of the solutions were sealed in glass tubing and heated in the oil bath. The tubes were cooled and opened, and the water was evaporated under a stream of air at 100 °C (oil bath). Although these conditions are rather drastic, they do not hydrolyze the dipeptide significantly. The dipeptides were separated by TLC after heating. This demonstrated that they were still present as the dipeptides. Only a very slight amount of hydrolysis occurs under these nearly neutral conditions. Dipeptides require strong acid (6 N HCl), high temperature (110 °C), and 22 h for hydrolysis.

**Sample Derivatization. *N*-(Trifluoroacetyl)amino Acid Isopropyl Esters.** The dipeptides were hydrolyzed to the amino acids with 6 N hydrochloric acid at 100 °C for 22 h, and the aqueous acid was removed as described above. The last traces of moisture were removed by azeotropic distillation with dichloromethane and evaporation under a stream of air. To each dried amino acid residue was added 2-propanol/HCl (4 N, 1 mL). The tubes were resealed and heated for 2 h at 100 °C. The excess 2-propanol was removed under a stream of air, dichloromethane was added, and the solvent was evaporated again. Derivatization was completed by adding 1-1.5 mL of trifluoroacetic anhydride in dichloromethane (30%). After the mixture had remained 20 min at room temperature, the excess reagent was removed by a stream of air. The residue was taken up in dichloromethane and transferred to small rubber-capped vials. There was no detectable racemization due to hydrolysis of peptide compounds or due to derivatizations.

**Gas Chromatography.**[21] Triplicate GC analyses were run on each sample using appropriate isothermal conditions at 140 °C. A stainless steel capillary column (150 ft × 0.02 in.) coated with an optically active mixed-phase consisting of 60% *N*-docosanoyl-L-valyl-*tert*-butylamide and 40% *N*-octadecanoyl-L-valyl-L-valylcyclohexyl ester was used. In all instances base line resolution was obtained for the D and L enantiomeric amino acid derivatives. The gas chromatograph used was an HP 5880A with electronic integration and a FID detector. The carrier gas was nitrogen.

**Buffer Concentration Study.** The ionic strengths of the samples were made identical by adding sodium chloride to the samples which were not of the highest buffer concentration (0.100 M). For example, the ionic strength of the 0.025 M phosphate buffer was made equal to that of the 0.100 M solution ($\mu$ = 0.1695) by adding 0.854 g of NaCl to 100 mL of the 0.025 M buffer.

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**Registry No.** Val-Pro-OMe·HCl, 95500-47-3; Val-Pro (DKP), 2854-40-2; Gly-Val-OMe·HCl, 79638-93-0; Gly-Val (DKP), 16944-60-8; Val-Gly-OMe·HCl, 2421-57-0; Ala-Pro-OMe·HCl, 71067-42-0; Ala-Pro (DKP), 36357-32-1; Ile-Pro-OMe·HCl, 104465-31-8; Ile-Pro (DKP), 57089-60-8; Gly-Ala-OMe·HCl, 59095-76-0; Gly-Ala (DKP), 4526-77-6; Ala-Gly-OMe·HCl, 23404-09-3; Gly-Ile-OMe·HCl, 104465-32-9; Gly-Ile (DKP), 59652-63-0; Ile-Gly-OMe·HCl, 2421-59-2; Ala-Pro, 13485-59-1; Val-Pro, 20488-27-1; Ile-Pro, 37462-92-3; Ala-Gly, 687-69-4; Val-Gly, 686-43-1; Ile-Gly, 868-28-0; Gly-Ala, 3695-73-6; Gly-Val, 1963-21-9; Gly-Ile, 19461-38-2; Phe-Gly, 721-90-4; Gly-Leu, 869-19-2; Gly-Phe, 3321-03-7; Me-Gly-Ala, 53846-71-2; Me-Gly-Leu, 98951-55-4; Me-Gly-Phe, 17123-28-3; Me-Gly-Val, 98998-74-4; Me-Gly-Ile, 104465-33-0; Ac-Gly-Ala, 79806-70-5; Ac-Gly-Leu, 29852-55-9; Ac-Gly-Phe, 13716-72-8; β-Ala-Ala, 34322-87-7; β-Ala-Leu, 17136-25-3; β-Ala-Phe, 17136-28-6; β-Ala-Val, 17136-26-4; β-Ala-Ile, 104465-34-1.

# Isomerization of the Hydridoalkylrhodium Complexes Formed on Oxidative Addition of Rhodium to Alkane C-H Bonds. Evidence for the Intermediacy of $\eta^2$-Alkane Complexes

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**Abstract:** The products of insertion of the coordinatively unsaturated fragment Cp*RhL (Cp* = $\eta^5$-$C_5Me_5$; L = $PMe_3$) into alkane C-H bonds are generated by irradiation of Cp*(L)$RhH_2$ or thermal decomposition of Cp*(L)Rh(neopentyl)(H), at temperatures below -30 °C in alkane solvents. The hydridoalkylrhodium products can be synthesized independently, also at low temperature, from the corresponding haloalkyl complexes by lithiation with *t*-BuLi followed by protonation. Alternatively, the highly nucleophilic complex Li[Cp*(L)RhH], prepared by deprotonation of Cp*(L)$RhH_2$, leads to the alkylhydridorhodium complexes upon treatment with alkyl tosylates R-OTs. When Cp*RhL is generated in mixtures of linear alkanes, only the products of insertion into primary C-H bonds are observed, even at -100 °C. The relative rate constants for the formation of these products correlate directly with the number of secondary C-H bonds in the alkane. This suggests that insertion occurs initially into all the C-H bonds of the alkane, but that even at very low temperatures the secondary insertion products rearrange quickly, and intramolecularly, to the primary products. We suggest that this rearrangement occurs through the intermediacy of $\eta^2$-C-H alkane complexes. Further studies provide support for this idea. The synthetic procedures summarized above can be used to prepare regiospecifically $^2H$ and $^{13}C$ labeled alkyl hydrides at low temperatures. Warming these complexes to temperatures above -80 °C in aromatic solvent reveals isotope rearrangements which confirm that the alkylhydridorhodium complexes are capable of interconverting with one another intramolecularly at rates competitive with or in some cases faster than they undergo reductive elimination. For example, rearrangement of the $^{13}C$, $^2H$-labeled ethylhydridorhodium and the (1-methylcyclopropyl)methylhydridorhodium complexes has been used to show that the Cp*(L)Rh fragment migrates and inserts most rapidly into the $\alpha$ position of the alkyl group followed by migration to the $\beta$ and $\gamma$ positions; reductive elimination is the slowest process which occurs. The kinetic isotope effect for oxidative addition of [Cp*(L)Rh] into the C-H bonds of hexane (determined by competition techniques) is small [$(k_H/k_D)$ = 1.1 ± 0.1], whereas that for reductive elimination (obtained from directly measured rates) from the ethylhydridorhodium complex is both large and inverse [$(k_H/k_D)$ = 0.5 ± 0.1]. These results provide further support for the existence of intermediate $\eta^2$-C-H alkane complexes.

Several organotransition-metal systems are now known in which intermolecular activation of alkane carbon-hydrogen bonds occurs. One important mode of reaction involves oxidative addition of relatively electron-rich, so-called "late" transition-metal complexes to C-H bonds in the alkane R-H, leading directly to isolable, or at least observable, insertion products R-M-H. Such alkane C-H oxidative addition has now been observed at iridium, rhodium, and rhenium centers.[1,2]

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**Table I.** Yields of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(R)(H)$ Prepared by Methods A, B, C, and D (See Text)

| R (compd no.) | yield[a] % (±5%) method A[b] | method B[c] | method C[d] | method D[e] |
|---|---|---|---|---|
| methyl (**2**) | | 91 | 93 | |
| ethyl (**3**) | 55 | | 91 | 75 |
| *n*-propyl | 65 | | | |
| *n*-butyl (**4**) | 62 | 86 | 89 | 83 |
| *n*-pentyl | 67 | | | 91 |
| *n*-hexyl (**5**) | 65 | | 90 | 82 |
| *n*-octyl | 68 | | | 93 |
| isobutyl (**6**) | 59 | | | 89 |
| neopentyl (**7**) | | 85 | | |
| (1-methylcyclopropyl)methyl (**8**) | 40[f] | | 92 | 44[f] |
| trimethylsilyl (**9**) | 76 | | | 92 |
| cyclopropyl (**10**) | 89 | 93 | | 95 |
| 2,2-dimethylcyclopropyl (**11a**) | 60[f] | 61[h] | | 24[f] |
| 2,2-dimethylcyclopropyl (**11b**) | 30[f] | 31[h] | | 24[f] |
| cyclobutyl | 53 | 87 | | 86 |
| cyclopentyl (**12**) | 35[g] | | | |

[a] NMR yields. [b] Yields based on **1** after 2 h of irradiation at 60 °C with a 450-W Hanovia Hg arc lamp. [c] Yields based on **13**, X = I. [d] Yields based on **13**, R = neopentyl, X = I. [e] Yields based on **1**. [f] A mixture of **8**, **11a**, and **11b** is produced on activation of dimethylcyclopropane. [g] Yield based on **1** after 1 h of irradiation at −60 °C with a 100-W Hg arc lamp. [h] A mixture of **11a** and **11b** is produced.

Much progress has been made toward understanding the mechanism of this reaction, and the critical step is now generally understood to involve a three center transition state involving the metal center and carbon and hydrogen atoms undergoing bond cleavage.[2f] However, a number of important mechanistic and structure/reactivity questions remain to be answered. One of the most intriguing concerns the factors which control selectivity in C–H oxidative addition—e.g., the higher inter/intramolecular selectivity observed for Ir and Rh but not for Re and the high primary/secondary selectivity observed for Rh and Re but not for Ir. An important concern in these selectivity studies is whether they are kinetic or thermodynamic. That is, the rates of formation of the disfavored products might be appreciable, but after formation they might rapidly rearrange to the observed products under the reaction conditions. Another question concerns the possible formation of metastable $\eta^2$- or $\sigma$-complexes, between the alkane and metal center, before actual insertion has taken place. Precedent for such intermediates comes from the discovery of

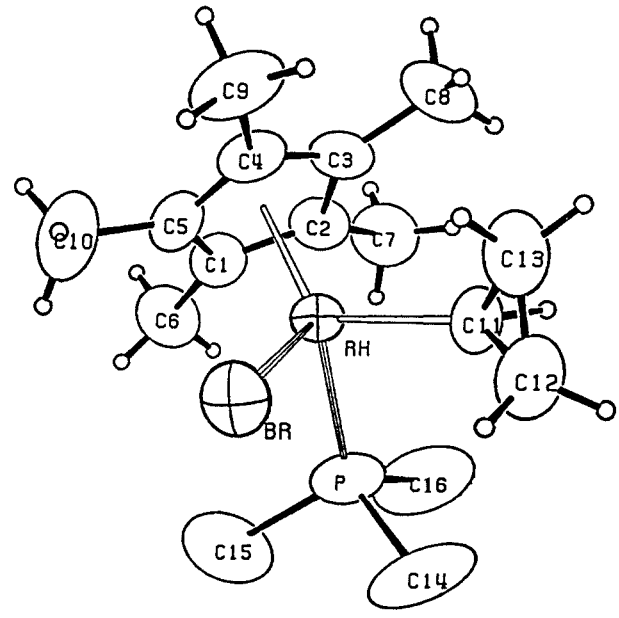


**Figure 1.** ORTEP diagram illustrating the structure of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_3H_5)Br$.

complexes having intramolecular $\eta^2$- (or so-called "agostic") interactions, which Green and Brookhart have suggested may represent "arrested" oxidative addition reactions.[4] In addition, stable complexes containing substantially intact $H_2$ ligands have recently been isolated and characterized.[5a-c]

In the rhodium series, secondary insertion products are formed from cyclic alkanes, but only primary products are formed from acyclic alkanes.[2m,n] The research summarized in this paper was initiated to investigate this perplexing result. Our findings provide evidence that the factors which control selectivity and the possible intervention of $\eta^2$-complexes are closely related phenomena. In addition, full experimental details of our rhodium C–H activation experiments,[2n] including several alternate syntheses of hydrido(alkyl)rhodium complexes, are described.

## Results and Discussion

**Synthesis of $Cp^*(PMe_3)Rh(R)(H)$.** The simplest method of synthesizing the alkylhydridorhodium complexes as reported in an earlier communication[2n] is by photolysis of $Cp^*(PMe_3)RhH_2$ (**1**)[7] at temperatures below −30 °C in the appropriate hydrocarbon solvent (method A, eq 1).[8] This general reaction is limited only

Method A

$$Cp^*(L)RhH_2 \xrightarrow[RH,\ -H_2]{-60°C,\ h\nu} Cp^*(L)Rh(R)(H) \qquad (1)$$

$Cp = \eta^5\text{-}C_5Me_5$, $L = PMe_3$

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(8) C–H activation by [Cp*(L)Rh] has also been reported by Jones and Feher, ref 1m.

by the requirement that the hydrocarbon solvent be liquid below −30 °C and occurs with high selectivity (>85%) to the alkyl hydride products. However complete conversion of **1** to the alkyl hydrides could not be accomplished, presumably due to the buildup of highly colored species. The alkyl hydrides were produced in varying yields with **1** as a major contaminant (Table I).

The alkyl hydride products (see Table I for compound numbers) are extremely labile complexes which decompose above −20 °C, precluding any attempts at isolation. They were identified by (a) $^1H$, $^{31}P$, and $^{13}C$ NMR spectrometry, (b) conversion to the more stable, isolable alkylhalorhodium complexes $Cp^*(PMe_3)Rh(R)(X)$ (**13**) on treatment with haloform, and (c) independent synthesis. The alkylhalorhodium complexes were fully characterized by NMR spectroscopy, elemental analysis, and independent synthesis from the reaction of $Cp^*(L)RhX_2$ (X = Cl, Br, and I) with the corresponding alkyllithium reagents. As reported earlier,[2n] crystals of the cyclopropyl(bromo)rhodium complex obtained after the treatment of the cyclpropyl hydride **10** with bromoform were used to solve its structure by X-ray diffraction. An ORTEP diagram of the structure is reproduced in Figure 1. Independent synthesis by methods B, C, and D (eq 2, 3, and 4) provided solutions of the alkyl hydride complexes, identical with those formed in method A in high yield but uncontaminated by rhodium dihydride **1** or other major impurities. The methods B and C also allowed regiospecific isotopic labeling of the complexes.

Method B (eq 2) is a more general preparation and involves the treatment of the alkyliodorhodium complex **13**, X = I with 2 equiv of *t*-BuLi to produce salts (presumably the lithium alkylrhodates **14**) followed by in situ protonation with ethanol to

Method B

$$Cp^*(L)Rh(R)(X) \;+\; 2\ t\text{-BuLi} \xrightarrow[-LiI,\ -isobutylene]{-78°C,\ -isobutane} \underset{\textbf{14}}{[Cp^*(L)Rh(R)]Li} \xrightarrow[-LiOC_2H_5]{-90°C,\ C_2H_5OH} Cp^*(L)Rh(R)(H) \qquad (2)$$

**13**, X = I

produce the alkyl hydrides. The reaction was used to generate a wide variety of complexes ranging from the very unstable neopentyl hydride **7** which decomposed at −60 °C with a half-life of 20 min to the more stable *n*-hexyl hydride **5** and cyclopropyl hydride **10** (Table I). However, the reaction could not be used to prepare the ethyl hydride **3** due to competing side reactions, nor was it successful for the (1-methylcyclopropyl)methyl hydride **8**, as the corresponding halide of this complex could not be synthesized.

In this sequence, formation of the lithium alkylrhodates **14** can only be presumed from the subsequent protonation chemistry, since all attempts at isolating these materials failed. The rhodates are quite soluble in nonpolar hydrocarbons (even *n*-butane), thus allowing generation of the alkyl hydrides in a wide variety of solvents. Formation of the rhodates is accompanied by the formation of isobutane, isobutylene, and lithium iodide. The volatile materials were removed by high vacuum techniques at −70 °C; the lithium iodide (and lithium ethoxide produced in the protonation step) were removed by filtration through alumina III at −90 °C. This was accomplished by the use of the apparatus shown in Figure 4.

Although less general, method C (eq 3) is particularly simple and involves the alkylation of the lithium hydridorhodate **15** with alkyl tosylates.[9] One disadvantage of this method is that due

Method C

$$\underset{\textbf{1}}{Cp^*(L)RhH_2} \;+\; n\text{-BuLi} \xrightarrow{-butane} \underset{\textbf{15}}{[Cp^*(L)Rh(H)]Li} \xrightarrow[-LiOts]{ROts} Cp^*(L)Rh(R)(H) \qquad (3)$$

to the slower rate of the alkylation step, the alkyl hydrides can only be produced at −60 °C or above thus precluding the observation of chemistry that occurs below this temperature. Fortunately, however, the method was well suited to the preparation of the ethyl hydride **3** and (1-methylcyclopropyl)methyl hydride **8** complexes which could not be prepared by method B. As with **4**, complete characterization of pure salt **15** was not successful. It was generated by treatment of the rhodium dihydride **1** in toluene with 1 equiv of *n*-butyllithium. NMR analysis of the material suggested that it is a complex mixture of monomers and oligomers in solution. Repeated attempts at obtaining it in crystalline form gave (somewhat irreproducably) a yellow crystalline or amorphous material which analyzed correctly for the stated formula. The complex is extremely air and water sensitive both in solution and in the solid state. Thus treatment of a toluene-$d_8$ solution of the material with 1 equiv of methanol at −78 °C resulted in the instantaneous formation of the rhodium dihydride **1** in quantitative yield as determined by $^1H$ NMR. Exposure to air resulted in the formation of many decomposition products. Reaction with unhindered primary alkyl tosylates proceeded cleanly (though slowly at −60 °C) in pentane/$Et_2O$ to yield the alkyl hydrides in high yields (80–95%), based on NMR analysis. The reaction mixtures after alkylation contained lithium tosylate and small amounts of alkyl tosylates as contaminants. These materials were removed by filtration through alumina III at −60 °C by the use of the apparatus shown in Figure 4. The reaction can be also be carried out with alkyl triflates, but no advantage was gained over the use of the more easily synthesized alkyl tosylates.

Methyl-, ethyl-, or *n*-butylhydridorhodium complexes **2**, **3**, and **4**, respectively, were prepared in this way. However, attempts at alkylation with secondary alkyl tosylates resulted only in the formation of rhodium dihydride **1**, presumably by proton abstraction. Interestingly, while attempts at alkylation with neopentyl tosylate failed, alkylation with (1-methylcyclopropyl)methyl tosylate proceeded cleanly to give **8**. Even though this system is "neopentyl-like," the reaction works presumably because the position adjacent to the three-membered ring is both activated toward nucleophilic substitution and sterically less congested than the corresponding site in neopentyl tosylate. Attempts at alkylation of **15** with haloalkanes resulted in poor yields of the desired products.

The alkyl hydrides were also generated by *thermal* C–H activation of hydrocarbons (method D, eq 4). This method depends on the unique thermal lability of the neopentyl hydride **7** prepared

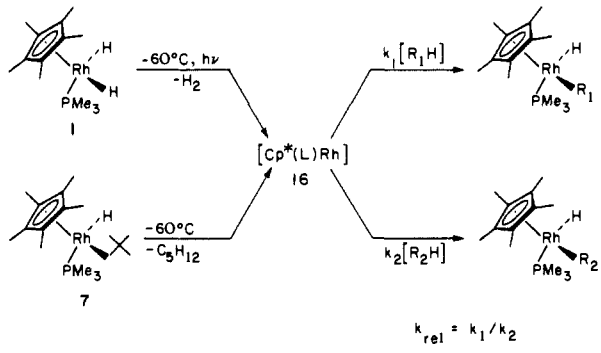
Method D

$$\underset{\textbf{7}}{Cp^*(L)Rh(neopentyl)(H)} \xrightarrow[-neopentane]{-60°C} \underset{\textbf{16}}{[Cp^*(L)Rh]} \xrightarrow{-60°C,\ RH} Cp^*(L)Rh(R)(H) \qquad (4)$$

by method B. This complex decomposes at −60 °C with a half-life of approximately 20 min in hydrocarbon solutions to produce neopentane and presumably the reactive intermediate $(Cp^*(L)Rh)$ **16** which can subsequently activate the C–H bonds of the solvent. Since all the other alkyl hydrides studied were stable at −60 °C, these products could be observed on decomposition of neopentyl hydride **7** in the appropriate solvent, and then converted to the more stable alkyl(halo)rhodium complexes **13** for full characterization. The reaction is clean and proceeds in high yield (Table I). As in the case of photochemical C–H activation the reaction is quite general and limited only by the requirement that the hydrocarbon solvent be liquid at temperatures below −60 °C.

Initial attempts at carrying out C–H activation with the parent cyclopentadienyl complex $(\eta^5\text{-}C_5H_5)(PMe_3)RhH_2$ were frustrated by its limited solubility in alkane solvents at low temperatures. Thus while the complex dissolves in, and readily activates, benzene (as evidenced by NMR analysis), it is only very sparingly soluble in *n*-hexane at −60 °C, and subsequent photolysis resulted in very poor yields of a new product presumed to be the *n*-hexyl hydride. Attempts at photolysis at temperatures above −30 °C resulted only in decomposition. The alkyl hydrides are stable complexes below −30 °C as evidenced by the synthesis of $(\eta^5\text{-}C_5H_5)(PMe_3)Rh(1\text{-}^{13}C\text{-ethyl})(D)$ at −60 °C by method C from the corresponding lithium hydridorhodate and (1-$^{13}$C)ethyl tosylate. This complex

**Scheme I**




showed comparable stability to the pentamethylcyclopentadienyl complex **3** and decomposed in toluene-$d_8$ at −20 °C to produce free ethane and the corresponding rhodium tolyl deuterides, identified by comparison of their NMR properties with those described earlier by Feher and Jones.[2m]

**C–H Activation of Acyclic Alkanes and Competition Studies.** Although secondary C–H insertion products are formed from reaction of [Cp*Rh($PMe_3$)] (**16**) with cycloalkanes such as cyclopentane and cyclohexane, activation of the (presumably) electronically similar secondary C–H bonds in acyclic alkanes has never been directly observed. Instead, photolysis of the rhodium dihydride **1** in *n*-butane even at −100 °C or thermal reductive elimination of the neopentyl hydride **7** at −60 °C in *n*-butane resulted only in the formation of the *n*-butyl hydride **4**.

The proton-coupled $^{13}C$ NMR spectrum is most diagnostic of the nature of the alkyl hydride. The carbon $\alpha$ to the rhodium atom typically appears furthest upfield as a characteristic doublet of doublets which is additionally split by the attached hydrogens. The furthest upfield resonance seen in the $^1H$ coupled $^{13}C$ NMR spectrum of the *n*-butyl hydride **4** obtained from C–H activation appears as a distinct triplet of doublet of doublets, indicating that the product is only the *n*-butyl hydride. These results were confirmed by several methods. The $^1H$ NMR spectrum in the hydride region (−10 to −20 ppm) of the alkyl hydrides is also very diagnostic of the type of alkyl hydride present. Secondary cycloalkyl hydrides such as the cyclohexyl or cyclopentyl hydrides typically show resonances between −15.0 and −15.5 ppm. Primary alkyl hydrides resonate further downfield, in the region −14.0 to −14.8 ppm. The activation of *n*-butane by both methods resulted in an alkyl hydride which showed only one hydride resonance. This appears in the "primary hydride region" at −14.73 ppm as a characteristic doublet of doublets due to coupling to Rh and P. Further confirmation of the structure of this hydride was obtained by comparison with solutions of *n*-butyl hydride **4** prepared independently. These solutions were obtained by the reaction of the hydrido anion **15** with *n*-butyl tosylate (see eq 3) and were found to be spectroscopically identical to the *n*-butyl hydride prepared by thermal and photochemical C–H activation of *n*-butane. By using similar techniques it was observed that *n*-hexane also gave only the product of activation at the primary C–H bond. Functionalization studies also support the conclusion that only primary C–H activation products are detectable in these reactions. Thus, treatment of the primary alkyl hydrides with bromoform at −100 °C resulted in quantitative formation of the corresponding primary bromoalkylrhodium complexes **13** (R = *n*-alkyl, X = Br). Treatment of these materials with bromine at −78 °C resulted in the formation of only 1-bromoalkane and Cp*(L)$RhBr_2$.

The first indication of the source of this unique selectivity came from competition studies designed to obtain the relative rate of activation of the C–H bonds of different hydrocarbons by (Cp*(L)Rh) (**16**). The competition experiments were conducted both by the thermal and photochemical generation of the intermediate **16** in mixtures of two hydrocarbons (Scheme I). The ratio of C–H-activated products in each experiment was obtained by $^1H$ and $^{31}P$ NMR analysis and by conversion of the alkyl hydrides to the more stable haloalkyl complexes. The relative rate constants for C–H bond activation were obtained from these ratios after correction for the relative concentrations and the number of C–H bonds of each hydrocarbon in the solvent. The results reported in Table II are referenced to cyclohexane, the reactivity of which has been arbitrarily set at 1.0.

**Table II.** Relative Rate Constants[a] ($k_{rel}$) for C–H Activation of Different Hydrocarbons by [($\eta^5$-$C_5Me_5$)($PMe_3$)Rh] Generated Photochemically by Irradiation of **1** and by Thermal Decomposition of **7**, Both at −60 °C

| hydrocarbon | $k_{rel}$ photochemical | $k_{rel}$ thermal |
|---|---|---|
| benzene[b] | 9.1 ± 0.6 | 4.5 ± 0.2 |
| toluene-$d_8$[c] | | 3.8 ± 0.3 |
| dimethylcyclopropane[d] | | 2.8 ± 0.1 |
| *n*-dodecane[e] | 6.1 ± 0.3 | 5.6 ± 0.3 |
| cyclopropane | 5.2 ± 0.3 | 2.3 ± 0.1 |
| *n*-decane[e] | 4.8 ± 0.5 | 4.6 ± 0.2 |
| *n*-octane[e] | 3.8 ± 0.1 | 3.9 ± 0.2 |
| cyclobutane | | 2.7 ± 0.2 |
| *n*-hexane[e] | 2.9 ± 0.3 | 2.6 ± 0.1 |
| *n*-hexane-$d_{14}$[e] | | 2.2 ± 0.1 |
| isobutane[e] | 2.8 ± 0.2 | |
| *n*-pentane[e] | 2.1 ± 0.1 | |
| *n*-butane[e] | 1.5 ± 0.2 | 1.8 ± 0.2 |
| cyclopentane | 1.5 ± 0.3 | |
| propane[e] | 1.3 ± 0.2 | 1.2 ± 0.1 |
| ethane | 1.0 ± 0.2 | 0.8 ± 0.2 |
| cyclohexane[f] | 1.0 ± 0.2 | 1.0 ± 0.1 |

[a] Relative rate constants are determined by generation of [($\eta^5$-$C_5Me_5$)($PMe_3$)Rh] in mixtures of two hydrocarbon solvents (see text). [b] Data obtained from a mixture of benzene/hexane in a 1:10 molar ratio, respectively. [c] Activation at both the benzyl and aryl positions is observed in a 0.74:1 ratio, respectively. [e] Only the primary alkyl hydrides are observed (see text). [f] Data obtained from a mixture of cyclohexane and tetramethylsilane in a 5:1 molar ratio, respectively.

Examination of the table shows that for unstrained saturated hydrocarbons, in each case, the relative rate constants ($k_{rel}$) obtained by the two methods are quite similar. However, relative rate constants determined by using hydrocarbons (benzene and cyclopropane) that form relatively stable insertion products mixed with those which form less stable products (*n*-alkanes) give different *apparent* photochemical and thermal $k_{rel}$ values. We believe this is because the hydridoalkyl products are photochemically quite unstable to reductive elimination and in the presence of aromatic compounds are converted to hydridoaryl complexes. Due to signal-to-noise problems, it was difficult to obtain accurate integration data at early dihydride photolysis times. Control experiments which demonstrated product photoisomerization were therefore carried out by irradiating independently generated hydride mixtures. For example, irradiation of toluene-$d_8$ solutions of the ethyl hydride **3** at −60 °C resulted in rapid reductive elimination of ethane and subsequent activation[2m] of the aryl C–D bonds of the solvent (eq 5). Also, irradiation of "thermal"

$$\underset{\mathbf{3}}{Cp^*(L)Rh(C_2H_5)(H)} \xrightarrow[-C_2H_6]{-60°C,\ h\nu,\ \text{toluene-}d_8} Cp^*(L)Rh(C_6D_4(CD_3))(D) \quad (5)$$

mixtures of ethyl hydride **3** and the phenyl(hydrido)rhodium complex in hexane/benzene resulted in rapid conversion of the alkyl to the phenyl hydride. On the basis of these experiments, we suggest that photochemical generation of Cp*RhL in benzene/alkane and cyclopropane/alkane mixtures initially produces product ratios similar to those formed thermally. However, rapid photochemical interconversion of the alkyl hydrides to the aryl and cyclopropyl hydrides occurs, changing the distributions to those recorded in Table I. Thus we conclude that both methods probably generate the same reactive intermediate, but the photochemical experiments are in some instances complicated by secondary photoinduced reactions.

Comparison of the relative rate constants for the activation of the series of straight chain alkanes reveals an interesting and surprising correlation. This is most easily seen graphically as shown in Figure 2. In the graph, the relative rate constants obtained by both methods are plotted against the number of

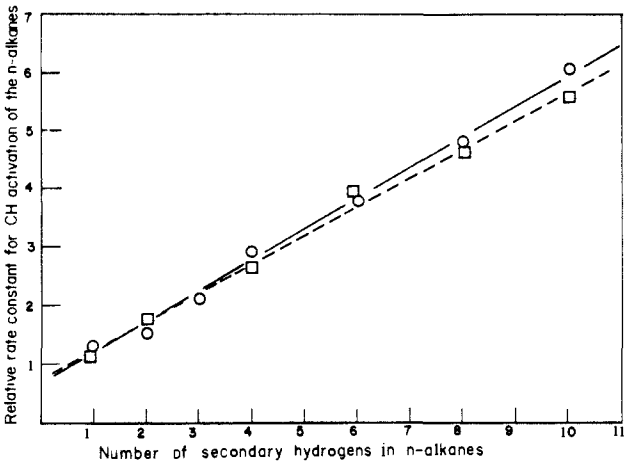



Figure 2. Plot of the relative rate constants ($k_{rel}$) for the activation of *n*-alkanes by [Cp*($PMe_3$)Rh] generated photochemically (○) from **1** and thermally (□) from **1** vs. the number of methylene hydrogens in the *n*-alkane. Note: in all cases only primary C–H activation products were observed (see text).

secondary C–H bonds of each *n*-alkane. This reveals a direct correlation between the relative rate constants and the number of *secondary* C–H bonds of the alkanes. However, as stated above only the primary alkyl hydride, resulting from attack at the $CH_3$ groups, is formed in each case. The data therefore suggest that C–H activation actually occurs at both the primary and secondary C–H positions but that even at low temperatures the secondary activation product rearranges rapidly *and intramolecularly* to the primary C–H activation product.[10]

**Thermal Isomerization of Alkyl Hydrides: Label Scrambling in Hydridoethylrhodium Complexes.** To obtain direct evidence for the intramolecular migrations proposed above, we tried repeatedly to synthesize an acyclic secondary alkyl hydride and directly observe its rearrangement to a primary alkyl hydride. Unfortunately, all attempts at synthesis of such a complex failed. As described above, treatment of secondary tosylates with the hydrido anion **15** (eq 3) resulted only in the formation of dihydride **1**. Possibly consistent with the presumed thermal instability of secondary acyclic hydrides, attempts at synthesizing secondary acylic halides also failed. Thus, treatment of Cp*(L)$RhX_2$ (X = Cl, Br, and I) with isopropyllithium or isopropylmagnesium bromide resulted in the formation of complex mixtures of products. Although one of these could be identified as the desired isopropylhalorhodium complex by $^1H$ NMR, the material could not be purified, decomposing during attempts at crystallization or column chromatography.

In a second approach, we decided to investigate the possibility of degenerate rearrangements in observable alkyl(hydrido)rhodium complexes. A simple complex in which such a rearrangement could be studied is the doubly labeled (1-$^{13}$C)ethyl deuteride **3a** (Scheme II). This complex was synthesized by treatment of the lithium deuteriorhodate **15-*d*** with (1-$^{13}$C)ethyl tosylate at −60 °C. $^1H$ and $^{13}C$ NMR analysis indicated that while the $^{13}C$ label still resided in the $\alpha$-position, the deuteride had migrated almost completely into the alkyl ligand. However, the label was located only at the $\alpha$-carbon, resulting in the formation of (1-$^{13}$C,1-$^2$H)ethyl hydride **3b**, as shown in Scheme II. On warming the

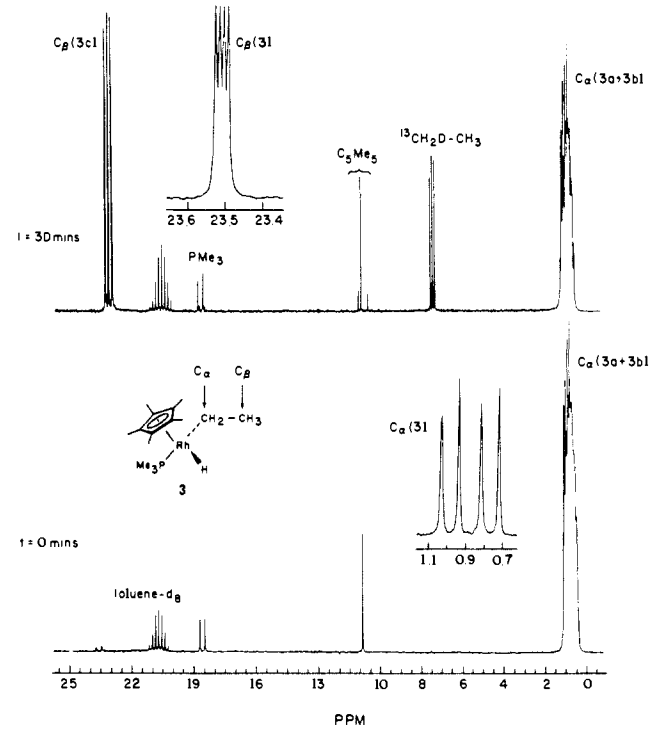
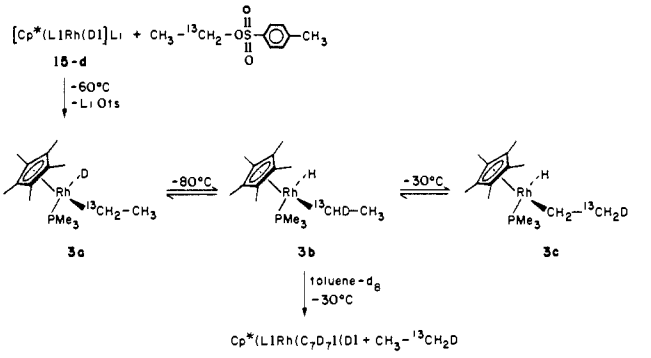



Figure 3. $^{13}C\{^1H\}$NMR spectra (toluene-$d_8$, −60 °C) of a mixture of (1-$^{13}$C)ethyl deuteride **3a** and (1-$^{13}$C,1-$^2$H)ethyl hydride **3b** ($t$ = 0 min) showing rearrangement to (2-$^{13}$C,2-$^2$H)ethyl hydride **3c**. Chemical shifts are reported in ppm downfield from $Me_4Si$. Inset spectra show $C_\alpha$ and $C_\beta$ resonances for the undeuterated $^{13}C$-labeled complex.

**Scheme II**




mixture of **3a** and **3b** to −25 °C rearrangement of the $\alpha$-$^{13}C$ label to the $\beta$ carbon of the ethyl ligand to produce **3c** was observed by $^{13}C$ analysis. Monitoring by $^{13}C\{^1H\}$ NMR spectroscopy at various times at −25 °C demonstrated this transformation and also provided evidence that *the deuterium remains attached to the labeled carbon* as rearrangement occurs (Figure 3). At $t$ = 0 the $^{13}C$ label of the mixture **3a** and **3b** is seen just below 0 ppm as a broad multiplet. A sharp four-line pattern in the undeuterated complex is due to rhodium and phosphorous coupling (see inset to Figure 3); the signal is further complicated in the mixture of deuterated complexes by overlap between the resonances of **3a** and **3b** and by additional deuterium coupling in **3b**. As $\beta$-migration occurs, the $\beta$-$^{13}C$ resonance grows at the expense of the $\alpha$-$^{13}C$ signal. This peak appears as a broad triplet (in contrast to a four narrow line pattern in the proton-coupled spectrum of the undeuterated complex; see insert) due to deuterium coupling and also the smaller Rh and phosphorus coupling. Independent experiments showed that the $\beta$-$^{13}C$ label without attached deuterium appears in the $^{13}C\{^1H\}$NMR spectrum at the same chemical shift as the most downfield shoulder of the triplet due to the deuterium labeled $\beta$-carbon. Thus if significant amounts of the $^{13}C$ label had entered the $\beta$-position without attached deuterium, a distorted triplet with a large downfield peak would have resulted. Importantly the $\beta$-carbon label in the scrambled complex appears

(9) (a) This chemistry is based on the analogous iridium chemistry described in ref 9b. (b) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502.

(10) If the rearrangement occurred simply by reductive elimination of the secondary alkyl hydrides (leading to kinetically free Cp*(L)Rh) and reoxidative addition to the primary C–H bonds, then the $k_{rel}$ for activation of the *n*-alkanes would not reflect attack at the secondary C–H bonds, and the correlation observed (Figure 2) would require another explanation. The correlation could also result if the inherent rate constant for activation of the primary C–H bonds of *n*-alkanes increased in some linear fashion due to a peculiar electronic effect which increases with the number of methylene groups. However this seems unlikely, especially for *n*-pentane and the higher homologues.

as a 1:1:1 triplet confirming that to greater than 90% accuracy the $^{13}C$ and $^{2}H$ labels always migrate together. At −25 °C reductive elimination to form (1-$^{13}$C,1-$^{2}$H)ethane is also occurring as evidenced by the appearance of a 1:1:1 triplet at 8.7 ppm. Thus the integrity of the $^{13}C-^{2}H$ bond is also maintained in this step.

A possible pathway by which the isomerization could occur involves rapid, reversible reductive elimination of free ethane. However, these isomerizations were typically carried out by using 0.025 M solutions of alkyl hydrides in toluene-$d_8$. Thus the maximum concentration of ethane can only be 0.025 M, which is small compared to that of toluene-$d_8$ (9.4 M). Therefore for the "isomerization" to occur by this pathway, the rate constant for oxidative addition to ethane would have to be 9.4/0.025 or 375 times larger than the rate constant for oxidative addition to toluene-$d_8$. The relative rate constant for activation of toluene-$d_8$ was determined to be actually larger than that for ethane (Table 1), allowing this mechanism to be ruled out. However, in order to test this possibility more rigorously, a toluene-$d_8$ solution of the perdeuterated ethyl complex **3-$d_6$** (0.025 M) was doped with a large excess of $C_2H_6$ (0.31 M). The mixture was warmed to −20 °C and analyzed by $^{1}H$ NMR. Throughout the course of the reaction no ethyl hydride **3** was formed, and only activation of toluene-$d_8$[2m] was observed.

The $\alpha$-exchange (**3a** ⇌ **3b**, Scheme II) was not directly observed in the above experiments, presumably because the process occurs rapidly at −60 °C, the temperature at which the complex was prepared. In order to monitor this process **3a** was synthesized at −90 °C. This was accomplished by deprotonation of the (1-$^{13}$C)ethyl hydride **3** with *n*-butyllithium at −78 °C, followed by quenching with EtOD at −90 °C. The formation of unscrambled **3a** was confirmed by $^{13}C$ and $^{2}H$ NMR analysis. Upon warming to −80 °C a rapid exchange occurred resulting in the deuterium migrating almost completely to the $\alpha$-carbon of the ethyl group. The equilibrium ratio of deuterium on the $\alpha$-carbon to that in the hydride position was determined by the $^{2}H$ NMR spectroscopy and found to be 4.5:1. The fact that this ratio is greater than the statistical value of 2:1 is due to an equilibrium isotope effect, most likely as a result of the higher stretching frequency of the $\alpha$-C–H bond as compared to the Rh–H bond. Further warming to −25 °C again produced correlated migration of $^{13}C$ and $^{2}H$ into the $\beta$-position, as observed with the hydridoethyl complex prepared at −60 °C by method C (Scheme II).

Analogous $\alpha$-rearrangements have been studied carefully by Norton and co-workers in $Cp_2W(CH_3)(D)$.[11,12] In these cases crossover studies indicated that the scrambling occurred by both intra- and intermolecular mechanisms. In order to determine if this was occurring in the $\alpha$- and $\beta$-exchange processes observed in the rhodium system, similar crossover studies were carried out. Thus a mixture of deuterated ethyl complex **3-$d_6$** and **3** was generated in toluene-$d_8$ (0.025 M and 0.028 M, respectively) by the use of the apparatus shown in Figure 4. The mixture was warmed to 20 °C, and the mixture of ethanes produced on reductive elimination was analyzed at low ionization energies by electron impact mass spectroscopy. The composition of ethane was found to consist of $C_2D_6$ and $C_2H_6$ with only minor amounts (<5%) of crossover products (eq 6). Thus, at the concentrations used in our experiments, the $\alpha$- and $\beta$-rearrangements appear to occur by intramolecular mechanisms.

$$\underset{\mathbf{3}}{Cp^*(L)Rh(C_2H_5)(H)} + \underset{\mathbf{3}\text{-}d_6}{Cp^*(L)Rh(C_2D_5)(D)} \xrightarrow[\text{toluene-}d_8]{-20°C} Cp^*(L)Rh(C_7D_7)(D) + C_2H_6 + C_2D_6 + C_2H_ND_{6-N} \quad (6)$$

(<5%, N = 1-5)

**Label Scrambling in Hydridocyclopropylrhodium Complexes: Stereochemistry of the Rearrangement.** Exchange of hydrogen between the metal-bound position and the carbon-bound positions in the hydridoalkylrhodium complexes studied here appears to be a general process, occurring rapidly at −80 °C with the methyl and neopentyl deuterides **2-*d*** and **7-*d***. In these systems, as with the hydridoethyl complex, rearrangement of label from the metal to $\alpha$ position occurs too rapidly to observe at −80 °C. The reaction requires a somewhat higher temperature, however, in the labeled hydridocyclopropylrhodium complex **10**. In this material the rearrangement can be observed to occur at a reasonable rate at −60 °C. Adding a substituent to the cyclopropyl ring, as in the dimethylcyclopropyl derivative **11** (Scheme III), transforms the carbon atom attached to the metal into a chiral center. Because the rhodium center is also chiral, this material exists as a mixture of two diastereomers (four enantiomers). In principle, therefore, examination of its rearrangement can provide information about the stereochemical requirements for the process.

In order to carry out such a study in a rigorous way, availability of each pure diastereomer, and an assignment of its structure, is needed. This is a difficult goal, especially in view of the thermal lability of these materials, and we were not able to achieve it completely. However, treatment of $Cp^*(L)RhI_2$ with 2,2-dimethylcyclopropyllithium gave the corresponding haloalkyl complex **13** (cf eq 2), and $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectrometry indicated that only *one* diastereomer of this material was produced in the reaction. Unfortunately, subsequent lithiation and deuteration of this complex at −90 °C resulted in the formation of both diastereomers of the corresponding deuterioalkyl complex **11-$d_1$**. However, partial selectivity was observed in this reaction;

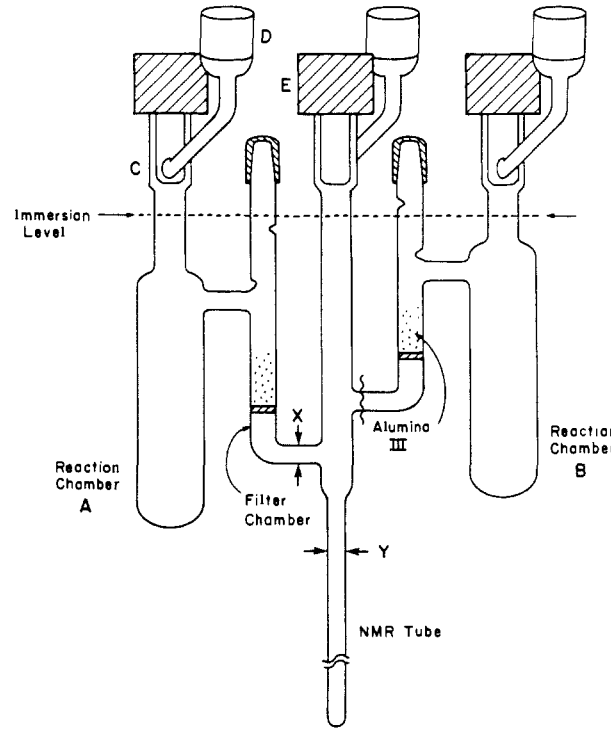
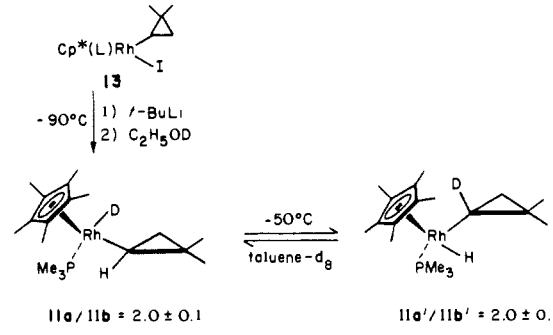


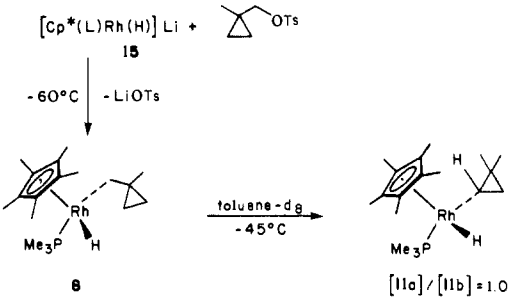

**Figure 4.** Illustration of the apparatus used in the preparation of the alkylhydridorhodium complexes: A, B, reaction chambers; C, E, teflon stopcocks; D, joint for connection to vacuum line; X, Y, points at which apparatus is separated by flame sealing.

**Scheme III**




(11) Bullock, R. M.; Headford, D. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.

**Scheme IV**




and examination of the $^1$H NMR spectrum of material carefully kept below −60 °C following its generation showed that (a) deuterium was restricted to the metal-bound position and (b) the two diastereomers of **11** had been produced in a 2:1, rather than a 1:1, ratio.

The two diastereomers have substantially different NMR spectra. Although this allowed us to distinguish the two complexes readily, we were not able to establish which of the diastereomers is the *R,R/S,S* and which is the *R,S/S,R* isomer. However, in order to make the following discussion as clear as possible (a) we will assume that the major product is the *S,S/R,R* diastereomer and (b) we illustrate the transformations summarized in Scheme III only for the metal-labeled *S,S* isomer **11a-*d*$_1$** and the metal-labeled *R,S* isomer **11b-*d*$_1$**.

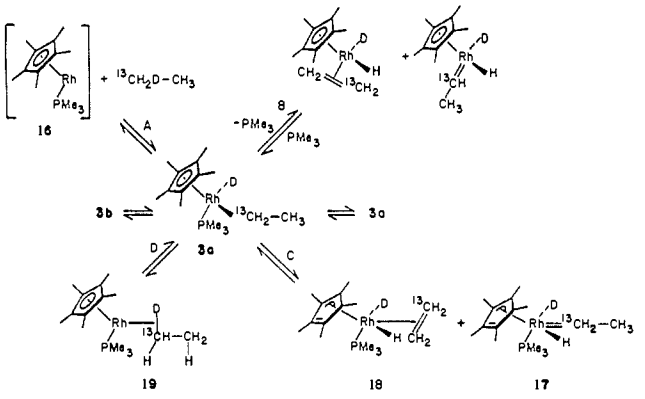
Upon warming the 2:1 mixture of diastereomers, assumed to be 66% **11a-*d*$_1$** and 33% **11b-*d*$_1$**, to −50 °C, $\alpha$-exchange was observed as evidenced by the appearance of resonances in the hydride region of the $^1$H NMR spectrum. However, *this label exchange occurs without any change in the 2:1 ratio of diastereomers.* This observation can be accounted for in only two ways: either 2:1 is the equilibrium ratio of diastereomers or label is interchanged without interconversions of the two diastereomers; i.e., the rearrangement occurs stereospecifically. That the latter situation is true is demonstrated by warming the solution further to −30 °C: here diastereomeric interchange was observed, leading to a 1:1 ratio, which must be the equilibrium ratio.

These results demonstrate that the exchange of hydrogen between the metal and $\alpha$ carbon centers cannot be occurring by an odd number of inversions of the two chiral centers (i.e., inversion at one center and retention at the other). Lacking a method for obtaining optically active complexes or for establishing the absolute stereochemistry of the diastereomers, we cannot at this point tell whether the rearrangement proceeds by retention or inversion at both centers. However, it does occur stereospecifically.

Having observed $\alpha$ and $\beta$-migrations of rhodium on alkane fragments, we sought to determine whether $\gamma$-migrations could occur. It would be especially revealing if the $\gamma$-migration could be observed in systems not possessing $\beta$-C–H bonds. The neopentyl hydride **7** was the first such system investigated. In order to observe any possible rearrangements the neopentyl deuteride **7-*d*$_1$** was prepared at −90 °C by method A. Analysis of the system by $^2$H NMR indicated that while $\alpha$-rearrangement readily occurred no $\gamma$-migration was observable below −60 °C. Further warming above this temperature resulted only in reductive elimination of the neopentane-$d_1$ and no $\gamma$-exchange was observed.

In retrospect this result was perhaps not unexpected. The ethyl hydride **3**, which is much more stable than the neopentyl hydride, shows comparable rates of reductive elimination and $\beta$-migration. Thus $\gamma$-migration, which should be less facile than the $\beta$-migration, would require a fairly stable system to allow observation. Such an alkyl hydride was found in (1-methylcyclopropyl)methyl hydride **8** (Scheme IV). This compound was synthesized according to method B by the alkylation of the hydrido anion **15** with (1-methylcyclopropyl)methyl tosylate. The resulting complex is stable at −60 °C but undergoes rapid $\gamma$-rearrangement at −45 °C in toluene-$d_8$, as illustrated in Scheme IV. This thermal isomerization was most easily followed by $^1$H NMR analysis of the hydride region (−10 to −20 ppm). At −60 °C the hydride resonance of **8** appears as a characteristic doublet of doublets at −14.55 ppm. As the toluene-$d_8$ solution is warmed to −45 °C almost quantitative rearrangement to the $\gamma$-position of the cyclopropyl ring is observed to occur with clean first-order kinetics ($k$ = (1.8 ± 0.1) × $10^{-4}$ $s^{-1}$) resulting in the formation of the two diastereomers of 2,2-dimethylcyclopropylhydridorhodium **11a** and **11b** in a 1:1 ratio. This is evidenced by the appearance of two sets of doublets of doublets at −14.14 and −14.45 ppm. The structures of these two products were confirmed by $^1$H and $^{13}$C analysis as well as by independent synthesis as described earlier and by conversion to the isolable 2,2-dimethyl(iodo)rhodium complex by treatment of the mixture of **11a** and **11b** with iodoform. In order to demonstrate that this process was occurring by an intramolecular mechanism, the relative rate constants for the activation of toluene-$d_8$ and free 1,1-dimethylcyclopropane by ($\eta^5$-$C_5Me_5$)$RhPMe_3$ **16** were determined from thermal competition experiments with the neopentyl hydride **7**. It was found that the relative rate constant for the activation of toluene-$d_8$ was 1.4 times greater than that for 1,1-dimethylcyclopropane (Table II). Thus the isomerization reactions carried out on a 0.025 M toluene-$d_8$ solution of **8** must be occurring by an intramolecular process.

**Scheme V**



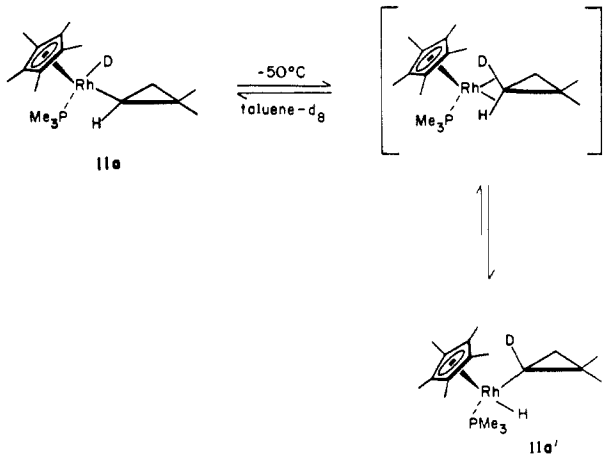

These observations of $\alpha$-, $\beta$- and $\gamma$-rearrangements unambiguously demonstrate that intramolecular rearrangements of alkyl hydrides can indeed occur. They lend strong credence to the proposal that the exclusive observation of primary C–H bond activation products from acyclic alkanes is a result of secondary to primary alkyl rhodium hydride rearrangements.

**Mechanism of Alkyl Hydride Rearrangements.** Several mechanisms can be proposed to explain the facile isomerizations observed. They are shown in Scheme V as mechanisms A, B, C, and D and illustrate the $\alpha$ and $\beta$ scrambling in $^{13}$C-labeled **3**. Mechanism A involves the dissociation of and subsequent reoxidative addition to the hydrocarbon substrate. This mechanism has already been ruled out by the doping and competition experiments discussed earlier. Mechanism B involves the reversible dissociation of $PMe_3$ followed by, or simultaneous with, reversible $\alpha$- and $\beta$-eliminations to produce intermediate dihydrido carbene or olefin species, respectively. This mechanism was ruled by experiments which establish that incorporation of $P(CD_3)_3$ into the alkylhydridorhodium complexes is very slow compared to the isomerization processes. Additionally, $PMe_3$ inhibition of the isomerization rate was not observed.

The two remaining mechanisms are C and D, both of which involve intramolecular processes. In mechanism C isomerization occurs by $\alpha$- and $\beta$-elimination to the carbene and alkene complexes **17** and **18**, respectively. These processes require expansion of the rhodium valence shell to 20 electrons or $\eta^5 \rightleftharpoons \eta^3$ "slippage" of the $C_5Me_5$ ring. In the case of $\beta$-rearrangement it is also required that the relationship of each ethylene carbon to the D and H atoms on Rh be maintained (i.e., no ethylene rotation or D/H interchange), because migration of $^{13}$C and $^2$H is correlated (Scheme II). We cannot rule out these specific combinations of restrictions, but they seem somewhat unlikely to us.

A more interesting way of interpreting our observations involves the possibility of the isomerization proceeding by a weakly coordinated alkane $\sigma$-complex **19**. Rearrangement can occur by intramolecular migration of the metal center to the $\alpha$-, $\beta$-, or

**Scheme VI**




γ-C–H bonds, followed by oxidative addition at the new positions. Importantly, the connectivity between the carbon and hydrogen atoms undergoing the reductive elimination or oxidative addition is never lost in this proposed mechanism. Thus, this would result in the β-isomerization in **3a** always occurring to place both the $^{13}C$ and $^{2}H$ atom into the β-position, as is observed. Mechanism D is also consistent with our observation that the α-isomerization in (2,2-dimethylcyclopropyl) deuteride **11-*d*$_1$** occurs with simultaneous retention or inversion at both centers (Scheme III). A possible transition state or intermediate consistent with mechanism D which allows α-isomerization to occur in **11-*d*** with simultaneous inversion at both the rhodium and α-carbon centers is shown in Scheme VI.[13]

The strongest piece of evidence favoring mechanism D over mechanism C is the observation that *rearrangements can occur past carbon positions which do possess β-C-H bonds*. Thus, as described above the metal fragment in (1-methylcyclopropyl)-methylrhodium hydride **8** undergoes at −45 °C rapid and quantitative intramolecular rearrangement from the γ-$CH_2$ to the C–H bonds of the cyclopropyl ring, producing the two diastereomers **11a** and **11b** (Scheme IV). Since **8** possesses no C–H bonds β to the metal center, β-hydrogen elimination processes can be ruled out rigorously, at least for the α- to γ-rearrangement. In view of the several considerations summarized above, intervention of $\eta^2$-C–H alkane complexes seems the most economical way to explain all the rearrangements observed in these systems.

The observation that the α-isomerization can occur rapidly at −80 °C indicates that the alkyl hydrides are in rapid equilibrium with the proposed σ-complex intermediate. We propose that reductive elimination (and so oxidative addition) which occurs more slowly, also proceeds via the same intermediate. Consistent with an early transition state leading to the intermediate is the observation that the kinetic isotope effect for oxidative addition to alkane C–H bonds is quite small but normal ($k_H/k_D$ for *n*-hexane = 1.2 ± 0.1; data obtained from Table I). This is expected because rate-determining precoordination of the alkane presumably involves little C–H bond breakage. Such an early transition state for oxidative addition would predict, in the absence of an intermediate, that the microscopic reverse step (reductive elimination) would show a large normal isotope effect. Contrary to this expectation, the isotope effect for reductive elimination is large but inverse ($k_H/k_D$ = 0.5 ± 0.1). This measurement was obtained by determining the rate of reductive elimination of ethane and ethane-$d_6$ from **3** and **3-*d*$_6$** in toluene-$d_8$ at −30 °C, respectively. Complexes **3** and **3-*d*$_6$** were prepared according to method B, both by the reaction of **15** and **15-*d*** with ethyl tosylate and ethyl-$d_5$ tosylate, respectively, and also with the corresponding triflates. The complexes were found to decompose with clean first-order kinetics over 4 half-lives with rate constants which were independent (within 10%) of the method of preparation. The rate constants measured are $k_{3\text{-}d_6}$ = (1.2 ± 0.1) × $10^{-4}$ $s^{-1}$; $k_3$ = (6.0 ± 0.6) × $10^{-5}$ $s^{-1}$. It is theoretically possible to observe inverse kinetic isotope effects in a reaction proceeding through a single rate-determining transition state.[14] However experimental precedent[14c,d,15] seems to indicate that inverse isotope effects appear in reactions involving rapid preequilibration with a transient intermediate which possesses increased zero-point energy relative to its precursor.

The intermediate alkane σ-complex proposed in mechanism D (Scheme V) is not without precedent. Photolysis studies of $Cr(CO)_6$ in alkane solutions and matrices[16] have provided both UV–vis and IR spectroscopic evidence for the formation of alkane-solvated $Cr(CO)_5$ intermediates. Such "solvated species" are presumably identical with alkane σ-complexes. Other indications that C–H bonds can act as ligands lie in the many known "agostic" C–H/metal interactions[4] and the recently discovered σ-complexes involving dihydrogen.[5a-c] Girolami and his co-workers have recently isolated and structurally characterized a complex containing side-bound B–H bonds in coordinated $BH_4$ groups.[5d] In theoretical studies on C–H insertion from both Hoffmann's and Goddard's groups, similar species have been proposed.[17] Goddard's GVB calculations predict that a species, in which Pd or Pt interacts with two C–H bonds of methane, is prone to rapid oxidative addition with a low but finite activation barrier of only 2–4 kcal/mol. Hoffmann has used the more approximate EHT method to predict a metastable "end-on" σ-complex; the alkane then rotates over a low barrier to give the inserted product. The intermediates we propose may involve end-on or side-on C–H interactions or one or more $\eta^2$-C–H interactions between the metal center and the alkane C–H bonds; our present evidence does not allow us to distinguish between these possibilities.

Finally, in order to explore the effect on the rearrangement of changing substituent and metal, reactions of the parent Cp complex ($\eta^5$-$C_5H_5$)($PMe_3$)Rh((1-$^{13}$C)ethyl)($^2$H) **20** and the isoelectronic iridium complex ($\eta^5$-$C_5Me_5$)Ir((1-$^{13}$C)ethyl)($^2$H) **21** were studied. The α- and β-rearrangements, as well as reductive elimination of (1-$^{13}$C,1-$^2$H)ethane from **20**, were found to occur at rates similar to those observed in the (pentamethylcyclopentadienyl)rhodium analogue **3a**. This provides additional evidence against mechanisms requiring $\eta^5 \rightleftharpoons \eta^3$ ring slippage, which should be more facile for the parent Cp ligand. It also suggests that the steric bulk of the cyclopentadienyl ligand does not greatly influence the stability of proposed σ-complex intermediates such as **19**.

(12) See, also: Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

(13) Only one enantiomer is shown for clarity.

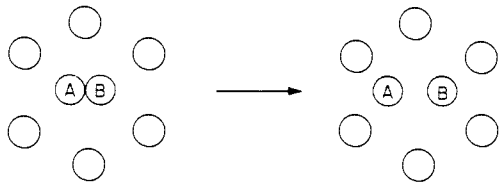
(14) The causes of inverse isotope effects have been discussed; see for example (a) Bigeleisen, J. *Pure. Appl. Chem.* **1964**, *8*, 217. (b) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley Interscience; New York, 1980; p 157. **Note Added in Proof.** A referee has disagreed with our interpretation of the inverse isotope effect and cities "Halpern's study of hydrogen transfer from $HMn(CO)_5$ to $R_2CCH_2$, where $k_H/k_D$ = 0.4" as an example of a system exhibiting an inverse isotope effect which "cannot involve anything more than a single, rate-determining step". The reaction studied by Halpern and Sweany (where the inverse isotope effect measured is for the overall process of addition of two hydrogen atoms to the C=C bond in β-methylstyrene) has in fact been proposed to proceed by a *reversible* preequilibrium between starting materials and radicals, followed by conversion of the radical pair to products (ref 14c,d). Both the CIDNP observed during this reaction and the formation of $HMn(CO)_5$ accompanying the reaction of $DMn(CO)_5$ with alkene are consistent with a reversible initial step. Thus the observations made on this system support, rather than contradict, the empirical correlation of an inverse isotope effect with the reversible preequilibrium formation of a transient intermediate. (c) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (d) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575.

(15) Isotope effects for other (presumably concerted) mononuclear alkane reductive eliminations typically fall in the range 2.2–3.3. The only inverse isotope effects reported for $L_nM(R)(H)$ systems are cases where R = aryl and strong evidence exists for preequilibration with an intermediate $\eta^2$-arene complex: cf (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. (b) Feher, F. J., Ph.D. Thesis, University of Rochester (New York), 1984.

(16) (a) Kelly, J. M.; Bent, D. V.; Herman, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259. (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (c) Hermann, H.; Grevels, F. W.; Henne, A.; Schuffner, K. *J. Phys. Chem.* **1982**, *86*, 5151. (d) Welch, J. A.; Peters, K. S.; Vaida, J. *Phys. Chem.* **1982**, *86*, 1941.

(17) (a) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 221. (b) Saillard, J. P.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2012. (c) Low, J. J.; Goddard, W. A., submitted for publication.

**Scheme VII**




Interestingly, in the iridium complex **21** only $\alpha$-rearrangements are observed. Unlike the analogous rhodium systems and also as observed in the $Cp^*(PMe_3)Ir(cyclohexyl)(D)$,[2f] this rearrangement requires elevated temperatures, only occurring slowly at 130 °C, and is competitive with reductive elimination of ethane. Perhaps consistent with the absence of a $\beta$-rearrangement pathway in this system is the observation made earlier[2a-f] that the iridium fragment [Cp*(L)Ir] will activate both secondary and primary C–H bonds of *n*-alkanes to give stable observable products.

**$\alpha$-Complexes or Solvent Cages?** In response to the comments of a referee, we add some remarks here concerning the possibility that the intermediates in these reactions might be "solvent caged" species with "no appreciable M/C–H interaction"; rather than $\sigma$-complexes.

There is no way to rigorously rule out solvent-caged species as intermediates in the isomerizations reported here. However, our problem with the solvent-caged hypothesis is straightforward. We know of no experimental precedent for the formation of solvent caged intermediates *in which the caged fragments have inherent reactivity toward solvent which is as high as or greater than their reactivity toward one another*. In our opinion, this is the central reason that the cage effect[18a] is so important in organic radical chemistry. Our point is best illustrated by the simple drawing in Scheme VII. The left side shows a reactant A–B surrounded by solvent molecules. Assume first that the A–B bond cleaves to give A and B and that these fragments are radicals. The inherent reactivity of the radicals toward the molecules making up the cage "wall" is typically rather low, whereas they normally react with one another (e.g., to give recombination or hydrogen atom transfer) with activation energies close to zero kcal/mol.[18b] Thus reactions between the caged partners can occur preferentially to reaction with the solvent and in competition with diffusion. In fact, even when good hydrogen atom donors are present in concentrations high enough to become part of the cage, evidence exists that they scavenge the caged radicals in competition with recombination.[18c]

The system described in this paper is rather different. Here A and B are Cp*RhL and alkane. In contrast to the situation with radicals, the inherent reactivity of one of these caged partners (the Rh fragment) toward the molecules making up the cage wall (an aromatic solvent) is actually *higher* than it is toward the alkane partner trapped in the cage. Yet, for some reason, the Rh center reacts preferentially—in some cases repeatedly—with C–H bonds in the alkane rather than with one of the several aromatic solvent molecules which make up the walls of the cage. It is clear, therefore, that the rhodium fragment must have *some* special relationship to the extruded hydrocarbon. Once again, we cannot rigorously rule out the possibility that the cage itself might somehow provide this special relationship (for example, by longer Rh wall distances compared to Rh alkane distances which are somehow maintained for relatively long time periods). However, it seems more reasonable to us to attribute this specificity to weak $\sigma$-complexation, especially in view of the extensive precedent which now exists for such interactions in agostic systems and $H_2$ complexes.[4,5]

## Summary and Conclusions

Several hydridoalkylrhodium complexes, $Cp^*(PMe_3)Rh(R)(H)$, prepared in this study were found to undergo degenerate rearrangements by migration of the [Cp*(L)Rh] fragment to the $\alpha$-, $\beta$- and $\gamma$-C–H bonds of the alkyl group. Reductive elimination to give kinetically free Cp*RhL, and $\alpha,\beta$-elimination/readdition pathways, were ruled out as possible mechanisms for the migrations by isotopic labeling, competition studies, and the observation that $\gamma$-rearrangements occur even when the alkyl group possesses no $\beta$-C–H bonds. We propose that these rearrangements occur via the intermediacy of alkane $\sigma$-complexes where the connectivity between the metal and the alkane substrate is probably a three-centered two-electron interaction.

The C–H activation of *n*-alkanes by rhodium results only in the formation of primary alkyl hydrides; no secondary alkyl hydrides are detected. The observation of the rhodium migrations coupled with the results of competition studies strongly suggests that this exclusive selectivity is thermodynamically founded. Thus we propose that both the primary and secondary C–H bonds are activated but that the secondary alkyl hydrides isomerize rapidly, even at very low temperature, via C–H alkane $\sigma$-complexes to the primary alkyl hydrides.

The $^2H$ isotope effect on oxidative addition of [Cp*(L)Rh] to alkane C–H bonds is small and normal ($k_H/k_D = 1.2 \pm 0.1$) while the isotope effect on the microscopic reverse (reductive elimination) is large and inverse. These observations are also consistent with the intermediacy of alkane $\sigma$-complexes.

These studies add to the growing body of evidence which suggests that oxidative addition to C–H bonds can occur via intermediates in which the $\sigma$-bonds of the alkanes act as Lewis basic ligands. It is our hope that complexes which specifically stabilize such interactions can be designed, so that $\sigma$-complexes may be isolated and fully characterized by X-ray and neutron diffraction.

## Experimental Section

All manipulations were conducted under a nitrogen atmosphere by using 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 high field 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-MHz high field Fourier transform spectrometer.

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 (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. Ultraviolet spectra (UV) were recorded on a Hewlett-Packard 8450A UV–vis spectrometer by using 1-cm path length quartz cells. Melting points were taken in glass capillary tubes in a Thomas-Hoover capillary melting point apparatus and were 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 vacuum jacketed column cooled by bubbling $N_2$ through a Dewar of liquid $N_2$ and then through the outer jacket of the column. All chromatography was performed under air-free conditions. 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 -$d_0$, 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% $H_2SO_4$, 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 having been stirred for 12 h, the solvents were vacuum transferred into a glass bomb for storage. Cyclopropane, propane, butane, and 1,1-dimethylcyclopropane were each 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 three freeze–pump–thaw cycles and vacuum transferred at −78 °C onto 1:5 sodium/potassium alloy. After having been stirred for 24 h at room temperature, the hydrocarbons were vac-

(18) (a) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; New York, Wiley-Interscience: 1973; Vol. I, Chapter 4. (b) Ingold, K. U. ref. 18a, Chapter 2. (c) Hammond, G. S.; Waits, H. P. *J. Am. Chem. Soc.* **1964**, *86*, 1911. Wu, C.-H. S.; Hammond, G. S.; Wright, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 538.

uum transferred into a glass bomb for storage. $CDCl_3$ was vacuum transferred from $P_2O_5$ and degassed by freeze–pump–thaw cycles. Bromoform and iodoform were fractionally crystallized and dried over $P_2O_5$. Trimethylphosphine was purchased from the Strem Company, dried over 1:5 sodium/potassium alloy, and always handled by vacuum transfer. CP grade ethane was obtained from Matheson and purified by 3 freeze–pump–thaw cycles before use. $AgBF_4$ 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. $NaBH_4$, $NaBD_4$, and 70% toluene solution of $Na^+[(CH_3OCH_2CH_2O)_2AlH_2]^-$ were obtained from the Aldrich Chemical Co. *p*-Toluenesulfonyl chloride (99%, Gold label), methylcyclopropylcarbinol, and cyclopropyl bromide were obtained from the Aldrich Chemical Co. and used as received. $Ba^{13}CO_3$ (99% $^{13}C$-enriched) and ethanol-$d_5$ were obtained from the Cambridge Isotope Laboratories and used as received. Methyl-$d_3$ iodide was obtained from MSD Isotopes and vacuum transferred from 4Å sieves prior to use. Cyclopropyllithium and 2,2-dimethylcyclopropyllithium were prepared according to the method of Seyferth[20] from the corresponding bromides. 2,2-Dimethylcyclopropyllithium was prepared from 1-bromo-2,2-dimethylcyclopropane[21] which was prepared from 1,1-dibromocyclopropane[22] according to referenced procedures. Cyclobutyllithium was prepared from cyclobutyl chloride which was purchased from Alfa Chemicals. Neopentyl-, isobutyl-, ethyl-, *n*-propyl-, *n*-hexyl-, and *n*-octyllithium were prepared according to the method of Gilman.[23] Cyclobutyl-, cyclopentyl-, and cyclohexyllithium were prepared from the corresponding chlorides according to the procedure of Applequist.[24] Other alkyllithium compounds were purchased from the Aldrich Chemical Company. All alkyllithium reagents were standardized prior to use by the procedure of Watson and Eastham.[25] Ethyl, *n*-butyl, and *n*-hexyl tosylates were prepared according to the method of Tipson.[26] $(\eta^5\text{-}C_5Me_5)(PMe_3)RhX_2$[7,27] (X = Cl, Br, and I) and trimethylphosphine-$d_9$[28] were prepared according to literature procedures. $RhCl_3$ (39.83% Rh) was obtained from Johnson-Matthey Inc.

**Low-Temperature Photolyses.** All UV irradiations were carried out at −60 °C unless otherwise stated. The UV apparatus consisted of a 450-W (or 100-Watt) medium pressure Conrad-Hanovia mercury immersion lamp in a double-jacketed quartz immersion well. The outer jacket was evacuated. This was immersed in a 4-L Dewar containing spectral grade methanol that was cooled to various temperatures by a Neslab ULT-80 refrigerated circulating cooler. UV irradiation experiments were performed by securing the vessel containing the sample to be photolyzed next to the immersion well in the methanol bath. All sample vessels were constructed of Pyrex glass.

**$(\eta^5\text{-}C_5Me_5)RhPMe_3H_2$[7] (1).** (a) $NaBH_4$ (98 mg, 2.62 mmol) was added to a stirred isopropanol solution (25 mL) of $Cp^*(L)RhCl_2$ (0.25 g, 0.649 mmol). The mixture was stirred for 8 h during which time the solution changed from bright orange to a light brown color. The solvent was removed in vacuo, and the residue was extracted twice with hexane. The combined extracts were filtered, concentrated in vacuo, and filtered through silica gel in a 60-mL glass fritted filter funnel with 20% diethyl ether/hexane as eluant. The solvent was removed, and the resulting pale yellow oil was further purified by crystallization from pentane at −40 °C. This yielded the product as large yellow plates in analytically pure form (143 mg, 60% yield). (b) The procedure was carried out as described above, except 50 mL of diethyl ether and $Na[(CH_3OCH_2CH_2O)AlH_2]$ (Red-al (Aldrich); 3.4 M in toluene, 0.21 mL) replaced the isopropyl alcohol and the $NaBH_4$ (70% yield): $^1H$ NMR ($C_6D_6$) δ 2.05 (d, $J$ = 1.8 Hz, 15 H), 1.06 (dd, $J$ = 9.5, 1.8 Hz, 9 H), −13.65 (dd, $J$ = 41.8, 29.8 Hz, 2 H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 98.63 (t, $J$ = 4 Hz, $C_5Me_5$), 16.14 (d, $J$ = 31 Hz, $PMe_3$), 9.41 (s, $C_5\mathit{Me}_5$); $^{31}P\{^1H\}$ NMR (THF-$d_8$) δ 8.11 (d, $J$ = 160.9 Hz); IR (hexane) 2099 $cm^{-1}$ ($\nu_{Rh\text{-}H}$); UV (hexane) $\lambda_{max}$ = 259 nm, $\epsilon = 1.6 \times 10^3$; MS, (70 ev), 316 ($M^+$); mp 36–38 °C. Anal. Calcd for $C_{13}H_{26}PRh$: C, 49.38; H, 8.29; P, 9.79. Found: C, 49.62; H, 8.24; P, 9.73.

**$(\eta^5\text{-}C_5Me_5)RhPMe_3D_2$ (1-$d_2$).** Silica gel (50 g) was heated (100 °C) in vacuo to remove most of the absorbed water. The silica gel was allowed to cool to 20 °C, and $D_2O$ (10 mL) was slowly added with vigorous shaking to ensure mixing. The treated silica gel was again heated in vacuo, and the $D_2O$ was removed. An additional 5 mL of $D_2O$ was added to the silica gel. After mixing and cooling to room temperature, the $D_2O$ was removed in vacuo without the application of heat. The treated silica gel (5 g) was used to prepare a chromatography column with 25% $Et_2O$/hexane as the eluant. The crude rhodium dideuteride 1-$d_2$ was prepared from the reaction of $Cp^*(L)RhCl_2$ (0.25 g, 0.649 mmol) with $NaBD_4$ (98 m, 2.62 mmol) in isopropyl alcohol as described earlier for the preparation of the rhodium dihydride. The hexane extracts containing the crude dideuteride were purified by flash chromatography through the deuterated silica gel column. Removal of the solvents yielded the material as a pale yellow oil which crystallized from pentane at −40 °C to yield the product as large yellow plate-like crystals which were pure by NMR [$^1H$ NMR ($C_6D_6$) 2.05 (d, $J$ = 1.8 Hz, 15 H), 1.06 (dd, $J$ = 9.5, 1.8 Hz, 9 H)]. Integration of the −13.6 ppm residual proton region against the $PMe_3$ resonance indicated that the product was >95% deuterated at the hydride positions: IR (hexane) 1535 $cm^{-1}$ ($\nu_{RhD}$).

**Preparation and Isolation of $(\eta^5\text{-}C_5Me_5)RhPMe_3(R)(X)$ (X = Cl, Br, and I) from $(\eta^5\text{-}C_5Me_5)RhPMe_3X_2$ and RLi.** This general procedure is illustrated for the preparation of the iodocyclopropylrhodium complex. An ether solution (10 mL) of cyclopropyllithium (0.92 mmol) was added dropwise to a stirred THF solution (30 mL) of $Cp^*(L)RhI_2$ (500 m, 0.88 mmol) cooled to −78 °C. The reaction was allowed to warm to 20 °C and stirred for 1 h. The reaction mixture changed from a dark red to a less intense orange color over the course of the addition. The solvent was removed in vacuo, and the residue was extracted with 10% $Et_2O$/hexane. The combined extracts were filtered, and the solvent was removed to yield the crude product as a red sticky residue. The residue was taken up in the minimum amount of 25% $Et_2O$/hexane and cooled to −40 °C. The product crystallized as red needles in analytically pure form (318 m, 74% yield): $^1H$ NMR ($C_6D_6$) δ 1.55 (d, $J$ = 2.7 Hz, 15 H), 1.23 (dd, $J$ = 10.2, 0.6 Hz, 9 H), 0–1.6 (m, 5 H); $^{13}C$ NMR (gated, THF-$d_8$) δ 99.5 (m, $C_5Me_5$), 17.8 (qd, $J$ = 131.2, 32.5 Hz, $PMe_3$), 12.12 (t, $J$ = 157.4 Hz, $CH_3$), 10.16 (q, $J$ = 127.1 Hz, $C_5\mathit{Me}_5$), 9.76 (t, $J$ = 162.6 Hz, $CH_2$), 1.72 (ddd, $J$ = 140.1, 34.4, 24 Hz, RhCH); $^{31}P\{^1H\}$ (THF-$d_8$) δ 5.47 (d, $J$ = 158.8 Hz); MS, 482 ($M^+$); mp 185 °C dec. Anal. Calcd for $C_{16}H_{29}IPRh$: C, 39.83; H, 6.01. Found: C, 39.59; H, 6.09.

The alkylbromorhodium and alkylchlororhodium complexes were prepared from the corresponding rhodium dibromide and rhodium dichloride complexes, respectively, exactly as described above.

**Data for other Cp*(L)Rh(R)(X) complexes prepared by this method**: R = ethyl, X = Br, 71% yield; $^1H$ NMR ($CDCl_3$) δ 1.67 (d, $J$ = 2.7 Hz, 15 H), 1.47 (dd, $J$ = 9.9, 0.8 Hz, 9 H), 1.14 (td, $J$ = 7.3, 1.0 Hz, 3 H) 1.8 (M, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 98.63 (M $C_5Me_5$), 25.21 (d, $J$ = 5.6 Hz, $RhCH_2CH_3$), 22.21 (dd, $J$ = 23.1, 13.4 Hz, $RhCH_2CH_3$), 15.23 (d, $J$ = 30.3 Hz, $PMe_3$) 9.78 (s, $C_5Me_5$); MS, 393 ($M^+ - C_2H_5$); mp 185 °C dec. Anal. Calcd for $C_{15}H_{29}PRhBr$: C, 42.58; H, 6.91; P, 7.32. Found: C, 42.57; H, 7.01; P, 7.12.

R = η-butyl, X = I, 83% yield, $^1H$ NMR ($C_6D_6$) δ 1.57 (d, $J$ = 2.7 Hz, 15 H), 2.0–1.0 (m),[29] 1.24 (dd, $J$ = 10.3, 0.5 Hz, 9 H); $^{13}C\{^1H\}$ ($C_6D_6$) δ 99.56 (m, $C_5Me_5$), 30.12 (s, $RhCH_2(CH_2)_2CH_3$), 28.21 (s, $RhCH_2(CH_2)_2CH_3$), 25.61 (dd, $J$ = 23.2, 14.2 Hz, $RhCH_2(CH_2)_2CH_3$), 16.81 (d, $J$ = 31.2 Hz, $PMe_3$), 9.98 (s, $C_5Me_5$), 9.61 (s, $Rh(CH_3CH_3)$; MS, 441 ($M^+ - C_4H_9$); mp 175 °C dec. Anal. Calcd for $C_{17}H_{33}IPRh$: C, 40.98; H, 6.63. Found: C, 40.42; H, 6.54.

R = η-hexyl, X = I, 85% yield; $^1H$ NMR ($C_6D_6$) δ 1.59 (d, $J$ = 2.6 Hz, 15 H), 2.0–1.0 (m),[29] 1.26 (dd, $J$ = 9.7, 0.7 Hz, 9 H); $^{13}C\{^1H\}$ ($C_6D_6$) δ 99.47 (M, $C_5Me_5$), 30.45 (s, $RhCH_2(CH_2)_4CH_3$), 29.21 (s, $RhCH_2(CH_2)_4CH_3$), 28.31 (s, $RhCH_2(CH_2)_4CH_3$), 27.21 (s, $Rh(CH_2)_5(CH_3)$, 24.31 (dd, $J$ = 23.1, 14.8 Hz, $RhCH_2(CH_2)_4CH_3$), 17.21 (d, $J$ = 30.6 Hz, $PMe_3$) 10.23 (s, $C_5\mathit{Me}_5$) 9.21 (s, $Rh(CH_2)_5CH_3$); MS, 441 ($M^+ - C_6H_{13}$); mp 165 °C dec. Anal. Calcd for $C_{19}H_{37}IPRh$: C, 43.34; H, 7.03. Found: C, 43.51; H, 7.21.

R = η-octyl, X = I, 65% yield; $^1H$ NMR ($C_6D_6$) δ 1.61 (d, $J$ = 2.7 Hz 15 H), 2.0–0.95 (m),[29] 1.25 (dd, $J$ = 9.7, 0.8 Hz, 9 H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 99.21 (m, $C_5Me_5$), 29.98 (s, $RhCH_2(CH_2)_6CH_3$), 29.58 (s, $RhCH_2(CH_2)_6CH_3$), 28.25 (s, $Rh(CH_2(CH_2)_6CH_3$), 28.05 (s, $RhCH_2(CH_2)_6CH_3$), 27.90 (s, $RhCH_2(CH_2)_6CH_3$), 27.51 (s, $Rh(CH_2(CH_2)_6CH_3$), 23.10 (dd, $J$ = 24.2, 13.9 Hz, $RhCH_2(CH_2)_6CH_3$), 17.32 (d, $J$ = 30.62 Hz, $PMe_3$), 10.13 (s, $C_5\mathit{Me}_5$), 9.85 (s, $Rh(CH_2)_7CH_3$); MS, 441 ($M^+ - C_8H_{17}$); mp 165 °C dec. Anal. Calcd for $C_{21}H_{41}IPRh$: C, 45.49; H, 7.40. Found: C, 45.79; H, 7.65.

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R = isobutyl, X = I, 53% yield; $^1$H NMR ($C_6D_6$) $\delta$ 2.45 (m, 1 H), 1 (d, $J$ = 2.3 Hz, 15 H), 1.4 (br m, 2 H), 1.19 (d, $J$ = 6.6 Hz, 3 H), 1.23 (d, $J$ = 6.5 Hz, 3 H), 1.01 (dd, $J$ = 8.8, 0.9 Hz, 9 H); $^{13}$C NMR (gated $C_6D_6$) $\delta$ 97.8 (M, $C_5Me_5$), 41.2 (d, $J$ = 126.2 Hz, RhCH$_2$CH(CH$_3$)), 24.5 (tdd, $J$ = 130.2, 23.8, 13.2 Hz, RhCH$_2$CH(CH$_3$)$_2$), 17.52 (qd, $J$ = 125.6, 30.9 Hz, PMe$_3$), 10.32 (q, $J$ = 126.3 Hz $C_5Me_5$), 10.21 (q, $J$ = 125.8 Hz, RhCH$_2$CH(CH$_3$)), 9.28 (q, $J$ = 126.1 Hz, RhCH$_2$CH(CH$_3$)$_2$); MS, 441 (M$^+$ - C$_4$H$_9$); mp 163 °C dec. Anal. Calcd for $C_{17}H_{33}IPRh$: C, 40.96; H, 6.62. Found: C, 40.59; H, 6.51.

R = neopentyl, X = I, 79% yield; $^1$H NMR (THF-$d_8$) $\delta$ 1.73 (d, $J$ = 2.8 H$_2$, 15 H), 1.55 (dd, $J$ = 10.1, 0.5 Hz, 9 H), 1.2–1.0 (m, 2 H), 1.05 (s, 9 H); $^{13}$C{$^1$H} ($C_6D_6$) $\delta$ 97.8 (m, $C_5Me_5$), 45.3 (s, RhCH$_2$C(CH$_3$)$_3$), 25.3 (dd, $J$ = 23.5, 15.7 Hz, RhCH$_2$C(CH$_3$)$_3$, 18.23 (d, $J$ = 31.1 Hz, PMe$_3$), 10.21 (s, $C_5Me_5$), 8.13 (s, RhCH$_2$C(CH$_3$)$_3$). MS, 512 (M$^+$); mp 165 °C dec. Anal. Calcd for $C_{18}H_{35}$ IPRh: C, 42.19; H, 6.84. Found: C, 42.08; H, 7.01.

R = trimethylsilyl, X = I, 88% yield; $^1$H NMR ($C_6D_6$) $\delta$ 1.50 (d, $J$ = 2.9 Hz, 15 H), 1.19 (dd, $J$ = 9.9, 0.8 Hz, 9 H), 0.49 (s, 9 H), 0.18 (dd, $J$ = 9.7, 0.6 Hz, 1 H), -0.40 (dd, $J$ = 10.1, 9.7 Hz, 1 H); $^{13}$C{$^1$H} ($C_6D_6$) $\delta$ 98.6 (m, $C_5Me_5$), 23.2 (dd, $J$ = 29.8, 11.2 Hz, RhCH$_2$Si(CH$_3$)$_3$), 20.5 (s, $C_5Me_5$), 16.56 (d, $J$ = 30.01 Hz, PMe$_3$) 1.21 (s, Rh CH$_2$Si(CH$_3$)$_3$); MS, 528 (M$^+$); mp 165 °C dec. Anal. Calcd for $C_{17}H_{35}SiIPRh$: C, 38.63; H, 6.63. Found: C, 38.4; H, 6.80.

R = cyclobutyl, X = I, 54% yield; $^1$H NMR ($C_6D_6$) $\delta$ 1.76 (d, $J$ = 2.8 Hz, 15 H), 2.0–1.0 (m),[29] 1.23 (dd, $J$ = 10.1, 0.6 Hz, 9 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 97.3 (m, $C_5Me_5$), 43.2 (s, $CH_2$)$_3$), 41.2 (s, (CH$_2$)$_3$), 38.3 (s, (CH$_2$)$_3$), 36.1 (dd, $J$ = 32.1, 21.2 Hz, RhCH), 17.2 (d, $J$ = 29.1 Hz, PMe$_3$), 10.1 (s, $C_5Me_5$); MS, 441 (M$^+$ - C$_4$H$_7$); mp 115 °C dec. Anal. Calcd for $C_{17}H_{31}IPRh$: C, 41.13; H, 6.25. Found: C, 41.35; H, 6.11.

R = cyclopentyl, X = I, 46% yield; $^1$H NMR ($C_6D_6$) $\delta$ 1.63 (d, $J$ = 2.8 Hz, 15 H), 2.2–1.3 (m),[29] 1.25 (dd, $J$ = 10.1, 0.7 Hz, 9 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 98.1 (m, $C_5Me_5$), 37.51 (s, (CH$_2$)$_4$), 36.81 (s, (CH$_2$)$_4$), 34.79 (dd, $J$ = 34.1, 22.1 Hz, RhCH), 27.14 (s, (CH$_2$)$_4$), 26.73 (s, (CH$_2$)$_4$), 15.21 (d, $J$ = 28.2 Hz, PMe$_3$), 9.51 (s, $C_5Me_5$); MS, 393 (M$^+$ - C$_5$H$_9$); mp 133 °C dec. Anal. Calcd for $C_{18}H_{33}IPRh$: 42.35; H, 6.47. Found: C, 42.61; H, 6.71.

R = cyclohexyl, X = Br, 39% yield; $^1$H NMR ($C_6D_6$) $\delta$ 1.68 (d, $J$ = 2.7 Hz, 15 H), 2.2–1.1 (m),[29] 1.31 (dd, $J$ = 9.8, 0.7 Hz, 9 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 96.8 (m, $C_5Me_5$), 37.21 (s, (CH$_2$)$_5$), 36.23 (s, (CH$_2$)$_5$), 35.81 (s, (CH$_2$)$_5$), 34.13 (dd, $J$ = 32.3, 21.5 Hz, RhCH), 29.31 (s, (CH$_2$)$_5$), 27.21 (s, (CH$_2$)$_5$, 16.31 (d, $J$ = 30.1 Hz, PMe$_3$), 9.21 (s, $C_5Me_5$); MS, 346 (M$^+$ - C$_8$H$_{11}$); mp 131 °C dec. Anal. Calcd for $C_{19}H_{35}IPRh$: C, 43.51; H, 6.68. Found: C, 43.27; H, 6.51.

R = 2,2-dimethylcyclopropyl, X = I, 83% yield; $^1$H NMR ($C_6D_6$) $\delta$ 1.69 (s, 3 H), 1.58 (d, $J$ = 2.9 Hz, 15 H), 1.46 (s, 3 H), 1.25 (dd, $J$ = 10.2, 0.6 Hz, 9 H), 1.13 (m, 1 H), 0.55 (m, 2 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 98.9 (m, $C_5Me_5$), 29.3 (s, C(CH$_3$)$_2$, 21.8 (s, C(CH$_3$)$_2$), 18.5 (d, $J$ = 31.2 Hz, PMe$_3$), 17.23 (s, C(CH$_2$)$_2$), 11.3 (s, CH$_2$), 10.5 (s, $C_5Me_5$), 2.31 (dd, $J$ = 35.1, 15.6 Hz, RhCH). MS, 441 (M$^+$ - C$_5$H$_9$); mp 175 °C dec. Anal. Calcd for $C_{18}H_{33}IPRh$: C, 42.35; H, 6.47. Found: C, 42.42; H, 6.55.

**[($\eta^5$-C$_5$Me$_5$)RhPMe$_3$H]$_x$Li$_x$ (15).** A solution of $n$-BuLi (66 $\mu$L, 2.5 M in $n$-hexane, 0.160 mmol) was added dropwise to a stirred toluene solution (5 mL) of the dihydride **1** (50 mg, 0.158 mmol) at -78 °C. The reaction mixture changed from a pale yellow to a bright orange during the course of the reaction. The mixture was allowed to warm to 20 °C and was stirred for 1 h. The toluene was removed in vacuo, and the resulting orange powder was washed with cold pentane (-40 °C) to remove any excess BuLi. The residue was taken up in the minimum amount of 50% toluene/hexane and cooled to -40 °C to yield the product as an amorphous (sometimes crystalline) orange material in analytically pure form (43 m, 85% yield). Anal. Calcd for $C_{13}H_{25}LiPRh$: C, 48.47; H, 7.76. Found: C, 48.21; H, 7.48.

Preparation of **15-$d_1$** was carried out exactly as described above from the dideuteride **1-$d_2$**.

**(1-$^{13}$C)Ethyl Tosylate, 55% $^{13}$C-Enriched.** This material was prepared by the method of Tipson[26] from (1-$^{13}$C)ethanol (55% $^{13}$C-enriched) and $p$-toluenesulfonyl chloride in pyridine. The (1-$^{13}$C)ethanol was prepared from barium carbonate-$^{13}$C by the procedure of Colborn and Vollhardt[30] which was adapted from the method of Calvin et al.[31]

**1,1,1,2,2-Pentadeuterioethyl Tosylate.** This material was prepared by the method of Tipson[26] from 1,1,1,2,2-pentadeuterioethanol purchased from Cambridge Isotope Laboratories and toluenesulfonyl chloride in pyridine.

**(1-Methylcyclopropyl)methyl Tosylate.** This material was prepared from methylcyclopropylcarbinol, $p$-toluenesulfonyl chloride, and colidine by the method of Bergstrom and Siegel.[32] It was found necessary to allow the reaction to stand at 10 °C for 36 h to avoid significant contamination by the $p$-toluenesulfonyl chloride in the isolated product. The material was purified by crystallization at -40 °C from 50% Et$_2$O/hexane. This yielded the product as large colorless crystals which melted below room temperature. Anal. Calcd for $C_{12}H_{16}SO_4$: C, 60.0; H, 6.66. Found: C, 60.4; H, 6.34.

**($\eta^5$-C$_5$H$_5$)RhPMe$_3$I$_2$.** Iodine (0.29 g, 1.15 mmol) dissolved in Et$_2$O (5 mL) was added dropwise to a stirred solution of ($\eta^5$-C$_5$H$_5$)RhPMe$_3$(C$_2$H$_4$)[30] (0.3 g, 1.1 mmol) in Et$_2$O (20 mL). Upon addition of the iodine the product precipitated as a black microcrystalline material. This material was filtered and dried to yield analytically pure product (0.5 g, 93% yield): $^1$H NMR ($CDCl_3$) $\delta$ 5.54 (d, $J$ = 1.82, 5 H), 2.02 (dd, $J$ = 10.2, 0.8 Hz, 9 H); $^{13}$C{$^1$H} ($CDCl_3$) $\delta$ 83.2 (m, $C_5H_5$), 16.21 (d, $J$ = 28.1 Hz, PMe$_3$). Anal. Calcd for $C_8H_{14}PRhI_2$: C, 19.28; H, 2.81. Found: C, 19.1; H, 2.55.

**($\eta^5$-C$_5$H$_5$)RhPMe$_3$H$_2$.** Na(CH$_3$OCH$_2$CH$_2$O)$_2$AlH$_2$ (Red-al) (0.85 mL, 1.13 M solution in toluene, 0.96 mmol) was slowly added to a stirred slurry of ($\eta^5$-C$_5$H$_5$)RhPMe$_3$I$_2$ (0.4 g, 0.80 mmol) in Et$_2$O (100 mL). The mixture was stirred for 4 h at 20 °C. The reaction mixture changed from a dark brown heterogeneous mixture to a pale yellow color over the course of the reaction. The solvent was removed in vacuo, and the residue was extracted several times with 25% Et$_2$O/hexane. The combined extracts were filtered, and the solvent was removed in vacuo. The material was purified by sublimation under high vacuum at 30 °C onto a -78 °C cooled condenser. The product was obtained in analytically pure form as a white flaky material (0.15 g, 75% yield): $^1$H NMR ($C_6D_6$) $\delta$ 5.24 (d, $J$ = 1.5 Hz, 5 H), 1.06 (dd, $J$ = 10.3, 0.7 Hz, 9 H), -13.93 (dd, $J$ = 38.5, 28.88 Hz, 2 H); $^{13}$C{$^1$H} ($C_6D_6$) $\delta$ 85.3 (m, $C_5H_5$), 17.2 (d, $J$ = 27.8 Hz, PMe$_3$); $^{31}$P{$^1$H} NMR ($C_6D_6$) $\delta$ 5.11 (d, $J$ = 158.2 Hz); IR (hexane) 2050 cm$^{-1}$ ($\nu_{Rh-H}$); UV (hexane) $\lambda_{max}$ = 275 nm, $\epsilon$ = 5.3 × 10$^3$; MS, 246 (M$^+$). Anal. Calcd for $C_8H_{16}PRh$: C, 39.04; H, 6.51. Found: C, 39.15; H, 6.73.

**Preparation of [($\eta^5$-C$_5$H$_5$)(PMe$_3$)RhH]Li.** This complex was prepared exactly as described above for the analogous complex **15** from the reaction of ($\eta^5$-C$_5$H$_5$)(PMe$_3$)RhH$_2$ (0.08 mmol) with $n$-BuLi (0.081 mmol) in toluene at -78 °C.

**Preparation of the Alkyl Hydrides by the Photolysis of ($\eta^5$-C$_5$Me$_5$)(PMe$_3$)RhH$_2$ in Hydrocarbon Solvents. Method A.** This method is exemplified by the following preparation of the cyclopropyl hydride **10**. NMR scale: cyclopropane (1.0 mL) was vacuum transferred onto the rhodium dihydride **1** (10 m, 0.032 mmol) in an NMR tube equipped with a vacuum stopcock. The tube was immersed in a methanol bath at -60 °C and irradiated for a specific period, typically 2 h. The cyclopropane was then removed under high vacuum while maintaining the temperature of the reaction mixture at -60 °C. The resulting residue was cooled to -196 °C, and 0.6 mL of toluene-$d_8$ containing tetramethylsilane (0.032 mmol) as internal standard was vacuum transferred into the tube. The tube was flame sealed, warmed to -60 °C, and analyzed by NMR spectroscopy at -60 °C. Integration of the $^1$H NMR resonances of C$_5$Me$_5$ vs. the internal standard showed that **10** was produced in 89% yield along with 8% of **1** as the only observable contaminant: $^1$H NMR (THF-$d_8$, -60 °C) $\delta$ 1.82 (d, $J$ = 1.6 Hz, 15 H), 1.36 (dd, $J$ = 9.8, 0.7 Hz, 9 H), 0.45 to -0.26 (m, 5 H), -15.18 (dd, $J$ = 45.0, 32.5 Hz, 1 H); $^{13}$C NMR (gated, THF-$d_8$, -60 °C) $\delta$ 97.2 (m, $C_5Me_5$), 19.11 (qd, $J$ = 128.5, 30.5 Hz, PMe$_3$), 12.81 (t, $J$ = 157.5 Hz, CH$_2$), 10.73 (q, $J$ = 126.0 Hz, $C_5Me_5$), 8.16 (t, $J$ = 161.1 Hz, CH$_2$), -4.95 (ddd, $J$ = 138.1, 38.06, 18.96 Hz, RhCH); $^{31}$P{$^1$H} (THF-$d_8$, -60 °C) 8.41 (d, $J$ = 160.9 Hz).

High-boiling solvents could not be removed at low temperatures by high vacuum techniques. In these cases the products were identified only on the basis of the $^1$H NMR resonance appearing in the hydride region (-10 to -25 ppm) and by conversion to the more stable haloalkyl complexes as described later.

Preparative scale: again, using the cyclopropyl hydride as an example, cyclopropane (10 mL) was vacuum transferred onto the rhodium dihydride **1** (100 m, 0.32 mmol) in a glass bomb equipped with a right angle stopcock. The bomb was immersed in a methanol bath at -60 °C and irradiated for 3 h. The cyclopropane solution of the product was then used in the subsequent conversion to the cyclopropyl(halo)rhodium complexes as described later.

Photochemical experiments with ($\eta^5$-C$_5$H$_5$)RhPMe$_3$H$_2$ were carried out as above, but with the light filtered through 2-mm thick uranium glass. Typical photolysis time was 1 h. NMR data for hydridoalkyl complexes ($\eta^5$-C$_5$Me$_5$)(PMe$_3$)Rh(R)(H) prepared by this method (see Table I for yields and conditions): **3**, R = ethyl; $^1$H NMR (toluene-$d_8$, -60 °C) $\delta$ 1.89 (d, $J$ = 1.8 Hz, 15 H), 1.63 (br t, $J$ = 8 Hz, 3 H), 1.5

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(br m, 1 H), 1.2 (br m, 1 H), 1.01 (dd, $J$ = 9, 0.9 Hz, 9 H), −14.64 (dd, $J$ = 49.67, 32.29 Hz, 1 H); $^{13}$C NMR (gated, toluene-$d_8$, −60 °C) $\delta$ 96.1 (t, $J$ = 4 Hz, $C_5Me_5$), 23.51 (qdd, $J$ = 127.1, 2.8, 1.6 Hz, $RhCH_2CH_3$), 18.84 (qd, $J$ = 128.3, 29.8 Hz, $PMe_3$), 10.87 (q, $J$ = 125.5 Hz, $C_5Me_5$), 0.88 (tdd, $J$ = 126.1, 26.65, 11.83 Hz, $RhCH_2CH_3$); $^{31}$P{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 7.81 (d, $J$ = 158.5 Hz).

**4**: R = *n*-butyl; $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.84 (d, $J$ = 1.8 Hz, 15 H), 1.8–1.1 (m),[29] 0.94 (dd, $J$ = 9 Hz, 9 H), −14.53 (dd, $J$ = 49.51, 32.40 Hz, 1 H); $^{13}$C NMR (gated, toluene-$d_8$, −60 °C) $\delta$ 96.25 (t, $J$ = 4 Hz, $C_5Me_5$), 41.6 (t, $J$ = 125.1 Hz, $RhCH_2(CH_2)_2CH_3$), 29.76 (t, $J$ = 125.3 Hz, $RhCH_2(CH_2)_2CH_3$), 21.38 (qd, $J$ = 131.01, 30.33 Hz, $PMe_3$), 14.71 (q, $J$ = 123.3 Hz, $Rh(CH_2)_3CH_3$), 11.63 (q, $J$ = 125.83 Hz, $C_5Me_5$), 8.29 (tdd, $J$ = 124.21, 26.93, 11.45 Hz, $RhCH_2(CH_2)_2CH_3$); $^{31}$P{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 7.79 (d, $J$ = 158.2 Hz).

**5**: R = *n*-hexyl; $^1$H NMR (toluene-$d_8$, −60 °C) 1.85 (d, $J$ = 2.3 Hz, 15 H), 1.8–0.9 (m),[29] 0.91 (dd, $J$ = 10.6, 0.8 Hz, 9 H), −14.55 (dd, $J$ = 49.9, 32.2 Hz, 1 H); $^{13}$C NMR (gated, toluene-$d_8$, −60 °C) $\delta$ 96.31 (br t, $J$ = 4 Hz, $C_5Me_5$), 39.12 (t, $J$ = 125.2 Hz, $RhCH_2(CH_2)_4CH_3$), 29.71 (t, $J$ = 125.4 Hz, $RhCH_2(CH_2)_4CH_3$), 26.81 (t, $J$ = 125.6 Hz, $RhCH_2(CH_2)_4CH_3$), 25.31 (t, $J$ = 125.5 Hz, $RhCH_2(CH_2)_4CH_3$) 18.31 (qd, $J$ = 130.9, 29.1 Hz, $PMe_3$), 14.31 (q, $J$ = 125.0 Hz, $Rh(CH_2)_5CH_3$), 10.58 (q, $J$ = 125.81 Hz, $C_5Me_5$), 8.40 (tdd, $J$ = 124.4, 26.82, 11.21 Hz, $RhCH_2(CH_2)_4CH_3$); $^{31}$P{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 7.73 (d, $J$ = 157.3 Hz).

R = *n*-octyl; $^1$H NMR (octane, −40 °C) $\delta$ −14.81 (dd, $J$ = 49.4, 32.1 Hz); $^{31}$P{$^1$H} NMR (octane, −40 °C) $\delta$ 6.21 (d, $J$ = 157.9 Hz).

**6**: R = isobutyl; $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.85 (m, 1 H), 1.76 (d, $J$ = 1.7 Hz, 15 H), 1.28 (d, $J$ = 8.1 Hz, 3 H), 1.19 (d, $J$ = 8.1 Hz, 3 H), 0.91 (dd, $J$ = 9.1, 0.85 Hz, 9 H), −14.05 (dd, $J$ = 50.6, 30.8 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 97.2 (t, $J$ = 4.2 Hz, $C_5Me_5$), 15.9 (s, $RhCH_2CH(CH_3)_2$) 13.31 (s, $RhCH_2CH(CH_3)_2$), 17.41 (d, $J$ = 29.5 Hz, $PMe_3$), 11.21 (s, $C_5Me_5$), 5.0 (dd, $J$ = 25.61, 12.1 Hz, $RhCH_2CH(CH_3)_2$); $^{31}$P{$^1$H} (toluene-$d_8$, −60 °C) $\delta$ 8.15 (d, $J$ = 157.3 Hz).

**9**: R = trimethylsilyl; $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.73 (d, $J$ = 1.8 Hz, 15 H), 0.94 (dd, $J$ = 10.1, 0.9 Hz, 9 H), 0.38 (s, 9 H), 0.2 (dd, $J$ = 10.1, 2.1 Hz, 1 H), −13.45 (dd, $J$ = 12.1, 10.1 Hz, 1 H); $^{13}$C{$^1$H} (toluene-$d_8$, −60 °C) $\delta$ 98.1 (br t, $J$ = 3.8 Hz, $C_5Me_5$), 17.21 (d, $J$ = 28.7 Hz, $PMe_3$), 10.72 (s, $C_5Me_5$), 9.1 (s, $RhCH_2Si(CH_3)_3$), −10.89 (dd, $J$ = 27.12, 10.3 Hz, $RhCH_2Si(CH_3)_3$); $^{31}$P{$^1$H}(toluene-$d_8$, −60 °C) $\delta$ 6.15 (d, $J$ = 157.2 Hz).

R = cyclobutyl; $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.79 (d, $J$ = 1.7 Hz, 15 H), 2.0–1.0 (m),[29] 1.01 (dd, $J$ = 9.1, 0.9 Hz, 9 H), −15.12 (dd, $J$ = 48.1, 31.2 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 98.3 (m, $C_5Me_5$), 25.2 (s, $(CH_2)_3$), 22.1 (s, $(CH_2)_3$), 21.2 (s, $(CH_2)_3$), 19.1 (*d*, $J$ = 29.6 Hz, $PMe_3$), 11.2 (s, $C_5Me_5$), 5.3 (d, $J$ = 33.1, 19.2 Hz, RhCH); $^{31}$P{$^1$H} toluene-$d_8$, −60 °C) $\delta$ 7.9 (d, $J$ = 154.5 Hz).

**12**: R = cyclopentyl; $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.9 (d, $J$ = 1.8 Hz, 15 H), 2.0–1.0 (m),[29] 0.95 (dd, $J$ = 9.1, 0.8 Hz, 9 H), −15.23 (dd, $J$ = 49.2, 30.8 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 97.31 (m, $C_5Me_5$), 35.3 (s, $CH_2)_4$), 34.21 (s, $(CH_2)_4$), 30.25 (s, $(CH_2)_4$), 29.35 (s, $CH_2)_4$), 19.8 (d, $J$ = 30.1, $PMe_3$), 10.54 (s, $C_5Me_5$), 7.21 (dd, $J$ = 30.2, 13.5 Hz, RhCH); $^{31}$P{$^1$H} (toluene-$d_8$, −60 °C) $\delta$ 9.5 (d, $J$ = 153.5 Hz).

R = cyclohexyl, 25% yield; $^1$H NMR (20% solution of cyclohexane in isobutane, −60 °C) $\delta$ −15.15 (dd, $J$ = 49.5, 30.2 Hz); $^{31}$P{$^1$H} (isobutane/cyclohexane, −60 °C) 6.66 (d, $J$ = 156.2 Hz).

**Preparation of ($\eta^5$-$C_5Me_5$)RhPMe$_3$(R)(H) from the Corresponding Alkyliodorhodium Complex. Method B.** This method is illustrated by the preparation of the neopentyl hydride **7** at −90 °C. An apparatus similar to that shown in Figure 4 but without the attached reaction chamber B, was used in these reactions. A 2% $Et_2O$/pentane slurry (0.5 mL) of **13**, R = neopentyl, X = iodide (32.2 m, 0.063 mmol), prepared from the rhodium diiodide, was placed in reaction chamber A. The reaction chamber was cooled to −196 °C, stopcock C was opened under a rapid stream of $N_2$ fed in from point D, and a pentane solution (0.2 mL) of *t*-BuLi (2.1 M in pentane, 0.05 mL, 0.120 mmol) was added to the reaction mixture via syringe. The mixture was warmed to −100 °C, and a glass rod equipped with rubber septum was inserted via stopcock C and used to stir the reaction mixture periodically over 3 h. The solution changed from bright red to pale orange as the lithium rhodate **14** (R = neopentyl) was produced over the course of the reaction. The stopcock was closed, and the reaction mixture was warmed to −78 °C. The pentane/$Et_2O$ was then removed under high vacuum. The resulting lithium neopentyl rhodate residue was cooled to −196 °C, and toluene-$d_8$/$Et_2O$-$d_{10}$ (3:1, 1.0 mL) was added by vacuum transfer. As the reaction chamber was warmed to −95 °C the rhodate dissolved, and the mixture was again cooled to −196 °C. Ethan-*d*-ol (0.063 mmol) was vacuum transferred into the reaction mixture, and the entire apparatus was then immersed to the level indicated in Figure 4 in a −95 °C bath. The mixture was agitated periodically over 30 min during which time it became pale yellow as the neopentyl hydride was formed. The solution was then filtered directly into the attached NMR tube by rapidly removing the entire apparatus from the cold bath and tilting to allow the solution to collect in the filter column containing alumina III. The apparatus was returned to the bath and by the application of a slight vacuum at stopcock E, the solution was made to collect in the NMR tube. The apparatus was cooled to −196 °C, and the NMR tube with attached stopcock was removed by flame sealing at point X. Tetramethylsilane (0.063 mmol) was added by vacuum transfer as internal standard, and the NMR tube was removed by flame sealing at point Y. Subsequent analysis by $^1$H NMR at −90 °C indicated that the neopentyl hydride was produced in 85% yield and was the only observable product: $^1$H NMR (toluene-$d_8$/$Et_2O$-$d_{10}$, 3:1 by volume, −90 °C) $\delta$ 1.74 (d, $J$ = 1.8 Hz, 15 H), 1.51 (br m, 2 H) 1.24 (s, 9 H), 0.89 (d, $J$ = 9 Hz, 9 H), −14.21 (dd, $J$ = 49.1, 30.1 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$) $\delta$ 96.8 (t, $J$ = 3.8 $H_2$, $C_5Me_5$), 36.81 (s, $RhCH_2C(CH_3)_3$), 31.5 (s, $RhCH_2C(CH_3)$), 18.12 (d, $J$ = 28.7 Hz, $PMe_3$), 10.51 (s, $C_5Me_5$), 9.71 (dd, $J$ = 25.51, 11.8 Hz, $RhCH_2C(CH_3)_3$); $^{31}$P{$^1$H} ((toluene-$d_8$, −80 °C) $\delta$ 8.05 (d, $J$ = 156.3 Hz).

Following are NMR data for other alkylhydridorhodium complexes, Cp*(L)Rh(R)(H), prepared by this method (see Table I for yields). **11a**: $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.82 (d, $J$ = 2.1 Hz, 15 H), 1.59 (s, 3 H), 1.58 (s, 3 H), 0.96 (dd, $J$ = 9.7, 0.8 Hz, 9 H), 0.5 to −0.2 (m, 3 H), −14.45 (dd, $J$ = 46.6, 31.1 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −60 °C) $\delta$ 96.3 (m, $C_5Me_5$), 23.5 (s, $CMe_2$), 19.3 (d, $J$ = 29.2 Hz, $PMe_3$), 18.31 (s, $C(CH_3)_2$), 16.74 (s, $C(CH_3)_2$), 10.63 (s, $C_5Me_5$), 8.31 (s, $CH_2$), −6.35 (dd, $J$ = 37.35, 19.21 Hz, $RhCH$); $^{31}$P{$^1$H} (toluene-$d_8$, −60 °C) $\delta$ 7.65 (d, $J$ = 157 Hz.

**11a-d**: $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.82 (d, $J$ = 2.1 Hz, 15 H), 1.59 (s, 3 H), 1.58 (s, 3 H), 0.96 (dd, $J$ = 9.7, 0.8 Hz, 0.5–0.2 (m, 34). Intergration of the −14.45 ppm residual proton region against the $PMe_3$ resonance indicated that the product was >95% deuterated at the hydride position.

**11b**: $^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.79 (d, $J$ = 2.0 Hz, 15 H), 1.37 (s, 3 H), 1.35 (s, 3 H), 0.95 (dd, $J$ = 0.3, 0.8 Hz, 9 H), 0.37–0.2 (m, 3 H), −14.14 (dd, $J$ = 47.72, 29.9 Hz, 1 H); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −60 °C) 96.8 (m, $C_5Me_5$), 24.1 (s, $CMe_2$), 18.51 (d, $J$ = 29.4 Hz, $PMe_3$), 18.51 (s, $C(CH_3)_2$), 13.25 (s, $C(CH_3)_2$), 11.51 (s, $C_5Me_5$), 9.81 (s, $CH_2$), −5.57 (dd, $J$ = 39.51, 19.71 Hz, RhCH); $^{31}$P{$^1$H} NMR (toluene-$d_8$, −60 °C) 7.31 (d, $J$ = 157.3 Hz).

**11b-*d***: $^1$H NMR (toluene-$d_8$, −60 °C) 1.79 (d, $J$ = 2.0 Hz, 15 H), 1.37 (s, 3 H), 1.35 (s, 3 H), 0.95 (dd, $J$ = 9.3, 0.8 Hz, 9 H), 0.37–0.2 (m, 3 H). Integration of the −14.14 ppm residual proton region against the resonance of $PMe_3$ indicated that the compound was >95% deuterated in the hydride position.

The NMR data for other compounds prepared by this method are identical with those listed under method A.

**Preparation of the Alkyl Hydrides from [($\eta^5$-$C_5Me_5$)RhPMe$_3$H]Li and Alkyl Tosylates. Method C.** This method is illustrated for the preparation of (1-$^{13}$C)ethyldeuteriorhodium complex **3a** (55% $^{13}$C-enriched). An apparatus similar to that shown in Figure 4, but without the attached chamber B, was used in these reactions. A pentane solution (0.6 mL) of the lithium deuteriorhodate complex **15** (20.2 m, 0.063 mmol) was placed in the reaction chamber A. The apparatus was immersed to level indicated in liquid $N_2$ while under a $N_2$ atmosphere. Stopcock C was opened under a rapid stream of $N_2$ fed in from point D, and a 2% $Et_2O$/pentane solution (0.3 mL) of (1-$^{13}$C)ethyl tosylate (51% $^{13}$C-enriched, 24 m, 0.126 mmol) was added via syringe to the contents of reaction chamber A. Stopcock C was closed, and the apparatus was warmed to −60 °C for 3 h. During the course of the reaction the solution changed from a bright orange to a light brown with the formation of a gelatinous precipitate of lithium tosylate. In preparation for filtering the solution into the NMR tube, the apparatus was placed in a dry ice/isopropanol bath at −78 °C. Filtering was accomplished by rapidly removing the entire apparatus from the viscous isopropanol bath and quickly tilting to allow the mixture to run into the filter chamber. The apparatus was returned to the cooling bath, and by application of a slight vacuum via stopcock E, the pale yellow pentane/$Et_2O$ solution of the ethyl hydride was made to collect in the NMR tube. The apparatus was cooled to −196 °C, evacuated via stopcock E, and the NMR tube with attached stopcock was removed by flame sealing at point X. The pentane/$Et_2O$ solution of **3a** was warmed to −60 °C, and the solvents were removed under high vacuum. The resulting pale yellow residue of the product was cooled to −196 °C, and toluene-$d_8$ (0.6 mL) and tetramethylsilane (0.063 mmol), as internal standard, were added by vacuum transfer. The NMR tube was removed by flame sealing at point Y. Subsequent analysis by $^1$H NMR at −60 °C indicated that **3a** and **3b** were produced in 87% yield as the only observable products [$^1$H NMR (toluene-$d_8$, −60 °C) $\delta$ 1.89 (d, $J$ = 1.8 Hz, 15 H), 1.63–1.2 (br multiplets of ethyl resonances), 1.01 (dd, $J$ = 9.0), 0.9 Hz, 9 H, −14.62 (dd, $J$ = 49.61, 32.10 Hz,)]. Integration of the hydride (−14.64 ppm) and ethyl

(1.63–1.2 ppm) residual proton regions against the $PMe_3$ resonance indicated that the compound was >95% monodeuterium labeled [$^{13}C\{^1H\}$ NMR (toluene-$d_8$, −60 °C) δ 96.1 (t, $J$ = 4 Hz, $C_5Me_5$), 23.51 (m, $RhCH_2CH_3$), 18.84 (d, $J$ = 29.9 Hz, $PMe_3$), 10.87 (s, $C_5Me_5$), 0.88 (m, RhCH)]. Integration of the $^{13}C$ satellite resonances of the β-carbon of the ethyl group (23.51 ppm) indicated that the material was approximately 55% $^{13}C$-enriched in the α-position of the ethyl group.

NMR data for other alkylhydridorhodium complexes prepared by this method (see Table I for yields) [**3-$d_6$**: $^1H$ NMR (toluene-$d_8$, −60 °C) δ 1.89 (d, $J$ = 1.8 Hz, 15 H), 1.01 (dd, $J$ = 9.0, 0.9 Hz, 9 H)]. Integration of the hydride (−14.64 ppm) and ethyl (1.63–1.2 ppm) residual proton regions against the $PMe_3$ resonance indicated that the compound was >95% deuterium labeled in these positions.

**8**: $^1H$ NMR (toluene-$d_8$, −60 °C) δ 1.79 (d, $J$ = 1.8 Hz, 15 H), 1.51 (s, 3 H), 1.15 (m, 2 H), 0.87 (dd, $J$ = 9.6, 0.8 Hz, 9 H), 0.3–0.7 (m, 3 H), −14.55 (dd, $J$ = 50.0, 30.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR (saturated toluene-$d_8$, −60 °C) δ 96.19 (m, $C_5Me_5$), 17.99 (dd, $J$ = 129.9, 27.85 Hz, $PMe_3$), 15.64 (s, *C*Me), 14.01 (q, $J$ = 124.8 Hz, $CH_3$), 10.56 (q, $J$ = 126.1 Hz, $C_5Me_5$), 5.62 (t, $J$ = 161.3 Hz, $CH_2$), 4.12 (t, $J$ = 159.4 Hz, $CH_2$), −6.12 (q dd, $J$ = 125.1, 39.1, 18.2 Hz, $RhCH_2$); $^{31}P\{^1H\}$ (toluene-$d_8$, −60 °C) δ 8.12 (d, $J$ = 155.6 Hz). The NMR data for the other compounds prepared by this method were identical with those listed under method A.

**Preparation of ($\eta^5$-$C_5H_5$)($PMe_3$)Rh((1-$^{13}$C)ethyl)(H) 55% $^{13}$C-Enriched.** The preparation of this complex was carried out by using [($\eta^5$-$C_5H_5$)($PMe_3$)RhH]Li and $CH_3{}^{13}CH_2OTs$, exactly as described above for [($\eta^5$-$C_5Me_5$)($PMe_3$)Rh($^{13}CH_2CH_3$)(**D**): $^1H$ NMR (toluene-$d_8$, −60 °C) δ 5.07 (s, 5 H), 0.91 (dd, $J$ = 10.0, 1.0 Hz, 9 H), 3.5–1.5 (m, 5 H), −14.76 (dd, $J$ = 43.29, 31.29 Hz, 1 H), $^{13}C\{^1H\}$ NMR (toluene-$d_8$, −60 °C) δ 87.5 (s, $C_5H_5$), 26.83 (m, $RhCH_2CH_3$), 19.25 (d, $J$ = 30.1 Hz, $PMe_3$), −6.81 (dd, $J$ = 25.8, 10.41 Hz, $RhCH_2CH_3$). Integration of the $^{13}C$-satellites of β-carbon of the ethyl group indicated that the material was approximately 55% $^{13}C$-enriched in the α-carbon position of the ethyl group.

**Preparation of Cp*($PMe_3$)Rh(R)(H) by Thermolysis of the Neopentyl Hydride 7 at −60 °C in Hydrocarbon Solvents. Method D.** These experiments are exemplified by the activation of *n*-butane. The neopentyl hydride **7** (0.063 mmol) was generated in η-butane solvent as described above in method A. The solution of **7** was then filtered at −100 °C into the NMR tube, and the NMR tube and attached stopcock were removed by flame sealing at point X. The solution was then warmed to −60 °C for 1 h to allow the reductive elimination of neopentane from **7** and subsequent C–H activation of the hydrocarbon solvent. The reaction mixture was then cooled to −78 °C, and the volatile materials were removed under high vacuum to yield a pale yellow residue of the η-butyl hydride **4**. The residue was cooled to −196 °C, and toluene-$d_8$ (0.6 mL) containing tetramethylsilane (0.063 mmol) as internal standard was added by vacuum transfer. The NMR tube was removed by flame sealing at point Y and warmed to −60 °C, and the contents were analyzed by $^1H$ and $^{31}P$ NMR. The *n*-butyl hydride was found to be the only product present and was formed in 83% yield based on the neopentyliodorhodium complex.

Additional evidence for the products produced in these reactions was obtained by converting the products to the more stable alkyl(halo)rhodium complexes **13** as described later under the photochemical competition experiments. Data for the compounds (see Table I for yields) prepared by this method are identical with those listed under method A.

**Preparation of ($\eta^5$-$C_5Me_5$)$RhPMe_3$(R)(X) (X = Cl, Br, and I) from the Corresponding Alkylhydridorhodium Complex.** This general method is illustrated for the cyclopropyliodorhodium complex. The cyclopropyl hydrido complex **10** was prepared by photolysis of a solution of the dihydride **1** (100 mg, 0.32 mmol) in cyclopropane (10 mL) at −70 °C as previously described. Iodoform (0.125 g, 0.32 mmol) dissolved in diethyl ether (3 mL) was slowly added to the photolysis mixture, maintaining the temperature below −60 °C. The reaction mixture immediately changed from a brown to an orange color upon addition of the iodoform. The solution was agitated and left at −70 °C for 1 h. The reaction mixture was evaporated in vacuo, and the resulting red residue was extracted several times with 5% diethyl ether/hexane until the extracts were no longer colored. The combined extracts were filtered, and the solvent was removed to yield the crude product as a red viscous oil. The material was taken up in the minimum amount of 20% $Et_2O$/hexane and cooled to −40 °C, yielding the cyclopropyliodorhodium as red needles (74 mg, 52% yield based on the dihydride **1**).

To prepare the alkyl chloride or bromide, the iodoform is replaced by chloroform or bromoform, respectively. The spectroscopic data for other Cp*(L)Rh(R)(X) complexes prepared by this method are identical with those listed for the alkylhalorhodium complexes prepared from the reaction of the rhodium dihalides with the corresponding alkyllithium. All the alkylhalorhodium complexes prepared by this method were obtained in analytically pure form. The yields obtained by this method are based on the alkyl hydrides as prepared by methods A and D: R = ethyl, X = Br, 45% (A), 52% (D); R = *n*-butyl, X = I, 49% (A), 54% (D); R = *n*-pentyl, X = I, 52% (A), 60% (D); R = *n*-hexyl, X = I, 48% (A), 55% (D); R = *n*-octyl, X = I, 47% (A), 54% (D); R = isobutyl, X = I, 35% (A), 39% (D); R = trimethylsilyl, X = I, 75% (A), 78% (D); R = cyclopropyl, X = I, 65% (D); R = 2,2-dimethylcyclopropyl, X = I, 69% (from thermal rearrangement of **8** obtained by method C); R = cyclobutyl, X = I, 29% (A), 38% (D); R = cyclopentyl, X = I, 25% (A), 29% (D); R = cyclohexyl, X = Br, 23% (A), 28% (D).

**Reaction of the Alkylrhodium Halides with Halogen.** These reactions are exemplified by the conversion of the ethyl hydride to bromoethane. The ethylhydridorhodium complex **3** was prepared from the rhodium dihydride **1** (50 mg, 0.16 mmol) and ethane as described above for the photochemical activation of cyclopropane. The ethane was replaced with methylcyclohexane-$d_{14}$ (0.6 mL) at −78 °C, and the ethyl hydride was converted to the ethylbromorhodium complex by reaction with bromoform (0.16 mmol) dissolved in methylcyclohexane-$d_{14}$ (0.2 mL) at −78 °C as described above for the cyclopropyl hydride. Without further purification, bromine (0.16 mmol) freshly dissolved in methylcyclohexane-$d_{14}$ (0.5 mL) was added to the solution at −50 °C. The mixture was left for 60 min in the dark and then allowed to warm to 20 °C. The volatiles were removed and trapped at −190 °C, *p*-dioxane (0.16 mmol) was added as an internal standard, and the mixture was analyzed by $^1H$ NMR, gas chromatography, and GC/MS. Each method of analysis indicated that bromoethane was formed in 51% yield based on the dihydride **1**. $^1H$ NMR analysis of the organometallic residue indicated that the rhodium fragment had been converted to Cp*(L)$RhBr_2$ in 87% yield.

In similar fashion the *n*-butyl and *n*-hexyl hydrides were converted to *n*-bromobutane and *n*-bromohexane in 47 and 59% yield, respectively. The ethylhydridorhodium complex could be converted to iodoethane in 48% yield by treatment with iodoform followed by iodine.

**Observation of Cp*(L)Rh((1-$^{13}$C)ethyl)(D) at −90 °C.** A pentane/$Et_2O$ solution of Cp*(L)Rh((1-$^{13}$C)ethyl)(H) (0.063 mmol) was prepared at −60 °C in an NMR tube equipped with a right angle stopcock as described in method B from the reaction between **15** and (1-$^{13}$C)ethyl tosylate. The solution was cooled to −196 °C, and *n*-BuLi (2.5 M in hexane, 50 μL, 0.063 mmol) was added via the stopcock. The stopcock was closed, and the reaction mixture was warmed to −78 °C for 3 h with periodic agitation. The reaction mixture changed from a pale yellow to deeper yellow as the lithium (1-$^{13}$C)ethyl rhodate was formed. The pentane/$Et_2O$ mixture was removed under high vacuum, and the resulting yellow residue of rhodate was cooled to −196 °C. Toluene-$d_0$/$Et_2O$ (3:1) (0.6 mL) was added by vacuum transfer, warmed to −78 °C to dissolve the rhodate, and recooled to −196 °C. Ethan-*d*-ol (0.063 mmol) was added by vacuum transfer, and the tube was warmed to −90 °C. After 30 min the tube was cooled to −196 °C, and the tube was removed by flame sealing. The tube was warmed to −90 °C, agitated periodically for 30 min to ensure dissolution of the complex, and analyzed at −90 °C and then at −60 °C by $^2H\{^1H\}$ NMR [$^2H\{^1H\}$ NMR (toluene-$d_0$/$Et_2O$-$d_0$; 3:1 by volume, −90 °C) δ −14.41 (dd, $J$ = 48, 32 Hz)]. No resonances where detected at 1.4 ppm (α-ethyl resonance) [$^2H\{^1H\}$ NMR (toluene-$d_0$/$Et_2O$-$d_0$, −60 °C) 1.4 (m, 0.81 H), −14.71 (dd, $J$ = 48, 32 Hz, 0.18 H)]. Warming to −25 °C resulted in deuterium distributed between the hydride α- and β-positions, as expected on the basis of the $^{13}C/^2H$ results described above.

**Photochemical Competition Experiments.** These experiments were carried out by the photolysis of the rhodium dihydride **1** at −60 °C in mixtures of tetramethylsilane and a second hydrocarbon. In a typical experiment hexane (0.917 mmol) and tetramethylsilane (0.917 mmol) were vacuum transferred into an NMR tube containing the dihydride **1** (10 mg, 0.032 mmol) and equipped with a vacuum stopcock. The tube was cooled to −60 °C and irradiated for 30 min as previously described. After photolysis the solvent was carefully removed under high vacuum while maintaining the temperature of the tube at −78 °C. The residue was cooled to −196 °C, and toluene-$d_8$ was added by vacuum transfer. The tube was flame sealed and warmed to −60 °C, and the ratio of products formed was determined by $^1H$ and $^{31}P$ NMR spectroscopy. Both methods of analysis indicated that (within 5% error) the ratio of trimethylsilyl hydride **9** to hexyl hydride **5** was 2:1.

High-boiling hydrocarbons could not be removed by high vacuum techniques. In these cases the mixture was analyzed by $^{31}P$ NMR and by observing the hydride region of the $^1H$ NMR spectrum (−10 to −25 ppm) obtained at −60 °C after a presaturation pulse was applied to the solvent peaks.

The results of the techniques of analysis discussed above were confirmed in selected cases by converting the mixture of alkylhydridorhodium complexes to the alkyliodorhodium complexes by treatment with $CHI_3$. This was accomplished by the use of the apparatus shown in Figure 5. Thus the NMR tube with the reaction mixture held at −196

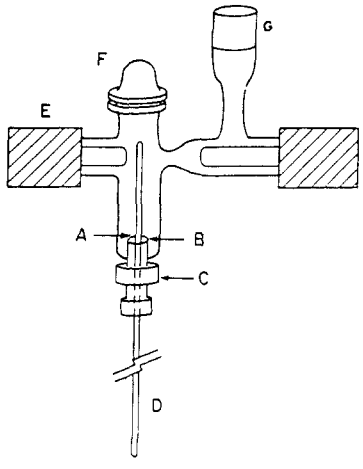


**Figure 5.** Illustration of the apparatus used to open flame sealed NMR tubes while maintaining the tube under an inert atmosphere and also at low temperatures if necessary: A, score mark on NMR tube; B, break point; C, Cajon adapter; D, NMR tube; E, plunger; F, removable cap; G, nitrogen inlet.

°C was first scored as indicated in the figure. It was then carefully inserted into the apparatus via the Cajon adaptor until the score mark rested against the break point. The Cajon fitting was then tightened, the apparatus was evacuated, and the plunger was tightened until the tube cracked at the score mark. The tube was warmed to −100 °C, and the apparatus was filled with $N_2$. The apparatus was opened at point F under a stream of $N_2$ fed in from point G, and $CHI_3$ (1 equiv) in $Et_2O$ (0.5 mL) was then allowed to run down the NMR tube slowly enough to prevent the reaction mixture from warming above −60 °C. The apparatus was recapped, and the reaction mixture was warmed to −60 °C and agitated periodically over the course of 1 h. The reaction mixture was then allowed to warm to room temperature, and the volatile materials were removed in vacuo. Toluene-$d_8$ was vacuum transferred onto the reaction mixture, and the tube was flame sealed and analyzed by $^1H$ NMR. The ratios of the alkylhalo complexes were obtained by integration of the respective resonances of the complexes. The results obtained by this technique were found in all cases to be consistent with those obtained by NMR analysis at the alkyl hydride stage.

**Thermal Competition Experiments.** These experiments were carried out by the thermolysis of the neopentyl hydride at −60 °C in a mixture of tetramethylsilane and a second hydrocarbon as described above for the thermal C−H activation of *n*-butane. The mixtures of products were analyzed as described for the photochemical competition experiments.

**Thermal Isomerization of ($\eta^5$-$C_5Me_5$)($PMe_3$)Rh(R)(H)**: These experiments are exemplified by the thermal isomerization of Cp*($PMe_3$)Rh((1-$^{13}$C)ethyl)(**D**) **3a** at −30 °C. A toluene-$d_8$ solution (0.6 mL) of the (1-$^{13}$C)ethyldeuteridorhodium complex **3a** was produced as described earlier by method C from the lithium deuteridorhodate complex **15-*d***and (1-$^{13}$C)ethyl tosylate in toluene-$d_8$ at −60 °C. The sample was examined by NMR spectroscopy initially at −60 °C and periodically at −25 °C until the isomerization was complete. The tube was cooled to −78 °C and cracked under a vacuum by using the apparatus shown in Figure 5. The ethane evolved, was analyzed by mass spectroscopy, and found to consist of 48% $C_2H_5D$ and 50% $^{13}CCH_4D$.

**Preparation, Isolation, and Thermal Isomerization of ($\eta^5$-$C_5Me_5$)IrP-$Me_3$((1-$^{13}$C)$C_2H_5$)(D), 55% $^{13}$C-Enriched.**[9b] *t*-BuLi (2.5 M/pentane, 206 μL, 0.51 mmol) was added dropwise to a stirred toluene solution (2 mL) of the Cp*($RMe_3$)$IrD_2$ (200 mg, 0.49 mmol) at −40 °C. The solution was allowed to warm to 20 °C and stirred for an additional 30 min. The solution was cooled to −40 °C, and a toluene solution (1.0 mL) of (1-$^{13}$C)ethyl tosylate (19.8 mg, 0.98 mmol) was added dropwise over the course of 10 min. The reaction mixture was allowed to warm to 20 °C and left stirring for 3 h. During the course of the reaction the solution changed from a bright yellow to a light brown with the formation of a gelatinous precipitate of lithium tosylate. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane solution was filtered and concentrated to 1.0 mL. The sample of crude product was purified by low-temperature (−100 °C) chromatography on alumina III with 5% $Et_2O$/pentane. The pure product eluted in the first fraction. The solvent was removed to yield the product as a pale yellow oil (108 mg, 51% yield) [$^1H$ NMR ($C_6D_6$) δ 1.88 (d, $J$ = 1.8 Hz, 15 H), 1.8−1.7 (m, 5 H), 1.25 (d, $J$ = 9.7 Hz, 9 H)]. Integration of the −17.94 ppm residual proton region against the $PMe_3$ resonance indicated that the complex was >95% deuterium substituted in the hydride position: [$^{13}$C NMR (gated, $C_6D_6$) 91.7 (d, $J$ = 3.4 Hz), 25.19 (q, $J$ = 125.6 Hz, $IrCH_2CH_3$), 19.12 (qd, $J$ = 126.1, 36.4 Hz, $PMe_3$), 10.33 (q, $J$ = 126.2 Hz, $C_5Me_5$), −20.93 (td, $J$ = 125.6, 7.7 Hz, $IrCH_2CH_3$)]. Integration of the $^{13}$C satellite resonances of the β-carbon of the ethyl group indicated that the complex was approximately 55% $^{13}$C-substituted at the α-carbon position of the ethyl group [$^{31}P\{^1H\}$ ($C_6D_6$) −43.1 (s); IR (neat) 1530 $cm^{-1}$ ($\nu_{Ir-D}$)].

The product (50 mg) was dissolved in toluene-$d_8$ (0.6 mL) and placed in an NMR tube, and the tube was flame sealed. The entire tube was immersed into an oil bath at 145 °C in the dark. At various time intervals the tube was removed, rapidly cooled in an ice bath at 0 °C, and examined by NMR spectroscopy (see text). After the isomerization was over (10 h), the tube was coled to −78 °C and cracked open by using the apparatus shown in Figure 5. The ethane evolved was examined by mass spectroscopy. The mixture was found to consist of 48% $C_2H_4D$ and 50% $^{13}CCH_4D$.

**Crossover Experiments. (a) Thermal Reductive Elimination of a Mixture of ($\eta^5$-$C_5Me_5$)$RhPMe_3(CH_3)$(H) and ($\eta^5$-$C_5Me_5$)$RhPMe_3$-$(CD_3)$(D) in Toluene-$d_8$.** The apparatus shown in Figure 4 was used. A pentane (0.6 mL) solution of the methylhydridorhodium complex **2** (0.063 mmol) was prepared in reaction chamber A by method A from the corresponding methyliodo complex and *t*-BuLi followed by ethanol quench. The solution was filtered into the NMR tube, and the pentane was removed under high vacuum at −78 °C. A pentane solution of the methyl-$d_3$ deuteride **2-$d_4$** was then similarly prepared in reaction chamber B from the methyl-$d_3$-iodorhodium complex (0.063 mmol) and *t*-BuLi followed by ethan-*d*-ol quench. The pentane solutions were filtered into the NMR tube, and the pentane was removed under high vacuum at −78 °C. Toluene-$d_8$ was vacuum transferred into the NMR tube at −196 °C, and the tube was removed by flame sealing at point Y. The mixture was examined by NMR spectroscopy at −70 °C and various higher temperatures up to 20 °C. The tube was cooled to −196 °C and cracked open under vacuum by using the apparatus shown in Figure 5. The mixture of methanes was analyzed by low-energy electron impact mass spectroscopy and the isotopic ratio obtained. The mixture was found to consist only of $CH_4$ and $CD_4$ with minor (<5%), $CH_ND_{4-N}$, N = 1, 2, 3. **(b) Thermal Reductive Elimination of a Mixture of ($\eta^5$-$C_5Me_5$)-$(PMe_3)Rh(C_2H_5)$(H) and ($\eta^5$-$C_5Me_5$)$RhPMe_3(C_2D_5)$(D) in Toluene-$d_8$.** The apparatus shown in Figure 4 was used in this experiment. A toluene-$d_8$ solution (0.5 mL) of the ethyl hydride **3** (0.062 mmol) was prepared in reaction chamber A from the lithium hydridorhodate complex **15** and ethyl tosylate as described earlier. The solution was filtered at −78 °C into the NMR tube. Similarly, a toluene-$d_8$ (0.5 mL) solution of the ethyl-$d_5$ deuteride **3-$d_6$** (0.062 mmol) was generated from the lithiumdeuteriorhodium complex **15-*d*** and ethyl-$d_5$ tosylate in reaction chamber B and filtered into the NMR tube at −78 °C. The apparatus was evacuated and sealed at point Y. The mixture was examined by NMR spectroscopy at −70 °C and various temperatures up to 20 °C. The tube was cooled to −78 °C and cracked open under vacuum by using the apparatus shown in Figure 5. The mixture of ethanes was analyzed by low-energy electron impact mass spectroscopy. The mixture was found to consist only of $C_2H_5$ and $C_2D_5$ with minor amounts of $C_2H_ND_{5-N}$ (<5%).

**Kinetic Experiments.** These experiments are exemplified by the thermal decomposition of the ethyl hydride **3**. A toluene-$d_8$ solution of **3** (0.063 mmol) was prepared in a NMR tube equipped with an attached right angle stopcock as described in method B. The solution was cooled to −196 °C, and a sealed capillary tube containing hexamethyldisiloxane (0.032 mmol) and rhodium dihydride **1** (0.032 mmol) in toluene-$d_8$ as external standards was added to the reaction mixture via the right angle stopcock. The NMR tube was evacuated, flame sealed, warmed to −90 °C, quickly placed into the NMR spectrometer probe, and allowed to equilibrate to −30 °C. The decomposition of **3** was followed by $^1H$ NMR by monitoring the disappearance of the peaks due to the Cp* and hydride ligands of **3** relative to the external standards. The decomposition was followed for 4 half-lives and was found to exhibit clean first-order kinetics with a rate constant of (6.0 ± 0.6) × $10^{-5}$ $s^{-1}$.

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**Registry No. 1**, 84624-03-3; **1-$d_2$**, 104338-08-1; **2**, 84624-01-1; **2-$d_4$**, 104338-10-5; **3**, 88825-25-6; **3a**, 104338-06-9; **3-$d_6$**, 104338-01-4; **4**, 104337-80-6; **5**, 104337-81-7; **6**, 104337-82-8; **7**, 104337-83-9; **8**,

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 $\pi$-Allyl Complexes

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**Abstract:** Generation of the coordinatively unsaturated fragment [Cp*RhL] (Cp* = $\eta^5$-$C_5Me_5$; 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 $\alpha$-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 $\beta,\beta$-dimethylrhodacyclobutane, $Cp^*(L)\overline{Rh\text{-}CH_2\text{–}CMe_2\text{–}CH_2}$. The possible intermediate formation of the isomeric $\alpha,\alpha$-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 $\pi$-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 $\beta$-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]

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