Molecular Structure in Solution. A sample of **4** was dissolved in *n*-butylbenzene, and the resulting solution was injected into a sample cell that consisted of a copper sample holder fitted with two Mylar windows as described in an earlier study.[33] The cell containing the solution was rapidly frozen with liquid nitrogen and mounted on the precooled cold finger of a Heli-tran cryostat. The ^{57}Fe Mössbauer parameters of this frozen (glassy) solution sample of **4** were identical with the values observed for the neat solid sample (Table I), and hence it can be concluded that there are no structural changes of the molecule between the neat crystalline solid and isolated molecules in solution that can be detected at the metal atom site. Thus probably it is valid to ascribe the structural and bonding parameters that are derived from solution spectroscopic techniques (^{1}H and ^{13}C NMR, infrared, etc.) in solvents as innocuous as *n*-butylbenzene to the structures that are derived from single-crystal X-ray diffraction experiments. The ^{57}Fe Mössbauer data thus provide a significant bridge between the structural inferences drawn from the two types of experiments that have been used to elucidate this new class of bis(pentadienyl)iron compounds.

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The Mechanism and Thermodynamics of Alkane and Arene Carbon-Hydrogen Bond Activation in $(C_5Me_5)Rh(PMe_3)(R)H$

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Abstract: The complexes $(C_5Me_5)Rh(PMe_3)(R)X$ (R = Me, Ph, *p*-tolyl, 3,4-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, 2,5-$C_6H_3Me_2$, and C≡CH—CH_2—CH_2—CH_2; X = Br) react with the hydride donors $Li^+[HB(sec\text{-}Bu)_3]^-$ or $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ to produce $(C_5Me_5)Rh(PMe_3)(R)H$. The complexes with R = alkyl or R = vinyl are unstable, undergoing rapid reductive elimination at 25 °C, but can be observed by ^{1}H NMR below −20 °C. $(C_5Me_5)Rh(PMe_3)(CH_3)H$ undergoes first-order reductive elimination with $k = (6.38 \pm 0.10) \times 10^{-5}$ s^{-1} at −17 °C. In contrast, $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ undergoes a more complicated first-order process in C_6D_6, producing C_6H_6 and $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ with the overall activation parameters $\Delta H^\ddagger$ = 30.5 ± 0.8 kcal/mol and $\Delta S^\ddagger$ = 14.9 ± 2.5 eu. The alkyl and aryl hydride complexes can also be generated by photochemical extrusion of H_2 from $(C_5Me_5)Rh(PMe_3)H_2$ in the presence of alkane or arene solvent. In a competition experiment, a 5.4:1 selectivity for benzene over cyclopentane was exhibited at −35 °C. Irradiation in toluene solvent at −45 °C produced products in which activation of all possible C-H bonds of toluene was observed: 57% meta, 36% para, 7% ortho, and <1% benzyl. Thermodynamically controlled competition between activation of benzene and toluene, *m*-xylene, *o*-xylene, or *p*-xylene showed preferences for benzene of 2.7, 12.1, 7.6, and 58.6. The aryl complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ were found to be in rapid equilibrium with their η^2-arene derivatives at temperatures above −15 °C. Mechanistic studies revealed a [1,2]-shift pathway around the ring with $\Delta H^\ddagger$ = 16.3 ± 0.2 kcal/mol and $\Delta S^\ddagger$ = −6.3 ± 0.8 eu for the derivative with R = 2,5-$C_6H_3Me_2$. Generation of the coordinatively unsaturated species $(C_5Me_5)Rh(PMe_3)$ in the presence of *p*-$[C_6H_4(t\text{-}Bu)_2]$ permitted the direct observation of an η^2-arene complex at −15 °C. The kinetics of C-H bond activation in this system are interpreted in terms of two distinct rate-determining reactions, arene coordination vs. alkane oxidative addition. The rhodium-phenyl bond is found to be about 13 kcal/mol stronger than the rhodium-methyl bond.

One of the most beneficial features of transition-metal complexes is their ability to promote chemical reactions in organic molecules. Oxidative addition is a fundamental process that produces a species capable of reacting in numerous ways characteristic of the molecule that has been activated.[1] For example, aldehydes and acid chlorides can be decarbonylated following oxidative addition of the C-H or C-Cl bonds.[2] The oxidative addition of alkyl and aryl halides produces organometallic complexes in which the metal-carbon bond can undergo a variety of insertion and elimination reactions, leading to substantial changes in the structure of the organic ligand.[3] Until recently, however,

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activation of the parent alkane molecules proved to be an elusive but potentially promising area for research.[4-6]

Many studies have been aimed at examining the chemistry of carbon-hydrogen (C-H) bonds with transition metals.[4-15] The reductive elimination of alkane from alkyl hydrido complexes led to the speculation that all such species would be thermodynamically unaccessible.[7] However, others were able to activate alkane C-H bonds intramolecularly, thereby reducing the entropic contribution to the free energy for the process.[8] The oxidative addition of alkane C-H bonds to metal ions has been known for several years, both in the gas phase[9] and in solution.[4] Similarly, isolation of metal atoms in hydrocarbon matrices also is believed to result in C-H activation,[10] as are reactions of hydrocarbons at metal surfaces.[11] Only recently have well-characterized solution reactions been reported in which alkane C-H bonds undergo a straightforward oxidative addition reaction in which an alkyl hydride complex is produced.[6]

The work with alkanes stands in marked contrast to the numerous examples of arene activation, both intermolecularly and intramolecularly, that have been known for many years.[12,13] Parshall has suggested that the arene may precoordinate to the metal in an η^2 fashion prior to activation,[14] a formulation that was postulated as early as 1965 by Chatt (eq 1).[15] The coordination of the arene can thereby provide a lower energy pathway for oxidative addition of the C-H bond, a route unavailable to alkanes.

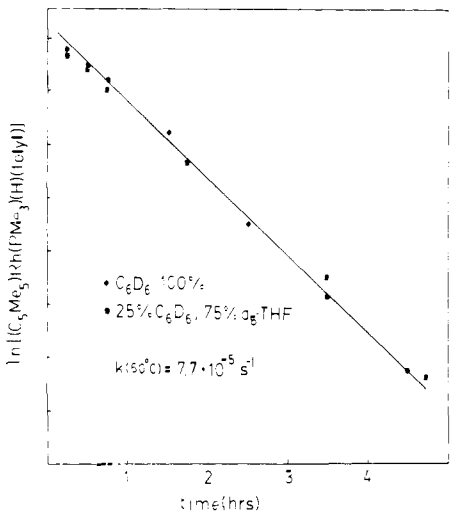
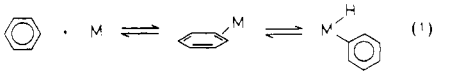


Figure 1. Solvent effect upon the rate of arene exchange for **6** in C_6D_6 at 60 °C.



In this paper, we provide evidence for the intermediacy of the η^2-arene complex along the pathway for oxidative addition/reductive elimination of arene C-H bonds. With the same metal complex alkane C-H activation and elimination can be observed, permitting a direct comparison of alkane vs. arene activation. The complexes are sufficiently convenient for study that reaction rates can be measured over a wide enough temperature range to give reliable activation parameters. Comparison of thermodynamic parameters allows an estimation of relative metal-alkyl vs. metal-aryl bond strengths in this series of permethylcyclopentadienyltrimethylphosphinerhodium(III) complexes. Preliminary communications of this work have recently appeared.[6c,12]

Results and Discussion

A. Preparation and Stability of Alkyl and Aryl Hydride Complexes. We have recently reported the preparation and conformational dynamics of a series of complexes of the general formula $(C_5Me_5)Rh(PMe_3)(R)X$ (X = Cl, Br, I; R = alkyl, aryl, vinyl, benzyl).[16] The aryl halide complexes all react with $Li^+[HB(sec\text{-}Bu)_3]^-$ or $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ at 25-30 °C in THF to give the corresponding air-sensitive hydride derivatives, $(C_5Me_5)Rh(PMe_3)(R)H$, in good yield. The boron- or aluminum-containing byproducts can be easily removed from the thermally stable aryl derivatives by rapid filtration through silica gel. Removal of solvent leaves the product as a slightly impure semisolid. The hydride substitution reactions employing $[HB(sec\text{-}Bu)_3]^-$ are curious in that the orange solution does not appear to react until the solvent is removed under reduced pressure, leaving a highly concentrated gummy residue. Reaction is accompanied by a lightening of the residue to a straw yellow color. In contrast, the $[H_2Al(OCH_2CH_2OCH_3)_2]^-$ reductions of the iodide complexes occur over a few minutes in THF solution.

Another method for preparing both alkyl and aryl hydride complexes involves removal of the halide ligand with $AgPF_6$ in THF, producing a THF-complexed rhodium(III) cation. Addition of the borohydride reagent at low temperature results in the instantaneous formation of the alkyl or aryl hydride. Thus, treatment of a THF-d_8 solution of $(C_5Me_5)Rh(PMe_3)(CH_3)Cl$ with 1 equiv of $Ag^+[PF_6]^-$ results in the formation of a solution whose ^1H NMR spectrum shows three doublets at δ 1.437 (J = 2.7 Hz, 15 H), 1.333 (J = 10.2 Hz, 9 H), and 0.616 (J = 7.5 Hz, 3 H) attributable to $[(C_5Me_5)Rh(PMe_3)(CH_3)(THF\text{-}d_8)]^+$.

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Table I. ^{1}H NMR Spectral Data

compound	prepn[a]	solvent[b]	temp, °C	chemical shift, δ (mult, *J* area)
$(C_5Me_5)Rh(PMe_3)(CH_3)H$ (1)	B	A	−60	−14.424 (dd, *J* = 48.3, 30.3 Hz, 1 H) −0.130 (dd, *J* = 5.1, 2.5 Hz, 3 H) 1.178 (d, *J* = 9.6 Hz, 9 H) 1.790 (d, *J* = 2.1 Hz, 15 H)
$(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (2)	A	B	25	−13.505 (dd, *J* = 49.5, 32.8 Hz, 1 H) 0.903 (dd, *J* = 9.8, 0.8 Hz, 9 H) 1.789 (d, *J* = 1.4 Hz, 15 H) 7.105 (m, 3 H) 7.640 (d, *J* = 7.1 Hz, 2 H)
$(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ (2-d_6)	C, D	B	25	0.902 (dd, *J* = 9.8, 0.8 Hz, 9 H) 1.790 (d, *J* = 1.5 Hz, 15 H)
$(C_5Me_5)Rh(PMe_3)(C_6D_4H)D$ (2-d_6) or $(C_6D_5)H$	B	C	−40	1.483 (d, *J* = 10.3 Hz, 9 H) 1.563 (d, *J* = 2.4 Hz, 15 H) 6.673 (s, para) 6.700 (s, meta) 7.279 (s, ortho) −13.858 (dd, *J* = 49.6, 32.6, hydride)
$(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)H$ (3)	C, D	B	25	−13.335 (dd, *J* = 53, 31 Hz, 1 H) 0.866 (d, *J* = 9.7 Hz, 9 H) 1.785 (d, *J* = 1.9 Hz, 15 H) 2.354 (s, 3 H) 2.630 (s, 3 H) 6.878 (d, *J* = 7.5 Hz, 1 H) 7.256 (d, *J* = 7.4 Hz, 1 H) 7.330 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)H_2$ (4)		B	25	−13.650 (dd, *J* = 41.8, 29.8 Hz, 2 H) 1.058 (d, *J* = 9.4 Hz, 9 H) 2.054 (br s, 15 H)
		C	25	−14.285 (dd, *J* = 41.8, 29.8 Hz, 2 H) 1.268 (dd, *J* = 10.1, 1.0 Hz, 9 H) 1.987 (d, *J* = 2.1 Hz, 15 H)
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4Me)H$ (*p*-6) (33%)[c]	A, B, C, D	B	25	−13.522 (dd, *J* = 49.1, 33.7 Hz, 1 H) 0.920 (d, *J* = 9.8 Hz, 9 H) 1.807 (d, *J* = 1.3 Hz, 15 H) 2.302 (s, 3 H) 6.987 (d, *J* = 7.5 Hz, 2 H) 7.551 (d, *J* = 7.5 Hz, 2 H)
$(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4Me)H$ (*m*-6) (67%)[c]	A, B, C, D	B	25	−13.522 (dd, *J* = 49.1, 33.7 Hz, 1 H) 0.920 (d, *J* = 9.8 Hz, 9 H) 1.807 (d, *J* = 1.3 Hz, 15 H) 2.335 (s, 3 H) 6.911 (d, *J* = 7.2 Hz, 1 H) 7.071 (t, *J* = 7.4 Hz, 1 H) 7.434 (d, *J* = 7.3 Hz, 1 H) 7.511 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)(n\text{-propyl})H$ (7)	C	C	−40	−14.963 (dd, *J* = 50, 32 Hz, 1 H) 0.840 (t, *J* = 7 Hz, 3 H) 1.278 (d, *J* = 9 Hz, 9 H) 1.820 (d, *J* = 1.8 Hz, 15 H) 1.20–1.45 (m, 4 H)[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-xylyl-}d_3)H$ (8a and 8b)	B	C	−22	−13.556 (dd, *J* = 52.6, 31.5 Hz, 1 H) 1.125 (d, *J* = 10.4 Hz, 9 H) 1.78 (br s, 15 H) 2.121 (s, 1.5 H) 2.214 (s, 1.5 H) 6.452 (d, *J* = 7.3 Hz, 1 H) 6.768 (d, *J* = 7.4 Hz, 1 H) 7.138 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)[p\text{-}C_6H_4(t\text{-Bu})_2]$ (10)	C	D	−20	1.816 (d, *J* = 2.5 Hz, 15 H) 3.879 (br dd, *J* = 4.9, 3.0 Hz, 2 H) 6.355 (s, 2 H)
$(C_5Me_5)Rh(PMe_3)(\overline{C=CHCH_2CH_2CH_2})H$	B	A	−30	−13.895 (dd, *J* = 49.2, 32.3 Hz, 1 H) 1.125 (d, *J* = 9.9 Hz, 9 H) 1.792 (br s, 15 H) 5.086 (br s, 1 H) 1.0–2.3 (m, 6 H)
$(C_5Me_5)Rh(PMe_3)(\overline{CH=CHCH_2CH_2CH_2})$	C	A	25	0.812 (d, *J* = 8.2 Hz, 9 H) 1.701 (d, *J* = 2.0 Hz, 15 H) 1.0–2.3 (m, 8 H)

Table I (*Continued*)

compound	prepn[a]	solvent[b]	temp, °C	chemical shift, δ (mult, *J* area)
$(C_5Me_5)Rh(PMe_3)[2,5\text{-}C_6H_3(i\text{-}Pr)_2]H$	C	B	25	−13.315 (dd, *J* = 56.3, 30.9 Hz, 1 H) 0.896 (dd, *J* = 9.8, 1.1 Hz, 9 H) 1.360 (d, *J* = 6.8 Hz, 3 H) 1.374 (d, *J* = 6.8 Hz, 6 H) 1.490 (d, *J* = 7.0 Hz, 3 H) 1.789 (d, *J* = 2.3 Hz, 15 H) 2.875 (sept, *J* = 6.9 Hz, 1 H) 3.886 (sept, *J* = 6.9 Hz, 1 H) 6.969 (dd, *J* = 7.8, 2.0 Hz, 1 H) 7.250 (d, *J* = 7.8 Hz, 1 H) 7.350 (br s, 1 H)
$(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$	A, C, D	B	25	−13.552 (dd, *J* = 46, 33 Hz, 1 H) 0.944 (d, *J* = 9.8 Hz, 9 H) 1.824 (d, *J* = 1.1 Hz, 15 H) 2.336 (s, 6 H) 6.702 (s, 1 H) 7.325 (s, 2 H)
$(C_5Me_5)Rh(PMe_3)(3,4\text{-}C_6H_3Me_2)H$	A, C, D	B	25	−13.539 (dd, *J* = 49.5, 32.7 Hz, 1 H) 0.937 (d, *J* = 9.8 Hz, 9 H) 1.826 (br s, 15 H) 2.205 (s, 3 H) 2.260 (s, 3 H) 6.957 (d, *J* = 7.4 Hz, 1 H) 7.378 (d, *J* = 7.3 Hz, 1 H) 7.496 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4Cl)H$ (50%)[e]	A	B	25	−13.472 (dd, *J* = 33, 12 Hz, 1 H) 0.968 (d, *J* = 10.1 Hz, 9 H) 1.687 (br s, 15 H) 7.302 (d, *J* = 8.4 Hz, 2 H) 7.588 (d, *J* = 7.5 Hz, 2 H)
$(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4Cl)H$ (50%)[e]	A	B	25	−14.351 (dd, *J* = 33, 12 Hz, 1 H) 0.968 (d, *J* = 10.1 Hz, 9 H) 1.687 (br s, 15 H) 6.923 (t, *J* = 7.6 Hz, 1 H) 7.283 (d, *J* = 7.2 Hz, 1 H) 7.709 (d, *J* = 7.4 Hz, 1 H) 7.971 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4OMe)H$ (76%)[e]	A	B	25	−13.482 (dd, *J* = 49.2, 32.6 Hz, 1 H) 0.912 (d, *J* = 9.4 Hz, 9 H) 1.793 (br s, 15 H) 3.531 (s, 3 H) 6.630 (dd, *J* = 7.8, 1.8 Hz, 1 H) 7.057 (t, *J* = 7.7 Hz, 1 H) 7.269 (br d, *J* = 7.0 Hz, 1 H) 7.388 (s, 1 H)
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4OMe)H$ (12%)[e]	A	B	25	−13.519 (dd, *J* = 49, 32 Hz, 1 H) 0.912 (d, *J* = 9.4 Hz, 9 H) 1.793 (br s, 15 H) 3.485 (s, 3 H) 6.844 (d, *J* = 7.9 Hz, 2 H) 7.480 (d, *J* = 7.1 Hz, 2 H)
$(C_5Me_5)Rh(PMe_3)(o\text{-}C_6H_4OMe)H$ (12%)[e]	A	B	25	−13.839 (dd, *J* = 51, 32 Hz, 1 H) 0.973 (d, *J* = 8.9 Hz, 9 H) 1.793 (br s, 15 H) 3.396 (s, 3 H) 6.533 (d, *J* = 8.1 Hz, 1 H) 6.904 (t, *J* = 6.7 Hz, 1 H) 7.982 (br d, *J* = 6.8 Hz, 1 H) 7.15[d]
$[(C_5Me_5)Rh(PMe_3)(C_6H_5)(THF)]^+ [PF_6]^-$		C	25	1.483 (d, *J* = 10.3 Hz, 9 H) 1.563 (d, *J* = 2.4 Hz, 15 H) 6.925 (t, *J* = 7.2 Hz, 1 H) 7.027 (t, *J* = 7.3 Hz, 2 H) 7.284 (d, *J* = 6.3 Hz, 2 H)
$[(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})(THF)]^+ [PF_6]^-$		C	−25	1.483 (d, *J* = 10.4 Hz, 9 H) 1.557 (d, *J* = 2.5 Hz, 15 H) 2.238 (s, 3 H) 6.934 (d, *J* = 7.9 Hz, 2 H) 7.106 (d, *J* = 7.9 Hz, 2 H)
$[(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)(THF)]^+ [PF_6]^-$		A	25	0.984 (s, 3 H) 1.460 (d, *J* = 10.6 Hz, 9 H)

Table I (*Continued*)

compound	prepn[a]	solvent[b]	temp, °C	chemical shift, δ (mult, J = area)
$[(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)(THF)]^+ [PF_6]^-$				1.610 (d, J = 1.6 Hz, 15 H) 2.256 (s, 3 H) 6.618 (d, J = 7.5 Hz, 2 H) 6.757 (d, J = 7.5 Hz, 2 H) 6.920 (s, 1 H)
$[(C_5Me_5)Rh(PMe_3)(2\text{-}CH_3\text{-}5\text{-}CD_3\text{-}C_6H_3)(THF)]^+ [PF_6]^-$		C	−50	1.496 (d, J = 10.5 Hz, 9 H) 1.584 (br s, 15 H) 2.215 (s, 3 H) 6.704 (d, J = 7.3 Hz, 1 H) 6.750 (d, J = 7.5 Hz, 1 H) 6.942 (s, 1 H)
$[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF)]^+ [PF_6]^-$		C	−40	1.483 (d, J = 10.3 Hz, 9 H) 1.563 (d, J = 2.4 Hz, 15 H)
$[(C_5Me_5)Rh(PMe_3)(\overline{C{=}CHCH_2CH_2CH_2})(THF)]^+ [PF_6]^-$		A	−50	1.319 (d, J = 10.6 Hz, 9 H) 1.564 (d, J = 2.4 Hz, 15 H) 5.029 (br s, 1 H) 1.0–2.3 (m, 6 H)

[a] A = via aryl halide complex; B = via THF complex; C = via photolysis of 4; D = via arene exchange. [b] A = 3:1 THF-d_8/C_6D_6; B = C_6D_6; C = THF-d_8; D = $C_6D_{11}CD_3$. [c] Multuplets obscured by PMe_3 resonance. [d] Obscured by residual protons in solvent. [e] NMR yield.

Treatment of this solution with 1 equiv of $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ in toluene at −40 °C produces $(C_5Me_5)Rh(PMe_3)(CH_3)H$, **1**, characterized by its ^1H NMR spectrum (Table I) and reaction chemistry (vide infra). Similarly, treatment of $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ with $Ag^+[PF_6]^-$ in THF-d_8 produces $[(C_5Me_5)Rh(PMe_3)(C_6H_5)(THF\text{-}d_8)]^+$, whose ^1H NMR spectrum shows a pair of doublets at δ 1.563 (J = 2.4 Hz, 15 H) and 1.483 (J = 10.3 Hz, 9 H), as well as resonances for the coordinated phenyl group (Table I). Addition of 1 equiv of $Li^+[HB(sec\text{-}Bu)_3]^-$ at −40 °C produces new resonances for the complexes $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (**2**).[17] The THF-complexed cations are stable in solution for several hours, but attempted isolation by removal of the solvent under reduced pressure results in decomposition, presumably due to the lability of the weakly complexed THF ligand.

The aryl hydride complexes are quite stable thermally and do not eliminate arene at an appreciable rate until heated. If a solution of **2** in 100.0% C_6D_6 is heated to 60 °C, a smooth first-order reductive elimination occurs to produce C_6H_6 (93% by mass spectroscopy), C_6H_5D (7%), and $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ (**2**-d_6). The origin of the small amount of C_6H_5D is not known, but the elimination is clearly highly intramolecular. Heating **2**-d_6 in C_6H_6 regenerates **2** cleanly. By monitoring the rate of conversion of **2** to **2**-d_6 over a 46 °C temperature range, the activation parameters for the formation of benzene from **2** were found to be $\Delta H^\ddagger$ = 30.5 ± 0.8 kcal/mol and $\Delta S^\ddagger$ = 14.9 ± 2.5 eu (Table II). The large positive value of $\Delta S^\ddagger$ is somewhat surprising since the transition state for reductive elimination *presumably* (see Mechanism Section) involves a highly ordered 3-center

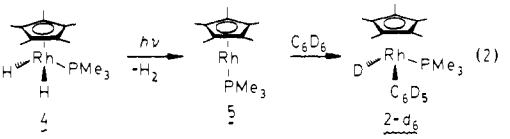
transition state. Other known reductive elimination reactions have negative or slightly positive entropies of activation.[18]

Aryl complexes with bulky substituents adjacent to the metal center are less stable than **2**, as would be expected. The *p*-xylyl derivative $(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)H$, **3**, also exchanges with C_6D_6 to form *p*-xylene and **2**-d_6 upon warming in C_6D_6. Activation parameters for the exchange calculated from rate data measured over an 18 °C range give $\Delta H^\ddagger$ = 29.3 ± 4.5 kcal/mol and $\Delta S^\ddagger$ = 19 ± 14 eu (Table II). The *p*-diisopropyl complex, $(C_5Me_5)Rh(PMe_3)[2,5\text{-}C_6H_3(CHMe_2)_2]H$, is even less stable, with a half-life for exchange with C_6D_6 of a few hours at room temperature.

The rate of the reductive elimination reaction has little dependence upon solvent polarity or ligating ability. Elimination of toluene from $(C_5Me_5)Rh(PMe_3)(tolyl)H$ proceeds at the same rate in both C_6D_6 and 25% C_6D_6/THF-d_8 (Figure 1).

The alkyl and vinyl hydride complexes are much less stable and were consequently prepared and studied in situ at temperatures below −20 °C. The methyl hydride complex, **1**, decomposes at −17 °C in THF-d_8 to produce methane and unidentified metal products.[19] If a small amount (10%) of C_6D_6 is added to a solution of **1**, then reductive elimination of methane is followed by oxidative addition of C_6D_6 to produce **2**-d_6. The kinetics for the elimination of methane from **1** in the presence of C_6D_6 is cleanly first order, with $k = (6.38 \pm 0.10) \times 10^{-5}$ s^{-1} at −17 °C. Attempts to obtain activation parameters for this reaction were unsuccessful, however, as the elimination rate showed a very strong temperature dependence implying that $\Delta S^\ddagger$ is both large and positive.

The third method for generation of alkyl and aryl halides is based upon the photochemically induced reductive elimination of dihydrogen from $(C_5Me_5)Rh(PMe_3)H_2$ (**4**). UV irradiation of the dihydride in C_6D_6 solution resulted in the rapid formation of **2**-d_6 presumably through the formation of coordinatively unsaturated $[(C_5Me_5)Rh(PMe_3)]$, **5** (eq 2). **2**-d_6 can be observed directly by ^1H NMR spectroscopy in 90% yield[20] or indirectly by conversion to $(C_5Me_5)Rh(PMe_3)(C_6D_5)Br$ upon addition of $CHBr_3$.



The tolyl derivatives $(C_5Me_5)Rh(PMe_3)(tolyl)H$, **6**, are potentially interesting in that four different isomers in which the ortho, meta, para, or benzylic C–H bonds have been activated are possible. However, irradiation of **4** in toluene solution *at 25 °C* produces only *m*-**6** and *p*-**6** in a 2:1 ratio. The same ratio of

(17) The hydridic reductions employing Ag^+ are always accompanied by the formation of small amounts of 5–10% of $(C_5Me_5)Rh(PMe_3)H_2$ (**4**) plus some free R–H.

(18) (a) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834. (b) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 295–296. (c) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *Ibid.* **1978**, *100*, 7577–7585.

(19) The nature of these decomposition products is under further investigation.

(20) Formation of a light-absorbing decomposition product limits the overall percent conversion in these irradiations.

Table II. Rate Constants and Activation Parameters for the Arene Exchange Reactions, $(C_5Me_5)Rh(PMe_3)(Ar)H + Ar'H \rightleftharpoons (C_5Me_5)Rh(PMe_3)(Ar')H + ArH$

Ar	Ar'	T, K	k,[a] s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
C_6H_5	C_6D_5	299.4	$(6.22 \pm 0.20) \times 10^{-7}$	26.03 ± 0.02
		324.9	$(3.15 \pm 0.08) \times 10^{-5}$	25.93 ± 0.02
		332.1	$(1.06 \pm 0.05) \times 10^{-4}$	25.72 ± 0.03
		345.3	$(6.73 \pm 0.30) \times 10^{-4}$	25.49 ± 0.03
2,5-$C_6H_3Me_2$	C_6D_5	295.5	$(2.67 \pm 0.20) \times 10^{-5}$	23.47 ± 0.04
		306.5	$(1.14 \pm 0.04) \times 10^{-4}$	23.49 ± 0.02
		313.7	$(4.50 \pm 0.12) \times 10^{-4}$	23.20 ± 0.02

[a] Errors are expressed as standard deviations of a least-squares fit of k to a decaying exponential.

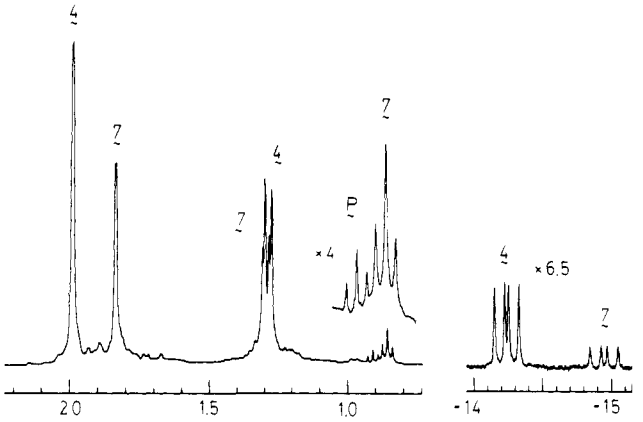


Figure 2. ^1H NMR spectrum of **7** in THF-d_8 at −40 °C (P = propane).

these two complexes is produced upon heating **2** to 60 °C in toluene for several hours, suggesting that this represents the thermodynamic distribution of the isomers of **6** (vide infra). Treatment of this mixture with $CHBr_3$ produces a 2:1 meta:para ratio of $(C_5Me_5)Rh(PMe_3)(tolyl)Br$ isomers.

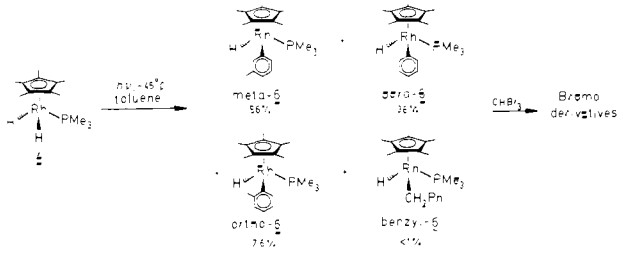
Due to the thermal instability of the alkyl hydrido derivatives similar to **1**, any attempt to activate alkane C–H bonds must be carried out at temperatures below −20 °C, where the products will be stable. In order to be able to directly observe the alkyl hydride adduct, a solvent that would evaporate below −20 °C (propane) was employed so that the excess solvent could be removed without destroying the oxidative addition product. Irradiation of **4** in liquid propane at −55 °C followed by removal of the propane at −40 °C (10^{-4} mm) and addition of THF-d_8 (−78 °C) produced the ^1H NMR spectrum shown in Figure 2. The triplet at δ 0.840 is assigned to the terminal methyl group in $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)H$, **7**. Doublets for the C_5Me_5 ring and PMe_3 ligand were observed at δ 1.820 (J = 1.8 Hz, 15 H) and 1.278 (J = 9 Hz, 9 H), as was a doublet of doublets for the hydride at δ −14.963 (J = 50, 32 Hz, 1 H). The four methylene hydrogens, being diastereotopic and coupled to rhodium, phosphorus, and each other, were not observed directly, although irradiation of the δ 1.20–1.45 region with a decoupling oscillator caused the triplet at δ 0.840 to collapse to a singlet. Additional evidence for the formulation of **7** as the *n*-propyl derivative includes the formation of propane at the expense of **7** upon warming to −15 °C and the conversion to the bromo derivative $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)Br$ upon addition of $CHBr_3$ at −78 °C. The latter was identified by comparison of its ^1H and ^{13}C NMR spectral data with that of an authentic sample.

B. Competition Experiments. The thermodynamic and kinetic selectivity of the coordinatively unsaturated species **5** for several substituted arenes and alkanes was investigated by generating **5** in mixtures of two solvents. The thermodynamic selectivity for different arenes was measured by heating **2** in a mixture of benzene and toluene, *o*-xylene, *m*-xylene, or *p*-xylene, the ratios of which were chosen so as to give approximately equal amounts of **2** and the aryl hydride complex (eq 3). After equilibration at 50 °C for 48 h, the solvent was removed (25 °C) and the products

Table III. Equilibrium Constants for the Arene Exchange Reactions at 50 °C, $(C_5Me_5)Rh(PMe_3)(Ar)H + Ar'H \rightleftharpoons (C_5Me_5)Rh(PMe_3)(Ar')H + ArH$

Ar	Ar'	[Ar'H]/[ArH]	[RhAr]/[RhAr']	K_{eq}
C_6H_5	tolyl	1.96	1.38	0.37
	o-xylyl	3.02	2.52	0.13
	m-xylyl	6.39	1.90	0.083
	p-xylyl	18.2	3.22	0.017

Scheme I



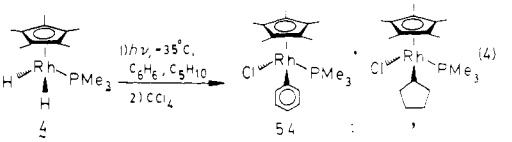
analyzed by ^1H NMR spectroscopy. The ratios of arenes used, products observed, and calculated values for K_{eq} are given in Table III.

$$(C_5Me_5)Rh(PMe_3)(C_6H_5)H + \underset{\mathbf{2}}{} \quad Ar\text{–}H \overset{K_{eq}}{\rightleftharpoons} (C_5Me_5)Rh(PMe_3)(Ar)H + C_6H_6 \quad (3)$$

As mentioned earlier, only the meta and para isomers of **6** were observed with toluene. Similarly, only the 3,4-xylyl, 3,5-xylyl, and 2,5-xylyl (**3**) isomers were observed upon equilibration of **2** with *o*-xylene, *m*-xylene, and *p*-xylene, respectively. The K_{eq} trend shows a distinct preference of **5** for oxidative addition to unhindered, less electron rich arenes. In no case (even *p*-xylene) is activation of the weakest C–H bond, i.e., the benzylic C–H bond, observed under conditions of thermodynamic control.

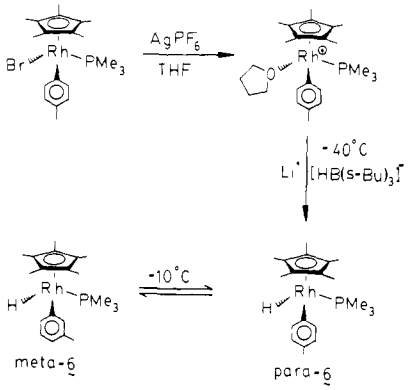
However, if **5** is generated by irradiation of **4** at low temperature, then the possibility of observing the kinetic selectivity of **5** exists. Indeed, irradiation of **4** in toluene at −45 ± 5 °C for 35 min (20% completion) produces a mixture of the isomers of **6** (Scheme I) that are analyzed by conversion to the bromo derivatives by addition of $CHBr_3$. The *m*-**6** and *p*-**6** isomers were found to be predominate, as evidenced by an isomeric distribution of 56% meta and 36% para in the $(C_5Me_5)Rh(PMe_3)(tolyl)Br$ mixture. However, the ortho isomer was now found in 7.6% yield and a trace (<1%) of the benzyl isomer could be detected. The latter possesses an ABXY pair of resonances characteristic of the diasteriotopic CH_2 group that are identical with those in an authentic sample of the bromide. This product distribution corresponds to only minor differences between the barriers to reaction ($\Delta G^{\ddagger}$) at the different sites, with the barriers for formation of *p*-**6**, *o*-**6**, and benzyl-**6** being 0.15, 0.9, and 2–3 kcal/mol higher than the barrier for formation of *m*-**6**.

The photolysis of **4** at low temperature also permits measurement of the kinetic selectivity of **5** for alkanes vs. arenes. Irradiation of **4** in a 5.1:1.0 ratio of cyclopentane:benzene at −35 ± 5 °C for 20 min (35% completion) followed by addition of CCl_4 at −78 °C produced a 0.94:1.00 ratio of the alkyl and aryl products (eq 4). This product ratio corresponds to a 5.4:1 preference of **5** toward benzene over cyclopentane, or a difference in the two barriers to reaction of 0.8 kcal/mol.

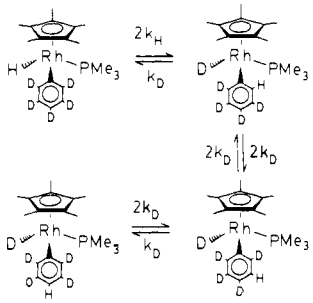


Finally, the kinetic selectivity between benzene and *p*-xylene was measured by a similar irradiation of **4** in a 1:5 mixture of benzene:*p*-xylene at 10 °C. The observed product ratio, measured

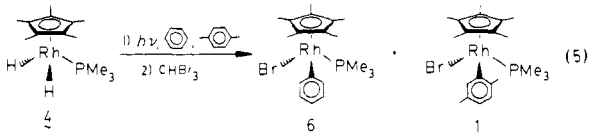
Scheme II



Scheme III



by conversion of **2** and **3** to their bromo derivatives with $CHBr_3$, was 1.2:1, which corresponds to a 6:1 selectivity for benzene over *p*-xylene (eq 5).



(5)

C. Isomerization of Aryl Hydrides. While the aryl hydride complexes **2** and **6** appear more thermally stable than the alkyl hydride complexes **1** and **7**, more informative experiments showed in fact that **2** and **6** were rapidly undergoing an isomerization process as if rapid and reversible intramolecular reductive elimination and oxidative addition were occurring. The first evidence for this process was provided by the reduction of $(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})Br$ with $Li^+[HB(sec\text{-}Bu)_3]^-$ in THF.[12] ^1H NMR spectral analysis of the products showed a 2:1 (thermodynamic) ratio of *m*-**6**:*p*-**6**. As the reaction had been carried out at temperatures below that required for the exchange of toluene with other arenes, the isomerization must have occurred intramolecularly at lower temperature. Proof for this hypothesis was obtained by treatment of $(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})Br$ with $Ag^+[PF_6]^-$ in THF-d_8, followed by addition of $Li^+[HB(sec\text{-}Bu)_3]^-$ at −40 °C. Low-temperature (−25 °C) ^1H NMR spectroscopy showed the conversion of the initial THF complex into *p*-**6**. Upon warming to −10 °C, *p*-**6** was then observed to slowly equilibrate with *m*-**6** (Scheme II).

The isomerization was found to proceed by a [1,2] shift process, as opposed to [1,3], [1,4], or random shifts, by monitoring the low-temperature behavior of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$, **2**-$d_5$. The complex was prepared at −40 °C in the same fashion as *p*-**6**. Upon warming to −14.5 °C, the initially vacant aromatic region of the ^1H NMR spectrum showed the growth of the isomer of **2**-d_5 with a hydrogen in the ortho position of the phenyl ligand. The isomer of **2**-d_5 with the hydrogen in the meta position grew in more slowly, followed by the para isomer (Figure 3A), until the equilibrium molar percentages of 46.7:17.9:17.6:16.9% were obtained. The rates for equilibrium can be calculated by using the reaction sequence shown in Scheme III. Only the two rate constants k_H and k_D are involved. The time evolution of the

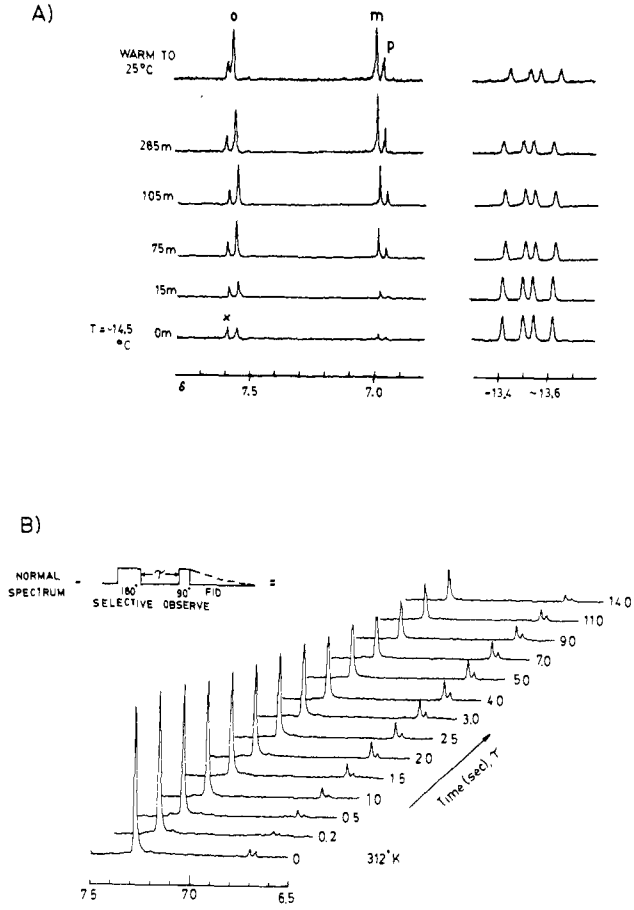


Figure 3. ^1H NMR spectra for the isomerization of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ at −14.5 °C: (A) by direct observation at −14.5 °C (the peak marked X is due to free benzene) and (B) by spin saturation transfer at 39 °C.

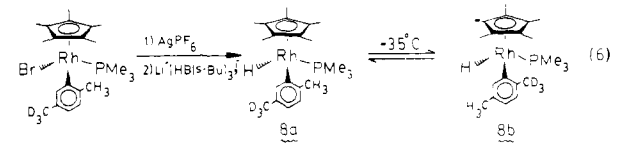
Table IV. Rate Constants for the Degenerate Isomerization of 3

T, K	k, s^{-1}	method[a]
238.5	$(2.492 \pm 0.090) \times 10^{-4}$	direct
285.4	0.0803 ± 0.0162	SST
292.2	0.1839 ± 0.0140	SST
299.3	0.4215 ± 0.0482	SST
306.2	0.6014 ± 0.0317	SST

[a] Direct = use of CD_3 label in **8a** to measure rate; SST = use of spin saturation transfer to measure rate.

complexes can be simulated by using the rate constants $k_H = (6.0 \pm 1.2) \times 10^{-5}\ s^{-1}$ and $k_D = (1.6 \pm 0.3) \times 10^{-4}\ s^{-1}$. The equilibrium isotope effect, k_H/k_D, is 0.37 and reflects the greater Rh–H bond strength. The above value for k_H gives a value of $\Delta G^{\ddagger}$ (−15 °C) of 20.0 kcal/mol for the isomerization of **2**. The [1,2] shifts in **2**-d_5 were also monitored by spin saturation transfer NMR spectroscopy at 39 °C. Irradiation of the ortho resonance (180° selective pulse) followed by a nonselective 90° pulse after a 0–15-s delay showed magnetization transfer from the ortho to the meta sites (Figure 3B).

The rate of the [1,2] shift in **3** was measured accurately over a 68 °C temperature range, allowing determination of the activation parameters for this degenerate isomerization. The rate was measured directly at 238.5 K by preparing complex **8a** (eq 6) from



(6)

the corresponding bromide with use of $Ag^+[PF_6]^-$ in THF-d_8 followed by $Li^+[HB(sec\text{-}Bu)_3]^-$. The methyl ^1H resonance at δ

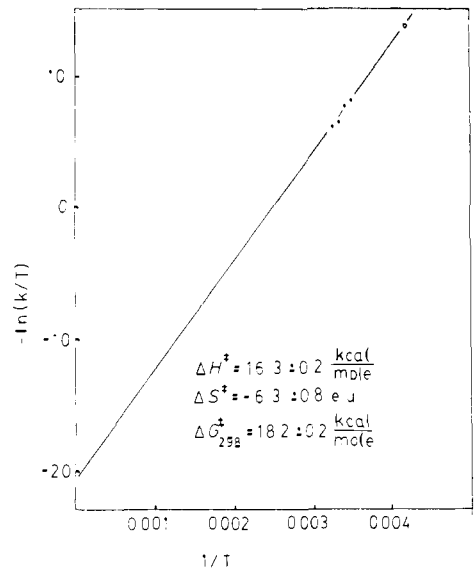
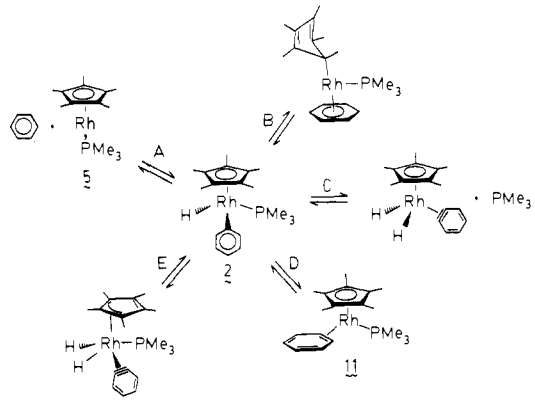


Figure 4. Eyring plot for the isomerization of **3**. X = spin saturation transfer, O = direct observation.

Scheme IV



2.214 was observed to slowly equilibrate with the methyl resonance at δ 2.121 in **8b**, where the rate of approach to equilibrium is governed by eq 7 (Table IV).

$$2\frac{[8a]}{[8a]_0} - 1 = e^{-2kt} \qquad (7)$$

The rate of isomerization in the 285 to 306 K region was measured by spin saturation transfer between the two singlets for the methyl groups in **3** (Table IV).[21] In this temperature range, longitudinal relaxation (T_1) is competitive with the isomerization process. The Eyring plot for these data is shown in Figure 4 and gives $\Delta H^{\ddagger} = 16.3 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -6.3 \pm 0.8$ eu for the isomerization of **3**. The negative value for $\Delta S^{\ddagger}$ indicates an ordered transition state for the isomerization process.

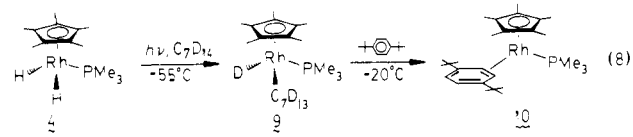
D. Mechanism of Isomerization: The η^2-Arene Complex. The complexity of the isomerization process in which three bonds are broken (C′–H′, Rh–H, Rh–C) and three bonds are formed (C–H, Rh–H′, Rh–C′) can be accommodated by several different reaction mechanisms. However, the selectivity of the isomerization allows many of these mechanisms to be discarded, as will now be discussed.

The extreme facility of the isomerization at room temperature in these aryl hydride complexes ($\Delta G^{\ddagger} = \sim 18$ kcal/mol) along with the observation of arene exchange only at higher temperatures ($\Delta G^{\ddagger} = \sim 26$ kcal/mol) rules out an isomerization process involving a reversible reductive elimination of the aryl hydride complex for generation of free arene and **5** (Scheme IV, mechanism A). Another possible mechanism is shown in Scheme IV, mechanism B, in which reductive elimination is concomitant with the formation of an η^6-arene ligand and the slipping of the η^5-C_5Me_5 ligand to η^1 coordination.[22a] This mechanism can be ruled out on the basis that the isomerization was shown to occur by a series of [1,2] shifts in **2**-d_5, not a random shift as would be expected for mechanism B in Scheme IV.

A third mechanism that does take into account the [1,2] nature of the isomerization involves the intermediacy of a benzyne complex (Scheme IV, mechanism C) similar to that proposed by Marks.[22b] As written, the reaction involves the dissociation of the PMe_3 ligand in order to avoid a 20-electron intermediate. However, addition of $P(CD_3)_3$ to complex **2** at 25 °C results in only slow exchange over several hours, during which time the isomerization has occurred many thousands of times. Consequently, mechanism C, Scheme IV, can be discarded.

Two mechanisms remain to be considered that are consistent with the above experiments. The simplest of these involves the direct reversible formation of an η^2-arene complex during the reductive elimination from the aryl hydride complex (Scheme IV, mechanism D). The other mechanism is a modification of C, Scheme IV, in which a benzyne complex is formed by displacing the η^5-C_5Me_5 ring to η^3 coordination, rather than dissociating PMe_3 (Scheme IV, mechanism E). The best evidence pointing toward the isomerization occurring by way of mechanism D, Scheme IV, is the direct observation of the unstable η^2-arene complex formed by the reaction of **5** with p-$C_5H_4(t\text{-}Bu)_2$ at low temperature. Similar such η^2-arene complexes have recently been observed.[23]

The experiment was performed by irradiating a solution of **4** and p-$[C_6H_4(t\text{-}Bu)_2]$ in perdeuteriomethylcyclohexane at −55 ± 5 °C, producing the complex $(C_5Me_5)Rh(PMe_3)(C_7D_{13})D$ (**9**) identified by its ^1H NMR resonance at δ 1.809 (d, J = 2.3 Hz) for the C_5Me_5 ligand (cf. **7**; the PMe_3 resonance was obscured by residual protons in the solvent). As the temperature was raised to −20 °C, the signal at δ 1.809 decayed as new resonances appeared at δ 6.355 (s, 2 H), 3.879 (dd, J = 4.9, 3.0 Hz, 2 H), and 1.816 (d, J = 2.5 Hz, 15 H) attributable to the η^2-arene complex $(C_5Me_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(t\text{-}Bu)_2]$, **10**. The singlet at δ 6.355 is assigned to the aromatic hydrogens opposite the site of η^2 coordination. The doublet of doublets at δ 3.879 are assigned to the aromatic hydrogens at the site of η^2 coordination, coupled to both rhodium and phosphorus (eq 8).



Further evidence for the formulation of **10** as an η^2-arene complex arises from the observation of partial spin saturation transfer from the free di-*tert*-butylbenzene resonance at δ 7.211 to the coordinated aromatic resonances of **10** at δ 6.355 and 3.879 at −10 °C. The intensity of the latter two peaks decrease markedly upon irradiation of the δ 7.211 resonance, indicating that the free arene is exchanging with the coordinated arene at a rate competitive with relaxation (T_1) of the aromatic protons.

The equilibrium between **10** and the species in which an aromatic C–H bond has undergone oxidative addition apparently lies heavily in favor of **10**. This is not unexpected, however, as it has already been seen that the stability of the aryl hydride complexes decreases upon going from phenyl to p-xylyl to p-diisopropyl.

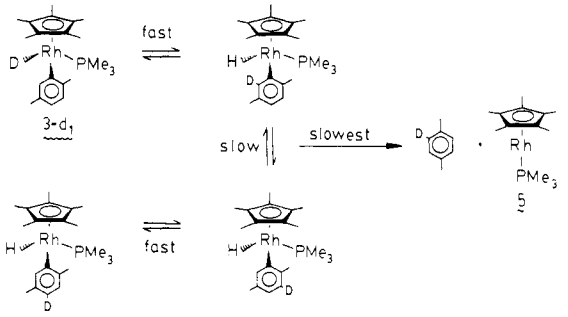
An interesting comparison can be made between these aryl hydride/η^2-arene interconversions and a vinyl hydride/η^2-olefin interconversion. The complex $(C_5Me_5)Rh(PMe_3)$-$(\overline{C{=}CH{-}CH_2{-}CH_2{-}CH_2})Br$ can be converted to the THF complex by treatment with $Ag^+[PF_6]^-$ in 3:1 THF-d_8/C_6D_6.

(21) Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406–410. Morris, G. A.; Freeman, R. *Ibid.* **1978**, *29*, 433–462.

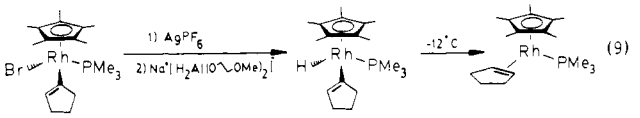
(22) (a) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793–794. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(23) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305–306. Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884–891.

Scheme V



$(C_5Me_5)Rh(PMe_3)(\overline{C{=}CH{-}CH_2{-}CH_2{-}CH_2})H$ can be observed upon addition of $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ at low temperature (Table I, eq 9). By warming the sample to −12 °C,



(9)

the ^1H NMR spectrum shows the direct conversion to the olefin complex, $(C_5Me_5)Rh(PMe_3)(\overline{CH{=}CH{-}CH_2{-}CH_2{-}CH_2})$. The same product is formed exclusively upon addition of the $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ to the bromide complex at 25 °C in C_6D_6 solution. If reductive elimination produced free cyclopentene and **5**, then reaction of **5** with the C_6D_6 solvent should have provided **2**-d_6. The observation of the cyclopentene complex, even in C_6D_6, suggests that the reductive elimination directly produces the olefin complex. The situation is similar to that for the aryl hydride/η^2-arene equilibration except that the equilibrium favors the olefin complex over the vinyl hydride complex. This change in the direction of the equilibrium is not so unexpected in light of the disruption of aromaticity that must occur upon formation of an η^2-arene complex.

One final aspect of the η^2-arene complexes pertains to the possibility of fluxional behavior or "ring whizzing" in this intermediate.[24] Were the η^2-arene complexes fluxional, then random shifts would have been observed in the isomerization rather than [1,2] shifts. One can still wonder, however, whether or not *any* fluxional behavior can be detected in these compounds. The only evidence for this type of behavior is provided by preparing $(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)D$ in C_6D_6. At 21 °C, the deuterium equilibrates with the hydrogen in the 6-position with a half-life of a few seconds, and the fluxional reaction to produce the isomers with the hydrogen in the 3 and 4 positions occurs with a half-life of 3 h. At this temperature, the arene exchange reaction to produce free xylene-d_1 and **2**-d_6 occurs competitively ($t_{1/2}$ = 8 h) and irreversibly (Scheme V). Since the fluxionalities in metal–polyene and metal–arene complexes generally have barriers of 5–10 kcal/mol,[24] the barrier to the formation of the aryl hydride complexes from the η^2-arene complexes is probably on the order of 4–8 kcal/mol.

Finally, the normal C_5H_5 derivatives have been found to behave similarly. Hydridic reduction of $(C_5H_5)Rh(PMe_3)(p\text{-tolyl})I$ produces a 2:1 ratio of *m*- and *p*-tolyl hydride complexes.

E. Mechanism and Thermodynamics of C–H Bond Activation. The wide variety of complexes described here and the ability to determine activation parameters for a number of reactions offers a unique opportunity for investigation of the mechanism and thermodynamics of C–H bond activation. Perhaps the most interesting observation in this work is that both arene and alkane C–H bonds can be activated by oxidative addition to a rhodium center competitively, even though the C–H bond energies differ by 6–10 kcal/mol. In order to understand this apparent dilemma between kinetic and thermodynamic considerations, the details of the mechanism of arene oxidative addition should be examined first.

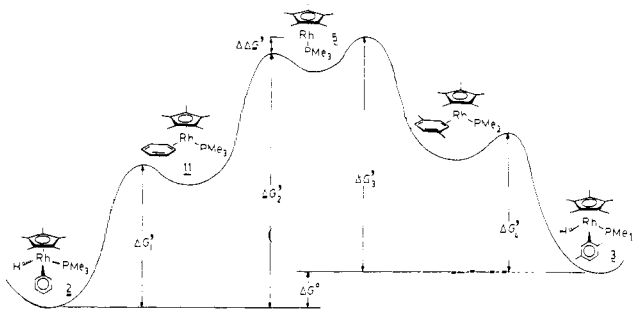
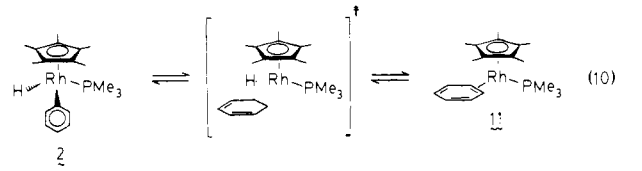


Figure 5. Qualitative free energy diagram for the interconversion of **2** and **3**: $\Delta G^\ddagger_1$(−15 °C) = 20.0 kcal/mol; $\Delta G^\ddagger_2$(25 °C) = 26.0 kcal/mol; $\Delta G^\ddagger_3$(25 °C) = 23.5 kcal/mol; $\Delta G^\ddagger_4$(25 °C) = 18.2 kcal/mol; $\Delta\Delta G^\ddagger$(10 °C) = 1.1 kcal/mol; $\Delta G°$(50 °C) = 2.4 kcal/mol.

In the experiments described earlier, it was demonstrated that the phenyl hydride complex **2** was in rapid equilibrium with the η^2-benzene complex **11** and that only slowly was the complexed benzene liberated from the rhodium metal center. The former process, with a negative entropy of activation, is consistent with an ordered transition state in which the reductive elimination proceeds directly to the η^2-arene complex (eq 10). Dissociation

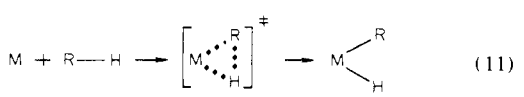


(10)

of the coordinated benzene from **11** to produce free benzene and **5** is slow (requires more energy) and also has an overall entropy of activation that is large and positive as is common for dissociative reactions. The free energy diagram for this process is included on the left side of Figure 5. The readily reversible reductive elimination to form the η^2-arene complex compared to the higher barrier for arene exchange is visible here. The relationship to the less stable *p*-xylyl complex **3** is also shown on the right side of Figure 5, with $\Delta G°$ representing the equilibrium between the two complexes at 50 °C. The 6:1 kinetic selectivity for benzene over xylene by **5** indicates that the highest barrier heights differ by 1.1 kcal/mol.

Although this free energy diagram has been constructed with use of data for the reductive elimination and dissociation of arenes, the principle of microscopic reversibility states that the lowest energy pathway for oxidative addition must also occur on the same potential energy surface; i.e., *oxidative addition of an arene to* **5** *must occur by precoordination of the arene in an* η^2 *fashion.* Thus, the hypothesis forwarded by Chatt and Parshall is well founded, at least for this series of compounds.

The mechanism of alkane activation is probably much simpler, involving the reaction of **5** with the alkane C–H bond in a side-on, concerted fashion (eq 11). The experiments described earlier



(11)

allow the addition of alkane oxidative addition to the free energy diagram for arene activation. From the rate of elimination of methane from **1**, a barrier to reductive elimination of 19.8 ± 0.1 kcal/mol at −17 °C can be calculated by using the Eyring equation. Since both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are known for both the aryl hydride isomerization and arene exchange reactions, these barrier heights ($\Delta G^\ddagger$) can be adjusted to the temperature at which the methane reductive elimination was measured (−17 °C). The difference between the two barrier heights for the reaction of coordinatively unsaturated **5** with benzene or methane ($\Delta\Delta G^\ddagger$) is assumed to be small, on the basis of the following two con-

(24) Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257–266. Browning, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97–101. Vrieze, K.; van Leeuwen, P. W. N. M. *Prog. Inorg. Chem.* **1971**, *14*, 1–63.

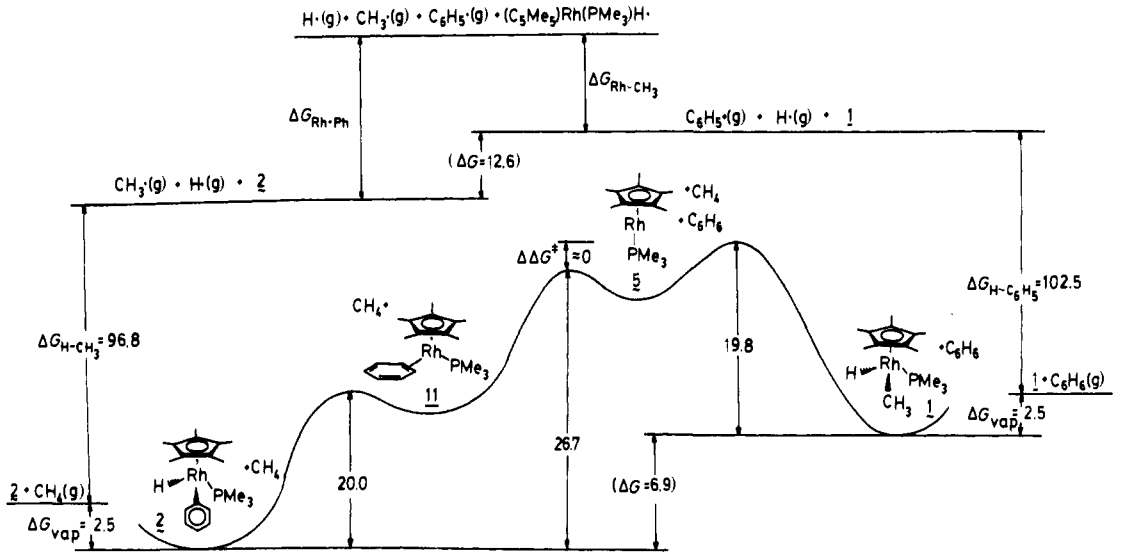


Figure 6. Free energy diagram for arene and alkane activation at −17 °C. All values are in kcal/mol. Values in parentheses are derived from the other measured numbers.

siderations. First, the competition between benzene and cyclopentane for **5** showed a slight preference for benzene ($\Delta\Delta G^{\ddagger}$ = 0.8 kcal/mol). Second, the activation of propane C-H bonds showed a preference for primary C-H bonds over secondary, which would lead to the expectation that methane C-H bonds should be slightly preferred over cyclopentane C-H bonds. The value of $\Delta\Delta G^{\ddagger}$ is probably only reduced from 0.8 kcal/mol for cyclopentane to near zero for methane, as the C-H bonds in methane are substantially stronger than those at a primary or secondary center.[25] The resulting free energy diagram for benzene, methane, and **5** is shown in Figure 6.

Some interesting conclusions can be drawn from the diagram. First, it is seen that reaction of **5** with both arene and alkane is competitive but that while the rate-determining step toward alkane activation involves a 3-center transition state, the rate-determining step for arene activation involves coordination of **5** to the arene π system. The two rate-limiting transition states are quite different, and it is apparent that the barrier to reaction with arene has little to do with the arene C-H bond strength. The well-documented kinetic selectivity of metal complexes toward electron-deficient arenes[18c] can also be accounted for in terms of better coordination to the arene π system in the electron-deficient arene. Also, the kinetic selectivity of **5** for benzene and *p*-xylene (6:1) can be interpreted as reflecting the number of double bonds available for coordination (6 for benzene, 2 for *p*-xylene), whereas the thermodynamic selectivity (60:1) reflects steric hindrance in the aryl hydride complexes.

Second, the diagram shows that the barrier to reductive elimination from the alkyl hydride is comparable to the barrier to reductive elimination from the aryl hydride. In the latter case, however, the arene remains coordinated to the metal, giving an overall macroscopically observable stability to the aryl hydride complexes. This feature may also be true of other known aryl hydride complexes.

The third conclusion that can be drawn from these studies requires the formation of the Born-Haber cycle shown in the perimeter of Figure 6. Starting with the lowest energy state for the system of **2** plus methane dissolved in benzene, the methane is first evaporated from solution ($\Delta G°$(−17 °C) = 2.5 kcal/mol)[26] and the methane C-H bond cleaved homolytically ($\Delta G°$(−17 °C) = 96.8 kcal/mol.[27] Starting instead with the right-hand side of the diagram with **1** dissolved in benzene, the benzene is first evaporated ($\Delta G°$(−17 °C) = 2.5 kcal/mol)[28] and the phenyl-hydrogen bond cleaved ($\Delta G°$(−17 °C) = 102.5 kcal/mol).[29] The two states arrived at by these constructions differ by the difference in free energy ($\Delta\Delta G°$) between the rhodium-phenyl and rhodium-methyl bond. If it is assumed that the entropy of cleavage of these two bonds is identical, and that the heats of solution and sublimation of **1** and **2** are the same,[30] then the difference between the rhodium-phenyl and the rhodium-methyl bond strengths ($\Delta\Delta H°$(−17 °C)) is calculated to be 12.6 ± 1.0 kcal/mol. This is substantially larger than the difference between the benzene and methane C-H bond strengths ($\Delta\Delta H°$ = 6 kcal/mol).[27,29] It is not clear whether this increased difference is due to a stronger rhodium-phenyl or a weaker rhodium-methyl bond primarily. While the combined error in these thermodynamic measurements and estimated quantities is moderately large, it is clear that the metal-phenyl bond must be substantially stronger than the metal-methyl bond. The higher metal-phenyl bond strength also indicates that there is an overall thermodynamic preference for arene activation over alkane activation in addition to the kinetic effect discussed earlier.

Conclusion

The activation of C-H bonds in arenes by the coordinatively unsaturated intermediate $(C_5Me_5)Rh(PMe_3)$ has been shown to proceed by way of the initial rate-determining formation of an η^2-arene complex. The latter rapidly and reversibly undergoes an intramolecular oxidative addition reaction to produce stable but labile aryl hydride complexes. Alkanes on the other hand undergo oxidative addition to give alkyl hydride complexes that are thermally unstable above −20 °C. The transition states for alkane and arene activation are energetically similar but structurally very different, the latter actually resembling the transition state for coordination of a metal to an olefin. A large difference

(25) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976.

(26) With use of data from Evans (Evans, E. D.; Battino, R. J. *J. Chem. Thermodyn.* **1971**, *3*, 753–760) $\Delta E°_{vap}$ = 1.737 kcal/mol, $\Delta S°_{vap}$ = −0.7 eu. Since $\Delta H° = \Delta E° + \Delta(PV) = \Delta E° + \Delta nRT$ = 2.33 kcal/mol, ΔG_{vap}(256 K) = 2.5 kcal/mol.

(27) With use of data from ref 25 for $CH_4(g) = CH_3·(g) + H·(g)$, $\Delta H°$ = 104.3 kcal/mol and $\Delta S°$ = 29.3 eu. Therefore, $\Delta G°$(256 K) = 96.8 kcal/mol.

(28) With use of data from Karapet'yants (Karapet'yants, M. Kh. "Thermodynamic Constants of Inorganic and Organic Compounds"; Humphrey Science Publishers: Ann Arbor, London, 1970) for C_6H_6 (l) → C_6H_6 (g), $\Delta H°_{vap}$ = 8.10 kcal/mol, $\Delta S°_{vap}$ = 22.0 eu. Therefore, ΔG_{vap}(256 K) = 2.5 kcal/mol.

(29) With use of data from ref 25 for C_6H_6 (g) = $C_6H_5·$ (g) + H· (g), $\Delta H°$ = 110.8 kcal/mol, $\Delta S°$ = 32.5 eu. Therefore, ΔG(256 K) = 102.5 kcal/mol.

(30) It is assumed that the values for ΔG sublimation are equal for **1** and **2**. Cf.: Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67–71. Evans, A.; Mortimer, C. T.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *85*, 101–103; **1974**, *72*, 295–297. Ashcroft, S. J.; Mortimer, C. T. *J. Organomet. Chem.* **1970**, *24*, 783–786. Mortimer, C. T.; McNaughton, J. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1265–1267. Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Livingston, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613–1618. Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124–7126.

was found between the metal–aryl and metal–alkyl bond energies in these compounds.

These results have implications with regard to arene/alkene selectivities. Other complexes with similar geometries such as $(C_5Me_5)Ir(PMe_3)(R)H$ and $(C_5Me_5)Ir(CO)(R)H$ also show a modest selectivity between arenes and alkanes, perhaps for the same reasons as outlined here. On the other hand, more sterically crowded complexes such as Cp_2WRH,[31] $CpMo(DMPE)H_3$,[32] and $(C_5Me_5)_2LuR$[6d] show a much higher selectivity for benzylic and alkane C–H bonds that can be attributed to the difficulty in forming η^2-arene complexes. Further examinations of other systems that are known to activate arene C–H bonds are underway and will continue to address the importance of arene coordination in C–H activation.

Experimental Section

Most of the rhodium complexes described in this paper are extremely sensitive toward oxygen and halogenated solvents. All operations were performed under a nitrogen atmosphere, either on a high vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. dri-lab which was free of halogenated solvents. Rhodium trichloride (42.9% Rh) was obtained as a generous loan from Johnson Matthey, Inc. The syntheses of the starting materials with the general formula $(C_5Me_5)Rh(PR'_3)RX$ have been described elsewhere.[16]

Tetrahydrofuran (THF) and diethyl ether were distilled from dark purple solutions of sodium benzophenone ketyl under vacuum. Aliphatic and aromatic hydrocarbon solvents were vacuum distilled from dark purple solutions of potassium benzophenone ketyl containing tetraglyme. Before distillation, aliphatic hydrocarbon solvents were stirred for 48 h over two portions of concentrated H_2SO_4, washed successively with saturated $KMnO_4$ in 10% H_2SO_4, three portions of H_2O, and one portion of saturated Na_2CO_3, and dried over $CaCl_2$. Cyclopentene was vacuum distilled (25 °C (10^{-4} mm)) from calcium hydride after three freeze–pump–thaw cycles. Bromoform was purified by fractional crystallization and was degassed (3 cycles) before use. Carbon tetrachloride was vacuum distilled (25 °C (10^{-4} mm)) from P_2O_5 and degassed (3 cycles) before use. $Ag^+[PF_6]^-$ was obtained from Strem Chem. Co. $Li^+[HBEt_3]^-$, $Li^+[DBEt_3]^-$, and $Li^+[HB(sec\text{-}Bu)_3]^-$ were obtained from Aldrich Chemical Co. as 1 M solutions in THF. $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ was obtained from Aldrich Chemical Co. as a 70% (w:w) toluene solution. It was occasionally used as such but was more often used as a 0.5 N solution, which was prepared by diluting 7 mL of the commercially available solution to 100 mL with toluene. 1,4-Diisopropylbenzene and 1,4-di-*tert*-butylbenzene were obtained from Aldrich Chemical Co. The former was vacuum distilled (50 °C (10^{-4} mm)) from a small amount of CaH_2, and the latter was used without further purification. Propane was obtained from J. T. Baker Chemical Co. and was purified by three freeze (−196 °C)–pump–thaw (−30 °C) cycles before use.

Low temperatures were maintained with use of liquid nitrogen (LN_2, −196 °C), CH_3OH/LN_2 (−95 °C), acetone/dry ice (−78 °C), $CH_3OH/H_2O(45:55)/LN_2$ (−40 C), $CH_3OH/H_2O(30:70)/LN_2$ (−20 °C), and ice water (0 °C) baths. Other low temperatures were maintained by adding LN_2 to methanol. Flash filtration chromatography was performed as previously described.[16]

Routine ^1H NMR spectra were recorded on a Varian EM-390 NMR spectrometer. High-field ^1H (400.13 MHz) and ^{31}P (162.00 MHz) NMR spectra were recorded on a Bruker WH-400 NMR spectrometer. ^1H NMR spectra are reported in units of δ (ppm downfield from internal tetramethylsilane) but were most often measured relative to residual ^1H resonances in the deuterated solvents, C_6D_6 (δ 7.150), THF-d_8 (δ 1.730), $CDCl_3$ (δ 7.261), or relative to internal Dow Corning silicone lubricant at δ 0.286 in C_6D_6 or δ 0.102 in THF-d_8. ^{31}P NMR spectra are reported in units of δ (ppm downfield from a coaxially mounted sealed capillary of 30% H_3PO_4). The temperature for NMR experiments was regulated by a Bruker BVT-1000 temperature control unit (±0.1 °C). Temperatures were calibrated by using standard methanol calibration samples obtained from Wilmad Glass Co. C_6D_6 and THF-d_8 (Stohler Isotope Co.) were vacuum distilled (25 °C (10^{-4} mm)) from sodium benzophenone ketyl and stored in glass ampules fitted with Teflon stopcocks. Cyclohexane-d_{12} (Stohler) and methylcyclohexane-d_{14} (Merck Co.) were vacuum distilled (25 °C (10^{-4} mm)) from potassium benzophenone ketyl containing a very small amount of tetraglyme. $CDCl_3$ (Aldrich) was vacuum distilled from P_2O_5 (25 °C (10^{-4} mm)).

Electron impact mass spectral analyses were conducted on a VG 7035 gas chromatograph/mass spectrometer at 5, 20, or 70 eV. Gas chromatography was performed by using a Hewlett-Packard 5710A Gas Chromatograph with a 10 ft × $^1/_8$ in. 5% SE-30/Chromosorb WAW column (150 °C, 20 mL/min). Low-temperature photolysis reactions were conducted with use of a low-pressure mercury lamp (Hanovia No. 831691). The reaction vessel consisted of an NMR tube connected to a ground glass joint with a side arm attached. The side arm was fitted with a rubber septum to permit the introduction of reagents, and the ground glass joint was attached to a stopcock adapter to permit connection to a vacuum line. The photolysis was performed through a methanol filled Dewar flask which had 1 in. circular quartz windows. The temperature of the vessel was maintained by adding LN_2 to the methanol which was efficiently stirred by a small magnetic stir bar at the bottom of the Dewar flask. For quenching experiments, the quenching reagent was slowly added via syringe, making sure that the reagent had sufficient time to cool to reaction temperature as it flowed down the walls of the NMR tube.

Preparation of $(C_5Me_5)Rh(PMe_3)H_2$ (4). This compound has been recently reported by Maitlis.[33] $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (2.6 mL of 0.5 N solution in toluene, 5 equiv) was added to a suspension of $(C_5Me_5)Rh(PMe_3)X_2$ (X = Cl, Br, I) (0.26 mmol) in benzene (5 mL). The mixture was stirred for 15 min at 25 °C and the volatiles removed to give a milky residue. The gum was dissolved in THF (0.5 mL), hexane (2.5 mL) added to precipitate the salts, and the mixture flash chromatographed on SiO_2 (5:1, v:v, hexane/THF). Removal of the volatiles under vacuum (25 °C (10^{-2} mm)) afforded a pale yellow gum (66 mg, 81%) which resisted all recrystallization attempts. Since **4** is extremely air sensitive and mildly light sensitive, it was generally used immediately.

Preparation of Aryl Hydrides from $(C_5Me_5)Rh(PMe_3)(Ar)X$ (X = Cl, Br). $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (0.5 mL of a 0.5 N toluene solution, 0.125 mmol) was added to a THF solution (5 mL) of $(C_5Me_5)Rh(PMe_3)(C_6H_5)X$ (X = Cl or Br, 0.120 mmol). The THF was removed under vacuum to leave an orange gum which gradually turned to a straw yellow color over a period of 15–30 min. The residue was dissolved in 0.15 mL of THF, diluted to 1 mL with hexane, and then flash chromatographed on a small column (15 × 20 mm) of silica gel with use of 5:1 (v:v) hexane/THF as eluent. Removal of the solvent (25 °C (10^{-1} mm)) gave a pale yellow gum which slowly solidified upon standing. The product is extremely soluble in all solvents with which it does not react. The reaction is very clean and produces **2** in quantitative (NMR) yield before chromatography. However, **2** is mildly reactive toward all chromatography adsorbents which have been examined and purification results in an unavoidable loss of material. When flash chromatographic techniques with short columns and rapid elution rates are used, **2** can be isolated in yields as high as 85%.

The reaction is general and was used to prepare a large variety of aryl hydride complexes (Table I). The products, which were obtained as thick, pale yellow gums, existed as equilibrium mixtures of isomers (see text) containing activated C–H bonds in all possible aryl positions. Most of these products are more sensitive than **2** toward chromatography. The reaction can also be accomplished by using a wide variety of other hydride reagents ($Li^+[HBEt_3]^-$, $Li^+[HB(sec\text{-}Bu)_3]^-$, $K^+[HB(O\text{-}i\text{-}Pr)_3]^-$) and likewise only proceeds in the gum phase. $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ is the best reducing agent because the aluminum-containing byproducts are not eluted during chromatography.

Preparation of Aryl Hydrides from $(C_5Me_5)Rh(PMe_3)(Ar)I$. $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (0.21 mL of a 0.5 N toluene solution, 0.0525 mmol) was added to a THF solution (1 mL) of $(C_5Me_5)Rh(PMe_3)(C_6H_5)I$ (27 mg, 0.0518 mmol). The color of the reaction mixture gradually changed from orange to pale yellow over 35 min. The solvent was removed (25 °C (10^{-2} mm)) and the residue was flash chromatographed as above. Removal of the solvent afforded a yellow semisolid (13 mg, 60%). The product obtained from the reduction of the iodide complex was identical with that obtained from the chloride and bromide complexes except that it was contaminated by 5–10% of the dihydride, **4**. The separation of **2** and **4** by chromatography could not be effectively accomplished so that the reductions of iodide complexes, although conveniently performed in solution, are not of much preparative value.

Preparation of Aryl Hydrides via THF Complexes. A THF-d_8 solution (0.4 mL) of $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ (20 mg, 0.042 mmol) was added to $Ag^+[PF_6]^-$ (10.6 mg, 0.0419 mmol). The mixture was stirred for 2 min and then filtered into an NMR tube through a small wad of cotton which had been tightly wedged into a pipet. An NMR spectrum of the burgundy solution exhibited resonances which were assigned to the THF adduct, $[(C_5Me_5)Rh(PMe_3)(C_6H_5)(THF\text{-}d_8)]^+$ (Table I). Attempts to isolate this complex by slowly removing the THF-d_8 and adding

(31) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35.
(32) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Chem. Commun.* **1981**, 186–187.
(33) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003–2008.

hexane to precipitate the salt resulted in decomposition. Addition of $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (15 μL of a 70% toluene solution, 0.053 mmol) at 25 °C instantly produced a pale yellow solution which showed two sets of rhodium hydride resonances at δ −13.858 (dd, J = 49.6, 32.6 Hz) and −14.289 (dd, J = 42.6, 30.1 Hz) in a 9:2 ratio, respectively. Flash chromatography as before and evaporation of the solvent afforded a pale yellow gum which consisted of a 9:1 mixture of **2** and **4**. Other hydride reagents ($Li^+[HBEt_3]^-$, $K^+[HB(O\text{-}i\text{-}Pr)_3]^-$) were equally capable of reducing the THF adduct but were accompanied by the formation of dihydride **4**.

Arene Exchange Reactions. A solution of freshly prepared **2** (11 mg, 0.028 mmol) in 0.4 mL of C_6D_6 (100.0% D) was carefully freeze–pump–thaw degassed and sealed under vacuum. The sample was heated at 60 °C for 16 h, and the volatiles were then distilled (25 °C (10^{-3} mm)) into one arm of a short-path vacuum distillation apparatus. The mass spectrum (5 eV) showed small peaks at m/e 78 (C_6H_6) and 79 (C_6H_5D, 14% of m/e 78) as well as very large peaks at m/e 83 and 84 which were observed in the pure C_6D_6. No peaks were seen at m/e 80, 81, or 82. The peak at m/e 79 corresponded to a 93:7 mixture of C_6H_6/C_6H_5D after correction for the natural abundance of ^{13}C. The nonvolatiles from the reaction were dissolved in C_6H_6 (0.4 mL), carefully freeze–pump–thaw degassed, sealed under vacuum, and heated at 60 °C for 16 h. The nonvolatile portion of this reaction exhibited an NMR (C_6D_6) spectrum that was identical with that of **2**. The NMR sample was evaporated to give a straw yellow gum which was converted to a 2:1 mixture of *m*-**6** and *p*-**6** by heating the residue in a sealed tube containing toluene (0.4 mL).

The arene exchange reaction is quite general and was used to prepare a wide variety of metal-activated aryl hydride complexes. As benzene is thermodynamically favored over most other arenes (Table III), it was usually necessary to either employ very large excesses of the substituted arene or else replace the solvent with fresh solvent during the course of the reaction in order to obtain complete exchange.

Formation of Aryl Hydride Complexes by Photolysis of 4. A solution of freshly prepared **4** (12 mg, 0.038 mmol) in C_6D_6 (0.5 mL) was placed in an NMR tube and capped with a rubber septum. The solution was irradiated with a low-pressure mercury arc lamp while maintaining the sample at 25 ± 5 °C with an air stream. The photolysis was initially relatively efficient and the evolution of dihydrogen was clearly visible. After 20 min an NMR spectrum revealed that the reaction had proceeded to nearly 60% completion. After 1.5 h of photolysis only traces of the dihydride remained. Although the reaction mixture had darkened considerably the yield of **2** was greater than 90% by NMR. The photolysis of **4** in the presence of arenes is a very general method for the preparation of C–H activated arene complexes. In some instances the photolysis is complicated by a decomposition reaction that darkens the solution to the point where dihydrogen elimination from **4** is extremely inefficient. Prolonged photolysis under these conditions eventually consumes all of **4**, but the final photolysis solution is extremely dark brown and only low yields of impure activated arenes are obtained after flash chromatography. The decomposition appears to be at least partially due to small amounts of impurities in the starting dihydride. Different batches of **4** showed behavior varying from almost no decomposition to extensive decomposition when the reactions were carried out under similar conditions. Lowering the temperature of the photolysis solution and varying the wavelength or intensity of the light did relatively little to reduce the decomposition. The use of dilute solutions (<0.02 M) did substantially reduce the amount of decomposition. By using carefully purified **4** and dilute photolysis solutions a variety of activated arenes were prepared (Table I).

Preparation of $(C_5Me_5)Rh(PMe_3)(CH_3)H$ (1). A 3:1 (v:v) THF-d_8/C_6D_6 solution (0.4 mL) of $(C_5Me_5)Rh(PMe_3)(CH_3)Cl$ (10 mg, 0.275 mmol) was added to $Ag^+[PF_6]^-$ (7.0 mg, 0.0276 mmol). The mixture was stirred for 2 min and then filtered through a small, tightly packed cotton plug into an NMR tube. The tube was capped with a 5-mm rubber septum and lowered into the probe of the NMR spectrometer which had been previously cooled to −70 °C. An NMR spectrum at −70 °C exhibited three doublets at δ 0.616 (J = 7.5 Hz, 3 H), 1.333 (J = 10.2 Hz, 9 H), and 1.437 (J = 2.7 Hz, 15 H) as expected for $[(C_5Me_5)Rh(PMe_3)(CH_3)(THF\text{-}d_8)]^+$. The NMR tube was cooled to −95 °C in a CH_3OH cold bath and $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (6 μL of a 7.14 N toluene solution, 0.022 mmol) was added. The tube was quickly shaken and rapidly lowered into the −70 °C NMR probe. After slowly warming the probe to −60 °C, an NMR spectrum was recorded, showing the presence of two rhodium complexes (5:1) in a combined yield (NMR) of approximately 90%. The major product, **1**, exhibited two four-line resonances centered at δ −14.424 (dd, J = 48.3, 30.3 Hz, 1 H) and δ −0.130 (dd, J = 5.1, 2.5 Hz, 3 H). (The minor product was **4**.) The NMR probe was gradually warmed to −17 °C, at which temperature a slow, first-order disappearance of **1** was observed. The integrated intensities of the methyl group of **1** (relative to Dow Corning silicone lubricant) were used in determining the rate constant for reductive elimination.[12] As the decomposition of **1** progresses there are steady increases in the resonances associated with methane (δ 0.176) and **2**-d_6 (δ 1.793 (d, J = 1.9 Hz, 15 H, 1.108 (d, J = 10.1 Hz, 9 H)). When the same reaction sequence was performed in the absence of C_6D_6 as a cosolvent, the decomposition of **1** gave a very complex mixture of unidentifiable products.

Observation of $(C_5Me_5)Rh(PMe_3)(n\text{-propyl})H$ (7). With use of the 5-mm NMR tube photolysis vessel described previously, a solution of **4** (6 mg, 0.019 mmol) in hexane was carefully evaporated under high vacuum (10^{-4} mm). Propane which had been purified by three freeze–pump–thaw cycles was then condensed into the reaction vessel at −78 °C. The contents were mixed by repeatedly swirling the tube in a −50 °C CH_3OH/H_2O cold bath. The propane solution was irradiated at −55 ± 5 °C for 1.5 h. The apparatus was attached to a high-vacuum line, cooled to −78 °C, and the propane carefully removed (10^{-4} mm). When only a brownish residue remained the vessel was warmed to −35 °C and the high vacuum applied for 15 min. The tube was cooled to −78 °C, THF-d_8 carefully added by vacuum distillation (25 °C (10^{-4} mm)), and the tube sealed under high vacuum. The NMR tube was then rapidly lowered into the probe of the NMR spectrometer which had been previously cooled to −40 °C. After thermal equilibration an NMR spectrum revealed one major product besides the unreacted **4**, δ −14.963 (dd, J = 50, 32 Hz, 1 H), 0.840 (t, J = 7 Hz, 3 H), 1.278 (d, J = 9 Hz, 9 H), and 1.820 (d, J = 1.8 Hz, 15 H). This product was assigned to be the *n*-propyl derivative **7** on the basis of the observation of the triplet at δ 0.840. There was no evidence for the formation of the isomeric isopropyl hydride. The methylene resonances, being both diasteriotopic and coupled to several nuclei, were not observed directly but are believed to fall partially under the PMe_3 resonance, as irradiation of the δ 1.20–1.45 region causes the triplet at δ 0.840 to collapse to a singlet. Further support for the formulation for **7** was obtained by warming the solution to −15 °C, at which temperature propane (δ 0.892 (t, J = 7 Hz), 1.317 (sept, J = 7 Hz)) is produced as **7** decomposes.

In a separate experiment, **7** was generated and the excess propane removed as described above. THF was carefully added at −78 °C by vacuum distillation (25 °C (10^{-4} mm)), and the contents mixed by gently swirling at −40 °C. The tube was cooled to −78 °C, and a fivefold excess of $CHBr_3$ (25% in THF) added carefully, producing an instantaneous reaction. The red mixture was swirled at −78 °C for 10 min and then allowed to warm to 25 °C over 15 min. The THF was removed (25 °C (10^{-4} mm)), $CDCl_3$ added by vacuum distillation, the tube sealed under vacuum, and an NMR spectrum recorded at 25 °C. Besides residual solvent resonances, the spectrum exhibited only resonances for $(C_5Me_5)Rh(PMe_3)Br_2$ and $(C_5Me_5)Rh(PMe_3)(n\text{-propyl})Br$ in a 2:1 ratio.[16] There is no evidence for the formation of the isopropyl complex.

Isomerization of *p*-6 to *m*-6. A THF-d_8 solution (0.4 mL) of $Ag^+[PF_6]^-$ (5.3 mg, 0.021 mmol) was added to $(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})Br$ (9.3 Mg, 0.018 mmol). The mixture was stirred for 5 min and then filtered through a cotton plug into an NMR tube. The tube was capped with a rubber septum and lowered into the probe of the NMR spectrometer at −25 °C. An NMR spectrum exhibited resonances expected for the THF complex (Table I). The NMR tube was cooled to −40 °C in a CH_3OH/H_2O cold bath and $Li^+[HB(sec\text{-}Bu)_3]^-$ (23 μL of a 1 M THF solution, 0.023 mmol) carefully added. After mixing, the tube was rapidly lowered into the −25 °C NMR probe and a spectrum recorded. The aromatic region of the spectrum consisted of a large AB pattern (δ 6.530 (d, J = 8.8 Hz, 2 H), 7.108 (d, J = 6.7 Hz, 2 H)) and several much smaller resonances (δ 6.466 (d, J = 7.3 Hz, 1 H), 6.561 (t, J = 7.5 Hz, 1 H), 7.016 (d, J = 7.3 Hz, 1 H), 7.117 (s, 1 H)). Decoupling experiments later confirmed that these resonances were due to *p*-**6** and *m*-**6**, respectively. The metal hydride region showed two sets of resonances in a 7.3:1 ratio (δ −13.928 (dd, J = 49.5, 32.9 Hz), −14.313 (dd, J = 41.8, 29.7 Hz)) corresponding to the two unresolved tolyl hydrides and dihydride **4**, respectively. The spectrum did not change after 1 h at −25 °C. The probe was slowly warmed to −10 °C, and a series of spectra recorded over 35 min at −10 °C showed the resonances corresponding to *p*-**6** gradually decreasing in intensity and the smaller resonances associated with *m*-**6** increasing. Upon warming to 25 °C, an equilibrium mixture of 33% *p*-**6** and 67% *m*-**6** was obtained.

Isomerization of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$. A THF-$d_8$ solution (0.4 mL) of $Ag^+[PF_6]^-$ (7.2 mg, 0.0285 mmol) was added to $(C_5Me_5)Rh(PMe_3)(C_6D_5)Br$ (13.5 mg, 0.0284 mmol). The mixture was stirred for 2 min and then filtered through a cotton plug into an NMR tube. The tube was capped with a rubber septum and lowered into the probe of the NMR spectrometer at −40 °C. In addition to the residual solvent resonances, the NMR spectrum exhibited only the two doublets expected for $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF\text{-}d_8)]^+$ at δ 1.483 (d, J = 10.3 Hz, 9 H) and 1.563 (d, J = 2.4 Hz, 15 H). The NMR tube was cooled to

−78 °C in a dry ice/acetone bath and $Li^+[HB(sec\text{-}Bu)_3]^-$ (30 μL of a 1 M THF solution, 0.030 mmol) carefully added. After mixing, the tube was rapidly lowered into the −40 °C probe and a spectrum recorded. The aromatic region of the spectrum consisted of 4 very small singlets at δ 7.288, 7.279, 6.700, and 6.673 corresponding to free benzene, ortho, meta, and para hydrogens. The hydride region exhibited two sets of resonances in a 7:2 ratio (δ −13.858 (dd, J = 49.6, 32.6 Hz), −14.289 (dd, J =v 42.6, 30.1 Hz)) corresponding to **2**-d_5 and **4**, respectively. Upon warming to −14.5 °C the intensity of the ortho resonance increased dramatically relative to the meta and para resonances (Figure 3). After 15 min the amount of hydride which had isomerized into the ortho position was 5 times the amount which had been isomerized into the meta position and more than 10 times that which had been isomerized into the para position. After the sample had been allowed to fully equilibrate (25 °C) and the relative intensities of the ortho, meta, and para resonances were 2:2:1 and the combined intensities were 1.85 times the integrated intensity of the metal–hydride resonance.

Low-Temperature Photolysis of 4 in Toluene. A solution of **4** (12.5 mg, 0.0395 mmol) in toluene (2 mL) was irradiated at −45 ± 5 °C for 30 min. The solution was cooled to −78 °C and then quenched by addition of a 10-fold excess of 25% $CHBr_3$ in THF. After warming to 25 °C, the volatiles were removed (25 °C (10^{-4} mm)) and an NMR spectrum recorded in C_6D_6. The mixture consisted of approximately 80% $(C_5Me_5)Rh(PMe_3)Br_2$ and a 20% yield of the combined tolyl bromide complexes as calculated from the integrated intensities of the C_5Me_5 and PMe_3 resonances. The relative amounts of the *o*-, *m*-, and *p*-tolyl bromide complexes could be obtained from the integrated intensities of the benzylic methyl resonances (ortho, δ 2.985 and 2.215, 7.6%; meta, δ 2.311, 55.8%; para, δ 2.280, 36.6%). Only traces (<1%) of the benzyl isomer were observed.[16]

Low-Temperature Isomerization of 8a. A THF-d_8 solution (0.3 mL) of $(C_5Me_5)Rh(PMe_3)(2\text{-}CH_3\text{-}5\text{-}CD_3\text{-}C_6H_3)Br$ was added to $Ag^+[PF_6]^-$ (4.9 mg, 0.0194 mmol). The mixture was stirred for 2 min at 25 °C and then filtered through a small cotton plug into an NMR tube. The tube was capped with a rubber septum and lowered into the probe of the NMR spectrometer at −50 °C, and an NMR spectrum was recorded (Table I). The tube was cooled to −78 °C in an acetone/dry ice bath and $Li^+[HBEt_3]^-$ (20 μL of a 1 M THF solution, 0.020 mmol) added carefully. The contents were mixed by rapidly lowering the sample into the −50 °C probe and spinning the sample at 80 Hz. An NMR spectrum recorded at −50 °C showed that the reduction gave a 73:27:5 mixture of **8a**:**8b**:**4**. The probe was raised to −35 °C and a slow first-order approach to equilibrium was observed in which the xylyl methyl group was equally distributed between the 2-position (δ 2.214) and the 5-position (δ 2.121).

Spin Saturation Transfer in 3. A sample of **3** was prepared by heating a mixture of **6a** and **6b** in xylene for 12 h at 50 °C, removing the volatiles (25 °C (10^{-4} mm)), and then repeating the procedure. The pale yellow residue which remained after removing the volatiles a second time was dissolved in C_6D_6 (0.4 mL) and transferred to an NMR tube fitted with a vacuum adapter. The tube was sealed under vacuum after three freeze–pump–thaw degas cycles. The two-site spin saturation transfer experiment (180–τ_x–90°–FID) was performed by using the two xylyl methyl singlets according to previously published procedures.[21] There was no difference in the calculated rates or T_1's whether the selective 180° pulse was applied to the upfield (δ 2.354) or the downfield (δ 2.630) xylyl methyl resonance. The data in Table IV were obtained by applying the selective 180° pulse to the resonance at δ 2.630.

Kinetics of Arene Dissociation in 2 and 3. A stock solution of **2** was prepared by dissolving the complex in C_6D_6 (2 mL) and the solution then divided into four portions in NMR tubes attached to ground glass joints. After a freeze–pump–thaw cycle each tube was sealed under 600 mm of nitrogen. The disappearance of **2** was quantified by monitoring the integrated intensity of the ortho protons (δ 7.640) on the phenyl ring. Dow Corning silicone lubricant was used as an internal standard (Table II).

A similar procedure was used to prepare three sample tubes containing **3**. The disappearance of **3** was quantified by monitoring the decrease in the sum of the integrated intensities of the xylyl methyl groups at δ 2.630 and 2.354 (Table II).

Cyclopentane/Benzene Competition. With use of the photolysis vessel previously described, the dihydride **4** (13 mg, 0.041 mmol) was irradiated for 20 min at −30 to −40 °C in 3 mL of cyclopentane/benzene (5.10:1.00 molar ratio). The reaction mixture was carefully quenched at −40 °C with 25% CCl_4 in THF. The volatiles were removed (25 °C (10^{-2} mm)), C_6D_6 distilled into the tube, and an NMR spectrum recorded. The mixture contained three products: $(C_5Me_5)Rh(PMe_3)$(cyclopentyl)Cl in 18% yield,[16] $(C_5Me_5)Rh(PMe_3)(C_6H_5)Cl$ in 19% yield,[16] and $(C_5Me_5)Rh(PMe_3)Cl_2$ in 63% yield. The ratio of the cyclopentyl to phenyl complexes was determined by the relative integrations of the corresponding PMe_3 resonances (0.94:1). This corresponds to a 5.4-fold kinetic preference for benzene over cyclopentane in the activation process.

Preparation of $(C_5Me_5)Rh(PMe_3)[\eta^2\text{-}C_6H_4(t\text{-}Bu)_2]$. A hexane solution of freshly prepared dihydride **4** (2 mg, 0.006 mmol) and 1,4-di-*tert*-butylbenzene (6 mg, 0.032 mmol) was pipetted into an NMR tube fitted with a ground glass joint and the hexane carefully removed (25 °C (10^{-4} mm)). Methylcyclohexane-d_{14} (0.3 mL) was vacuum distilled (25 °C (10^{-4} mm)) into the NMR tube and the tube sealed under vacuum. The reaction mixture was photolyzed for 45 min at −55 ± 5 °C. After cooling to −78 °C, the tube was rapidly lowered into the probe of the NMR spectrometer, which had been previously cooled to −50 °C. After 10 min the sample temperature was raised to −30 °C and a spectrum was recorded. Besides resonances for the starting dihydride **4**, a new resonance was observed at δ 1.809 (d, J = 2.3 Hz) and is attributed to the methylcyclohexyl complex **9** on the basis of the similarity of the chemical shift to that of **1** and **7**. Upon warming to −20 °C, a gradual decay of this product is observed as new resonances appear at δ 6.355 (s, 2 H), 3.879 (dd, J = 4.9, 3.0 Hz), and 1.816 (d, J = 2.5 Hz, 15 H) attributable to the η^2-arene complex **10**. In addition to these resonances, other resonances at δ 1.916 (s, 15 H) and −14.510 (5 lines, J = 20 Hz, 1 H) gradually appear. These resonances are believed to be due to a product (X) derived from oxidative addition of **5** to the unreacted dihydride **4**. When the reaction mixture is warmed to −10 °C the resonances assigned to **10** vanish altogether and only the resonances attributable to **4** and X remain. If this mixture is allowed to warm to 25 °C, X decomposes and unreacted **4** is the only unidentifiable material in the reaction mixture. When the reaction was repeated with a larger amount of 1,4-di-*tert*-butylbenzene (25 mg, 0.131 mmol), the photolysis mixture had a much larger amount of **10** relative to **9**. Upon warming to −20 °C the decay of **9** produced **10** almost exclusively. Only traces of X were observed.

The large excess of 1,4-di-*tert*-butylbenzene in the NMR experiment necessitated the use of a multiple peak suppression sequence to enhance the dynamic range of the signal digitizer. This was easily accomplished by alternate gated-decoupling of the 1,4-di-*tert*-butylbenzene resonances at δ 1.278 and 7.211. At −15 °C, this peak suppression procedure only suppresses the 1,4-di-*tert*-butylbenzene resonances. However, at −12 °C, where a slow decomposition of **10** begins, suppression of the δ 7.211 resonance also markedly suppresses the arene resonances associated with **10**. When only the δ 1.278 resonance of the di-*tert*-butylbenzene is suppressed there is no effect on the arene resonances of **10**, thus demonstrating that the η^2-arene is rapidly exchanging ($k \simeq 1/T_1$) with the free di-*tert*-butylbenzene in solution.

Preparation and Decomposition of the Cyclopentenyl Hydride Complex. A 3:1 (v:v) THF-d_8/C_6D_6 solution (0.4 mL) of $(C_5Me_5)Rh(PMe_3)(\overline{C{=}CH{-}CH_2{-}CH_2{-}CH_2})Br$ (6.1 mg, 0.0132 mmol) was added to $Ag^+[PF_6]^-$ (3.3 mg, 0.0131 mmol). The mixture was stirred for 5 min and then filtered through a cotton plug into an NMR tube. The tube was capped with a rubber septum and lowered into the probe of the NMR spectrometer at −50 °C. An NMR spectrum showed the presence of resonances expected for the THF complex (Table I). $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ (50 μL of a 0.5 N toluene solution, 0.0125 mmol) was carefully added after the tube was cooled to −78 °C in a dry ice/acetone bath. After mixing, the tube was again rapidly lowered into the −50 °C probe and a spectrum recorded. Besides a small amount of **4** (10%), two new rhodium complexes were observed. The major component (75%) had resonances at δ 1.564 (d, J = 2.4 Hz, 15 H), 1.125 (d, J = 9.9 Hz, 9 H), 5.086 (s, 1 H), and −13.859 (dd, J = 49.2, 32.3 Hz, 1 H) and was assigned to the cyclopentenyl complex $(C_5Me_5)Rh(PMe_3)(\overline{C{=}CH{-}CH_2{-}CH_2{-}CH_2})H$. The minor component showed resonances at δ 1.701 (d, J = 2.0 Hz, 15 H) and 0.962 (d, J = 8.6 Hz, 9 H) and is assigned to the cyclopentene complex $(C_5Me_5)Rh(PMe_3)(\overline{CH{=}CH{-}CH_2{-}CH_2{-}CH_2})$, which is formed at the expense of the cyclopentenyl complex upon warming to −12 °C. The half-life for the conversion is approximately 15 min. The cyclopentene complex, eventually formed in 90% yield, was identical with a sample prepared upon irradiation of **4** in cyclopentene solvent. No **2**-d_6 was detected, which would have resulted from the reaction of **5** with solvent (C_6D_6).

A control experiment showed that benzene could compete with cyclopentene for **5**. A 3:1 (v:v) THF/C_6H_6 solution (0.4 mL) of **4** (10 mg, 0.032 mmol) and cyclopentene (6.0 μL, 0.064 mmol) was photolyzed for 10 min at 25 °C. The volatiles were removed (25 °C (10^{-4} mm)) and an NMR spectrum (C_6D_6) recorded. Approximately 23% of the dihydride complex had been consumed, producing only **2** and no cyclopentene complex.

Low-Temperature Quenching of 6 with $CHBr_3$. A solution of **6** (11 mg, 0.027 mmol) in toluene (2 mL) was cooled to −78 °C. Bromoform (75 μL of a 25% solution in THF, 0.21 mmol) was added slowly, making sure it had sufficient time to cool to reaction temperature while flowing down the walls of the vessel. An instantaneous reaction occurred, producing a bright orange solution which was then evaporated (25 °C (10^{-2} mm)).

An NMR spectrum (C_6D_6) of the orange residue only exhibited resonances for the corresponding *m*- and *p*-tolyl bromide complexes. The ratio of the integrated intensities of the tolyl methyl resonances (meta, δ 2.309, 69%; para, δ 2.279, 31%) was within the experimental limit of error of the ratio of the starting materials (67:33).

Preparation of α,α,α-Trideuterio-2-bromo-*p*-xylene. The compound was prepared in 4 steps from methyl *p*-toluate and used for the preparation of **8a** as previously described.[16] Monobromination of methyl *p*-toluate (3.5 g) with $AlCl_3/Br_2$[34] gave methyl 3-bromotoluate (2.45 g, 46%) as a colorless liquid after Kugelrohr distillation (140 °C (10 mm)). Reduction of the ester (1.29 g) with lithium aluminum deuteride using standard procedures[35] afforded 2-methyl-5-hydroxymethyl-d_2-bromobenzene in 84% yield (0.96 g) after Kugelrohr distillation (110 °C (10 mm)). Treatment of the deuterated alcohol (0.80 g) with PMe_3 in CCl_4[36] followed by solvent removal, ether extraction, and concentration afforded 2-methyl-5-chloromethyl-d_2-bromobenzene in 90% crude yield. Reduction of the crude alkyl chloride with lithium triethylborodeuteride in ether followed by a standard aqueous workup afforded the desired 2-bromo-α,α,α-trideuterio-*p*-xylene in 83% overall yield from the benzylic alcohol. The product was purified by preparative gas chromatography prior to use (6 ft × 1/4 in. 10% SE-30/Chromosorb WAW, 140 °C, 20 mL/min). ^1H NMR ($CDCl_3$) δ 2.351 (s, 3 H), 7.001 (dd, J = 7.7, 1.2 Hz, 1 H), 7.105 (d, J = 7.6 Hz, 1 H), 7.358 (d, J = 0.9 Hz, 1 H).

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Registry No. 1, 84624-01-1; **2**, 81971-46-2; **2**-d_5, 88704-00-1; **2**-d_5 (ortho isomer), 88704-33-0; **2**-d_5 (meta isomer), 88704-34-1; **2**-d_5 (para isomer), 88704-35-2; **2**-d_6, 84624-02-2; **3**, 88704-01-2; **4**, 84624-03-3; *p*-**6**, 81971-48-4; *m*-**6**, 81971-47-3; **7**, 84624-04-4; **8a**, 88704-02-3; **8b**, 88704-03-4; **10**, 88704-04-5; $(C_5Me_5)Rh(PMe_3)(C{=}\overline{CHCH_2CH_2CH_2})H$, 88704-05-6; $(C_5Me_5)Rh(PMe_3)(\overline{CH{=}CHCH_2CH_2CH_2})$, 88704-06-7; $(C_5Me_5)Rh(PMe_3)[2,5\text{-}C_6H_3(i\text{-}Pr)_2]H$, 88704-07-8; $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$, 88704-08-9; $(C_5Me_5)Rh(PMe_3)(3,4\text{-}C_6H_3Me_2)H$, 88704-09-0; $(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4CF_3)H$, 88704-10-3; $(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4CF_3)H$, 88704-11-4; $(C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4OMe)H$, 88704-12-5; $(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4OMe)H$, 88704-13-6; $(C_5Me_5)Rh(PMe_3)(o\text{-}C_6H_4OMe)H$, 88704-14-7; $[(C_5Me_5)Rh(PMe_3)(C_6H_5)(THF)]^+[PF_6]^-$, 88704-16-9; $[(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})(THF)]^+[PF_6]^-$, 88704-17-0; $[(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)(THF)]^+[PF_6]^-$, 88704-19-2; $[(C_5Me_5)Rh(PMe_3)(2\text{-}CH_3\text{-}5\text{-}CP_3\text{-}C_6H_3)(THF)]^+[PF_6]^-$, 88704-21-6; $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF)]^+[PF_6]^-$, 88704-23-8; $[(C_5Me_5)Rh(PMe_3)(\overline{C{=}CHCH_2CH_2CH_2})(THF)]^-[PF_6]^-$, 88704-25-0; $(C_5Me_5)Rh(PMe_3)Cl_2$, 80298-79-9; $(C_5Me_5)Rh(PMe_3)Br_2$, 88704-26-1; $(C_5Me_5)Rh(PMe_3)I_2$, 88704-27-2; $(C_5Me_5)Rh(PMe_3)(C_6H_5)Cl$, 88704-28-3; $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$, 81971-44-0; $(C_5Me_5)Rh(PMe_3)(C_6H_5)I$, 88704-29-4; $(C_5Me_5)Rh(PMe_3)(CH_3)Cl$, 84623-98-3; $(C_5Me_5)Rh(PMe_3)(p\text{-tolyl})Br$, 81971-45-1; $(C_5Me_5)Rh(PMe_3)(2\text{-}CH_3\text{-}5\text{-}CD_3\text{-}C_6H_3)Br$, 88704-30-7; $(C_5Me_5)Rh(PMe_3)(C{=}CH)$, 88704-31-8; $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$, 22722-98-1; $Li^+[HBEt_3]^-$, 22560-16-3; $Li^+[HB(sec\text{-}Bu)_3]^-$, 38721-52-7; $K^+[HB(O\text{-}i\text{-}Pr)_3]^-$, 42278-67-1; $AgPF_6$, 26042-63-7; C_6D_5H, 13657-09-5; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; propane, 74-98-6; cyclopentane, 287-92-3; 1,4-di-*tert*-butylbenzene, 1012-72-2; cyclopentene, 142-29-0; α,α,α-trideuterio-2-bromo-*p*-xylene, 88704-32-9; C_6H_6, 71-43-2.

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Stepwise Reductive Acidolysis of $OsH_4(PMe_2Ph)_3$. Mechanism of Hydrogen Elimination/Ligand Addition

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Abstract: The polyhydride $OsH_4(PMe_2Ph)_3$ (**1**) reacts with either $HBF_4{\cdot}OEt_2$ or Ph_3CPF_6 and CH_3CN to give $[fac\text{-}Os(PMe_2Ph)_3(CH_3CN)_3]X_2$ (**6**) (X = BF_4, PF_6). The acidolysis reaction proceeds in stepwise fashion through several intermediate species. Using limiting reagent quantities (acid and CH_3CN), it is possible to either isolate or spectrally characterize $OsH_5(PMe_2Ph)_3^+$ (**2**), $OsH_3(PMe_2Ph)_3(CH_3CN)^+$ (**3**), *mer,cis*-$OsH(PMe_2Ph)_3(CH_3CN)_2^+$ (**4**), and *mer*-$Os(PMe_2Ph)_3(CH_3CN)_3^{2+}$ (**5**) on the pathway to **6**. Additionally, kinetic and labeling studies indicate that H_2 substitution by CH_3CN occurs via a preequilibrium H_2 loss and subsequent trapping by CH_3CN. The X-ray diffraction structure of **6** (X = PF_6) is also reported.

The syntheses and certain reaction pathways of transition-metal phosphine polyhydrides are becoming increasingly well developed. This is particularly true for compounds containing third-row transition metals, in addition to various $MoH_4(PR_3)_4$ derivatives.[1] The polyhydrides are characterized by high formal metal oxidation states and coordination numbers, as well as a strong adherence to the 18-electron rule. This latter restriction, coupled with the relative kinetic inertness of third-row compounds, has led to diverse efforts aimed at activating polyhydrides for intermolecular processes. One approach has been complexation with Lewis acids in the hope of enhancing the susceptibility of the transition-metal center to nucleophilic attack;[2-6] it is not always clear that the

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