Contribution from the Department of Chemistry,
University of Rochester, Rochester, New York 14627

Effects of Phosphine on Structure and Reductive Elimination Reactions of $(C_5Me_5)Rh(PR_3)PhH$ Complexes

William D. Jones* and Valerie L. Kuykendall

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The complexes $(C_5Me_5)Rh(PR_3)X_2$, $(C_5Me_5)Rh(PR_3)PhX$, $(C_5Me_5)Rh(PR_3)PhH$, and $(C_5Me_5)Rh(PR_3)H_2$ have been prepared for several members of the series where X = Cl or Br and PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $PMe_2(t\text{-}Bu)$, $PMe_2(n\text{-}Bu)$, or $P(n\text{-}Bu)_3$. The rates at which the phenyl hydride complexes reductively eliminate benzene have been measured. Four members of the series have been structurally characterized, and a comparison is made between the steric and electronic requirements of the phosphine and the rate of benzene elimination, showing the importance of both effects. The complex $(C_5Me_5)Rh(PPh_3)PhBr$ crystallizes in the triclinic space group $P\bar{1}$, with a = 15.707 (6) Å, b = 19.218 (5) Å, c = 10.419 (3) Å, α = 100.94 (2)°, β = 98.25 (3)°, γ = 105.04 (3)°, V = 2920 (4) Å^3, and Z = 4. The complex $(C_5Me_5)Rh(PMePh_2)PhBr$ was also structurally characterized, crystallizing in the monoclinic space group $P2_1/n$, with a = 13.421 (4) Å, b = 11.918 (4) Å, c = 17.085 (3) Å, β = 107.54 (2)°, V = 2606 (2) Å^3, and Z = 4. The complex $(C_5Me_5)Rh(PMe_2Ph)PhBr$ crystallized in the monoclinic space group $P2_1/n$ with a = 17.042 (4) Å, b = 15.94 (1) Å, c = 19.314 (8) Å, β = 115.53 (3)°, V = 4733 (8) Å^3, and Z = 8.

Many complexes have been found to be active for the oxidative addition of carbon-hydrogen bonds.[1] In many of the early studies of these reactions, intramolecular pathways were observed that led to the general belief that intermolecular activation was difficult.[2] The effects of ring size on the reaction were often cited as the reason for favoring the intramolecular activation. Several early examples of C-H bond activation not only formed five-membered rings, but also involved ligands that would put the bond to be activated close to the metal center.[3] In this way, the entropy loss in forming the metallacycle and the enthalpy requirements were minimized. Metallacycle formation served as a means of relieving steric crowding.

In the present study, we have investigated the effects of steric and electronic variations in the stability of a series of phosphine complexes of the type $(C_5Me_5)Rh(PR_3)PhH$, where PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $PMe_2(t\text{-}Bu)$, $PMe_2(n\text{-}Bu)$, and $P(n\text{-}Bu)_3$. In particular, we wanted to see if orthometalation of the phosphine phenyl group to give a four-membered metallacycle could be induced with the more crowded phosphines. Earlier studies in our laboratory examined the stabilities of five-membered arene and alkane intramolecular activation products.[4] The X-ray structures of the phenyl bromide precursors have also been examined to see if any obvious steric factors control the chemistry. It was found that both steric and electronic effects of the phosphine contribute to the overall stability of the $(C_5Me_5)Rh(PR_3)PhH$ complexes.

Results

Preparation of $(C_5Me_5)Rh(PR_3)PhH$ Complexes. A variety of phosphine complexes of the type $(C_5Me_5)Rh(PR_3)X_2$, where X = Cl or Br and PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, $PMe_2(t\text{-}Bu)$, $PMe_2(n\text{-}Bu)$, and PBu_3, were synthesized by cleaving the appropriate halide-bridged dimer $[(C_5Me_5)RhCl_2]_2$ or $[(C_5Me_5)RhBr_2]_2$ with 2 equiv of phosphine. These derivatives were characterized by elemental analysis and ^1H, ^{31}P, and ^{13}C NMR spectroscopies (Tables I-III). The phenyl complexes $(C_5Me_5)Rh(PR_3)PhBr$ were synthesized from the dihalide complexes as described earlier for the PMe_3 derivative[5] from the reaction of the appropriate dibromide complex $(C_5Me_5)Rh(PR_3)Br_2$ with PhMgBr (3 equiv). Recrystallization from CH_2Cl_2 layered with hexane afforded X-ray quality red-orange crystals in high yield. Alternatively, the chloro derivatives could be prepared in a similar fashion and then heated with NaBr (or NaI) to exchange the halide.

Reaction of the phenyl bromide (or chloride) complexes with hydride reagents led to the formation of the air-sensitive phenyl hydride complexes, analogous to the PMe_3 derivative.[6] The procedure involves treatment of a THF solution of the halide complex with $Li[HB(s\text{-}Bu)_3]$. Stirring the solution at 22 °C for 4 h results in an orange to yellow color change. Solvent removal and flash chromatography through silica (5:3 hexane-THF) produced a tan to green solution of the phenyl hydride complex. It was noted that the sensitivity of the complex to chromatography on silica gel increased with increasing phenyl substitution of the PR_3 ligand, so that the PPh_3 derivative did not even survive chromatography despite its presence in the crude reaction mixture. Consequently, this complex was not isolated in pure form but was only identified in the reaction mixture containing borohydride salts. Phosphine derivatives prepared in this fashion are listed in Tables I-III, which give ^1H, ^{31}P, and ^{13}C NMR data for these derivatives.

The dihydride complexes $(C_5Me_5)Rh(PR_3)H_2$ were synthesized in a manner analogous to that used for the similar PMe_3 complex.[6] The halide complex $(C_5Me_5)Rh(PR_3)Cl_2$ was treated with 3-5 equiv of sodium bis(methoxyethoxy)aluminum hydride (Red-Al). Flash chromatography using a 3:5 THF-hexane solution as eluent on a packed silica gel column (2 cm × 3 cm) yielded a colorless solution of the dihydride complex. Alternatively, $(PPN)BH_4$ could be employed in place of the Red-Al for the dihalide to dihydride reaction. In this case, the dichloride was placed in an ampule with 12 equiv of $(PPN)BH_4$ and slurried in THF. The $(PPN)BH_4$ reagent required a longer time to effect the same reaction as the Red-Al, as the solution changed from orange to milky white. After a few hours, a mixture of desired dihydride complex and $(C_5Me_5)Rh(PMe_2Ph)HCl$ was obtained. Stirring for a longer time period (24 h) resulted in the conversion of the monohydride complex to the dihydride complex. The product was then isolated by solvent removal and extraction with hexane. The $(PPN)BH_4$ was employed only in the instances when the more reactive Red-Al resulted in decomposition of the rhodium complex. In either case, the starting material employed could be the bromo analogue $(C_5Me_5)Rh(PR_3)Br_2$, with longer reaction times required.

X-ray Structure Determinations. Single-crystal X-ray structure determinations were carried out for the phenyl bromide complexes where PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, and PMe_3[5] as it was desirable to see how steric crowding at the metal changed with phosphine cone angle and if this was in turn reflected in a decrease in the nearest approach of an ortho position of a phosphine phenyl group to the metal center. The solutions followed directly from Patterson maps, with the PPh_3 and PMe_2Ph derivatives having

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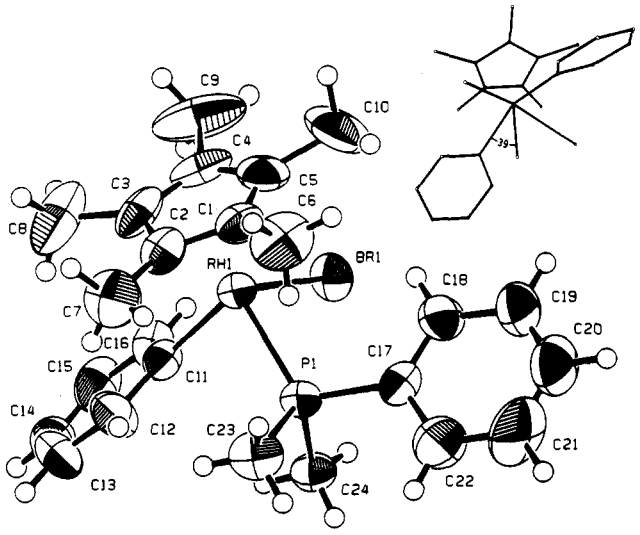


Figure 1. ORTEP plot of $(C_5Me_5)Rh(PMe_2Ph)PhBr$. Ellipsoids are shown at the 50% probability level. The inset shows the projection down the P–Rh bond.

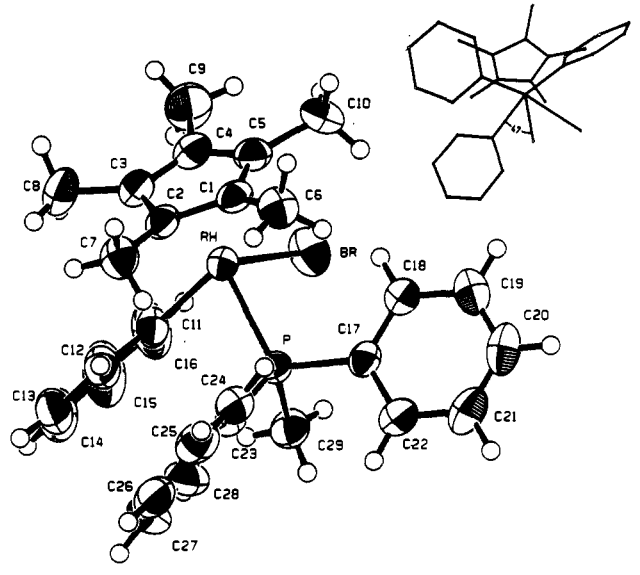


Figure 2. ORTEP plot of $(C_5Me_5)Rh(PMePh_2)PhBr$. Ellipsoids are shown at the 50% probability level. The inset shows the projection down the P–Rh bond.

two crystallographically independent molecules in the asymmetric unit. ORTEP plots are shown in Figures 1–4 and selected bond distances and angles in Table IV. In all molecules, the Rh–phenyl plane lies at a similar angle to the Rh–P vector. The insets show the view down the P–Rh bond, and demonstrate how similar the geometries of the aryl rings are in the solid state. The dihedral angles between C11–Rh–P–$C_{phosphine}$ vary from 37 to 39 to 47 to 60° upon progressing from PMe_3 to PPh_3.

Examination of the structure of $(C_5Me_5)Rh(PMe_2Ph)PhBr$ displayed in Figure 1 and Table IV shows that the complex crystallizes in the monoclinic crystal system, space group $P2_1/n$, with two molecules per asymmetric unit. The Rh1–P1 and Rh2–P2 distances are 2.270 and 2.277 Å, respectively. The distance from the rhodium center to the ortho carbon positions on the phenyl ring of the phosphine was examined. The smallest Rh–ortho C distance was found to be 3.602 Å, while the largest was 3.729 Å.

The ORTEP plot for the complex $(C_5Me_5)Rh(PMePh_2)PhBr$ is shown in Figure 2. The molecule crystallizes with one molecule per asymmetric unit in the monoclinic crystal system, space group $P2_1/n$. The Rh–P distance is 2.289 Å, and the shortest distance from rhodium to ortho carbon on phosphine is 3.189 Å, while the longest is 3.691 Å.

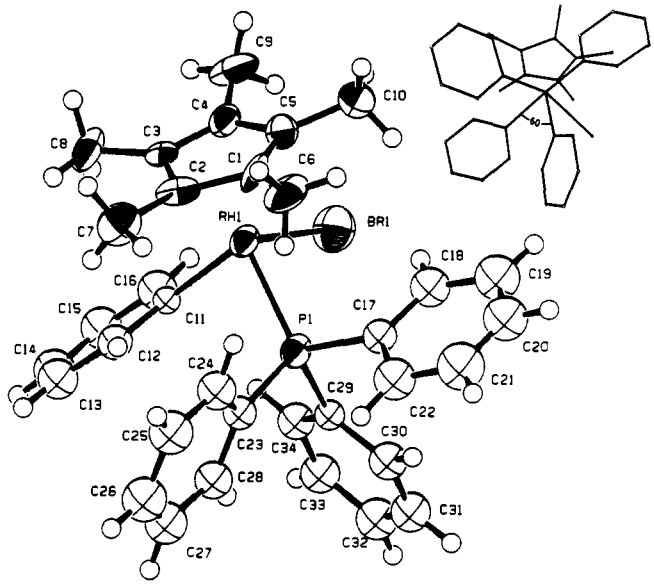


Figure 3. ORTEP plot of $(C_5Me_5)Rh(PPh_3)PhBr$. Ellipsoids are shown at the 50% probability level. The inset shows the projection down the P–Rh bond.

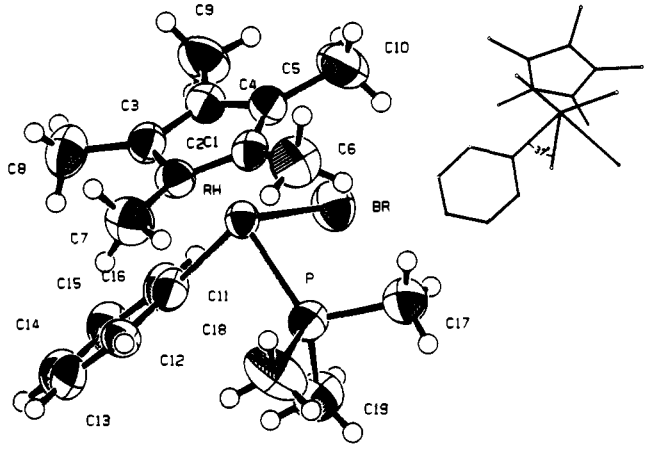
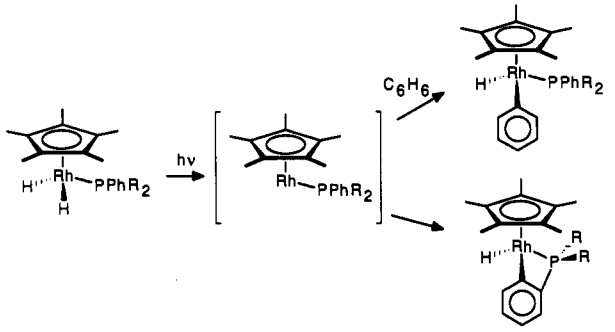


Figure 4. ORTEP plot of $(C_5Me_5)Rh(PMe_3)PhBr$. Ellipsoids are shown at the 50% probability level. The inset shows the projection down the P–Rh bond.

The ORTEP for complex $(C_5Me_5)Rh(PPh_3)PhBr$ is shown in Figure 3. The molecule crystallizes in the triclinic crystal system, $P\bar{1}$ space group with two molecules per asymmetric unit. The Rh1–P1 and Rh2–P2 distances are 2.295 and 2.317 Å, respectively. The shortest Rh–ortho C distance is 3.403 Å, while the longest is 3.826 Å, both of which are longer than in the $PMePh_2$ complex.

The nearest distance from the ortho carbon of the phenyl group of a phosphine to the rhodium center decreases in the following order: $(C_5Me_5)Rh(PMe_2Ph)PhBr$ (3.602 Å) > $(C_5Me_5)Rh(PPh_3)PhBr$ (3.403 Å) > $(C_5Me_5)Rh(PMePh_2)PhBr$ (3.189 Å). While the bulkiness of the phosphine increases in the order $PMe_2Ph < PMePh_2 < PPh_3$, a decrease in the metal–ortho carbon distance is not automatically produced, as might be expected with complexes of very similar geometries. This may be due in part to the increase in the rhodium–phosphorus distance as the bulkiness of the phosphine increases. The trend (distances) found was as follows (for two molecules per unit cell, distances are averaged): $(C_5Me_5)Rh(PMe_2Ph)PhBr$ (2.274 Å) < $(C_5Me_5)Rh(PMePh_2)PhBr$ (2.289 Å) < $(C_5Me_5)Rh(PPh_3)PhBr$ (2.306 Å). This trend may reflect the ability of the metal center to accommodate the phosphine. The less sterically demanding the phosphine, the closer it will be able to approach the metal center. This is also true of $(C_5Me_5)Rh(PMe_3)PhBr$ whose structure was reported earlier with a rhodium–phosphorus distance of 2.248 Å.[5]

Scheme I



As a consequence of these structural studies, it may not be correct to expect an increase in a tendancy for intramolecular orthometalation in the order $(C_5Me_5)Rh(PPh_3) > (C_5Me_5)Rh(PMePh_2) > (C_5Me_5)Rh(PMe_2Ph)$. All rhodium–phenyl distances were similar (2.07 ± 0.01 Å). The bulkiness of the phosphine is also reflected in the increase in the P–Rh–Br bond angles (86.3 to 90.2°). The major effect of phenyl substitution on the phosphine ligand therefore manifests itself in a slight rotation around the Rh–P bond, rather than any pronounced changes in the metal inner coordination sphere. All of these complexes display hindered rotation about the metal–phenyl bond, and the triarylphosphine derivatives show hindered rotation about the metal–phosphorus bond, attesting to the crowdedness at the metal center.[5]

Photochemical Reactivity in Benzene. Irradiation of $(C_5Me_5)Rh(PMe_2Ph)H_2$ presumably results in the loss of dihydrogen and production of the 16-electron coordinatively unsaturated intermediate $[(C_5Me_5)Rh(PMe_2Ph)]$. This intermediate can then either react intermolecularly with the benzene solvent to form a phenyl hydride complex or undergo an intramolecular reaction with the ortho position of a phenyl group of the phosphine ligand to yield the metallacycle (Scheme I).

A solution of $(C_5Me_5)Rh(PMe_2Ph)H_2$ in C_6D_6 in a sealed NMR tube was irradiated for 30 min, and the solution was examined by ^1H NMR spectroscopy. Examination of the hydride region of the spectrum showed no new hydride resonances, indicating that no intramolecular reaction had occurred. Examination of the remainder of the spectrum revealed the formation of a single product: C_5Me_5, δ 1.640 (s, 15 H); PMe_2Ph, δ 1.009 (d, J = 9.2 Hz, 3 H) and 1.296 (d, J = 9.2 Hz, 3 H). Repetition of the experiment with C_6H_6 in place of C_6D_6 now displayed additional resonances in the hydride and phenyl regions of the ^1H NMR spectrum: δ 7.05 (m, 6 H), 7.09 (m, 2 H), 7.388 (t, 2 H), −13.024 (dd, J = 47.0, 32.0 Hz, 1 H). The NMR spectrum of the product was identical with that of independently prepared phenyl hydride complex. As the sample was left at room temperature, no new products were observed to form.

The complexes $(C_5Me_5)Rh(PMePh_2)H_2$ and $(C_5Me_5)Rh(PPh_3)H_2$ were examined for inter vs intramolecular reaction in C_6D_6 as was done for $(C_5Me_5)Rh(PMe_2Ph)H_2$. In each case, a single new product was formed. Repetition of the photolyses in C_6H_6 led to a new hydride resonance, as well as additional phenyl resonances. The products were assigned as the phenyl hydride complexes $(C_5Me_5)Rh(PMePh_2)PhH$ and $(C_5Me_5)Rh(PPh_3)PhH$ based upon comparison of the spectroscopic data with data for the independently synthesized materials. Similar irradiations of $(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]H_2$, $(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]H_2$, and $(C_5Me_5)Rh[P(n\text{-}Bu)_3]H_2$ in benzene solution also gave only one product, which could be identified from the ^1H and ^{31}P NMR spectra as the phenyl hydride complexes. No evidence for metallacycle formation was noted.

Photochemical Reactivity in Hydrocarbon Solvents. Attempts were made to directly observe metallacycles by photochemical production of the 16-electron intermediates $[(C_5Me_5)Rh(PR_3)]$ from the dihydride complexes in deuterated methylcyclohexane solvent. The methylcyclohexane is not expected to form a stable alkyl hydride complex with these rhodium complexes at room temperature, as other alkyl hydrides have been found to eliminate alkane above −20 °C.[6-8] In general, these irradiations for the PPh_3, $PMePh_2$, and PMe_2Ph complexes led to mixtures of small amounts of hydride-containing products (see Experimental Section) that could not be identified or isolated due to their instability. If any of these species correspond to intramolecular activation products, they must be thermally or photochemically unstable to the reaction conditions.

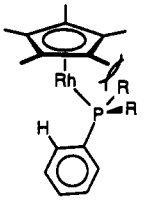


Figure 5. Steric interactions in $[(C_5Me_5)Rh(PR_2Ph)]$ favoring cyclometalation.

Thermal Reactions of $(C_5Me_5)Rh(PR_3)PhH$ Complexes in Benzene. The rates at which a variety of $(C_5Me_5)Rh(PR_3)(C_6D_5)D$ complexes lose benzene was determined by monitoring their rate of ligand exchange with benzene solvent. Plots of ln [concentration] vs time were linear, giving the first-order rate constant for benzene reductive elimination (and dissociation of the η^2-arene complex).[6] A summary of the reaction half-lives and ligand cone angles are given in Table V. It should be noted that these rates are for elimination of C_6D_6 and include an isotope effect, which was previously determined to be $k_H/k_D = 0.51$ for the PMe_3 derivative.[9]

Discussion

Earlier studies in our group investigated the thermodynamic and kinetic factors controlling intramolecular vs intermolecular cyclization in both aliphatic and aromatic C–H bond activation reactions.[4] These studies showed that, in the formation of 5-membered metallacycle rings in neat hydrocarbon solvent, the intramolecular product is thermodynamically preferred by ~2 kcal/mol for the aromatic system and by ~5 kcal/mol for the aliphatic system. However, the kinetic selectivities were just the opposite, with intermolecular reaction with the solvent being faster than the intramolecular cyclizations.

For the current study, complexes with differing steric and electronic factors were investigated by variation of the phosphine ligand in a series of $(C_5Me_5)Rh(PR_3)Cl_2$ complexes. The initial phosphines examined were PMe_2Ph, $PMePh_2$, and PPh_3, with the steric bulk increasing in the order $PMe_2Ph < PMePh_2 < PPh_3$ as determined by a "cone angle" (θ) measurement performed by Tolman in 1970 (122, 136, 145°, respectively).[10] The steric interactions that were expected to lead to more favorable intramolecular reaction by destabilization of the ground state of the noncyclometalated species are indicated in Figure 5, showing nonbonding interactions between the C_5Me_5 ring and the groups on the phosphine.

The only product formed upon irradiation of the dihydride $(C_5Me_5)Rh(PMe_2Ph)H_2$ in benzene was the phenyl hydride complex. No evidence of a product from an intramolecular reaction was observed. In the case of the previously examined $(C_5Me_5)Rh(PMe_2CH_2Ph)PhH$ complex, which can form the five-membered ring metallacycle $(C_5Me_5)Rh(PMe_2CH_2C_6H_4)H$, a slight kinetic preference (1.86:1.00 at 25 °C) for intermolecular reaction over intramolecular reaction was observed in neat benzene solvent.[4] When a four-membered ring metallacycle is examined, the preference is now substantially different, as the intermolecular reaction occurs exclusively. Furthermore, the formation of the five-membered ring metallacycle was thermodynamically much more favored than intermolecular formation of the phenyl hydride

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Table I. ^{1}H NMR Data and Yields for the Complexes $(C_5Me_5)Rh(PR_3)XY$

complex	solvent	chemical shift, ppm: C_5Me_5	chemical shift, ppm: PR_3 (and Ph)	% yield
$(C_5Me_5)Rh(PMe_3)Cl_2$	*a*	1.663 (d, J = 3.4 Hz, 15 H)	1.591 (d, J = 11.2 Hz, 9 H)	94
$(C_5Me_5)Rh(PMe_2Ph)Cl_2$	*a*	1.429 (d, J = 3.3 Hz, 15 H)	1.863 (d, J = 12.1 Hz, 6 H), 7.342 (m, 3 H), 7.849 (t, J = 9.2 Hz, 2 H)	82
$(C_5Me_5)Rh(PMePh_2)Cl_2$	*a*	1.395 (d, J = 3.6 Hz, 15 H)	2.128 (d, J = 12.0 Hz, 3 H), 7.435 (m, 6 H), 7.812 (t, J = 8.9 Hz, 4 H)	87
$(C_5Me_5)Rh(PPh_3)Cl_2$	*a*	1.349 (d, J = 3.4 Hz, 15 H)	7.354 (br s, 9 H), 7.808 (t, J = 8.6 Hz, 6 H)	99
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Cl_2$	*b*	1.299 (d, J = 3.0 Hz, 15 H)	0.948 (d, J = 13.6 Hz, 9 H), 1.413 (d, J = 10.6 Hz, 6 H)	47
$(C_5Me_5)Rh(PCy_3)Cl_2$	*a*	1.564 (d, J = 2.6 Hz, 15 H)	2.376 (q, J = 11.4 Hz, 3 H), 2.145 (d, J = 12.6 Hz, 6 H), 1.786 (br s, 6 H), 1.687 (br s, 3 H), 1.229 (t, J = 8.7 Hz, 9 H), 1.536 (br s, 6 H)	
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]Cl_2$	*a*	1.625 (d, J = 3.0 Hz, 15 H)	0.902 (t, J = 7.3 Hz, 9 H), 1.358 (q, J = 7.3 Hz, 6 H), 1.479 (dtt, J = 9.2, 7.1, 6.0 Hz, 6 H), 1.994 (dt, J = 10.3, 6.8 Hz, 6 H)	
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Cl_2$	*a*	1.657 (d, J = 3.3 Hz, 15 H)	0.922 (t, J = 7.2 Hz, 3 H), 1.558 (d, J = 11.5 Hz, 6 H), 1.952 (dt, J = 9.0, 7.7 Hz, 2 H), 1.38 (m, 2 H), 1.48 (m, 2 H)	20
$(C_5Me_5)Rh(PMe_3)Br_2$	*a*	1.770 (d, J = 3.5 Hz, 15 H)	1.681 (d, J = 11.3 Hz, 9 H)	
$(C_5Me_5)Rh(PMe_2Ph)Br_2$	*a*	1.530 (d, J = 3.9 Hz, 15 H)	1.983 (d, J = 11.3 Hz, 6 H), 7.439 (m, 3 H), 7.886 (m, 2 H)	83
$(C_5Me_5)Rh(PMePh_2)Br_2$	*a*	1.510 (d, J = 3.4 Hz, 15 H)	2.309 (d, J = 11.2 Hz, 3 H), 7.429 (m, 6 H), 7.810 (dd, J = 9.1 Hz, 4 H)	100
$(C_5Me_5)Rh(PPh_3)Br_2$	*a*	1.484 (d, J = 3.4 Hz, 15 H)	7.308 (br s, 9 H), 7.742 (br s, 6 H)	99
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Br_2$	*a*	1.782 (d, J = 3.0 Hz, 15 H)	1.230 (d, J = 13.9 Hz, 9 H), 1.677 (d, J = 10.2 Hz, 6 H)	16
	b	1.415 (d, J = 2.8 Hz, 15 H)	0.941 (d, J = 13.7 Hz, 9 H), 1.556 (d, J = 10.2 Hz, 6 H)	
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]Br_2$	*a*	1.76 (d, J = 3.0 Hz, 15 H)	0.92 (t, J = 8.3 Hz, 9 H), 1.36 (q, J = 5.5 Hz, 6 H), 1.53 (m, 6 H), 2.05 (m, 6 H)	100
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Br_2$	*a*	1.765 (d, J = 3.3 Hz, 15 H)	0.925 (t, J = 7.2 Hz, 3 H), 1.661 (d, J = 11.2 Hz, 6 H), 1.990 (m, 2 H)	98
$(C_5Me_5)Rh(PEt_3)Br_2$	*a*	1.756 (d, J = 2.8 Hz, 15 H)	1.143 (dt, J = 15.2, 7.6 Hz, 9 H), 2.126 (dq, J = 8.7, 8.2 Hz, 6 H)	
$(C_5Me_5)Rh(PMe_2Ph)I_2$	*a*	1.740 (d, J = 3.9 Hz, 15 H)	2.177 (d, J = 10.8 Hz, 6 H), 7.428 (m, 3 H), 7.911 (m, 2 H)	64
$(C_5Me_5)Rh(PMePh_2)I_2$	*a*	1.743 (d, J = 3.4 Hz, 15 H)	2.600 (d, J = 10.3 Hz, 3 H), 7.411 (m, 6 H), 7.787 (t, J = 9.2 Hz, 4 H)	100
$(C_5Me_5)Rh(PMe_2Ph)PhCl$	*a*	1.353 (d, J = 2.7 Hz, 15 H)	1.391 (d, J = 14 Hz, 3 H), 1.586 (d, J = 10.3 Hz, 3 H), 6.942 (t, J = 6.9 Hz, 1 H), 6.995 (t, J = 7.2 Hz, 2 H), 7.393 (br s, 3 H), 7.847 (m, 2 H)	57
$(C_5Me_5)Rh(PMePh_2)PhCl$	*a*	1.372 (d, J = 2.9 Hz, 15 H)	1.522 (d, J = 10.2 Hz, 3 H), 6.896 (br s, 3 H), 7.361 (m, 10 H), 7.634 (t, J = 9.3 Hz, 2 H)	50
$(C_5Me_5)Rh(PPh_3)PhCl$	*a*	1.291 (d, J = 2.7 Hz, 15 H)	6.807 (t, 7.0 Hz, 1 H), 6.963 (br s, 5 H), 7.171 (m, 3 H), 7.419 (m, 8 H), 7.596 (d, J = 1.4 Hz, 1 H), 7.824 (br s, 2 H)	43
$(C_5Me_5)Rh(PMe_3)PhBr$	*a*	1.555 (d, J = 2.6 Hz, 15 H)	1.338 (d, J = 10.4 Hz, 9 H), 6.827 (q, J = 6.5 Hz, 2 H), 6.876 (t, J = 6.8 Hz, 1 H)	88
$(C_5Me_5)Rh(PMe_2Ph)PhBr$	*a*	1.421 (d, J = 1.9 Hz, 15 H)	1.535 (d, J = 10.2 Hz, 3 H), 1.601 (d, J = 9.2 Hz, 3 H), 6.951 (m, 3 H), 7.820 (t, J = 7.9 Hz, 2 H), 7.393 (m, 3 H)	84
$(C_5Me_5)Rh(PMePh_2)PhBr$	*a*	1.383 (d, J = 2.7 Hz, 15 H)	1.594 (d, J = 10.0 Hz, 3 H), 6.853 (br s, 3 H), 7.303 (m, 10 H), 7.567 (t, J = 8.9 Hz, 2 H)	66
$(C_5Me_5)Rh(PPh_3)PhBr$	*a*	1.345 (d, J = 2.7 Hz, 15 H)	6.823 (m, 3 H), 7.016 (m, 2 H), 7.143 (m, 3 H), 7.396 (m, 6 H), 7.817 (t, J = 9.0 Hz, 2 H), 7.33 (t, J = 7.4 Hz, 1 H), 7.58 (d, J = 11.4 Hz, 1 H)	
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]$-PhBr	*a*	1.550 (d, J = 1.8 Hz, 15 H)	1.375 (d, J = 7.4 Hz, 3 H), 1.157 (d, J = 13.7 Hz, 9 H), 0.957 (d, J = 9.7 Hz, 3 H), 6.887 (m, 2 H), 6.912 (m, 1 H), 7.104 (br s, 1 H), 8.108 (br s, 1 H)	10
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]PhBr$	*a*	1.544 (d, J = 2.2 Hz, 15 H)	0.813 (t, J = 6.8 Hz, 9 H), 1.231 (m, 9 H), 1.321 (m, 3 H), 1.683 (dq, J = 12.4, 4.0 Hz, 3 H), 1.822 (m, 3 H), 6.855 (m, 3 H), 7.040 (br s, 1 H), 7.975 (br s, 1 H)	
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]$-PhBr	*a*	1.869 (d, J = 2.6 Hz, 15 H)	1.144 (t, J = 6.9 Hz, 3 H), 1.557 (d, J = 10.2 Hz, 3 H), 1.623 (d, J = 10.1 Hz, 3 H), 1.61 (m, 4 H), 2.07 (m, 2 H), 7.15 (m, 3 H)	
$(C_5Me_5)Rh(PMe_3)H_2$	*b*	2.065 (s, 15 H)	1.056 (d, J = 10.2 Hz, 9 H), −13.623 (dd, J = 41.8, 29.8 Hz, 2 H)	
$(C_5Me_5)Rh(PMe_2Ph)H_2$	*b*	1.945 (d, J = 1.2 Hz, 15 H)	1.359 (d, J = 9.5 Hz, 6 H), 7.062 (m, 3 H), 7.543 (dd, J = 9.9, 8.0 Hz, 2 H), −13.300 (dd, J = 40.9, 29.7 Hz, 2 H)	
$(C_5Me_5)Rh(PMePh_2)H_2$	*b*	1.891 (s, 15 H)	1.713 (d, J = 9.2 Hz, 3 H), 7.026 (d, J = 6.4 Hz, 2 H), 7.078 (t, J = 7.6 Hz, 4 H), 7.550 (dd, J = 10.4, 7.8 Hz, 4 H), −13.168 (dd, J = 39.8, 29.1 Hz, 2 H)	
$(C_5Me_5)Rh(PPh_3)H_2$	*b*	1.878 (s, 15 H)	7.017 (m, 9 H), 7.663 (m, 6 H), −13.010 (dd, J = 38.9, 28.0 Hz, 2 H)	
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]H_2$	*b*	2.068 (s, 15 H)	0.896 (d, J = 13.9 Hz, 9 H), 1.058 (d, J = 8.6 Hz, 6 H), −14.117 (dd, J = 39.2, 29.1 Hz, 2 H)	
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]$	*b*	2.102 (s, 15 H)	0.888 (t, J = 7.2 Hz, 9 H), 1.297 (q, J = 7.0 Hz, 6 H), 1.405 (d, J = 3.5 Hz, 12 H), −14.075 (dd, J = 39.1, 29.2 Hz, 2 H)	
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]H_2$	*b*	2.076 (s, 15 H)	1.075 (d, J = 9.3 Hz, 6 H), 0.861 (t, J = 7.2 Hz, 3 H), 1.256 (m, 4 H), 1.40 (m, 2 H), −13.780 (dd, J = 40.8, 30.0 Hz, 2 H)	
$(C_5Me_5)Rh(PEt_3)H_2$	*b*	2.071 (s, 15 H)	1.255 (dq, J = 8.1, 8.0 Hz, 6 H), 0.872 (dt, J = 15.7, 7.7 Hz, 9 H), −14.111 (dd, J = 38.7, 29.0 Hz, 2 H)	
$(C_5Me_5)Rh(PMe_3)PhH$	*b*	1.786 (s, 15 H)	0.904 (d, J = 10.2 Hz, 9 H), 7.102 (m, 3 H), 7.628 (d, J = 7.1 Hz, 2 H), −13.512 (dd, J = 49.0, 32.4 Hz, 1 H)	
$(C_5Me_5)Rh(PMe_2Ph)PhH$	*b*	1.640 (s, 15 H)	1.009 (d, J = 9.2 Hz, 3 H), 1.296 (d, J = 9.2 Hz, 3 H), 7.05 (m, 6 H), 7.09 (m, 2 H), 7.388 (t, J = 9.2 Hz, 2 H), −13.024 (dd, J = 47.0, 32.0 Hz, 1 H)	
$(C_5Me_5)Rh(PMePh_2)PhH$	*b*	1.645 (s, 15 H)	1.398 (d, J = 9.0 Hz, 3 H), 7.058 (m, 9 H), 7.455 (t, J = 9.2 Hz, 2 H), 7.595 (d, J = 6.4 Hz, 2 H), −12.899 (dd, J = 47, 32 Hz, 1 H)	

Table I (Continued)

complex	solvent	chemical shift, ppm: C_5Me_5	chemical shift, ppm: PR_3 (and Ph)	% yield
$(C_5Me_5)Rh(PPh_3)PhH$	*b*	1.604 (d, J = 1.8 Hz, 15 H)	6.987 (m, 14 H), 7.445 (dd, J = 9.7, 8.1 Hz, 6 H), −12.472 (dd, J = 47.2, 30.4 Hz, 1 H)	
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]PhH$	*b*	1.773 (s, 15 H)	0.652 (d, J = 8.9 Hz, 3 H), 0.820 (d, J = 13.9 Hz, 9 H), 1.023 (d, J = 8.5 Hz, 3 H), 7.089 (m, 3 H), 7.626 (br s, 2 H), −13.984 (dd, J = 46.2, 30.6 Hz, 1 H)	
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]PhH$	*b*	1.838 (s, 15 H)	0.866 (t, J = 7.2 Hz, 9 H), 1.216 (m, 6 H), 1.376 (br s, 12 H), 7.08 (m, 3 H), 7.684 (br s, 2 H), −13.624 (dd, J = 45.1, 32.2 Hz, 1 H)	
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]PhH$	*b*	1.803 (d, J = 2.0 Hz, 15 H)	0.821 (t, J = 7.1 Hz, 3 H), 0.832 (d, J = 9.8 Hz, 3 H), 0.995 (d, J = 9.2 Hz, 3 H), 1.19 (m, 6 H), 7.13 (m, 3 H), 7.67 (d, J = 5.7 Hz, 2 H), −13.492 (dd, J = 47.1, 32.2 Hz, 1 H)	
$(C_5Me_5)Rh(PEt_3)PhH$	*b*	1.800 (d, J = 1.7 Hz, 15 H)	1.245 (dq, J = 8.1, 7.9 Hz, 6 H), 0.776 (dt, J = 15.0, 7.6 Hz, 9 H), 7.12 (m, 3 H), 7.670 (m, 2 H), −13.667 (dd, J = 44.9, 31.5 Hz, 1 H)	

[a] $CDCl_3$ solvent. [b] C_6D_6 solvent.

Table II. $^{31}P\{^1H\}$ NMR Data for the Complexes $(C_5Me_5)Rh(PR_3)XY$

complex	solvent	chem shift, ppm
$(C_5Me_5)Rh(PMe_3)Cl_2$	*a*	8.787 (d, J = 137 Hz)
$(C_5Me_5)Rh(PMe_2Ph)Cl_2$	*a*	11.356 (d, J = 136 Hz)
$(C_5Me_5)Rh(PMePh_2)Cl_2$	*a*	22.439 (d, J = 146 Hz)
$(C_5Me_5)Rh(PPh_3)Cl_2$	*a*	28.244 (d, J = 141 Hz)
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Cl_2$	*a*	26.587 (d, J = 136 Hz)
$(C_5Me_5)Rh(PCy_3)Cl_2$	*a*	33.660 (d, J = 134 Hz)
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]Cl_2$	*a*	22.251 (d, J = 137 Hz)
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Cl_2$	*a*	13.457 (d, J = 136 Hz)
$(C_5Me_5)Rh(PMe_3)Br_2$	*a*	3.719 (d, J = 137 Hz)
$(C_5Me_5)Rh(PMe_2Ph)Br_2$	*a*	8.862 (d, J = 143 Hz)
$(C_5Me_5)Rh(PMePh_2)Br_2$	*a*	18.959 (d, J = 142 Hz)
$(C_5Me_5)Rh(PPh_3)Br_2$	*a*	27.893 (d, J = 147 Hz)
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Br_2$	*a*	21.289 (d, J = 140 Hz)
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]Br_2$	*a*	18.572 (d, J = 137 Hz)
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Br_2$	*a*	8.729 (d, J = 137 Hz)
$(C_5Me_5)Rh(PEt_3)Br_2$	*a*	24.424 (d, J = 138 Hz)
$(C_5Me_5)Rh(PMe_2Ph)PhCl$	*a*	9.697 (d, J = 154 Hz)
$(C_5Me_5)Rh(PMePh_2)PhCl$	*a*	27.027 (d, J = 155 Hz)
$(C_5Me_5)Rh(PPh_3)PhCl$	*a*	38.074 (d, J = 158 Hz)
$(C_5Me_5)Rh(PMe_3)PhBr$	*a*	2.949 (d, J = 153 Hz)
$(C_5Me_5)Rh(PMe_2Ph)PhBr$	*a*	8.426 (d, J = 154 Hz)
$(C_5Me_5)Rh(PMePh_2)PhBr$	*a*	27.836 (d, J = 156 Hz)
$(C_5Me_5)Rh[P(n\text{-}Bu_3)]PhBr$	*a*	18.777 (d, J = 152 Hz)
$(C_5Me_5)Rh(PMe_3)H_2$	*b*	7.258 (d, J = 151 Hz)
$(C_5Me_5)Rh(PMe_2Ph)H_2$	*c*	22.256 (d, J = 125 Hz)
$(C_5Me_5)Rh(PPh_3)H_2$	*b*	60.493 (d, J = 160 Hz)
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]H_2$	*b*	26.587 (d, J = 136 Hz)
$(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]H_2$	*b*	40.946 (d, J = 152 Hz)
$(C_5Me_5)Rh(PMe_3)PhH$	*b*	5.549 (dd, J = 154, 45 Hz[d])
$(C_5Me_5)Rh(PMePh_2)PhH$	*b*	39.804 (d, J = 154 Hz)
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]PhH$	*b*	33.743 (dd, J = 156, 45 Hz[d])

[a] $CDCl_3$ solvent. [b] C_6D_6 solvent. [c] C_6D_{12} solvent. [d] Hydride coupling.

complex. For the four-membered ring metallacycle, the intermolecular phenyl hydride complex is now the kinetic as well as the thermodynamically preferred product. It is possible that metallacycle formation occurs as a kinetically preferred reaction even in benzene solvent, but such a species would have to be labile as it is not observed in the presence of benzene or in an alkane solvent. It is also possible that the difficulty of η^2-complexation of the phosphine aromatic ring raises the barrier for oxidative addition to its C–H bond.

In comparison, the bulkier phosphines $PMePh_2$ and PPh_3 were examined with the notion that a larger phosphine might be more amenable to intramolecular cyclization due to a more crowded ground state. In the irradiation of $(C_5Me_5)Rh(PMePh_2)H_2$ and $(C_5Me_5)Rh(PMe_2Ph)H_2$ in benzene, only intermolecular solvent activation was observed. Although the C–H bond in the ortho position of a phenyl group of the phosphine is closer to the metal center in the PPh_3 and $PMePh_2$ complexes than for the PMe_2Ph analogue (as evidenced by X-ray structure determination), this does not manifest itself as a reactivity difference. Regardless of the bulkiness of the phosphine, all complexes undergo only intermolecular solvent activation upon irradiation in benzene to form the phenyl hydride complexes. It is interesting to compare these results to those of the iridium analogue reported by Bergman.[11] In this case, the intermediate $[(C_5Me_5)Ir(PPh_3)]$ reacted in benzene solvent to give both $(C_5Me_5)Ir(PMe_3)PhH$ and the cyclometalated product $(C_5Me_5)Ir(PPh_2C_6H_4)H$. In hydrocarbon solvent, cyclometalation was the exclusive reaction pathway. In the case of iridium, the metallacycle product is much more stable.

Steric effects do appear to be important, however, in the rate of benzene elimination from the phenyl hydride complexes. As can be seen from viewing the PMe_3 through PPh_3 entries in Table V, the rate of reaction increases as the bulkiness, or cone angle, of the phosphine increases. While this effect can be explained in terms of destabilization of the ground state due to steric interactions, it should be kept in mind that reductive elimination of benzene leads first to the intermediate η^2-benzene complex prior to loss of benzene.[12] The effect of the phosphine on the η^2-arene complex might also be considered to be important, but the rate-limiting step for benzene loss involves the dissociation of the arene, and examination of model geometries suggests that steric interaction with the phosphine should be felt minimally in this transition state. These phosphines also differ, however, in their electronic properties. As the number of phenyl groups on the phosphine increases, there is a reduction in the electron donation to the metal center relative to PMe_3. Comparison of phosphines that are more similar electronically would allow better determination of the steric component of the reaction. Examination of the entries for PMe_3, $P(n\text{-}Bu)_3$, and $PMe_2(t\text{-}Bu)$ provides this comparison, as these phosphines are more electronically similar in that they contain only alkyl groups. As the cone angle in this series increases from 118 to 132 to 139°, there is a concomitant increase in rate of benzene loss from 3.35×10^{-7} to 2.4×10^{-6} to 6.6×10^{-6} s^{-1}. Overall, the rate of benzene elimination from the phenyl hydride complexes clearly increases as steric demands increase.

In addition to the steric component, however, there is also an electronic effect of the phosphine on the rate as indicated by comparison of phosphines which are different electronically, yet have similar cone angles. This is seen by the pairwise comparison of PMe_2Ph with PMe_3 and of $PMePh_2$ with $PMe_2(t\text{-}Bu)$. These pairs of phosphines have similar cone angles of 122 and 118° and 136 and 139°, respectively, yet the complexes containing these phosphines display different rates of 1.08×10^{-6} and 3.35×10^{-7} s^{-1}) and 1.11×10^{-5} and 6.6×10^{-6} s^{-1}. Consequently, the differences in rate of exchange of phenyl hydride in complexes with different phosphines is attributed not only to a steric effect but also in part to an electronic effect as well. These effects are difficult to separate in a quantitative manner.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of nitrogen in a Vacuum Atmospheres Dri-Lab drybox or on

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Table III. Off-Resonance-Decoupled ^{13}C NMR Data for the Complexes $(C_5Me_5)Rh(PR_3)XY$

complex	chem shift,[a] ppm (δ)[a]	
	C_5Me_5	PR_3 + phenyl
$(C_5Me_5)Rh(Me_2Ph)Cl_2$	9.27 (q), 99.08 (dd)	128.69 (ddd), 131.11 (d), 133.82 (dd)
$(C_5Me_5)Rh(PMe_2Ph)PhBr$	9.17 (s), 99.35 (dd)	122.22 (s), 127.91 (d), 129.73 (s), 131.57 (d)
$(C_5Me_5)Rh(PMePh_2)Br_2$	9.82 (q), 99.60 (s)	19.92 (d), 128.58 (s), 131.09 (d), 134.13 (dd)
$(C_5Me_5)Rh(PMePh_2)PhBr$	9.66 (s), 100.23 (dd)	16.30 (d), 122.76 (s), 127.79 (s), 128.17 (dd), 130.14 (s), 130.18 (d), 132.93 (d), 133.5 (s), 134.00 (s), 134.50 (s), 135.53 (d), 156.96 (d), 157.37 (d)
$(C_5Me_5)Rh(PPh_3)Cl_2$	8.76 (s), 99.05 (s)	127.80 (dd), 130.28 (s), 134.58 (dd)
$(C_5Me_5)Rh(PPh_3)PhCl$	9.31 (s), 100.91 (d)	122.57 (s), 127.64 (m), 128.40 (d), 129.58 (m), 130.38 (m), 131.68 (m), 134.13 (m), 135.27 (m), 135.70 (m), 139.47 (m)
$(C_5Me_5)Rh(PPh_3)Br_2$	9.98 (d), 100.10 (dd)	128.41 (dd), 131.05 (s), 135.42 (dd)
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]Cl_2$	9.04 (s), 98.39 (dd)	26.19 (d), 24.76 (d), 24.94 (d), 13.49 (s)
$(C_5Me_5)Rh[P(n\text{-}Bu)_3]PhBr$	10.23 (s), 99.92 (dd)	14.14 (s), 24.94 (d), 26.24 (s), 26.58 (d), 30.78 (s), 122.44 (s), 125.97 (s), 136.20 (s), 139.64 (s), 142.62 (s), 157.57 (d)
$(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Cl_2$	10.26 (d), 98.14 (dd)	27.66 (d), 34.33 (d), 76.87 (s)
$(C_5Me_5)Rh(PCy_3)Cl_2$	10.47 (d), 98.91 (dd)	28.43 (m), 30.60 (m), 37.60 (m), 40.86 (m)

[a] $CDCl_3$ solvent.

a high-vacuum line with the use of Schlenk techniques. All hydrocarbon solvents were distilled from purple solutions of potassium/benzophenone/tetraglyme prior to use. $CDCl_3$ for use in the drybox was stirred over P_2O_5 overnight, stirred over molecular sieves (4A), and then vacuum distilled from the sieves. $CHCl_3$ and CH_2Cl_2 were stirred over P_2O_5 for a day and stored over $CaCl_2$. All phosphines employed were purchased from Strem Chemical Co. and were used without further purification with the exception of PMe_3 and PPh_3. PMe_3 was vacuum distilled (10^{-3} mmHg, 25 °C) prior to use, while PPh_3 was recrystallized from dichloromethane/ethanol and dried under vacuum (10^{-3} mmHg). $[(C_5Me_5)RhCl_2]_2$ and $(C_5Me_5)Rh(PMe_3)H_2$ were prepared according to the procedure of Maitlis et al.[13] $(C_5Me_5)Rh(PMe_3)Cl_2$ was prepared by using the procedure of Jones and Feher.[4]

Superhydride (lithium triethylborohydride) was purchased from Aldrich Chemical Co. as a 1.0 M solution in THF, and was titrated prior to use with a 1.06 M solution of *tert*-butylalcohol with 1,10-phenanthroline as an indicator. Red-Al [sodium bis(methoxyethoxy)-aluminum dihydride] was purchased from Aldrich as a 3.4 M solution in toluene, and was diluted with toluene or tetrahydrofuran to form solutions that were 0.1–0.5 M. The solution was titrated by measuring the amount of hydrogen gas evolved upon reaction with water. *tert*-Butyllithium and *n*-butyllithium were purchased from Aldrich. Aryl Grignard reagents were prepared as before.[5] Analtech Uniplate silica gel plates (2000 μm) were used for thick-layer chromatography. Silica used for flash chromatography was 60PF254 Kieselgel from EM Reagents.

Photolyses were carried out using an Oriel Arc Lamp with a high-pressure 200-W Hg/Xe lamp. A water filter was used to absorb infrared radiation, and a Pyrex filter was employed to select only wavelengths >300 nm. ^1H (400-MHz) and ^{31}P (162-MHz) NMR spectra were recorded on a Bruker WH-400 spectrometer. ^{13}C (75-MHz) NMR spectra were recorded on a GE QE-300 spectrometer. ^1H NMR shifts were measured relative to residual ^1H resonances in the deuterated solvents C_6D_6 (δ 7.15) and C_6D_{12} (δ 1.38). ^{31}P NMR spectra were reported in units of δ (chemical shifts are referred to external 10% H_3PO_4 δ 0.0 ppm)). ^{13}C NMR were measured relative to the deuterated solvent resonance ($CDCl_3$, δ 77.0 ppm). C_6D_6, C_6D_{12}, and C_7D_{14} were purchased from MSD Isotopes Merck Chemical Division Co. and were vacuum distilled from potassium–benzophenone prior to use. Elemental analyses were performed by Desert Analytics-Organic Microanalysis Laboratory. An Enraf-Nonius CAD4 diffractometer was used for the X-ray crystal structure determination. Infrared spectra were recorded on a Mattson Sirius 100 spectrometer. Electron-impact mass spectra were taken on either a VG 7035 or a Nermag R10-10C mass spectrometer at 70 eV.

General Procedure for the Preparation of $(C_5Me_5)Rh(PR_3)X_2$. Where PR_3 was a liquid at room temperature (e.g. PMe_2Ph), the following procedure was used. $[(C_5Me_5)RhCl_2]_2$ (150 mg, 0.243 mmol) was dissolved in anhydrous CH_2Cl_2. Dimethylphenylphosphine (80 μL, 0.51 mmol) measured via an airtight syringe was added to the dimer solution. The solution was stirred for 30 min at room temperature and the solvent then removed under vacuum. Recrystallization of the solid from CH_2Cl_2/hexanes provided the product as an orange powder (178 mg, 0.40 mmol) in 82% yield.

Where PR_3 was a solid at room temperature (e.g. PPh_3), the following procedure was used. $[(C_5Me_5)RhCl_2]_2$ (247 mg, 0.444 mmol) was weighed into a flask with 2.04 equiv of PPh_3 (237 mg, 0.904 mmol). Anhydrous CH_2Cl_2 was condensed into the flask, and the solution was stirred for 30 min. Recrystallization from CH_2Cl_2/hexane yielded the product as orange-red crystals (484 mg, 0.847 mmol) in 95% yield. Other complexes were prepared in this manner with different phosphines as listed in Table I–III with yields and NMR data. The complexes where X = Br or I were prepared similarly by starting with $[(C_5Me_5)RhX_2]_2$ in place of $[(C_5Me_5)RhCl_2]_2$. Anal. Calcd (found) for $(C_5Me_5)Rh(PPh_3)Cl_2$: C, 58.86 (59.00); H, 5.29 (5.25). Calcd (found) for $(C_5Me_5)Rh[P(n\text{-}Bu_3)]Cl_2$: C, 51.67 (51.98); H, 8.28 (8.23). Calcd (found) for $(C_5Me_5)Rh(PMePh_2)Br_2$: C, 46.18 (46.41); H, 4.72 (4.57). Calcd (found) for $(C_5Me_5)Rh(PMePh_2)Cl_2$: C, 54.25 (54.24); H, 5.54 (5.45). Calcd (found) for $(C_5Me_5)Rh(PEt_3)Cl_2$: C, 44.99 (44.70); H, 7.08 (6.88).

Preparation of $PMe_2(t\text{-}Bu)$. PMe_2Cl (0.240 mL, 0.293 g, 3.03 mmol) was placed in a 100-mL septum-capped two-neck flask and dissolved in 10 mL of THF. The solution was cooled to −40 °C and a solution of *tert*-butyllithium in pentane (1.73 mL, 2.94 mmol) was added dropwise via syringe. The solution was stirred for 1 h at −40 °C, warmed to 22 °C, and stirred for an additional hour. The phosphine and solvent were vacuum distilled (22 °C, 10^{-3} mm) leaving behind a yellow residue and yielding a colorless solution. The phosphine was not isolated from the THF/pentane solvent, but was used directly in reaction with the rhodium dimer as described below. Assuming 100% reaction (no starting material remains by ^1H NMR spectroscopy), the solution is 3.03 mmol in 5.3 mL or 0.57 M.

Preparation of $(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]X_2$. $[(C_5Me_5)RhCl_2]_2$ (98.3 mg, 0.159 mmol) was dissolved in anhydrous CH_2Cl_2. To this solution was added 3.6 equiv of the 0.57 M THF/pentane $PMe_2(t\text{-}Bu)$ solution prepared above (0.57 mmol, 1.00 mL). The solution was allowed to stir for 1 h. Column chromatography was performed with 4% THF in CH_2Cl_2. The first band to emerge was the desired material. Recrystallization from CH_2Cl_2 layered with hexane produced an orange-red powder (68.5 mg, 0.149 mmol) in 47% yield. The analogous complex with bromide in place of chloride was prepared similarly by starting with $[(C_5Me_5)RhBr_2]_2$ in place of $[(C_5Me_5)RhCl_2]_2$. The NMR data for these compounds are listed in Tables I–III. Anal. Calcd (found) for $(C_5Me_5)Rh[PMe_2(t\text{-}Bu)]Cl_2$: C, 44.99 (44.15); H, 7.08 (6.90).

Preparation of $PMe_2(n\text{-}Bu)$. The procedure was followed as for $PMe_2(t\text{-}Bu)$. A solution of *n*-butyllithium in hexane (1.01 mmol, 0.95 mL) was added dropwise via syringe to a −40 °C solution of PMe_2Cl (0.08 mL, 0.098 g, 1.01 mmol) in THF under nitrogen. The solution was stirred for 1 h at −40 °C, warmed to 22 °C, and stirred for 2 h. The phosphine was vacuum transferred (25 °C, 10^{-3} mmHg) to yield (assuming 100% reaction) 10 mL of a 0.10 M solution.

Preparation of $(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Cl_2$. An aliquot of $PMe_2(n\text{-}Bu)$ solution in THF–hexane (3.4 mL, 0.339 mmol) was added to a solution of $[(C_5Me_5)RhCl_2]_2$ in 25 mL of anhydrous CH_2Cl_2. The solution was stirred for 1 h. Thick-layer chromatography was performed with 4% THF in CH_2Cl_2 as the eluent. Two bands were obtained with starting material eluting more slowly (R_f = 0.14) than product (R_f = 0.5). Recrystallization from a CH_2Cl_2 solution layered with hexane yielded red needlelike crystals (0.0273 g, 0.064 mmol) in 20% yield. The NMR data for this compound is given in Tables I–III. Anal. Calcd (found) for $(C_5Me_5)Rh[PMe_2(n\text{-}Bu)]Cl_2$: C, 44.99 (45.06); H, 7.08 (7.00).

Preparation of $(C_5Me_5)Rh(PMe_3)H_2$. The procedure of Maitlis was followed.[13] $(C_5Me_5)Rh(PMe_3)Cl_2$ (7.3 mg, 0.019 mmol) was dissolved in 5 mL of anhydrous THF and sodium bis(methoxyethoxy)aluminum

(13) Kang, J. W.; Mosely, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977.

Table IV. Selected Distances (Å) and Angles (deg) in $(C_5Me_5)Rh(PR_3)PhBr$ Complexes[a]

$(C_5Me_5)Rh(PMe_3)PhBr$[b]			
Distances			
Rh–Br	2.533 (2)	P–C17	1.813 (10)
Rh–P	2.248 (3)	P–C18	1.818 (10)
Rh–C11	2.054 (9)	P–C19	1.834 (10)
Angles			
Br–Rh–P	86.3 (1)	C11–Rh–CEN	123.0
Br–Rh–C11	94.4 (3)	Rh–P–C17	113.6 (3)
P–Rh–C11	88.0 (3)	Rh–P–C18	116.9 (4)
Rh–C11–C12	122.3 (6)	Rh–P–C19	118.4 (4)
Rh–C11–C16	121.0 (6)	C17–P–C18	103.4 (5)
Br–Rh–CEN	120.9	C17–P–C19	101.9 (5)
P–Rh–CEN	133.0	C18–P–C19	100.2 (5)
$(C_5Me_5)Rh(PMe_2Ph)PhBr$[c]			
Distances			
Rh1–Br1	2.524 (2)	P1–C17	1.835 (6)
Rh1–P1	2.270 (2)	P1–C23	1.823 (7)
Rh1–C11	2.082 (6)	P1–C24	1.819 (6)
Angles			
Br1–Rh1–P1	88.80 (6)	C11–Rh1–CEN	122.2
Br1–Rh1–C11	91.8 (2)	Rh1–P1–C17	115.5 (2)
P1–Rh1–C11	88.7 (2)	Rh1–P1–C23	116.2 (2)
Rh1–C11–C12	124.1 (5)	Rh1–P1–C24	114.8 (2)
Rh1–C11–C16	119.8 (5)	C17–P1–C23	103.2 (3)
Br1–Rh1–CEN	122.4	C17–P1–C24	103.0 (3)
P1–Rh1–CEN	131.7	C23–P1–C24	102.2 (3)
$(C_5Me_5)Rh(PMePh_2)PhBr$			
Distances			
Rh–Br	2.543 (1)	P–C17	1.833 (5)
Rh–P	2.289 (2)	P–C23	1.830 (5)
Rh–C11	2.065 (5)	P–C29	1.815 (5)
Angles			
Br–Rh–P	89.48 (5)	C11–Rh–CEN	124.1
Br–Rh–C11	94.5 (1)	Rh–P–C17	116.8 (1)
P–Rh–C11	84.7 (1)	Rh–P–C23	115.2 (2)
Rh–C11–C12	121.5 (4)	Rh–P–C29	114.9 (2)
Rh–C11–C16	122.3 (4)	C17–P–C23	102.9 (2)
Br–Rh–CEN	119.1	C17–P–C29	103.6 (2)
P–Rh–CEN	133.8	C23–P–C29	101.6 (2)
$(C_5Me_5)Rh(PPh_3)PhBr$[c]			
Distances			
Rh1–Br1	2.525 (3)	P1–C17	1.85 (2)
Rh1–P1	2.295 (5)	P1–C23	1.82 (2)
Rh1–C11	2.08 (1)	P1–C29	1.84 (1)
Angles			
Br1–Rh1–P1	90.2 (1)	C11–Rh1–CEN	121.9
Br1–Rh1–C11	95.5 (4)	Rh1–P1–C17	110.5 (5)
P1–Rh1–C11	87.4 (4)	Rh1–P1–C23	116.5 (5)
Rh1–C11–C12	122 (1)	Rh1–P1–C29	120.5 (5)
Rh1–C11–C16	121 (1)	C17–P1–C23	103.8 (7)
Br1–Rh1–CEN	117.4	C17–P1–C29	102.3 (7)
P1–Rh1–CEN	134.4	C23–P1–C29	101.1 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] From ref 4. [c] Values are for one of two crystallographically independent molecules.

Table V. Rates of Benzene Loss from $(C_5Me_5)Rh(PR_3)(C_6D_5)D$ Complexes

PR_3	cone angle, deg	T, °C	k, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
PMe_3	118	23	$3.35\ (17) \times 10^{-7}$	26.1
PMe_2Ph	122	23	$1.08\ (5) \times 10^{-6}$	25.4
$PMePh_2$	136	24.5	$1.11\ (6) \times 10^{-5}$	24.2
PPh_3	145	23	$3.85\ (19) \times 10^{-4}$	21.9
$PMe_2(t\text{-}Bu)$	139	24.5	$6.6\ (3) \times 10^{-6}$	24.5
$PMe_2(n\text{-}Bu)$	123	24.5	$1.25\ (3) \times 10^{-5}$	24.1
$P(n\text{-}Bu)_3$	132	24.5	$2.4\ (1) \times 10^{-6}$	25.1

hydride (Red-Al) (0.56 mL, 0.095 mmol, 5 equiv) added to the solution. After 30 min, the solvent was removed, leaving a yellow waxy material, which was subjected to flash chromatography using 5/3 (v:v) hexane–THF as an eluent. Removal of solvent from the eluent yielded a pale oil that was used immediately for the photochemical experiments. The thermal instability of the complexes precluded analyses. This procedure was used to prepare all dihydrides listed in Table I except for the PPh_3 derivative, the preparation of which is described below.

Preparation of $(C_5Me_5)Rh(PPh_3)H_2$. $(C_5Me_5)Rh(PPh_3)Cl_2$ (10.8 mg, 0.0189 mmol) was reacted with 5 equiv Red-Al (0.0945 mmol, 0.56 mL), and flash chromatography was performed as described above. The resulting $(C_5Me_5)Rh(PPh_3)H_2$ solution also contained some free PPh_3 by ^1H NMR spectroscopy. The product was dissolved in THF, and $[(C_5Me_5)RhCl_2]_2$ (3 mg, 0.005 mmol) was added to the solution (to complex the free PPh_3). After the mixture was stirred for 30 min, the solvent was removed under vacuum and the desired $(C_5Me_5)Rh(PPh_3)H_2$ extracted with hexane and filtered through a cotton-plugged pipet. This resulted in a sample free of unwanted free PPh_3.

General Procedure for the Preparation of $(C_5Me_5)Rh(PR_3)H_2$ via $(PPN)BH_4$. $(C_5Me_5)Rh(PPh_3)Cl_2$ (16.2 mg, 0.0284 mmol) and 12.5 equiv $(PPN)BH_4$ (87.1 mg, 0.356 mmol) were placed in an ampule and THF distilled in. The suspension was stirred for 8 h in the dark, producing a milky white precipitate and a colorless solution. The solvent was removed and the product extracted with hexane and filtered twice through cotton plugs wedged tightly into pipets. Complexes with phosphines other than PPh_3 were also prepared via this method. In all cases, however, small amounts of impurities were present as evidenced by ^1H NMR resonances in the 6.9–7.7 ppm region (C_6D_6). These complexes could also be prepared starting with the bromo derivatives $(C_5Me_5)Rh(PR_3)Br_2$ in place of $(C_5Me_5)Rh(PR_3)Cl_2$.

General Procedure for the Preparation of $(C_5Me_5)Rh(PR_3)PhX$. The earlier published procedure was followed,[5] described here for R = Me. $(C_5Me_5)Rh(PMe_3)Br_2$ (0.413 g, 0.872 mmol) was dissolved in anhydrous THF and the solution cooled to −40 °C. A Grignard solution of PhMgBr in THF (3 equiv, 2.62 mmol, 4.4 mL) was added dropwise to the −40 °C solution via airtight syringe. The solution was stirred for 30 min, warmed to 22 °C, and stirred for an additional 30 min. An aliquot of a saturated NH_4Br–H_2O solution (0.2 mL) was added to the reaction mixture. The solvent was removed (22 °C, 10^{-3} mmHg), and the product was extracted with CH_2Cl_2 and filtered through a fine glass filter. Column chromatography on silica (4% THF–CH_2Cl_2) gave the desired complex as the first band to emerge. Recrystallization from CH_2Cl_2–hexane afforded an orange powder (0.360 g, 0.764 mmol) in 88% yield. The complexes with phosphines other than PMe_3 were prepared in the same manner. The yields for the preparation of these complexes along with their NMR data is presented in Table I–III. The complexes where X = Cl were prepared similarly, starting with the dichloro-substituted starting material, using phenylmagnesium chloride and saturated NH_4Cl to quench the solution. Anal. Calcd (found) for $(C_5Me_5)Rh(PMe_2Ph)PhCl$: C, 58.97 (57.72); H, 6.39 (6.36). Calcd (found) for $(C_5Me_5)Rh(PMe_2Ph)PhBr$: C, 54.05 (54.08); H, 5.86 (5.82). Calcd (found) for $(C_5Me_5)Rh(PMePh_2)PhBr$: C, 58.51 (58.78); H, 5.59 (5.62). Calcd (found) for $(C_5Me_5)Rh(PPh_3)PhBr$: C, 62.12 (61.23); H, 5.37 (5.30).

General Procedure for the Preparation of $(C_5Me_5)Rh(PR_3)PhH$. $(C_5Me_5)Rh(PMe_3)PhBr$ (24.8 mg, 0.0526 mmol) was dissolved in THF and 5 equiv of lithium tri-*sec*-butylborohydride (L-Selectride) (0.26 mL, 0.26 mmol) added via syringe. The solution was stirred for 6 h (22 °C) to yield a colorless to yellow solution. Solvent removal and flash filtration through silica with 5:3 (v:v) hexane–THF resulted in a tan to green solution of the desired product. Complexes with phosphines other than PMe_3 reacted similarly. As the bulk of the phosphine increased, however, shorter reaction times and less L-selectride was required, as listed: PMe_2Ph, 3.1 equiv, 4 h; $PMePh_2$, 1.6 equiv, 2 h; PPh_3, 1.2 equiv, 1 h; $P(n\text{-}Bu)_3$, 3 equiv, 30 min.

In the case of the PPh_3 complex, some free PPh_3 was produced under these reaction conditions. To rid the sample of this free PPh_3, the solution obtained after flash chromatography was stirred over a few milligrams of $[(C_5Me_5)RhCl_2]_2$, and the solvent was removed. The desired product was extracted with hexane and filtered through a cotton wad packed tightly into pipet. These complexes could also be synthesized with chloride in place of bromide for starting material, as listed in Tables I–III. The thermal instability of the complexes precluded analyses.

Irradiation of $(C_5Me_5)Rh(PR_3)H_2$ in Benzene-d_6. The general procedure is described here for $PR_3 = PMe_2Ph$. $(C_5Me_5)Rh(PMe_2Ph)H_2$ (0.028 mmol) was dissolved in C_6D_6 and placed in an NMR tube attached to a ⅞ 14/20 ground-glass joint. The joint was fitted with an adapter and flame-sealed under vacuum following three cycles of freeze–pump–thaw degassing. Alternatively, an NMR tube fitted with a J. Young resealable Teflon valve could be used in place of the flame-sealed tube. The sample was irradiated and examined periodically by ^1H NMR spectroscopy. In all cases, resonances for the corresponding phenyl deuteride $(C_5Me_5)Rh(PR_3)(C_6D_5)D$ were observed as the major product.

Table VI. Summary of Crystallographic Data for $(C_5Me_5)Rh(PR_3)PhBr$ Complexes

	PR_3 = PMe_2Ph	PR_3 = $PMePh_2$	PR_3 = PPh_3
formula	$RhBrPC_{24}H_{31}$	$RhPBrC_{29}H_{33}$	$RhPBrC_{34}H_{35}$
mol wt	533.29	595.36	657.44
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	17.042 (4)	13.421 (4)	15.707 (6)
b, Å	15.94 (1)	11.918 (4)	19.218 (5)
c, Å	19.314 (8)	17.085 (3)	10.419 (3)
α, deg	90	90	100.94 (2)
β, deg	115.53 (3)	107.54 (2)	98.25 (3)
γ, deg	90	90	105.04 (3)
V, Å^3	4733 (8)	2606 (2)	2920 (4)
ρ_{calc}, g cm^{-3}	1.50	1.52	1.50
Z	8	4	4
temp, °C	23	23	23
radiation (monochromator)	Mo, 0.71073 Å (graphite)		
μ, cm^{-1}	25.65	23.39	20.96
range of transm factors	0.74–1.00	0.78–1.16	0.85–1.16
R_1	0.033	0.030	0.051
R_2	0.041	0.031	0.057

Irradiation of $(C_5Me_5)Rh(PMe_2Ph)H_2$ in Methylcyclohexane-d_{14}. $(C_5Me_5)Rh(PMe_2Ph)H_2$ (0.0494 mmol) was dissolved in methylcyclohexane-d_{14} and placed in an NMR tube attached to a ground-glass joint. The solution was freeze–pump–thaw degassed and flame-sealed under vacuum. The sample was irradiated (180 W) with cooling by a jet of compressed air. After irradiation for 5 min at 23 °C, a new hydride resonance was observed: δ −13.922 (dd, J = 29, 13 Hz). After 35 min of irradiation, no hydrides remained, aside from a small amount of starting material. Other new resonances after 35 min of irradiation were as follows: δ 1.740 (s), 1.744 (s), 1.858 (s), 1.874 (s), 7.189 (m), 7.243 (t, J = 7.4 Hz), 7.284 (br, s), 7.349 (m), 7.610 (br m), 7.781 (m).

Irradiation of $(C_5Me_5)Rh(PMePh_2)H_2$ in Methylcyclohexane-d_{14}. The same procedure was carried out as described for the complex where PR_3 = PMe_2Ph. Upon irradiation of $(C_5Me_5)Rh(PMePh_2)H_2$ (0.0403 mmol) for 30 min, the new resonances observed were a singlet at δ 1.507 in addition to multiple small phenyl region resonances and multiple resonances in the −12.9 to −13.4 ppm region. Following irradiation for an additional 30 min, new resonances are observed: δ 13.207 (dd, J = 44.9, 31.9 Hz), 1.506 (s); 1.791 (s), 1.913 (s) in a ratio of 0.36:1.5:1.0:1.0, respectively. No change was observed to occur by ^{1}H NMR spectroscopy while the mixture was left to stand at room temperature for 26 days.

Irradiation of $(C_5Me_5)Rh(PPh_3)H_2$ in Cyclohexane-d_{12}. A solution of $(C_5Me_5)Rh(PPh_3)H_2$ (0.0198 mmol) in deuterated cyclohexane was placed in an NMR tube attached to a ground-glass joint. The solution was freeze–pump–thaw degassed three times and flame-sealed under vacuum. Upon irradiation for 150 min, the amount of starting material was reduced and a new complex was observed with a singlet in the ^{1}H NMR spectrum at 1.3 ppm. The solvent was removed and the product dissolved in C_6D_6. The major product was identified as $(C_5Me_5)Rh(PPh_3)_2$ (δ 1.583 (s, C_5Me_5)), by comparison with an authentic sample.

Exchange of C_6H_6 into $(C_5Me_5)Rh(PR_3)(C_6D_5)D$. The $(C_5Me_5)Rh(PR_3)(C_6D_5)D$ complexes were prepared by irradiation of the dihydride in C_6D_6 as previously described. The complex with the desired phosphine was then dissolved in C_6H_6 and placed in an NMR tube attached to a ground-glass joint. The solution was freeze–pump–thaw degassed and a small amount of deuterated benzene condensed into the tube (to permit locking of the NMR spectrometer). The tube was then flame-sealed under vacuum and the reaction followed by ^{1}H NMR spectroscopy. The exchange of benzene into the complex was measured via integration of the doublet of doublets for the hydride resonance verses the integration of the pentamethylcyclopentadienyl resonance. The rates for this reaction for complexes with various phosphines are listed in Table V.

X-ray Structural Characterization of $(C_5Me_5)Rh(PMe_2Ph)PhBr$, $(C_5Me_5)Rh(PMePh_2)PhBr$, and $(C_5Me_5)Rh(PPh_3)PhBr$. In each case, well-formed orange crystals of the compound were prepared by slow crystallization from CH_2Cl_2–hexane solution. Lattice constants were obtained from 25 centered reflections with values of χ between 5 and 70°. Cell reduction with the program TRACER revealed primative crystal systems. Data were collected on the crystals at ambient temperature in accord with the parameters in Table VI. The unique space group $P2_1/n$ was assigned as for $(C_5Me_5)Rh(PMe_2Ph)PhBr$ and $(C_5Me_5)Rh(PMePh_2)PhBr$ on the basis of systematic absences. For $(C_5Me_5)Rh(PPh_3)PhBr$, the space group was assigned as the centric choice $P\bar{1}$ on the basis of $N(z)$ statistics. The correctness of this choice was confirmed by successful solution of the Patterson map, showing two distinct rhodium atoms in general positions. In each case, the structures were expanded using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[14] Full least squares anisotropic refinement of the structure with hydrogens placed in idealized positions (U_{iso} = 1.2U_{carbon}) based upon a difference Fourier map was carried out on the PMe_2Ph and $PMePh_2$ structures. For the PPh_3 structure, only the rhodium, bromine, phosphorus, and C_5Me_5 carbons were refined anisotropically. The remaining carbons were refined isotropically, with hydrogens placed in idealized positions (U_{iso} = 1.2U_{carbon}) based upon a difference Fourier map.

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Supplementary Material Available: Tables S-I–S-XIII, listing crystallographic information, bond distances and angles, anisotropic thermal parameters, and coordinates of atoms (31 pages); Tables S-XIV–S-XVI, listing calculated and observed structure factors (71 pages). Ordering information is given on any current masthead page.

(14) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV, Tables 2.2B and 2.3.1.