temp, °C	NAD⁺		NADP⁺		PEG-NAD⁺	
	10	11	10	11	10	11
25	20.3	13.3	20.7	12.3	16.6	9.9
38	67.5	43.3	67.5	39.5	56.4	31.8

doublet at −7.2 ppm clearly indicates the hydride ligand (Figure 8).

With complexes 6 and 7 the NADH formation slows down very much with time, indicating that in these cases hydride transfer is the rate-determining step. 13 and 14 behave similarly.

In the case of complex 10, we studied the influence of the buffer system (sodium phosphate or Tris/HCl) and the formate counterion (sodium or ammonium) on the turnover frequency. With sodium phosphate buffer the pH optimum for the reduction of NAD⁺ by sodium formate is obtained at pH 8 due to increasing hydrogen formation at lower pH values. At higher pH the labile aquo ligand is replaced by the stronger coordinated hydroxy ligand, slowing down the ligand exchange by formate (eq 9). In the presence of ammonium formate as the reducing agent the pH optimum is found at pH 6. Under more basic conditions the free ammonia seems to act as a monodentate ligand for the rhodium central atom, which is more difficult to exchange by formate (eq 9). Tris/HCl buffer slows down the NADH formation drastically. This

may also be explained by the action of Tris as a strong ligand to rhodium, making the starting complex more stable.

In the case of complexes 10 and 11 it could also be shown that not only NAD⁺, but also NADP⁺ and PEG-NAD⁺ (PEG MW 20 000) can be reduced catalytically by sodium formate (Table III). The turnover frequency of 10 is identical for NAD⁺ and NADP⁺ and about 20% lower for the high molecular weight cofactor PEG-NAD⁺. 11 behaves very similarly; however, because of the binding to PEG the turnover frequencies are between 30 and 40% lower. The reaction rate in the presence of 11 is also independent of the NAD⁺ concentration. The activation energies for the reduction of NAD⁺ and PEG-NAD⁺ catalyzed by 10 (E_A(NAD⁺) = 16.3 kcal·mol⁻¹, E_A(PEG-NAD⁺) = 16.4 kcal·mol⁻¹) and 11 (E_A(NAD⁺) = 15.3 kcal·mol⁻¹, E_A(PEG-NAD⁺) = 16.8 kcal·mol⁻¹) were determined by rate measurements at different temperatures (17.3, 25.7, 32.1, 40.0 °C). The increase of the molecular weight of the cofactor as well as of the complex does not influence the activation energy. This is important for the application of 11 as a catalyst for the chemical cofactor regeneration for enzymatic reactions in a flow-through membrane reactor.[10]

Ring Migration Reactions of (C₅Me₅)Rh(PMe₃)H₂. Evidence for η³ Slippage and Metal-to-Ring Hydride Migration

William D. Jones,* Valerie L. Kuykendall, and Anthony D. Selmeczy

Department of Chemistry, University of Rochester, Rochester, New York 14627

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The reactions of (C₅Me₅)Rh(PR₃)H₂ (PR₃ = PMe₃, PMe₂Ph, PMePh₂, PPh₃) with D₂ gas occur quickly at 25 °C, leading to the stepwise exchange of hydrogen for deuterium. Kinetic studies indicate a second-order reaction mechanism involving rhodium and deuterium. (C₅Me₅)Rh(PMe₃)H₂ also reacts with PMe₃ at 40 °C to give C₅Me₅H and HRh(PMe₃)₄, a reaction that also displays bimolecular kinetics. Isotope effect studies show no rate difference with the dideuteride rhodium complex. The mechanism(s) of these reactions are discussed in light of the kinetic requirements. The reactions of (C₅Me₅)Rh(PR₃)(Ph)H with H₂ have also been studied and found to lead to (C₅Me₅)Rh(PR₃)H₂.

Introduction

Reactions of metal cyclopentadienyl complexes and their methylated derivatives have been the subject of intense study over the past few decades. While in many cases this ligand has been present as a spectator for much of the chemistry that occurs at either the metal center or a coordinated ligand, there is also good evidence for noninnocent involvement of this η⁵ ligand. In particular, the importance of η⁵ → η³ ring slippage[1] and metal-to-ring

migration reactions[2] have both been cited in recent literature.

Complexes of the general formula (C₅R₅)M(L)(R)H and (C₅R₅)ML₂ (M = Rh, Ir; R = H, Me; L = PMe₃, CO, C₂H₄) have been found to be generally very active for the activation of C–H bonds.[3] While most evidence points toward

(1) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* 1987, *87*, 307–318 and references therein. Rerek, M. E.; Basolo, F. *Organometallics* 1983, *2*, 372–376. Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* 1966, *88*, 1657–1663. Cramer, R. E.; Seiwell, L. P. *J. Organomet. Chem.* 1975, *92*, 245–252.

(2) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1974, 1324–1331. Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath D. V.; Holt, E. M. *J. Am. Chem. Soc.* 1986, *108*, 7222–7227. Green, M. L. H. *Pure Appl. Chem.* 1978, *50*, 27–35. Jones, W. D.; Maguire, J. A. *Organometallics* 1985, *4*, 951–953. Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* 1974, 516–517. Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1974, 1324–1331. Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 794–795.

RhH₂ + D₂   RhD₂ + H₂
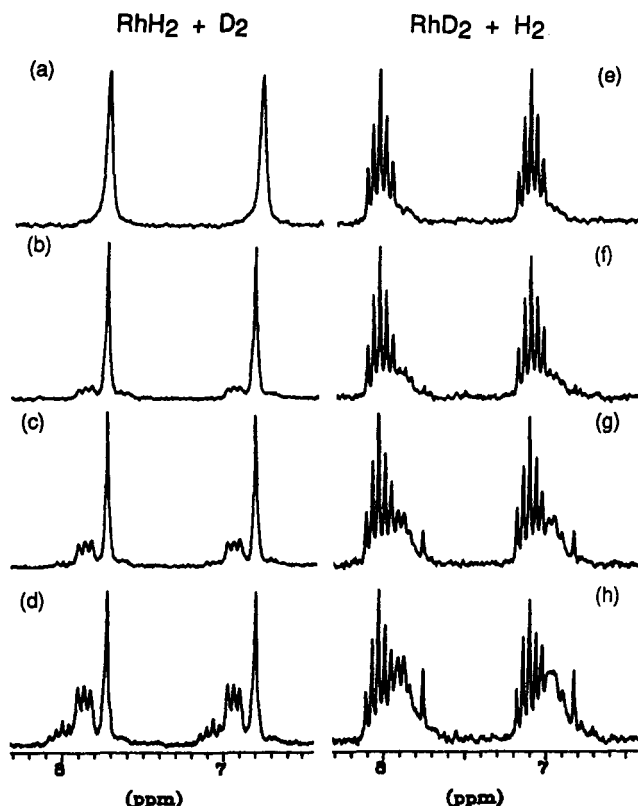
Figure 1. ^{31}P NMR spectra for the reaction of (C₅Me₅)Rh-(PMe₃)H₂ (0.082 M) with D₂ (700 mm) (a) prior to D₂ addition, (b) after 1 h, (c) after 3 h, and (d) after 5 h and of (C₅Me₅)Rh-(PMe₃)D₂ (0.078 M) with H₂ (700 mm) (e) prior to D₂ addition, (f) after 1 h, (g) after 3 h, and (h) after 5 h.
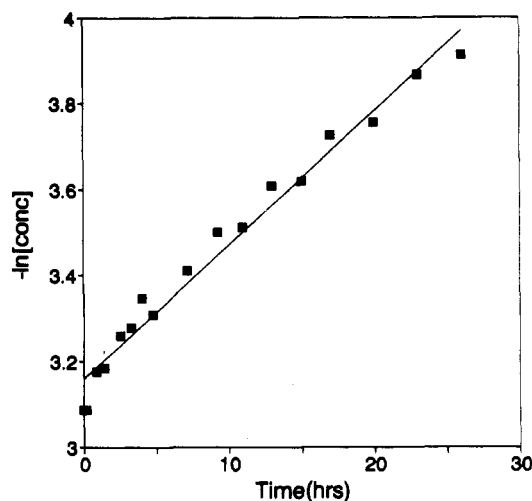
Figure 2. First-order plot for the reaction of (C₅Me₅)Rh(PMe₃)H₂ (0.046 M) with D₂ (601 mm, 2.5 mM).

the intermediacy of reductive elimination/oxidative addition pathways involving the 16-electron intermediate (C₅R₅)M(L), reports of $\eta^5 \rightarrow \eta^3$ ring slippage have also appeared to explain C–H bond activation and ligand substitution.[4] In this paper we report reactions of a series

(3) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100. Bergman, R. G.; Janowicz, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939. Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 1537–1550. Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725. Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–7191. Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734–1736. Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810–1817. Belt, S. T.; Duckett, S. B.; Haddleton, D. M.; Perutz, R. N. *Organometallics* **1989**, *8*, 748–759.
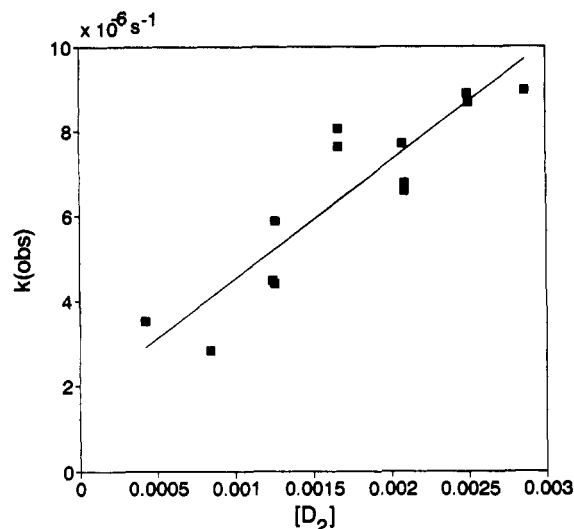

Figure 3. Plot of k_{obs} vs [D₂] for the reaction of (C₅Me₅)Rh-(PMe₃)H₂ with D₂ at 25 °C.

of complexes of the type (C₅Me₅)Rh(PR₃)H₂, where PR₃ = PMe₃, PMe₂Ph, PMePh₂, and PPh₃. The studies indicate that the C₅Me₅ ring participates in these not-so-common pathways in reactions with hydrogen and PMe₃.

Results

Reaction of (C₅Me₅)Rh(PR₃)H₂ with Deuterium.

The reaction of (C₅Me₅)Rh(PMe₃)H₂ (1) with deuterium gas at 25 °C in C₆D₆ solution was found to lead to the incorporation of deuterium into the hydride positions of the molecule. By ^{1}H NMR spectroscopy, the hydride resonance at δ –13.650 (dd, J = 41.8, 29.8 Hz) was observed to gradually disappear over several hours time. Monitoring the reaction by ^{31}P{^{1}H} NMR spectroscopy indicates that the exchange of deuterium occurs in a stepwise fashion, first generating 1-d_1 and then producing 1-d_2 (eq 1). The

$$(1)$$
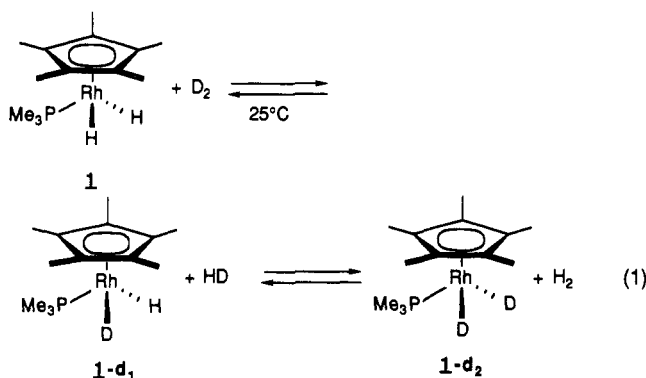
presence of each deuterium on the metal center induces an isotopic perturbation of the resonance of ~0.14 ppm downfield. In addition, the deuterium (I = 1) also couples to phosphorus (J_{P-D} = 6 Hz) giving rise to a 1:1:1 triplet for (C₅Me₅)Rh(PMe₃)HD and a 1:2:3:2:1 quintet for (C₅Me₅)Rh(PMe₃)D₂ (Figure 1a–d). A similar experiment reacting (C₅Me₅)Rh(PMe₃)D₂ with H₂ shows the gradual conversion to (C₅Me₅)Rh(PMe₃)HD and then (C₅Me₅)-Rh(PMe₃)H₂ (Figure 1e–h).

The rate of this reaction was probed as a function of the concentration of 1 and D₂. The reactions were conducted in sealed NMR tubes in which good contact between the liquid and gas phases was maintained by keeping the

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Table I. Reaction of (C₅Me₅)Rh(PMe₃)H₂ with D₂ in C₆D₆ Solution at 25 °C[a]

[C₅Me₅)Rh(PMe₃)H₂], M	$P(D_2)$, mm	$10^3[D_2]$, M[b]	$10^6 k_{obs}$, s⁻¹
0.0457	101 (1)	0.421 (8)	3.52
0.0457	201 (1)	0.838 (8)	2.83
0.0457	298 (1)	1.24 (1)	4.48
0.0179	301 (1)	1.26 (1)	4.40
0.0327	301 (1)	1.26 (1)	5.88
0.0178	399 (1)	1.66 (1)	8.05
0.0457	400 (1)	1.67 (1)	7.63
0.0457	498 (1)	2.08 (1)	7.70
0.0179	501 (1)	2.09 (1)	6.58
0.0327	501 (1)	2.09 (1)	6.78
0.0178	599 (1)	2.50 (1)	8.87
0.0457	601 (1)	2.51 (1)	8.67
0.0179	687 (1)	2.87 (1)	10.3
0.0327	687 (1)	2.87 (1)	8.95

[a]Errors are estimated at ±10% for k_{obs} and ±5% for [D₂]. [b]Calculated by using the Henry's Law constant for hydrogen in benzene (K_H = 3.17 × 10⁻³ M/atm).[20]

samples on their sides in the dark. Under these conditions, reproducible rates (±10%) could be obtained. Figure 2 shows a typical first-order plot (excess D₂ gas was employed in each run, although the concentration in solution is less than that of 1) for the exchange of one deuterium into 1, and Figure 3 shows how the observed pseudo-first-order rate constants vary with the concentration of D₂. The scatter in the k_{obs} data is attributed to the difficulties in measuring kinetics of fast reactions involving gas/liquid phase mixing, but it is clear that the reaction is first order in both 1 and D₂ gas (Table I).

The exchange reaction does not appear to be catalyzed by acid, base, or glass. Addition of pyridine (pK_b = 8.75) or acetic acid (pK_a = 5.0) was found to have no significant effect upon the rate of H/D exchange of 1 with D₂. Use of a Teflon-lined NMR tube for the experiment was also found to have no effect upon the rate. Also, the use of different reducing agents for preparing the dihydride (PPN⁺BH₄⁻ or Red-Al) had no effect upon the rate. Adding a drop of mercury did not effect the rate of H/D exchange.

1 also catalyzes H/D exchange between H₂ and D₂ gas. Treatment of a solution of 1 in C₆D₆ with ~300 mm each of the two gases led to the observation of a 1:1:1 triplet for HD in the ¹H NMR spectrum at δ 4.423 (J = 42.8 Hz), in addition to the singlet for H₂ at δ 4.460.

The other dihydrides (C₅Me₅)Rh(PPh₃)H₂ (2), (C₅Me₅)Rh(PPh₂Me)H₂, and (C₅Me₅)Rh(PPhMe₂)H₂ also react with deuterium in a similar fashion to give the corresponding dideuterides over several hours. In each case, HD is observed in solution. (C₅Me₅)Rh(PPh₃)H₂ also catalyzes the exchange between H₂ and D₂ gas, as was observed with 1.

2 was found to undergo an independent slow H/D exchange with benzene solvent. When a solution of the complex in 100.0% C₆D₆ was heated to 62 °C for several days, a singlet at δ 7.15 was observed to appear in the ¹H NMR spectrum of the sample. Confirmation of the formation of C₆D₅H came from GC/MS examination of the sample, showing a peak at m/e = 83 (2.1% of m/e = 84 after correction for 1.6% present prior to exchange.). A similar experiment with C₆H₆ and D₂ failed to show evidence for exchange by mass spectroscopy, since the natural-abundance M + 1 peak of benzene was greater than the amount of C₆H₅D produced by exchange.
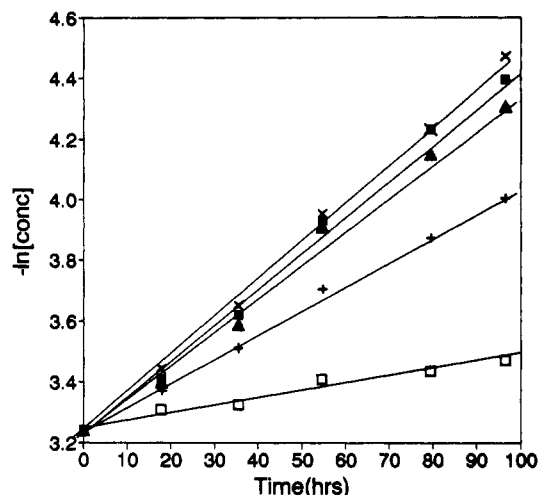
Figure 4. First-order plot for the reaction of (C₅Me₅)Rh(PMe₃)H₂ with PMe₃ at 40 °C. [PMe₃] = 0.038 M (□), 0.117 M (+), 0.235 M (▲), 0.313 M (■), and 0.471 M (×).

Table II. Reaction of (C₅Me₅)Rh(PMe₃)H₂ with PMe₃ in C₆D₆ Solution at 40 °C {[(C₅Me₅)Rh(PMe₃)H₂] = 0.039 M}

[PMe₃]	$10^6 k_{obs}$, s⁻¹	[PMe₃]	$10^6 k_{obs}$, s⁻¹
0.038 ± 0.001	0.97 (5)	0.313 ± 0.002	3.36 (17)
0.117 ± 0.002	2.00 (11)	0.471 ± 0.002	3.61 (19)
0.235 ± 0.002	3.03 (14)		

Attempts to catalyze solvent exchange with 1 failed. Solutions of 1 in C₆H₆/THF-d_8, C₆D₆/cyclohexene, or C₆D₆/cyclohexane mixed solvents showed no evidence for H/D exchange after several weeks at room temperature.

Reaction of (C₅Me₅)Rh(PMe₃)H₂ with PMe₃. The reaction of 1 with PMe₃ was found to occur more slowly than the reaction with D₂, and heating to 40 °C was required to obtain comparable rates. The products of the reaction are pentamethylcyclopentadiene and the known[6] hydride HRh(PMe₃)₄ (eq 2), formed in good yield (NMR analysis). None of the bis(phosphine) complex (C₅Me₅)-Rh(PMe₃)₂ is seen.

$$+ \ HRh(PMe_3)_4 \qquad (2)$$
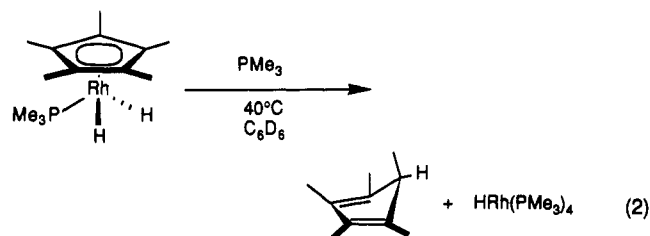
Similar results are obtained upon treatment of 1 with P(CD₃)₃ at 25 °C, although the product is mostly HRh-[P(CD₃)₃]₄. Free PMe₃ is observed by ³¹P NMR spectroscopy. At intermediate times (22 days), the PMe₃ resonance of 1 in the ¹H NMR spectrum remains at an area of 9 relative to the C₅Me₅ resonance with area 15. Consequently, the PMe₃ ligand in 1 does not appear to be labile or undergo exchange with free P(CD₃)₃ under the reaction conditions, although exchange is apparently facile in the HRh(PMe₃)₄ product.

The kinetics of this reaction were probed by varying the concentration of PMe₃ (in excess) and rhodium. As with deuterium, the reactions were found to follow pseudo-first-order kinetics (Figure 4). However, a plot of the observed rate constant vs PMe₃ concentration is now curved, with k_{obs} approaching a limiting value of ~4 × 10⁻⁶

(5) Kunin, A. J.; Johnson, C. E.; Maguire, J. A.; Jones, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1987**, *109*, 2963–2968.

(6) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 126–131.
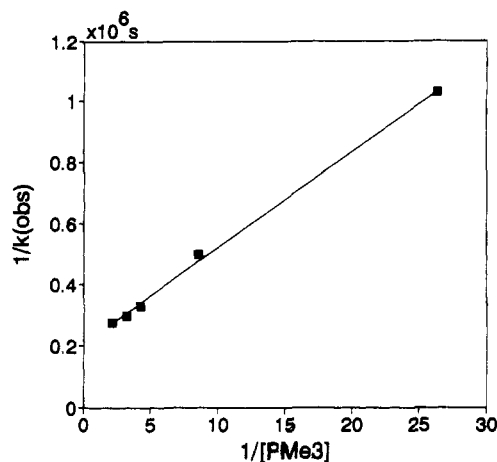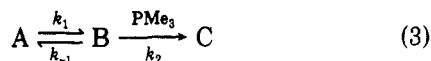
Figure 5. Plot of $1/k_{obs}$ vs $1/[PMe_3]$ for the reaction of $(C_5Me_5)Rh(PMe_3)H_2$ with PMe_3 at 40 °C.

s^{-1} at the highest PMe_3 concentrations (Table II). This type of behavior is typical of preequilibrium/saturation kinetics, as described generally in eq 3. The double-re-

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{PMe_3}{k_2} C \qquad (3)$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2} \frac{1}{[PMe_3]} \qquad (4)$$

ciprocal rate expression given in eq 4 can be derived under steady-state conditions, leading to the plot shown in Figure 5. From this plot, the intercept gives a value for the limiting rate $k_1 = 4.8 \times 10^{-6}$ s^{-1} and the slope gives k_2/k_{-1} = 6.6 M^{-1}.

Isotope Effects. A competition experiment was employed in order to probe the kinetic isotope effect in the reaction of 1 with PMe_3. An equimolar solution of 1 and 1-d_2 was prepared and treated with excess PMe_3 (0.9 M) in C_6D_6 at 40 °C. The reaction was monitored by ^{31}P NMR spectroscopy, showing the loss of 1 and 1-d_2 and the growth of $HRh(PMe_3)_4$ and $DRh(PMe_3)_4$. From first-order plots of the extent of reaction (Figure 6), it was determined that $k_H/k_D \cong 1.07$ (5).

Hydrogenation Reactions. 1 was also found to be a slow catalyst for the hydrogenation of olefins. It was discovered that placing cyclohexene (0.99 mmol) into an NMR tube with a solution of 1 (0.011 mmol) and hydrogen gas led to the hydrogenation of the cyclohexene to cyclohexane, evident from the appearance of a resonance at δ 1.395 in the ^1H NMR spectrum (eq 5). A total of 7.9 turnovers had taken place after 40 days at 25 °C.
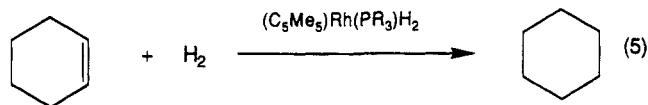
If the reaction is carried out with deuterium gas in place of hydrogen gas, deuterium is incorporated into the cyclohexane produced, as determined by the appearance of a resonance at δ 1.343 in the ^2H NMR spectrum. It was interesting to note that deuterium becomes incorporated not only into the cyclohexane produced, but also into the cyclohexene starting material as well, as seen by resonances for cyclohexene-d_n at δ 1.429 and 1.836 in the ^2H NMR spectrum.

Complex 2 was found to perform a similar hydrogenation of cyclohexene, although the rate was approximately twice that of complex 1. Eight turnovers had taken place after 23 days in the presence of 2 at 25 °C. A new complex was also formed, as seen by the appearance of new resonances

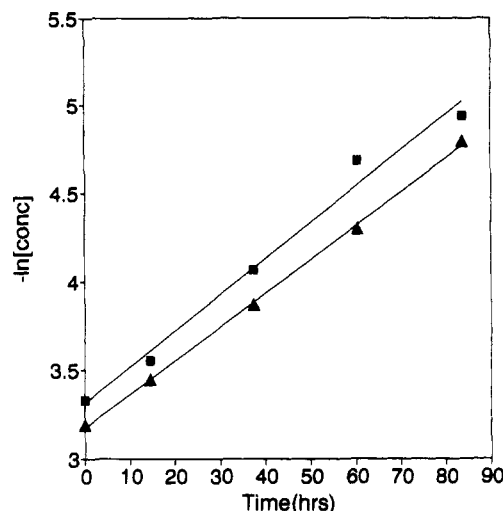**Figure 6.** Plots of (■) ln [1] vs time and (▲) ln [1-d_2] vs time.

in the ^1H NMR spectrum at δ 1.582 (15 H) and 7.754 (4 H) with other resonances partially obscured by those for the starting material. A new ^{31}P NMR resonance was observed at δ 57.69 (d, J = 224 Hz) in C_6D_6, the large coupling being indicative of rhodium in the +1 oxidation state. The complex was identified as $(C_5Me_5)Rh(PPh_3)_2$ by comparison of spectral data with an independently prepared sample. This complex must be formed upon decomposition of 2, since no other source of PPh_3 is present. After 44 days, the ratio of the bis(phosphine) complex to 2 is 1:2, or ca. half of the starting material has been converted to product (since 2 equiv of 2 are required to produce 1 equiv of product).

This decomposition product is not observed in the hydrogenation of ethylene by 2, although another complex is formed in this case. Placing ethylene over a solution of 2 in C_6D_6 in the absence of added hydrogen at 60 °C results in the hydrogenation of the ethylene to ethane, as determined by the appearance of a new resonance in the ^1H NMR spectrum at δ 0.791. The new metal-containing product that results has NMR resonances at δ 1.638 (d, J = 1.6 Hz, 15 H), 7.067 (m, 9 H), and 7.652 (t, J = 8.4 Hz, 6 H). The product was identified as $(C_5Me_5)Rh(PPh_3)(C_2H_4)$ by independent synthesis of the material, as per Diversi.[7] The ^1H NMR resonances for the coordinated ethylene are not observed in C_6D_6. In $CDCl_3$, however, one ethylene resonance appears at δ 1.084 (m, 2 H).

Reactions of $(C_5Me_5)Rh(PR_3)(Ph)H$ with Hydrogen. The complexes $(C_5Me_5)Rh(PR_3)(Ph)H$ (PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3) have been prepared by reaction of the corresponding phenyl chloride complexes with $[(sec\text{-}butyl)_3BH]^-$, as described elsewhere.[8] It was found that these complexes slowly undergo reaction with H_2 gas in C_6D_6 solution to give the dihydrides (eq 6). With excess
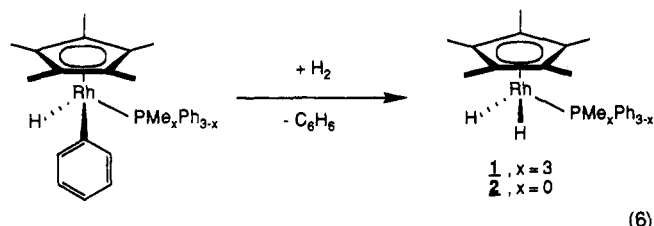
(6)

(7) Diversi, P.; Ingrosso, G.; Lucherini, A.; Martinelli, P.; Benetti, M.; Pucci, S. *J. Organomet. Chem.* **1979**, *165*, 253–263.

(8) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663. Jones, W. D.; Kuykendall, V. L. *Inorg. Chem.*, in press.

**Table III. Reaction of $(C_5Me_5)Rh(PR_3)(Ph)H$ with H_2 in Benzene**

complex	$P(H_2)$, atm	temp, °C	k_{obs}, s^{-1}	ΔG^*, kcal/mol
$(C_5Me_5)Rh$-$(PPh_3)(Ph)H$	0.855	68	1.9 (2) × 10^{-2}	22.9 (1)
$(C_5Me_5)Rh$-(PPh_2Me)-$(Ph)H$	0.851	68	5.5 (5) × 10^{-4}	25.3 (1)
$(C_5Me_5)Rh$-$(PPhMe_2)$-$(Ph)H$	0.896	62	2.2 (2) × 10^{-5}	27.0 (1)
$(C_5Me_5)Rh$-$(PMe_3)(Ph)H$	0.882	25	3.3 (3) × 10^{-8}	27.5 (1)

hydrogen the reactions go to completion, whereas with 1 equiv of hydrogen (i.e., no added H_2) an equilibrium appears to be established. Furthermore, exchange with C_6D_6 solvent to give $(C_5Me_5)Rh(PR_3)(C_6D_5)D$ was observed to occur prior to formation of the dihydride. The rates of reaction with H_2 were determined from plots of ln (concentration) vs time with excess hydrogen present, giving the rate constants and free energy barriers shown in Table III. Reaction with D_2 at 60 °C gives $(C_5Me_5)Rh(PMe_3)D_2$ and C_6H_6, although any $(C_5Me_5)Rh(PMe_3)HD$ formed at intermediate times would rapidly exchange with the D_2 gas under these conditions.

Discussion

The recent literature has provided several important examples of the importance of $\eta^5 \rightarrow \eta^3$ slippage of the cyclopentadienyl ligand in ligand substitution processes. Basolo has proposed this slippage in explaining the associative nature of ligand substitution processes in CpRh-$(CO)_2$ and related derivatives.[1] The "indenyl effect" is well documented and cited as evidence for η^3 intermediates.[9] Casey has also seen several examples in which CO substitution by PMe_3 proceeds by way of $\eta^5 \rightarrow \eta^1$ ring slippage and has even isolated and structurally characterized the intermediates with reduced hapticity.[10] Other examples in the literature provide evidence for the formation of η^1- or η^0-Cp ligands upon reaction of η^5-Cp complexes with entering ligands.[11]

When the reactions of dihydride 1 were studied, the only thermal pathway anticipated for this stable Rh(III) 18-electron complex was the reductive elimination of H_2 to generate the reactive species [$(C_5Me_5)Rh(PMe_3)$]. The hydrogenation of $(C_5Me_5)Rh(PR_3)(Ph)H$ indicated that while H_2 reacts more slowly than benzene solvent with [$(C_5Me_5)Rh(PR_3)$], the dihydride was the thermodynamically preferred product.[12] Since the barrier for loss of benzene from $(C_5Me_5)Rh(PMe_3)(Ph)H$ to give [(C_5Me_5)-

Scheme I. Ring Slip Mechanism for H_2/D_2 Exchange
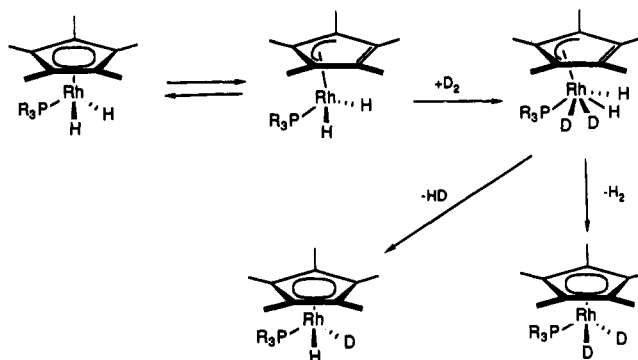
$Rh(PMe_3)$] had been measured previously[8] and the selectivity of [$(C_5Me_5)Rh(PMe_3)$] for H_2 vs benzene was determined in the above experiment, only the barrier for the reductive elimination of H_2 from 1 needed to be determined in order to compare the free energies of $(C_5Me_5)Rh(PMe_3)H_2$ and $(C_5Me_5)Rh(PMe_3)(Ph)H$.

In an attempt to measure the rate at which 1 thermally eliminates H_2 (by looking at exchange with D_2), the unexpected stepwise H/D exchange results were obtained. If a simple reductive elimination of H_2 and oxidative addition of D_2 were occurring, then the first (and only) product formed should have been $(C_5Me_5)Rh(PMe_3)D_2$. The intermediacy of $(C_5Me_5)Rh(PMe_3)HD$ as the first observed product is totally inconsistent with a simple reductive elimination/oxidative addition mechanism. Furthermore, the rate of H/D exchange between 1 and D_2 at 25 °C was much faster ($\tau_{1/2} \cong 1$–6 h) than the exchange of C_6D_6 into $(C_5Me_5)Rh(PMe_3)H_2$, the rate of the latter exchange being so slow that no reaction was observed after several months. The exchange with D_2 was found to be independent of added acid, base, or mercury (a known poison for heterogeneous catalysts[13]) and was demonstrated not to be catalyzed by the glass vessel.

Two other mechanisms can be imagined for the observed H/D exchange of 1. In one, a ring slippage step opens a vacant coordination site at the metal center. Oxidative addition of D_2 followed by reductive elimination of HD would lead to the observed intermediate 1-d_1 (Scheme I). As long as the $\eta^5 \rightarrow \eta^3$ ring slip is rapid and reversible, the reaction rate will be first order in [D_2]. This pathway may not seem feasible in that it requires a Rh(V) intermediate, but Maitlis has characterized several similar Rh(V) and Ir(V) complexes such as $(C_5Me_5)Rh(H)_2(SiMe_3)_2$,[14] and Bergman has characterized $(C_5Me_5)IrH_4$.[15] It is curious to note that in the latter complex, exchange with D_2 was believed to occur by a mechanism not involving reductive elimination of H_2, although it was not reported if the exchange was stepwise or pairwise.

In the present system, it was demonstrated that the PMe_3 is not labile under the reaction conditions so that the requisite intermediate would have to be [$(\eta^3$-$C_5Me_5)$-$Rh(PMe_3)H_2D_2$], not $(\eta^5$-$C_5Me_5)RhH_2D_2$. A more serious problem with this pathway, however, is that it would seem likely that this species could lose H_2 as well as HD (although loss of HD is statistically preferred), which in turn

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(12) The rate of the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with H_2 (k = 3.3 × 10^{-8} s^{-1}) is about 10 times slower than the rate at which C_6D_6 exchanges into the molecule (k = 4.8 × 10^{-7} s^{-1}) at 25 °C, indicating that reaction with benzene is faster than reaction with H_2.

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$$\frac{k_1 k_2}{k_{-1}} \sim 2.77 \times 10^{-3} \ M^{-1} s^{-1}$$
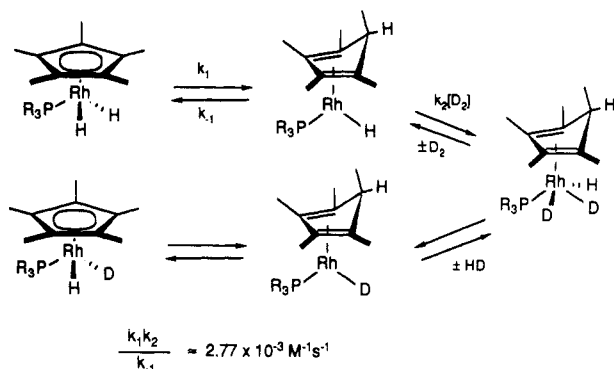
would lead to the simultaneous formation of both $(C_5Me_5)Rh(PMe_3)HD$ and $(C_5Me_5)Rh(PMe_3)D_2$. The ratio of 1-d_1 to 1-d_2 can be seen to be at least 5:1 from the ^{31}P NMR spectrum. The HD complex is clearly the first formed species beginning with either $(C_5Me_5)Rh(PMe_3)D_2$ or $(C_5Me_5)Rh(PMe_3)H_2$ (Figure 1). Consequently, a substantial isotope effect preferring the elimination of HD over H_2 can be ruled out, since D_2 would also have to be eliminated more rapidly, giving rise to the initial formation of $(C_5Me_5)Rh(PMe_3)H_2$ in the reaction of $(C_5Me_5)Rh-(PMe_3)D_2$ with H_2. In fact, the initial ratio of $RhD_2/RhHD$ in the reaction of $(C_5Me_5)Rh(PMe_3)H_2$ with D_2 can be seen to be the same as the initial ratio of $RhH_2/RhHD$ in the reaction of $(C_5Me_5)Rh(PMe_3)D_2$ with H_2, indicating that the isotope effects upon the product ratio are negligible. The possible intermediacy of an η^2-dihydrogen complex cannot be ruled out, however, in which case a preference for maintaining the deuterium–deuterium and deuterium–hydrogen bonds would be expected. Consequently, the initial preference for forming $(C_5Me_5)Rh(PMe_3)HD$ does not in itself completely rule out a tetrahydride intermediate.

A second possible mechanism involves the initial migration of a hydride ligand to the C_5Me_5 ring, effectively a reductive elimination reaction that produces a 16-electron Rh(I) intermediate. This species can then oxidatively add D_2 and reductively eliminate HD to generate $(C_5Me_5)Rh-(PMe_3)HD$ (Scheme II). A similar sequence was proposed by Bercaw to explain the formation of i-BuD upon treatment of $(C_5Me_5)_2ZrH(i$-Bu) with D_2 at -78 °C.[16] This mechanism has the advantage that no high oxidation state Rh species are involved, and that the HD complex is the only product that can be formed initially. Graham and Rest have put forth a similar migration to explain the incorporation of deuterium into the neopentyl hydride product upon irradiation of $CpIr(CO)D_2$ in the presence of neopentane.[17]

Both of these mechanisms fit the kinetic expressions given in eq 3 (with D_2 replacing PMe_3) provided that the initial step is rapid and reversible relative to the bimolecular step with D_2. The slope of a plot of k_{obs} vs $[D_2]$ gives the value for $k_1 k_2/k_{-1}$ of 2.77 (34) $\times 10^{-3} M^{-1} s^{-1}$. The rate was not observed to level off, since insufficient D_2 pressures were employed to saturate the rate.

In an attempt to trap the $(\eta^4$-$C_5Me_5H)Rh$ intermediate, PMe_3 was added to the solution. Instead of observing an intermediate, however, the formation of $HRh(PMe_3)_4$ and C_5Me_5H occurred. The reaction proceeded more slowly

and was found to depend on the concentration of PMe_3 up to about 0.3 M. Higher ligand concentrations did not result in an increase in rate. During the course of these investigations, Maitlis reported the observation of HRh-$(PMe_3)_4$ in similar reactions of both 1 and other rhodium silane complexes with phosphine.[18]

As mentioned above, the rate saturation behavior found in the reaction with PMe_3 fits with a mechanism involving a reversible unimolecular preequilibrium followed by a rate-determining reaction with PMe_3 (eq 3). The two mechanisms shown in Schemes III and IV (related to those shown in Schemes I and II) both fulfill this prerequisite. Consequently, the only obvious way to determine if the metal–hydrogen bond is being broken in (or prior to) the rate-determining step was to measure the kinetic isotope effect for the reaction of PMe_3 with 1 or 1-d_2. This ratio was measured in a competition experiment with $[PMe_3]$ $\cong 0.9$ M, where the preequilibrium is irreversible and the initial ring slippage or migration of H or D to the ring determines the overall rate of reaction. The kinetic isotope effect can be estimated for either mechanism under these conditions as described below.

If the mechanism in Scheme III is occurring in the reaction of 1 with PMe_3, then no isotope effect is anticipated since the Rh–H and Rh–D bonds remain intact in both the preequilibrium and rate-determining step involving PMe_3. If the hydride migration mechanism shown in Scheme IV is occurring, however, then the reaction of 1-d_2 is expected to proceed slightly faster than the reaction of 1, since a stronger C–D bond (with a lower zero-point energy difference) is formed with 1-d_2. Since k_D is expected to be larger than k_H, the ratio k_H/k_D should be less than 1. A typical value for this kinetic isotope effect would be 0.5–0.7 on the basis of reductive elimination reactions of similar rhodium and iridium aryl and alkyl hydrides.[19]

The lack of any significant isotope effect in the reaction of 1 with PMe_3 ($k_H/k_D \cong 1$) therefore is most consistent with the $\eta^5 \rightarrow \eta^3$ ring slip mechanism shown in Scheme III. It might seem likely, therefore, that the D_2 exchange reaction with 1 would also involve the same ring slip in the initial step as shown in Scheme I. However, the observed rate of the D_2-exchange reaction at 25 °C (~ 1 atm of D_2) is 1×10^{-5} s^{-1}, which is already much faster ($\sim 20x$) than the reactions involving PMe_3 despite the ~ 100-fold lower concentration of the former. The rate of H/D exchange with 1 atm of D_2 at 25 °C is twice as fast as the rate-limiting ring slip reaction in the PMe_3 experiments at 40 °C ($k_1 = 5 \times 10^{-6}$ s^{-1}). Consequently, the H/D exchange reaction must by proceeding by a different mechanism than the PMe_3 ring displacement reaction. Since the ring displacement reaction is believed to occur by way of the ring slip mechanism in Scheme III, the hydride-to-ring migration mechanism in Scheme I is most consistent with the observations pertaining to the H/D-exchange reaction.

The ability of 1 and 2 to catalyze the hydrogenation of olefins is also very surprising in light of their coordinative saturation. Since the PMe_3 ligand is not labile, a simple mechanism involving phosphine loss, olefin coordination and insertion into the rhodium–hydrogen bond, and reductive elimination of alkane can be ruled out. Pathways can be envisioned derived from either of the two mechanisms seen for the reactions with D_2 or PMe_3, but current data cannot distinguish which is operating. The obser-

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Scheme III. Ring Slip Mechanism for PMe₃ Displacement of C₅Me₅H
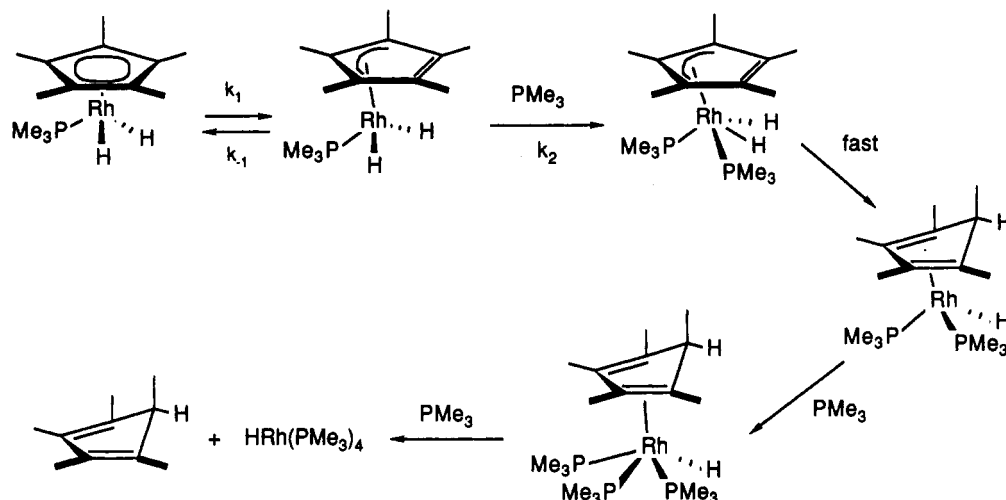
Scheme IV. Hydride Migration Mechanism for PMe₃ Displacement of C₅Me₅H

$k_1 = 4.8 \times 10^{-6}$ s⁻¹ $\dfrac{k_2}{k_{-1}} = 6.6$ M⁻¹
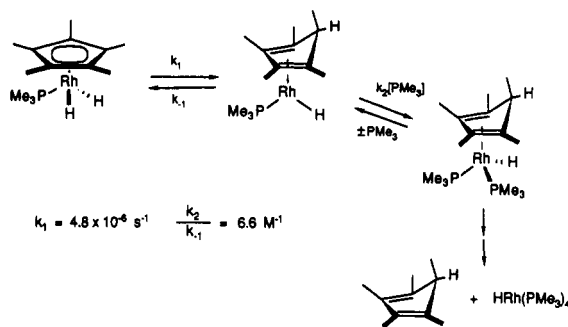
vation of deuterium incorporation into the cyclohexene indicates that β-elimination can compete with reductive elimination in the intermediate cyclohexyl hydride.

Conclusions

In summary, the complexes $(C_5Me_5)Rh(PR_3)(Ph)H$ are found to react with hydrogen to give the thermodynamically preferred dihydrides. The complex $(C_5Me_5)Rh(PMe_3)H_2$ has not been found to thermally reductively eliminate dihydrogen. Rather, this complex reacts bimolecularly with D_2 to give initially $(C_5Me_5)Rh(PMe_3)HD$ and then $(C_5Me_5)Rh(PMe_3)D_2$ by what is believed to be an initial migration of a hydride ligand from the metal to the C_5Me_5 ring. In contrast, reaction with PMe₃ leads to displacement of the C_5Me_5H ring by way of a pathway that is most consistent with an initial $\eta^5 \rightarrow \eta^3$ ring slip. The diversity of pathways open to these complexes in reactions with different substrates demonstrates that the energies of mechanistically distinct modes of reaction must lie close in energy and that generalization of reaction mechanisms must not be made without adequate investigation.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen or on a high-vacuum line with the use of Schlenk techniques. PMe₃ was purchased from Strem Chemical Co. and was used after vacuum distillation (25 °C, 10^{-3} mm). Benzene was distilled from purple solutions of benzophenone ketyl. The complexes $(C_5Me_5)Rh(PR_3)(Ph)H$ and $(C_5Me_5)Rh(PR_3)H_2$ were prepared as described elsewhere.[8] D_2 was purchased from Scott Specialty Gases and was purified by passage through a Scott Specialty Gases "Oxygen Trap" to remove any water or oxygen present.

¹H (400 MHz) and ³¹P (162 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. ¹H NMR shifts were measured relative to residual ¹H resonances in the deuterated solvent: C_6D_6 (δ 7.15). ³¹P NMR spectra were reported in units of δ (chemical shifts are referred to external 10% H_3PO_4 at δ 0.0 ppm). C_6D_6 was purchased from MSD Isotopes Merck Chemical Division and was vacuum-distilled from potassium-benzophenone prior to use.

Reaction of $(C_5Me_5)Rh(PPh_3)H_2$ with D_2. $(C_5Me_5)Rh(PPh_3)H_2$ (0.015 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was placed in a resealable NMR tube. The solution was subjected to three freeze-pump-thaw degas cycles and frozen with an ice bath. Deuterium gas was admitted to the NMR tube (663 mm) on the high-vacuum line. The solution was maintained at 24.5 °C in the absence of light. The reaction to produce $(C_5Me_5)Rh(PPh_3)D_2$ was monitored by ¹H NMR integration of the hydride resonance at δ -13.010 versus the C_5Me_5 resonance at δ 1.878. After 130 h, the solution was again freeze-pump-thaw-degassed, and H_2 (677 mm) was placed over the solution. The back-reaction to re-form 2 was then monitored.

Reaction of $(C_5Me_5)Rh(PMe_3)H_2$ with D_2. The reaction was performed as described for the PPh₃ analogue. $(C_5Me_5)Rh(PMe_3)H_2$ (0.019 mmol) was placed in a resealable NMR tube in C_6D_6. Deuterium gas (661 mm) was placed over the solution. The reaction was maintained at room temperature in the absence of light and followed by ¹H NMR spectroscopy via integration of the hydride resonance at δ -13.623 versus the C_5Me_5 resonance at δ 2.065. The ³¹P{¹H} NMR spectrum showed a doublet at δ 6.49 ($J = 150$ Hz), a doublet of 1:1:1 triplets at δ 6.63 ($J = 151$, 6 Hz), and a doublet of 1:2:3:2:1 quintets at δ 6.76 ($J = 150$, 6 Hz).

A sample that had been exhaustively exchanged with excess D_2 with freeze-pump-thaw-degassed and placed under 1 atm of H_2. The reverse reaction to produce $(C_5Me_5)Rh(PMe_3)HD$ and $(C_5Me_5)Rh(PMe_3)H_2$ was monitored by ³¹P NMR spectroscopy as described above.

Reaction of $(C_5Me_5)Rh(PMePh_2)H_2$ with D_2. The reaction was performed as described for the PPh₃ analogue. $(C_5Me_5)Rh(PMePh_2)H_2$ (0.017 mmol) was placed in a resealable NMR tube in 0.5 mL of C_6D_6. Dioxane (5 mm, 0.049 L, 293 K, 0.011 mmol) was condensed into the NMR tube as an internal standard. Deuterium gas (648 mm) was placed over the solution. The reaction was heated to 62 °C, and the reaction was followed by ¹H NMR spectroscopy via integration of the hydride resonance at -13.154 ppm versus the C_5Me_5 resonance at 1.892 ppm.

Reaction of $(C_5Me_5)Rh(PMe_2Ph)H_2$ with D_2. The reaction was performed as described for the PPh₃ analogue. $(C_5Me_5)Rh(PMe_2Ph)H_2$ (0.020 mmol) was placed in a resealable NMR tube in 0.5 mL of C_6D_6. Dioxane (3 mm, 0.049 L, 296 K, 0.008 mmol) was condensed into the NMR tube as an internal standard. Deuterium gas (668 mm) was placed over the solution. The reaction was heated to 62 °C, and the reaction was followed by ¹H NMR spectroscopy via integration of the hydride resonance at -13.300 ppm versus the C_5Me_5 resonance at 1.945 ppm.

Reaction of (C₅Me₅)Rh(PMe₃)H₂ with H₂ and D₂. (C₅Me₅)Rh(PMe₃)H₂ (0.020 mmol) was dissolved in 0.5 mL of C₆D₆, and the solution was placed in a resealable NMR tube. The solution was freeze–pump–thaw-degassed three times and frozen with liquid nitrogen. Deuterium gas (324 mm) was placed over the sample on the high-vacuum line, followed by hydrogen gas (275 mm). The sample was maintained at 23 °C and the reaction followed by ¹H NMR spectroscopy.

Reaction of (C₅Me₅)Rh(PPh₃)H₂ with H₂ and D₂. The same procedure was followed as for the PMe₃ analogue. (C₅Me₅)Rh-(PPh₃)H₂ (0.013 mmol) was placed in a resealable NMR tube in 0.5 mL of C₆D₆ with D₂ (355 mm) and H₂ (320 mm). Resonances for H₂ and HD were immediately (~10 min) observed in the ¹H NMR spectrum.

Reaction of (C₅Me₅)Rh(PPh₃)H₂ with C₆H₆/THF-*d*₈. (C₅Me₅)Rh(PMe₃)H₂ (0.043 mmol) was dissolved in 0.55 mL of a 5:1 mixture of C₆H₆ and THF-*d*₈, and the solution was placed into a resealable NMR tube. The sample was maintained at 24.5 °C, and the solution was monitored via ¹H NMR spectroscopy for 4 days. No exchange occurred.

Reaction of (C₅Me₅)Rh(PMe₃)H₂ in C₆D₆/C₆H₁₀. The same procedure was carried out as for the C₆H₆/THF-*d*₈ solvent mixture. (C₅Me₅)Rh(PMe₃)H₂ was dissolved in 0.5 mL of C₆D₆, and the solution was placed in a resealable NMR tube. To this was added 0.2 μL of cyclohexane. The sample was freeze–pump–thaw-degassed three times and maintained at 24.5 °C for 10 days. The reaction was monitored by ¹H NMR spectroscopy.

Reaction of (C₅Me₅)Rh(PMe₃)H₂ in C₆D₆/C₆H₁₂. The same procedure was carried out as for the C₆H₆/THF-*d*₈ solvent mixture. (C₅Me₅)Rh(PMe₃)H₂ was dissolved in 0.5 mL of C₆D₆, and the solution was placed in a resealable NMR tube. To this was added 0.2 μL of cyclohexane. The sample was freeze–pump–thaw-degassed three times and maintained at 24.5 °C for 10 days. The reaction was followed by ¹H NMR spectroscopy, showing no evidence for H/D exchange.

Thermolysis of (C₅Me₅)Rh(PPh₃)H₂ in C₆H₆ in the Presence of D₂. (C₅Me₅)Rh(PPh₃)H₂ (0.21 mmol) was dissolved in 0.6 mL of C₆H₆, and the solution was placed in a resealable NMR tube. The solution was freeze–pump–thaw-degassed three times and frozen (0 °C). Deuterium gas (638 mm) was admitted to the tube, and the solution was heated to 62 °C in a silicone oil bath. The reaction was followed by ²H NMR spectroscopy, monitoring the growth of a resonance for deuterated benzene at 7.15 ppm. After 142 h, a mass spectrum was taken of the reaction mixture to analyze the size of the *m/e* 78–84 peaks, showing no statistically significant increase in the *m/e* 79 peak above the natural abundance (6.6%).

Thermolysis of (C₅Me₅)Rh(PPh₃)H₂ in C₆D₆ in the Presence of H₂. (C₅Me₅)Rh(PPh₃)H₂ (0.011 mmol) was dissolved in 99.96% C₆D₆, and the solution was placed into a resealable NMR tube and freeze–pump–thaw-degassed three times. Dioxane (3 mm, 20 °C, 52.4 μL, 0.0086 mmol) was condensed into the NMR tube as an internal standard. The solution was cooled to 0 °C, and H₂ (676 mm) was admitted to the tube. The tube was heated to 62 °C, and the appearance of the resonance for C₆H₆ at 7.15 ppm in the ¹H NMR spectrum was monitored with time. After 42 days, a gas chromatograph/mass spectral analysis of the *m/e* 78–84 fragments was performed as described in the text.

Methods for Ruling Out Adventitious H/D Exchange Catalyst. (1) Silica. (C₅Me₅)Rh(PMe₃)Cl (10.9 mg, 0.028 mmol) was reacted with 4 equiv Red-Al (0.113 mmol, 0.67 mL) in THF. After stirring for 10 min, the sample was divided into two portions. One portion was subjected to flash chromatography through silica gel as previously described.[8] The second portion was subjected to flash chromatography through alumina. The resulting (C₅Me₅)Rh(PMe₃)H₂ from each chromatography was dissolved in C₆D₆, and the solution was placed into separate resealable NMR tubes. After three freeze–pump–thaw degas cycles, the samples were frozen with liquid nitrogen and deuterium gas was placed over each of the samples (605 and 578 mm of D₂, respectively) on the high-vacuum line. The tubes were left at room temperature (23 °C) in the dark, and the reaction was monitored with time with ¹H NMR spectroscopy by integration of the hydride resonance at −13.623 ppm. Plots of ln [1] vs time exhibit rate constants of 0.0201 and 0.0178 h⁻¹ for the samples filtered through alumina and silica, respectively. Attempts at the same reaction with the

PPh₃ analogue (C₅Me₅)Rh(PPh₃)H₂ were not successful due to the decomposition that results when the filtration through alumina is carried out, as evidenced by the presence of multiple resonances in the ¹H NMR spectrum.

(2) Involvement of Base. (C₅Me₅)Rh(PPh₃)H₂ (0.029 mmol) was dissolved in 1.0 mL of C₆D₆, and the solution was divided into two samples in separate resealable NMR tubes. To one tube was added pyridine (0.05 mL). The solutions were subjected to three freeze–pump–thaw degas cycles and frozen with liquid nitrogen, and deuterium gas (663 mm) was admitted to the tubes. The samples were kept at room temperature (23 °C) in the dark, and the reaction was followed by ¹H NMR spectroscopy via integration of the hydride resonance at δ −13.010 versus the C₅Me₅ resonance at δ 1.878. After 31 h, the sample with no added pyridine was 77% complete while the pyridine tube was 23% complete. The samples were freeze–pump–thaw-degassed three times and frozen with liquid nitrogen. A mixture of H₂ (311 mm) and D₂ (342 mm) was placed over the samples. Both H₂ and HD were observed in the ¹H NMR spectrum of both samples as a singlet at δ 4.46 and a triplet at δ 4.44. When the samples were heated to 62 °C for 13 h, a substantial increase in the amount of HD present was observed in both samples. No other major changes in the samples were observed.

(3) Involvement of Acid. (C₅Me₅)Rh(PPh₃)H₂ (0.028 mmol) was placed into a resealable NMR tube in 0.5 mL of C₆D₆, and acetic acid (0.05 mL, 0.88 mmol, 30 equiv) was added. No change in the starting rhodium complex was noted by ¹H NMR spectroscopy. The acetic acid appeared at δ 1.55 (s, 3 H) and 12.36 (br s, 1 H). The sample was subjected to three freeze–pump–thaw degas cycles and frozen with liquid nitrogen. A mixture of H₂ (302 mm) and D₂ (315 mm) was placed over the sample, and the reaction was followed by ¹H NMR spectroscopy. HD formation was observed at a rate comparable to that for experiments performed in the absence of added acid.

(4) Involvement of the Glass NMR Tube. (C₅Me₅)Rh-(PPh₃)H₂ (0.030 mmol) was dissolved in 1.0 mL of C₆D₆, and the solution was divided into two portions. One portion was placed in a resealable NMR tube as usual. The second sample was placed in a Wilmad Glass Teflon NMR tube liner, which was placed inside a resealable NMR tube. The solutions were freeze–pump–thaw-degassed three times and frozen in liquid nitrogen, and deuterium gas (665 mm) was admitted on the high-vacuum line. The tubes were maintained at room temperature (23 °C) in the dark, and the reaction was followed by ¹H NMR spectroscopy. After 5 days, the samples were freeze–pump–thaw-degassed three times and frozen with liquid nitrogen. A mixture of D₂ and H₂ was placed over the samples: nonlined tube, 300 mm of D₂ + 323 mm of H₂; lined tube, 296 mm of D₂ + 326 mm of H₂. The HD produced was observed in the ¹H NMR spectrum of both samples.

Kinetics of the Reaction of (C₅Me₅)Rh(PMe₃)H₂ with D₂ in C₆D₆. (C₅Me₅)Rh(PMe₃)H₂ (0.036 mmol) was dissolved in 0.3 mL of C₆D₆, and the solution was divided into three 0.1-mL portions. Each portion was placed into a resealable NMR tube. The samples were freeze–pump–thaw-degassed three times and diluted by condensation of C₆D₆ into the tubes to a volume of 0.49 mL, yielding a concentration of 0.0178 M/tube. The solutions were frozen (77 °K), and D₂ was admitted to the tubes on the high-vacuum line (197, 399, and 599 mm of D₂). The tubes were maintained at 24.5 °C, and the reaction was monitored via integration of the ¹H NMR hydride resonance versus the C₅Me₅ resonance.

This procedure was carried out for other concentrations of rhodium complex and D₂ as follows: (C₅Me₅)Rh(PMe₃)H₂ = 0.0179 M, *P*(D₂) = 301, 501, 687 mm; (C₅Me₅)Rh(PMe₃)H₂ = 0.0327 M, *P*(D₂) = 301, 501, 687 mm; (C₅Me₅)Rh(PMe₃)H₂ = 0.0457 M, *P*(D₂) = 101, 201, 298, 400, 498, 601 mm.

The same procedure was also repeated with the reaction being followed by the ³¹P NMR appearance of resonances for (C₅Me₅)Rh(PMe₃)HD at δ 6.630 (dt, *J* = 151, 6.3 Hz) and (C₅Me₅)Rh(PMe₃)D₂ at δ 6.764 (dqn, *J* = 150, 6.5 Hz). In this case, the concentration of starting material was 0.022 M, and the D₂ pressures used were 201, 409, and 609 mm. In addition, to one tube was added a drop of mercury.

Reaction of Cyclohexene with (C₅Me₅)Rh(PMe₃)H₂ and Hydrogen. (C₅Me₅)Rh(PMe₃)H₂ (0.011 mmol) was placed in a

resealable NMR tube in 0.5 mL of C_6D_6. Cyclohexene (0.010 mL, 0.099 mmol) was added to the tube via syringe under nitrogen. The solution was subjected to three freeze–pump–thaw degas cycles and frozen with liquid nitrogen. Hydrogen gas was admitted to the NMR tube (673 mm, ~0.06 mmol) on the high-vacuum line. The sample was placed in a constant-temperature room (24.5 °C), and the reaction was followed by ¹H NMR spectroscopy. The starting cyclohexene has the following ¹H NMR resonances: δ 1.887 (m, 4 H), 1.506 (m, 4 H), 5.68 (s, 2 H). Cyclohexane was produced, as observed by an ¹H NMR resonance at δ 1.395 (br s, 12 H). After 40 days, 7.9 turnovers had taken place.

Reaction of Cyclohexene with (C₅Me₅)Rh(PMe₃)H₂ and Deuterium. The reaction was carried out as described for the analogous hydrogenation reaction with deuterium gas substituted for hydrogen gas. (C₅Me₅)Rh(PMe₃)H₂ (0.017 mmol) was placed in a resealable NMR tube in 0.5 mL of C_6D_6. Cyclohexene (0.010 mL, 0.099 mmol) was added, and the solution was subjected to three freeze–pump–thaw degas cycles. Deuterium gas (669 mm, ~0.06 mmol) was placed over the liquid nitrogen frozen sample. After 49 days at 24.5 °C, the cyclohexene had been converted to cyclohexane. The ²H NMR spectrum exhibited a resonance at δ 1.343 indicative of deuterium incorporation into the cyclohexane.

Reaction of Cyclohexene with (C₅Me₅)Rh(PPh₃)H₂ and Hydrogen. The reaction was carried out as described for the PMe₃ analogue. (C₅Me₅)Rh(PPh₃)H₂ (0.042 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was placed in a resealable NMR tube with cyclohexene (0.02 mL, 0.20 mmol) and hydrogen gas (676 mm). After 23 days at 24.5 °C, the maximum number of approximately eight turnovers had occurred, while cyclohexene still remained in solution. The sample was again frozen in liquid nitrogen, and additional hydrogen (621 mm) was admitted to the NMR tube on the high-vacuum line. After 44 days, the cyclohexene was all converted to cyclohexane. The solvent was removed, and the solid product was dissolved in fresh C_6D_6. New resonances were present in the ¹H and ³¹P NMR spectra: ¹H δ 1.582 (s, 15 H), 7.754 (dd, J = 12.1, 6.9 Hz, 4 H) (remaining resonances obscured by starting material); ³¹P δ 57.695 (d, J = 224 Hz). The relative proportions of the starting material and product were 2:1. The product was identified as (C₅Me₅)Rh(PPh₃)₂ by comparison with an independently synthesized sample.

Thermolysis of (C₅Me₅)Rh(PPh₃)H₂ with Ethylene. (C₅Me₅)Rh(PPh₃)H₂ (0.020 mmol) was placed in a resealable NMR tube in C_6D_6, and the solution was subjected to three freeze–pump–thaw degas cycles. Dioxane (10 mm, 0.0173 L, 293 K, 0.0095 mmol) was condensed into the NMR tube on the vacuum line as an internal standard. The sample was frozen with an ice/water bath, and ethylene (665 nm) was placed over the sample. The sample was heated to 60 °C, and the reaction was followed by ¹H NMR spectroscopy. The starting ethylene appeared in the ¹H NMR spectrum as a singlet at δ 5.245 ppm. The C₅Me₅ resonance of the starting material decreased with time. As the reaction continued, ethane was observed (0.791 ppm), as well as a new product: δ 1.638 (d, J = 1.6 Hz, 15 H), 7.067 (m, 9 H), 7.652 (t, J = 8.4 Hz, 6 H). The solvent was removed, and the solid product was dissolved in fresh C_6D_6. The product formed was identified as (C₅Me₅)Rh(PPh₃)(C₂H₄), as confirmed by independent synthesis.

Reaction of Ethylene with (C₅Me₅)Rh(PPh₃)H₂ and Hydrogen. (C₅Me₅)Rh(PPh₃)H₂ (0.013 mmol) was dissolved in C_6D_6, placed in a resealable NMR tube, and freeze–pump–thaw-degassed three times. The solution was frozen with an ice/water bath, and ethylene (290 mm, 0.012 mmol) was admitted to the NMR tube. The solution and ethylene were frozen with liquid nitrogen, and hydrogen (303 mm, 0.016 mmol) was admitted to the NMR tube. The reaction was carried out at 23 °C and followed by ¹H NMR spectroscopy. The initial ¹H NMR spectrum exhibits resonances for ethylene (δ 5.226) as well as ethane (δ 0.791). Starting material was present along with a small amount of (C₅Me₅)Rh(PPh₃)(C₂H₄) in a 9.1:1 ratio. After 6 days, no ethylene remained; a large resonance for ethane and a small resonance for H₂ were present. At this time, the ratio of starting material to (C₅Me₅)Rh(PPh₃)(C₂H₄) was still about the same (7:1).

Independent Synthesis of (C₅Me₅)Rh(PPh₃)(C₂H₄). Diversi et al. have previously synthesized this complex.[7] No characterization data were reported, however, so the complex was synthesized here following the same procedure. (C₅Me₅)Rh(C₂H₄)₂

(0.011 g, 0.0374 mmol) was placed in a flask with PPh₃ (0.010 g, 0.0381 mmol) and dissolved in 10 mL of toluene. The flask was fitted with a septum-capped reflux condenser, and the solution was heated under nitrogen flow with stirring for 3 h at 124 °C. Removal of solvent and dissolution in CDCl₃ yielded a mixture of starting material (15%) and (C₅Me₅)Rh(PPh₃)(C₂H₄) (85%). ¹H NMR (CDCl₃) δ 1.084 (m, 2 H); 1.565 (d, J = 1.3 Hz, 15 H), 7.484 (m, 12 H), 7.663 (dd, J = 11.9, 7.6 Hz, 3 H); (C_6D_6) δ 1.639 (d, J = 1.2 Hz, 15 H), 7.08 (m, 9 H), 7.66 (t, J = 8.5 Hz, 6 H) [lit.:[7] δ 1.76 (15 H), 1.77 (2 H), 1.25 (2 H)].

Reaction of (C₅Me₅)Rh(PMe₃)H₂ with P(CD₃)₃. (C₅Me₅)Rh(PMe₃)H₂ (0.054 mmol) was dissolved in 1.2 mL of C_6D_6 and divided into two portions, each of which was placed into an NMR tube attached to a ground glass joint. A solution of P(CD₃)₃ (0.0808 mmol) in 1.0 mL of C_6D_6 was divided into three portions. One portion was placed into one of the NMR tubes above, while two portions were placed into the other to yield tubes with 0.0269 and 0.0538 mmol of P(CD₃)₃, respectively. The samples were maintained at 24.5 °C in the dark. The reaction was monitored by integration of the ¹H NMR resonance for coordinated PMe₃ versus that for the pentamethylcyclopentadienyl ligand.

Thermolysis of (C₅Me₅)Rh(PMe₃)H₂ with PMe₃ in C_6H_{12}. (C₅Me₅)Rh(PMe₃)H₂ (0.0730 mmol) was dissolved in 0.5 mL of cyclohexane and placed into a resealable NMR tube. The solution was freeze–pump–thaw-degassed three times and 4 equiv of PMe₃ (0.283 mmol) condensed into the sample. The sample was maintained at 24 °C. After 12 days, the reaction to form HRh(PMe₃)₄ was 26% complete, as determined by ¹H NMR spectroscopy. The sample was heated to 70 °C for 6.5 h, at which time very little starting material remained. The product exhibited a ¹H NMR resonance at δ −12.55 (dqn). Solvent removal and the addition of C_6D_6 allowed a more thorough examination by ¹H NMR spectroscopy: δ 0.851 (d, J = 12.6 Hz), 1.301 (s), −12.278 (dqn, J = 13.6 Hz) in a ratio of 35:44:1. ³¹P{narrow band ¹H} NMR: δ −19.421 (dd, J = 146, 10.4 Hz), 30.407 (s) in a ratio of 24.1:21.3. (The latter resonance and the ¹H resonance at 1.301 are assigned to O=PMe₃.) GC analysis of the solution using a capillary column (Supelcowax 10, 30 m) at 100 °C showed the formation of pentamethylcyclopentadiene in >90% yield by comparison to an authentic sample.

Kinetics of the Reaction of (C₅Me₅)Rh(PMe₃)H₂ with PMe₃. (C₅Me₅)Rh(PMe₃)H₂ (0.129 mmol) was dissolved in 2.4 mL of C_6D_6 and divided into six portions, each of which was placed into an NMR tube attached to a ground glass joint. The solutions were freeze–pump–thaw-degassed three times on the vacuum line, and C_6D_6 was condensed into each tube to bring the solution to 0.55 mL, so that the rhodium complex concentration was 0.039 M. PMe₃ was measured out on the vacuum line into a 17.35-mL ampule and was condensed into each tube as follows: tube no. 1, no PMe₃; tube no. 2, 22 mm of PMe₃ (0.0208 mmol, 0.97 equiv); tube no. 3, 68 mm of PMe₃ (0.0645 mmol, 3.0 equiv); tube no. 4, 137 mm of PMe₃ (0.129 mmol, 6.0 equiv); tube no. 5, 182 mm of PMe₃ (0.240 mmol, 8.0 equiv); tube no. 6, 247 mm of PMe₃ (0.259 mmol, 12.0 equiv). The NMR tubes were then flame-sealed under vacuum and heated to 40 °C in a silicone oil bath. The reactions were followed by ¹H NMR spectroscopy. The concentrations of starting 1 and the product HRh(PMe₃)₄ was determined from the relative percentages in solution. The percentage determination was carried out via an average of the two values obtained for the integration of the C₅Me₅ resonance for 1 versus the PMe₃ resonance for HRh(PMe₃)₄ and by comparison of the hydride resonances for the two complexes. The first tube containing no added PMe₃ was used for corrections in concentration due to any decomposition.

Isotope Effects in the Reaction of (C₅Me₅)Rh(PMe₃)H₂ and (C₅Me₅)Rh(PMe₃)D₂ with PMe₃. Two samples of (C₅Me₅)Rh(PMe₃)H₂ (0.052 mmol each) in C_6D_6 (0.52 mL) were prepared, and one was reacted with D₂ gas for 2 days to generate (C₅Me₅)Rh(PMe₃)D₂ (>90% D). The solution was freeze–pump–thaw-degassed and mixed with the (C₅Me₅)Rh(PMe₃)H₂ solution. Examination of the mixture by ³¹P NMR spectroscopy revealed a 40:14:46 ratio of $1\text{-}d_2$:$1\text{-}d_1$:1. A 0.105-mL aliquot of PMe₃ (1.03 mmol, ~10 equiv, 0.9 M) was introduced into the sample and the reaction monitored by inverse gated ³¹P{¹H} NMR spectroscopy over the next 4 days. The areas of the resonances for $1\text{-}d_2$, 1, and HRh(PMe₃)₄ were used to determine the per-

centage of each complex, and plots of ln (concentration) vs time were made to determine the competitive rates of reaction. From the slopes of these lines during the first 2 half-lives of reaction, $k_H = 5.66\ (0.41) \times 10^{-6}\ s^{-1}$ and $k_D = 5.28\ (0.10) \times 10^{-6}\ s^{-1}$.

Equilibration of $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ with 1 Equiv of H_2. $(C_5Me_5)Rh(PPh_3)H_2$ (13.5 mg, 0.024 mmol) was dissolved in C_6D_6, and the solution was placed in an NMR tube attached to a ground glass joint. The solution was freeze–pump–thaw-degassed and flame-sealed under vacuum. Irradiation of the sample was carried out (180-W Hg lamp, $\lambda > 300$ nm) with cooling by a jet of compressed air. After irradiation for 30 min, only 1% of the starting material remained, with the only product being $(C_5Me_5)Rh(PPh_3)(C_6D_5)D$. The sample was placed in the dark at 24 °C. After 97 days, the sample exhibited a ratio of 1.25:1.00 for $(C_5Me_5)Rh(PPh_3)H_2$:$(C_5Me_5)Rh(PPh_3)(C_6D_5)D$. ¹H NMR (C_6D_6): $(C_5Me_5)Rh(PPh_3)H_2$ δ −13.009 (dd, $J = 38.8, 28.7$ Hz, 2 H), 1.876 (d, $J = 1.8$ Hz, 15 H), 7.017 (m, 9 H), 7.663 (m, 6 H); $(C_5Me_5)Rh(PPh_3)(C_6D_5)D$ δ 1.604 (d, $J = 1.8$ Hz, 15 H), 6.987 (m, 9 H), 7.445 (dd, $J = 9.7, 8.1$ Hz, 6 H).

Reaction of $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ with Excess Added H_2. $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ (0.0026 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was placed in an NMR tube attached to a resealable Teflon valve. 1,4-Dioxane (0.01 mL, 10.3 mg, 0.117 mmol) was added to the tube via syringe to serve as an internal standard. The solution was freeze–pump–thaw-degassed three times and cooled to 0 °C with an ice bath. Hydrogen gas was placed above the solution (650 mm, 0.07 mmol, 26 equiv) by filling the vacuum line with hydrogen and opening the Teflon valve. The sample was heated at 68 °C in the dark and the reaction monitored periodically by ¹H NMR spectroscopy to determine the rate of formation of $(C_5Me_5)Rh(PPh_3)H_2$.

Reaction of $(C_5Me_5)Rh(PMe_2Ph)(C_6H_5)H$ with H_2. $(C_5Me_5)Rh(PMe_2Ph)(C_6H_5)H$ (0.015 mmol) was dissolved in 0.5 mL of C_6D_6 and placed into a resealable NMR tube. The solution was subjected to three freeze–pump–thaw degas cycles. Dioxane (3 mm, 0.049 L, 296 K, 0.0080 mmol) was condensed into the NMR tube. The solution was cooled to 0 °C, and H_2 (681 mm) was placed over the solution. The sample was heated to 62 °C and the formation of $(C_5Me_5)Rh(PMe_2Ph)H_2$ monitored by the growth of the C_5Me_5 resonance in the ¹H NMR spectrum at δ 1.945 versus dioxane.

Reaction of $(C_5Me_5)Rh(PMePh_2)(C_6H_5)H$ with H_2. A solution of $(C_5Me_5)Rh(PMePh_2)(C_6H_5)H$ was prepared as above. The sample was cooled to 0 °C, and H_2 (647 mm) was placed over the solution. After 1 day at room temperature, the only change noted was a decrease in the hydride signal due to exchange with C_6D_6. The sample was heated to 68 °C, and the growth of the resonance in the ¹H NMR spectrum at δ 1.898 was monitored with time for the formation of $(C_5Me_5)Rh(PMePh_2)H_2$.

Reaction of $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ with H_2. A solution of $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (0.038 mmol) was prepared as above. Hydrogen (670 mm) was placed above the solution on the high-vacuum line. The ¹H NMR resonances for the C_5Me_5 ligands of starting material $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (δ 1.786) and of the product $(C_5Me_5)Rh(PMe_3)H_2$ (δ 2.065) were monitored with time, while the sample was maintained at 24.5 °C. (The reaction was too fast to monitor at 68 °C.)

Bromide Ion Catalyzed Dimerization of 3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane. Structure Determination and Ring Contraction of 2,2,6,6-Tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane and Synthesis of 2,2,4,4-Tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane

Young Tae Park, Georges Manuel, Robert Bau, Dong Zhao, and William P. Weber*

D. P. and K. B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Bromide ion catalyzed dimerization of 3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (I) yields *cis*- and *trans*-2,2,6,6-tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane (II). The structure of *trans*-II has been determined by a combination of ¹H, ¹³C, and ²⁹Si NMR spectroscopy and X-ray crystallography. *trans*-II crystallizes in the monoclinic space group $P2_1/n$, with $a = 7.105\ (3)$ Å, $b = 12.613\ (3)$ Å, $c = 15.455\ (5)$ Å, $\beta = 94.21\ (3)°$, and $V = 1381.2\ (8)$ Å³ for $Z = 2$. The structure was refined to a final agreement factor of 0.055 for 1374 reflections. Pyrolysis of II at 150 °C yields 2,2,4,4-tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (III) and 1,3-butadiene. The kinetics of this first-order ring contraction reaction of *trans*-II have been determined: $E_a = 32.2 \pm 1.5$ kcal/mol, $S = 1.3 \pm 0.2$ eu.

We wish to report the bromide ion catalyzed dimerization of 3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (I) to yield a mixture of *cis*- and *trans*-2,2,6,6-tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane (II). This high-yield
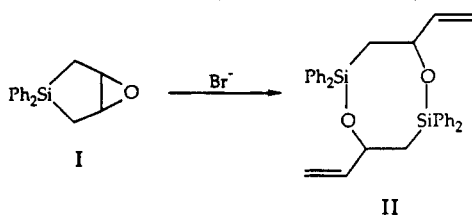
(87%) reaction is carried out at 80 °C in a mixed solvent system of acetone and benzene. The ratio of *cis*-II to *trans*-II is found to be highly dependent on the exact solvent composition used. Mixtures of *cis*-II and *trans*-II with compositions from 9/91 to 32/68 were obtained. The nature of this solvent effect is not understood. The molecular weight of II has been determined by mass spectroscopy. The structure of *trans*-II has been elucidated by ¹H, ¹³C, and ²⁹Si NMR spectroscopy as well as by X-ray crystallography (see Figure 1 for an ORTEP diagram of *trans*-II and Tables I and II for atomic coordinates and bond lengths and angles of *trans*-II) on a 9/91 mixture of