal Rearrangement of 1 in the Presence of [2-^{13}C]Rhodacyclobutane 4b. The cyclopropyl hydride **1** (0.047 mmol) was prepared in an NMR tube equipped with a right angle vacuum stopcock. The complex was cooled to −196 °C, and **4b** (16.0 mg, 0.047 mmol) dissolved in toluene-d_8 (0.20 mL) was carefully added via syringe (care was taken to avoid warming **1** above −60 °C). The tube was then evacuated, flame sealed, and deliberately warmed to −60 °C. The NMR tube was quickly placed into a NMR probe cooled to −60 °C and examined by ^1H and ^{13}C NMR spectroscopy. The tube was then allowed to warm to −20 °C and again analyzed by ^1H and ^{13}C NMR. ^{13}C NMR analysis indicated that the ^{13}C label remained only at the β position of the rhodacyclobutane. The NMR tube was cooled to −198 °C, cracked open as described in the accompanying paper,[23] and warmed to −78 °C. The cyclopropane evolved was analyzed by mass spectroscopy and found to consist only of [^{12}C]cyclopropane; no enriched [^{13}C]cyclopropane was detected.

Thermal Rearrangement of 2 in the Presence of 11. The 2,2-dimethylcyclopropyl hydride **2** (approximately 0.047 mmol) was prepared in an NMR tube equipped with a right angle vacuum stopcock. The complex was cooled to −100 °C and **11** (16.0 mg, 0.047 mmol) dissolved in toluene-d_8 (0.20 mL) was carefully added via syringe to the NMR tube so as to avoid warming the cyclopropyl hydride complex **2** above −60 °C. The solution was cooled to −190 °C, the tube was evacuated, and tetramethylsilane (Me_4Si, 0.047 mmol) and toluene-d_8 (0.4 mL) were added by vacuum transfer. The tube was flame sealed and warmed to −60 °C, and the amount of **11** was determined (relative to Me_4Si) by ^1H NMR from integration of the rhodacyclobutane and methyl resonances of **11** at 3.45, 2.57, and 1.53 ppm, respectively. The solution was warmed to −20 °C for 1 h, and the solution was examined by ^1H NMR. The complex **2** was found to have completely rearranged to **5** and **14** as described above. However, the amount of **11** relative to Me_4Si was found to be unchanged, indicating that the material did not isomerize under the reaction conditions.

Kinetics of the Thermal Rearrangement of 1 in Toluene-d_8 and THF-d_8. These experiments were carried out as described for the rearrangement of **1** in toluene-d_8, at 20 °C. The reaction was monitored by following, with ^1H NMR, the disappearance and appearance of the PMe_3 resonances of **1** and **4**, respectively, every 15 min for 5 h. The reactions were determined to follow first-order kinetics in both solvents from plots of $\ln([\mathbf{1}_0]/[\mathbf{1}_t])$ vs. $1/t$, giving rate constants of $(2.1 \pm 0.2) \times 10^{-4}$ s^{-1} in toluene-d_8 and $(2.3 \pm 0.2) \times 10^{-4}$ s^{-1} in THF-d_8.

The effects of added PMe_3 were determined by adding PMe_3 (10 equiv, 0.90 mmol) to **1** along with the toluene-d_8. The rearrangement of **1** was followed by ^1H NMR as described above. Under these conditions the reaction was found to follow clean first-order kinetics with a rate constant of $(2.0 \pm 0.3) \times 10^{-4}$ s^{-1}.

PMe_3 exchange was investigated by adding $P(CD_3)_3$ (3 equiv, 0.027 mmol) to **1** along with THF-d_8. $P(CD_3)_3$ exchange was evidenced by the appearance of free protiated PMe_3 (0.95 ppm, d, J = 2.5 Hz). After complete rearrangement of **1** had occurred, only ~0.1 equiv of free PMe_3 was found to be formed (determined by integration relative to the C_5Me_5 resonances of the products).

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