Articles

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

Preparation and Conformational Dynamics of $(C_5Me_5)Rh(PR'_3)RX$. Hindered Rotation about Rhodium–Phosphorus and Rhodium–Carbon Bonds

WILLIAM D. JONES* and FRANK J. FEHER

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Compounds with the general formula $[C_5Me_5]RhXR(PR'_3)$ have been prepared by the reactions of $[C_5Me_5]Rh(PR'_3)X_2$ and the corresponding Grignard or lithium reagent (X = Cl, Br, I; R = Me, c-C_5H_9, *n*-C_3H_7, CH_2CMe_3, C_6H_5, *o*-C_6H_4Me, *m*-C_6H_4Me, *p*-C_6H_4Me, 2,5-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, 3,4-$C_6H_3Me_2$, *p*-$C_6H_4CF_3$, *p*-C_6H_4F, *p*-C_6H_4OMe, *p*-$C_6H_4NMe_2$, $CH{=}CH_2$, $CMe{=}CH_2$, $C{=}CHCH_2CH_2CH_2$, $CH_2C_6H_5$; R′ = Me, C_6H_5, *p*-C_6H_4Me). The aryl derivatives show hindered rotation about the rhodium–aryl bond, with $\Delta H^* = 9.8 \pm 0.2$ kcal/mol and $\Delta S^* = -13.7 \pm 0.6$ eu for R′ = Me, X = Cl, and R = *p*-tolyl and $\Delta H^* = 11.0 \pm 0.2$ kcal/mol and $\Delta S^* = -9.8 \pm 0.6$ eu for R′ = C_6D_5, X = Br, and R = *p*-tolyl. ΔG^* for this hindered rotation was determined for several of the above compounds. In addition, the triarylphosphine complexes also show hindered rotation about the metal–phosphorus bond with $H^* = 15.7 \pm 0.2$ kcal/mol and $S^* = -2.8 \pm 0.2$ eu (X = Br, R = C_6D_5, R′ = *p*-tolyl) and $\Delta H^* = 14.3 \pm 0.3$ kcal/mol and $\Delta S^* = -1.8 \pm 1.2$ eu for $(C_5Me_5)Rh[P(p\text{-tolyl})_3]Br_2$. Both complete band shape analysis and spin saturation methods were used to determine rate constants. ΔG^* for rotation about the metal–aryl bond is insensitive to the nature of the para substituent on the aryl group but shows a moderate halide dependence and a stronger phosphine dependence. Single-crystal X-ray structural parameters for $[C_5(CH_3)_5]Rh[P(C_6H_5)_3](C_6H_5)Br$ are $a = 11.459$ (12) Å, $b = 9.008$ (6) Å, $c = 19.298$ (13) Å, $\beta = 90.03$ (2)°, $V = 1992$ Å^3, $Z = 4$, $d_{calcd} = 1.57$ g/cm^3, space group $P2_1/c$, $R = 4.68\%$, and $R_w = 6.15\%$ for the 2009 independent reflections with $F^2 \geq 3\sigma(F^2)$. The Rh–phenyl bond distance of 2.05 Å is typical for a rhodium sp^2-carbon bond and does not suggest any unusual π-bonding between the metal and the phenyl ligand.

Introduction

While the reaction of Grignard or lithium reagents with transition-metal halides has proven to be a general method for the introduction of organic ligands in transition-metal compounds, alkyl and aryl derivatives of the type $(C_5H_5)Rh(PR'_3)RX$ and $(C_5Me_5)Rh(PR'_3)RX$ have been scarcely investigated. Rausch and co-workers have reported the synthesis of $(C_5H_5)Rh(PPh_3)(Ph)I$ by the reaction of PhMgI with $(C_5H_5)Rh(PPh_3)I_2$,[1] and a low-yield monoalkylation reaction with the related C_5Me_5 derivative was studied by Maitlis.[2] Some dialkylations have been reported producing either dialkyl complexes or metallocycles of the type $(C_5Me_5)Rh(PPh_3)(\eta^2\text{-}(CH_2)_n)$,[3] but few other compounds of this type are known. We report here the preparation of a host of monoalkyl, -vinyl, and -aryl derivatives of the general formula $(C_5Me_5)Rh(PR'_3)RX$ by the action of vinyl or aryl Grignard or alkyllithium reagents upon the corresponding halide $(C_5Me_5)Rh(PR'_3)X_2$ (X = Cl, Br, I; R′ = Me, Ph, *p*-tolyl (*p*-tol); R = Me, c-C_5H_9, *n*-C_3H_7, CH_2CMe_3, C_6H_5, *o*-C_6H_4Me, *m*-C_6H_4Me, *p*-C_6H_4Me, 2,5-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, 3,4-$C_6H_3Me_2$, *p*-$C_6H_4CF_3$, *p*-C_6H_4F, *p*-C_6H_4OMe, *p*-$C_6H_4NMe_2$, $CH{=}CH_2$, $CMe{=}CH_2$, $CH_2C_6H_5$, and $C{=}CHCH_2CH_2CH_2$).

The study of rotational barriers in compounds is a topic of interest to chemists, as conformational stability is important in terms of understanding both chemical bonding and stereospecific reactivity. The aryl derivatives described here are unique in that they exhibit hindered rotation about both the metal–carbon and metal–phosphorus bonds. Other complexes have been shown to demonstrate hindered rotation about either the metal–carbon[4] or metal–phosphorus[5] σ-bond, but not both types of bonds in one molecule. The studies described here provide a firm basis for a barrier to rotation about a metal–aryl bond, for which there is one[4h] known example, including the evaluation of activation parameters. The dependence of the rotational barrier upon the nature of the para substituents on the aryl ligand also allows the electronic contribution to the hindered rotation to be evaluated separately from any steric or conformational effects.

Results

Preparation of Compounds. The dimer $[(C_5Me_5)RhCl_2]_2$ (**1a**) was first synthesized by Maitlis by heating $RhCl_3$ in the presence of hexamethyl(Dewar benzene).[2] The related iodide dimer, **1c**, was reported to be formed by treatment of the chloro-bridged dimer with NaI in acetone, and we have found that the bromo derivative, **1b**, can be prepared similarly.[6]

(1) Gardner, S. A.; Rausch, M. D. *Inorg. Chem.* **1974**, *13*, 997–999.
(2) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977.
(3) Kasahara, A.; Izumi, T.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1967**, *44*, 699. Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1977**, 52–53. Diversi, P.; Ingrosso, G.; Lucherini, A.; Martinelli, P.; Benetti, M.; Pucci, S. *J. Organomet. Chem.* **1979**, *165*, 253–263.
(4) (a) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045–3049. (b) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081–1083. (c) Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 814–821. (d) Wada, M.; Sameshima, K.; Nishiwaki, K.; Kawasaki, Y. *Ibid.* **1982**, 793–797. (e) Stanley, K.; Zelonka, R. A.; Thomson, J.; Fiess, P.; Baird, M. C. *Can. J. Chem.* **1974**, *52*, 1781–1786. (f) Pannell, K. H. *J. Chem. Soc., Chem. Commun.* **1969**, 1346–1347. (g) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529–5539. (h) Sharp, P. R.; Astruc, D.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *182*, 477–488.
(5) (a) Bushweller, C. H.; Hoogasian, S.; English, A. D.; Miller, J. S.; Lourandos, M. Z. *Inorg. Chem.* **1981**, *20*, 3448–3455. (b) Mann, B. E.; Masters, C.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc., Chem. Commun.* **1971**, 1103–1104. (c) Attig, T. G.; Clark, H. C. *J. Organomet. Chem.* **1975**, *94*, C49–C52. (d) Faller, J. W.; Johnson, B. V. *Ibid.* **1975**, *96*, 99–113.
(6) The compound was prepared in lower yield in methanol. See: Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359–364.

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These halo-bridged dimers are easily cleaved by phosphines[2] and provide quantitatively the initial compounds $(C_5Me_5)Rh(PR'_3)X_2$ (R′ = Me, X = Cl (**2a**), Br (**2b**), I (**2c**); R′ = Ph, X = Cl (**3a**), Br (**3b**), I (**3c**); R′ = p-C_6H_4Me, X = Cl (**4a**), Br (**4b**), I (**4c**); R′ = Et, X = Br (**5b**)) for the studies reported here. These dihalide derivatives can be interconverted (**2a** → **2b** → **2c**; **2a** → **2c**) by refluxing the metal complex with the appropriate sodium halide in acetone solvent for several hours.

Treatment of the complex **2a** with 1 equiv of halide-free methyllithium in THF solution at −40 °C produces the air-stable methyl complex $(C_5Me_5)Rh(PMe_3)MeCl$ (**6a**), which is isolated as orange crystals in 71% yield by chromatography on silica gel with 4% THF/CH_2Cl_2 as eluent. The ^1H NMR spectrum of the complex shows two doublets in a 15:9 ratio for the phosphorus-coupled methyl groups on the permethylcyclopentadienyl ring and the phosphine and a doublet of doublets for the rhodium-bound methyl group (Table I).

Other alkyl complexes of the type $(C_5Me_5)Rh(PMe_3)RX$ (X = Br, R = n-C_3H_7 (**7b**), CH_2CMe_3 (**9b**); X = Cl, R = C-C_5H_9 (**8a**)) are prepared similarly with use of lithium reagents (generated from lithium metal and alkyl halide) and **2b** or **2a**. Use of **2a** with the bromide-containing lithium reagents results in the formation of a mixture of chloro- and bromo-substituted derivatives due to partial halide exchange. Consequently, all syntheses were performed with reagents containing the same halogen.

Aryl derivatives can also be synthesized by treating compounds **2**, **3**, and **4** with aryl Grignard reagents. For example, $(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4Me)Cl$ (**10a**) is prepared by treating a THF solution of **2a** with 1 equiv of (p-C_6H_4Me)-MgCl. The solvent is removed under reduced pressure, leaving a light orange residue. Extraction with CH_2Cl_2 and rapid elution across silica gel to remove the magnesium salts provides a solution of **10a**, which is isolated in 90% yield by evaporating the solvent. The chloride can be substituted by bromide and iodide, forming **10b** and **10c**, respectively, by refluxing **10a** with the appropriate sodium halide in acetone for several hours.

A host of other aryl derivatives (**11**–**27**) were prepared in a similar fashion as listed in Tables I and II. Vinyl (**28b**), 2-propenyl (**29b**), and 1-cyclopentenyl (**30b**) derivatives were prepared by the reaction of the Grignard reagent with **2b**. The benzyl derivative, $(C_5Me_5)Rh(PMe_3)(CH_2C_6H_5)Br$ (**31b**), however, was not obtained upon treatment of **2b** with either benzyllithium or benzylmagnesium bromide. **31b** was obtained in 20% yield by reacting benzyl bromide and $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in THF solution, with most of the rhodium being converted into **2b**.

Dynamic NMR Studies. Compounds **3a**–**c** and **4b** all showed more complicated NMR spectra than would be expected for a coordinated triarylphosphine ligand with three equivalent aryl groups. The behavior of **4b** was simplest and showed two distinct p-tolyl methyl resonances at δ 2.385 (A) and δ 2.228 (B) in a 2:1 ratio at −44 °C, indicating an inequivalence of one of the three tolyl groups. At higher temperatures the peaks broadened and coalesced to a singlet, indicative of rapid exchange of the tolyl groups. Changes in the aromatic region were consistent with this process, showing two pairs of doublets in a 2:1 ratio at −44 °C and one pair of doublets at 40 °C. Complete band shape analysis (CBS) of the methyl resonances allowed determination of the rate constant (k) for interconversion of the three methyl groups according to eq 1 (see Experimental Section). An Eyring plot was used to determine the activation parameters ($\Delta H^\ddagger$ = 14.3 ± 0.3 kcal/mol, $\Delta S^\ddagger$ = −1.8 ± 1.2 eu) for this process.

$$A \underset{k}{\overset{2k}{\rightleftharpoons}} B \qquad (1)$$

All of the complexes containing rhodium–aryl bonds also showed temperature-dependent NMR spectra. The PMe_3-substituted p-tolyl derivatives demonstrated the least complex behavior, showing an AA′BB′ pattern in the low-temperature limit. For **10a** in $CDCl_3$, decoupling experiments indicated that the pair of widely separated doublets at δ 7.641 (J = 8 Hz, 1 H) and δ 6.850 (J = 8 Hz, 1 H) were coupled to one another, as are the doublets at δ 6.912 (J = 7 Hz, 1 H) and δ 6.768 (J = 7 Hz, 1 H). The widely separated resonances at δ 7.641 and 6.912 are assigned to the hydrogens ortho to the chiral rhodium center. The changes in the aromatic region of the ^1H NMR spectrum of **10a** with temperature are shown in Figure 1, along with simulated spectra calculated by CBS analysis assuming coupled A ⇄ A′ and B ⇄ B′ interconversions with the same rate constant k (see Experimental Section). Comparison of the calculated and observed spectra allowed k to be measured over a 131 °C temperature range. An Eyring plot (Figure 2) gives the activation parameters $\Delta H^\ddagger$ = 9.8 ± 0.2 kcal/mol and $\Delta S^\ddagger$ = −13.7 ± 0.6 eu for the dynamic process. A similar series of spectra were recorded for **23b**, allowing determination of its activation parameters by CBS analysis also (Table III).

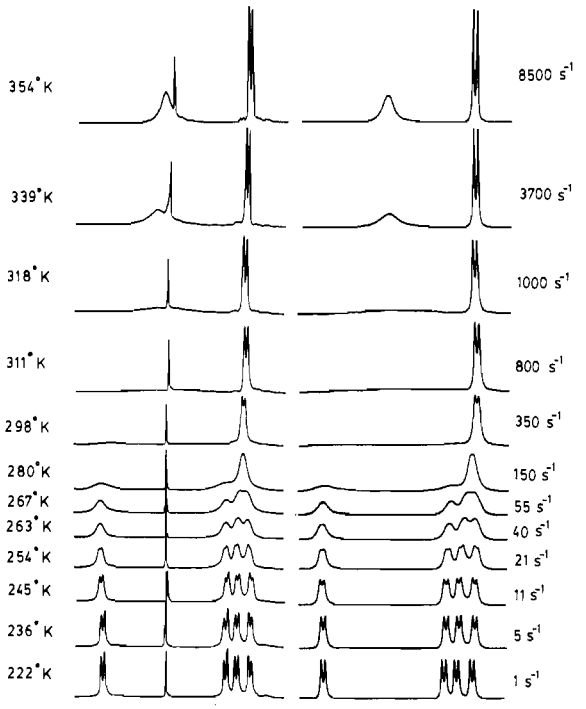

Figure 1. Observed (left) and calculated (right) ^1H NMR spectra for the δ 7.8–6.5 region of $(C_5Me_5)Rh(PMe_3)(p\text{-tol})Cl$ in $CDCl_3$ as a function of temperature.

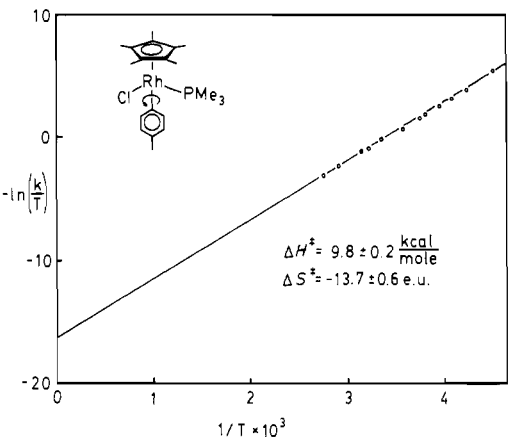

Figure 2. Eyring plot for the dynamic process in $(C_5Me_5)Rh(PMe_3)(p\text{-tol})Cl$.

Table I. Yields and ^{1}H NMR Data for the Compounds $(C_5Me_5)Rh(PR'_3)RX$[a]

compd						chem shifts[a]		
R'	R	X	no.	% yield	T, °C	C_5Me_5	PR'_3	other
Me	Cl	Cl	**2a**	99	25	1.712 (d, J = 3.4 Hz, 15 H)	1.633 (d, J = 11.7 Hz, 9 H)	
Me	Br	Br	**2b**	100	25	1.788 (d, J = 3.4 Hz, 15 H)	1.700 (d, J = 11.2 Hz, 9 H)	
Me	I	I	**2c**	100	25	2.003 (d, J = 3.3 Hz, 15 H)	1.846 (d, J = 10.8 Hz, 9 H)	
Ph	Cl	Cl	**3a**	100	−30	1.349 (d, J = 3.4 Hz, 15 H)	7.232 (m, 3 H; m, p) 7.458 (m, 6 H; m′, m″, p′, p″) 7.782 (dd, J = 11.2, 7.8 Hz, 4 H; o′, o″) 7.918 (dd, J = 9.3, 8.3 Hz, 2 H; o)	
Ph	Br	Br	**3b**	100	−30	1.485 (d, J = 3.4 Hz, 15 H)	7.232 (m, 3 H; m, p) 7.459 (m, 6 H; m′, m″, p′, p″) 7.725 (dd, J = 10.7, 6.8 Hz, 4 H; o′, o″) 7.886 (dd, J = 10.3, 7.3 Hz, 2 H; o)	
Ph	I	I	**3c**	100	−30	1.746 (d, J = 3.4 Hz, 15 H)	7.239 (m, 3 H; m, p) 7.459 (m, 6 H; m′, m″, p′, p″) 7.644 (dd, J = 10.3, 7.3 Hz, 4 H; o′, o″) 7.803 (dd, J = 9.8, 7.3 Hz, 2 H; o)	
p-tol	Br	Br	**4b**	98	−30	1.477 (d, J = 3.2 Hz, 15 H)	2.228 (s, 3 H; Me) 2.385 (s, 6 H; Me′, Me″) 6.997 (d, J = 7.3 Hz, 2 H; m) 7.225 (d, J = 7.3 Hz, 4 H; m′, m″) 7.632 (dd, J = 10.0, 8.0 Hz, 4 H; o′, o″) 7.726 (dd, J = 10.2, 8.3, 2 H; o)	
Et	Br	Br	**5b**	100	25	1.779 (d, J = 2.9 Hz, 15 H)	1.166 (dt, J = 15.1, 7.6 Hz, 9 H) 2.147 (dq, J = 15.7, 7.7 Hz, 6 H)	
Me	Me	Cl	**6a**	71	25	1.632 (d, J = 2.8 Hz, 15 H)	1.413 (d, J = 10.2, Hz, 9 H)	0.574 (dd, J = 7.1, 2.2 Hz, 3 H)
Me	*n*-C_3H_7	Br	**7b**	95	25	1.601 (d, J = 2.6 Hz, 15 H)	1.472 (d, J = 10.1, Hz, 9 H)	0.958 (t, J = 7.2 Hz, 3 H) 1.20 (m, 2 H) 1.85 (m, 2 H)
Me	c-C_5H_9	Cl	**8a**	95	25	1.617 (d, J = 2.9 Hz, 15 H)	1.432 (d, J = 10.1 Hz, 9 H)	1.3–2.1 (m, 9 H)
Me	CH_2CMe_3	Br	**9b**	95	25	1.625 (d, J = 2.8 Hz, 15 H)	1.494 (d, J = 10.2 Hz, 9 H)	1.036 (s, 9 H) 1.152 (dd, J = 18.1, 10.9 Hz, 1 H) 1.785 (m, 1 H)
Me	*p*-tol	Cl	**10a**	93	−50	1.555 (d, J = 2.6 Hz, 15 H)	1.301 (d, J = 10.5 Hz, 9 H)	2.222 (s, 3 H) 6.768 (dd, J = 7.4, 1.3 Hz, 1 H; 3-Ph) 6.850 (dd, J = 7.8, 1.3 Hz, 1 H; 5-Ph) 6.912 (d, J = 7.5 Hz, 1 H; 2-Ph) 7.641 (d, J = 7.7 Hz, 1 H; 6-Ph)
Me	*p*-tol	Br	**10b**	96	−50	1.631 (d, J = 2.4 Hz, 15 H)	1.406 (d, J = 10.3 Hz, 9 H)	2.250 (s, 3 H) 6.803 (d, J = 7.6 Hz, 1 H; 3-Ph) 6.843 (d, J = 7.9 Hz, 1 H; 5-Ph) 6.956 (d, J = 7.6 Hz, 1 H; 2-Ph) 7.812 (d, J = 7.9 Hz, 1 H; 6-Ph)
Me	*p*-tol	I	**10c**	97	−50	1.672 (d, J = 2.3 Hz, 15 H)	1.482 (d, J = 10.1 Hz, 9 H)	2.207 (s, 3 H) 6.745 (d, J = 7.6 Hz, 2 H; 3,5-Ph) 6.921 (d, J = 7.2 Hz, 1 H; 2-Ph) 7.964 (d, J = 6.9 Hz, 1 H; 6-Ph)

Me	Ph	Br	**11b**	87	−50	1.623 (d, J = 2.3 Hz, 15 H)	1.406 (d, J = 10.3 Hz, 9 H)	6.90–7.04 (m, 3 H; 3,4,5-Ph) 7.090 (d, J = 6.9 Hz, 1 H; 2-Ph) 7.943 (d, J = 7.3 Hz, 1 H; 6-Ph)
Me	Ph	I	**11c**	95	−50	1.684 (d, J = 2.7 Hz, 15 H)	1.498 (d, J = 10.1 Hz, 9 H)	6.908 (m, 3 H; 3,4,5-Ph) 7.074 (d, J = 7.3 Hz, 1 H; 2-Ph) 8.130 (d, J = 6.8 Hz, 1 H; 6-Ph)
Me	C_6D_5	Br	**12b**	94	25	1.623 (d, $J \pm 2.6$ Hz, 15 H)	1.401 (d, J = 10.3 Hz, 9 H)	
Me	p-$C_6H_4CF_3$	Br	**13b**	85	−50	1.595 (d, J = 2.6 Hz, 15 H)	1.380 (d, J = 10.4 Hz, 9 H)	7.128 (d, J = 6.6 Hz, 1 H; 3-Ph) 7.145 (d, J = 6.8 Hz, 1 H; 2-Ph) 7.190 (d, J = 7.8 Hz, 1 H; 5-Ph) 8.083 (d, J = 7.9 Hz, 1 H; 6-Ph)
Me	p-C_6H_4F	Br	**14b**	81	−50	1.589 (d, J = 2.5 Hz, 15 H)	1.372 (d, J = 10.3 Hz, 9 H)	6.715 (m, 1 H; 3-Ph) 6.738 (m, 1 H; 5-Ph) 6.940 (dd, J = 6.3, 6.3 Hz, 1 H; 2-Ph) 7.835 (dd, J = 6.9, 6.9 Hz, 1 H; 6-Ph)
Me	p-C_6H_4OMe	Br	**15b**	90	−50	1.596 (d, J = 2.6 Hz, 15 H)	1.369 (d, J = 10.3 Hz, 9 H)	3.741 (s, 3 H; OMe) 6.598 (dd, J = 8.1, 2.9 Hz, 1 H; 3-Ph) 6.640 (dd, J = 8.5, 2.9 Hz, 1 H; 5-Ph) 6.899 (d, J = 7.7 Hz, 1 H; 2-Ph) 7.777 (d, J = 8.1 Hz, 1 H; 6-Ph)
Me	p-$C_6H_4NMe_2$	Br	**16b**	79	−50	1.594 (d, J = 2.4 Hz, 15 H)	1.366 (d, J = 10.3 Hz, 9 H)	2.819 (s, 6 H; NMe) 6.538 (d, J = 8.1 Hz, 1 H; 3-Ph) 6.577 (d, J = 8.5 Hz, 1 H; 5-Ph) 6.850 (d, J = 7.9 Hz, 1 H; 2-Ph) 7.964 (d, J = 8.3 Hz, 1 H; 6-Ph)
Me	o-tol (2 isomers, 3:1)	Br	**17b**	92	25	1.602 (d, J = 3.0 Hz, 15 H)	1.500 (d, J = 10.1 Hz; major) 1.516 (d, J = 9.8 Hz; minor)	6.678 (t, J = 7.6 Hz, 1 H; 4-Ph) 6.831 (t, J = 7.2 Hz, 1 H; 5-Ph) 7.037 (d, J = 8.1 Hz, 1 H; 6-Ph) 7.071 (d, J = 7.6 Hz, 1 H; 3-Ph) 2.550 (s, 3 H; Me) [major] 6.744 (t, J = 8.1 Hz, 1 H; 5-Ph′) 6.831 (t, J = 7.2 Hz, 1 H; 4-Ph′) 6.987 (d, J = 7.8 Hz, 1 H; 3-Ph′) 8.066 (d, J = 8.3 Hz, 1 H; 6-Ph′) 2.309 (s, 3 H; Me′) [minor]
Me	m-tol (2 isomers, 55:45)	Br	**18b**	93	−50	1.595 (d, J = 2.1 Hz, 15 H)	1.371 (d, J = 10.3 Hz; major) 1.380 (d, J = 10.3 Hz; minor)	2.217 (s, 6 H; Me, Me′) 6.720 (m, 1 H; 5-Ph, 5-Ph′) 7.703 (d, J = 7.8 Hz, 0.45 H; 2-Ph) 6.85 (m, 2 H; 4,6-Ph, 2,4-Ph′) 7.744 (s, 0.55 H; 6-Ph′)
Me	2,5-$C_6H_3Me_2$ (2 isomers, 3:1)	Br	**19b**	89	25	1.599 (d, J = 2.9 Hz; major) 1.581 (d, J = 2.9 Hz; minor)	1.496 (d, J = 9.9 Hz; major) 1.519 (d, J = 8.5 Hz; minor)	2.178 (s, 3 H; 5-Me) 2.494 (s, 3 H; 2-Me) 6.648 (d, J = 7.4 Hz, 1 H; 4-Ph) 6.911 (s, 1 H; 6-Ph) 6.921 (d, J = 7.7 Hz, 1 H; 3-Ph) [major] 2.206 (s, 3 H; 5-Me′) 2.259 (s, 3 H; 2-Me′) 6.648 (d, J = 7.4 Hz, 1 H; 4-Ph′) 6.873 (d, J = 7.5 Hz, 1 H; 3-Ph′) 7.893 (s, 1 H; 6-Ph′) [minor]
Me	3,5-$C_6H_3Me_2$	Br	**20b**	83	−50	1.594 (d, J = 2.5 Hz, 15 H)	1.369 (d, J = 10.3 Hz, 9 H)	2.182 (s, 6 H; 3,5-Me) 6.551 (s, 1 H; 4-Ph)

Table I (*Continued*)

compd						chem shifts[a]		
R′	R	X	no.	% yield	T, °C	C_5Me_5	PR'_3	other
								6.653 (s, 1 H; 2-Ph) 7.528 (s, 1 H; 6-Ph)
Me	3,4-$C_6H_3Me_2$ (2 isomers, 3:2)	Br	21b	87	−50	1.595 (br s, 15 H)	1.363 (d, J = 10.2 Hz, 9 H)	2.123 (br s, 6 H; 3,4-Me) 6.68–6.77 (m, 2 H; 5,6-Ph, 2,5-Ph′) 7.591 (d, J = 7.8 Hz, 0.4 H; 6-Ph′) 7.632 (s, 0.6 H; 2-Ph)
Ph	*p*-tol	Br	22b	93	−30	1.330 (d, J = 2.5 Hz, 15 H)	6.810 (dd, J = 9.8, 8.4 Hz, 2 H; o) 7.024 (m, 2 H; m) 7.110 (m, 2 H; m′) 7.176 (t, 1 H; p) 7.417 (m, 6 H; o′, p′, m″, p″) 7.846 (dd, J = 11.3, 7.8 Hz, 2 H; o″)	2.194 (s, 3 H; Me) 6.093 (d, J = 6.8 Hz, 1 H; 2-Ph) 6.397 (d, J = 6.8 Hz, 1 H; 3-Ph) 6.849 (d, J = 6.9 Hz, 1 H; 5-Ph) 7.892 (d, J = 7.8 Hz, 1 H; 6-Ph)
C_6D_5	*p*-tol	Br	23b[b]	92	−50	1.317 (d, J = 2.2 Hz, 15 H)		2.143 (s, 3 H; Me) 6.126 (d, J = 7.6 Hz, 1 H; 2-Ph) 6.331 (d, J = 7.5 Hz, 1 H; 3-Ph) 6.774 (d, J = 7.9 Hz, 1 H; 5-Ph) 7.957 (d, J = 7.8 Hz, 1 H; 6-Ph)
Ph	Ph	Br	24b	88	−30	1.338 (d, J = 2.4 Hz, 15 H)	6.821 (m, 2 H; o′) 7.016 (m, 2 H; m′) 7.144 (m, 3 H; m, p′) 7.422 (m, 6 H; o, m″, p, p″) 7.831 (dd, J = 11.7, 7.3 Hz, 2 H; o″)	6.306 (d, J = 7.4 Hz, 1 H; 2-Ph) 6.566 (t, J = 7.1 Hz, 1 H; 3-Ph) 6.82 (1 H; 4-Ph)[c] 7.02 (1 H; 5-Ph)[c] 8.055 (d, J = 7.8 Hz, 1 H; 6-Ph)
p-tol	*p*-tol	Br	25b	96	−30	1.324 (d, J = 2.5 Hz, 15 H)	2.168 (s, 3 H; Me) 2.384 (s, 3 H; Me) 2.421 (s, 3 H; Me) 6.655 (dd, J = 10.3, 8.3 Hz, 2 H; o) 6.810 (dd, J = 7.8, 1.5 Hz, 2 H; m) 6.977 (dd, J = 10.3, 8.3 Hz, 2 H; o′) 7.182 (m, 4 H; m′, m″) 7.719 (dd, J = 10.7, 7.8 Hz, 2 H; o″)	2.198 (s, 3 H; Me) 6.120 (d, J = 7.6 Hz, 1 H; 2-Ph) 6.415 (d, J = 7.3 Hz, 1 H; 3-Ph) 6.841 (d, J = 7.8 Hz, 1 H; 5-Ph) 7.888 (d, J = 7.8 Hz, 1 H; 6-Ph)
p-tol	C_6D_5	Br	26b[b]	91	−35	1.342 (d, J = 2.9 Hz, 15 H)	2.151 (s, 3 H; Me) 2.378 (s, 3 H; Me) 2.407 (s, 3 H; Me) 6.721 (br d, J = 8.3 Hz, 2 H; m) 6.775 (dd, J = 10.3, 8.3 Hz, 2 H; o) 7.065 (dd, J = 9.8, 8.3 Hz, 2 H; o′) 7.204 (br d, J = 7.8 Hz, 2 H; m″) 7.248 (br d, J = 7.8 Hz, 2 H; m′) 7.757 (dd, J = 10.3, 8.3 Hz, 2 H; o″)	
Et	*p*-tol	Br	27b	88	−50	1.539 (br s, 15 H)	0.931 (dt, J = 14.8, 7.4 Hz, 9 H) 1.70 (m, 3 H) 1.88 (m, 3 H)	2.208 (s, 3 H; Me) 6.726 (d, J = 7.6 Hz, 1 H; 3-Ph) 6.759 (d, J = 8.1 Hz, 1 H; 5-Ph) 6.929 (d, J = 7.4 Hz, 1 H; 2-Ph) 7.811 (d, J = 7.6 Hz, 1 H; 6-Ph)
Me	$CH{=}CH_2$	Br	28b[d]	86	25	1.489 (d, J = 2.7 Hz, 15 H)	1.154 (d, J = 10.7 Hz, 9 H)	5.296 (d, J = 17.0 Hz, 1 H) 6.200 (d, J = 9.0 Hz, 1 H) 8.500 (dddd, J = 17, 9, 4.0, 1.8 Hz, 1 H)
Me	$CMe{=}CH_2$	Br	29b	86	−50	1.659 (d, J = 1.9 Hz, 15 H)	1.477 (d, J = 10.4 Hz, 9 H)	2.211 (s, 3 H)

							4.429 (br s, 1 H) 5.480 (br s, 1 H)
Me	$C{=}CH(CH_2)_3$	Br	**30b**[d]	67	25	1.484 (d, J = 2.8 Hz, 15 H)	1.176 (dd, J = 10.5, 0.6 Hz, 9 H)	1.940 (m, 2 H; 4-CH_2) 2.523 (m, 2 H; 3-CH_2) 2.631 (m, 1 H; 5-CH_2) 3.200 (m, 1 H; 5-CH_2) 5.152 (br s, 1 H; 2-CH)
Me	CH_2Ph	Br	31b	13	25	1.240 (d, J = 2.5 Hz, 15 H)	1.060 (d, J = 10 Hz, 9 H)	2.680 (ddd, J = 17, 16, 4 Hz, 1 H; CH_2) 3.700 (m, 1 H; CH_2) 7.010 (t, J = 7.4 Hz, 1 H; p) 7.173 (t, J = 7.3 Hz, 2 H; m) 7.630 (d, J = 6.8 Hz, 2 H; o)
Et	*p*-tol	I	**32c**[e]	74	−50	5.456 (d, J = 1.2 Hz, 5 H)	0.955 (dt, J = 15.5, 7.8 Hz, 9 H) 1.820 (m, 3 H) 2.025 (m, 3 H)	2.222 (s, 3 H; Me) 6.741 (d, J = 7.8 Hz, 2 H; m) 7.639 (d, J = 7.5 Hz, 2 H; o)
Et	I	I	**33c**[e]	93	25	5.684 (d, J = 1.5 Hz, 5 H)	1.169 (dt, J = 16.6, 7.8 Hz, 9 H) 2.290 (dq, J = 10.3, 7.6 Hz, 6 H)	

[a] In $CDCl_3$ solvent, except as noted. [b] THF-d_8. [c] Resonance obscured by PPh_3 resonance, but integrable. [d] C_6D_6. [e] C_5H_5 derivative.

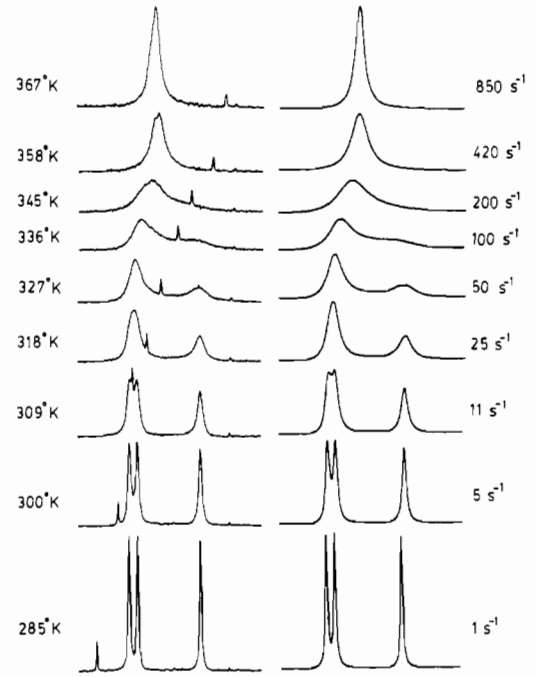

Figure 3. Observed (left) and calculated (right) ^1H NMR spectra for the δ 2.6–1.95 region of $(C_5Me_5)Rh[P(p\text{-tol})_3](C_6D_5)Br$ in THF-d_8 as a function of temperature.

For compounds **10a–c**, **11b**, **13b–16b**, and **27b** the free energy of activation was measured by determining the coalescence temperature (T_c) for the exchange of the ortho hydrogens. Equation 2 was then used to calculate the rate constant for interconversion ($\delta\nu$ = frequency difference between exchanging resonances at T_c) and $\Delta G^{\ddagger}$ obtained from the Eyring equation (Table III).[7]

$$k = \pi\delta\nu/2^{1/2} \tag{2}$$

The phenyl derivative **11b** also showed a temperature-dependent NMR spectrum, with the anticipated two ortho hydrogens appearing as doublets and the meta and para hydrogens appearing as a multiplet at low temperature. The increased complexity of the spectrum and the partial overlapping of some resonances prevented calculation of reliable activation parameters by CBS analysis for this molecule.

The ^1H NMR spectrum of the compound $(C_5Me_5)Rh[P(p\text{-tol})_3](C_6D_5)Br$ (**26b**) at 285 K shows a complex pattern in the aromatic region. Three separate pairs of doublets were observed for the tritolylphosphine ligand. In addition, three singlets were observed in the tolyl methyl region, indicating an inequivalence of all three tolyl groups. When the sample is heated to 378 K, the three singlets coalesce into a single resonance (Figure 3). CBS simulation of the spectra allows the determination of the rate constants for tolyl group interconversion over the temperature range 285–367 K.

At lower temperatures spin saturation transfer (SST) was used to measure the rate of interconversion of the tolyl methyl groups. This method is derived from a two-site exchange technique described by Dahlquist[8] and Morris.[9] In the experiment, irradiation of the singlet of **26b** at δ 2.172 (*A*) with a selective 180° pulse results in an inversion of the magnetization at that site. The interconversion of the tolyl groups transfers magnetization to the resonances at δ 2.402 (*B*) and δ 2.429 (*C*) with a rate constant k competitive with relaxation

(7) Sandström, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982, p 79.
(8) Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406–410.
(9) Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433–462.

Table II. $^{31}P\{^1H\}$ NMR,[a] ^{13}C NMR,[a] and Mass Spectral Data for the Compounds $(C_5Me_5)Rh(PR'_3)RX$

compd							
R'	R	X	no.	T, °C	^{31}P	^{13}C	mass spectrum
Me	Cl	Cl	**2a**	25	8.787 (d, J = 137 Hz)		384, 386, 388 (M^+)
Me	Br	Br	**2b**	25	3.733 (d, J = 137 Hz)		472, 474, 476 (M^+)
Me	I	I	**2c**	25	−2.520 (d, J = 138 Hz)		
Ph	Cl	Cl	**3a**	25	30.189 (d, J = 145 Hz)		
Ph	Br	Br	**3b**	25	27.988 (d, J = 148 Hz)		
Me	Me	Cl	6a	25		97.322 (s) 14.829 (qd, J = 129.2, 30.6 Hz) 9.120 (q, J = 127.3 Hz) −1.693 (qdd, J = 133.4, 24.2, 16.8 Hz)	349, 351 ($(M-15)^+$)
Me	n-C_3H_7	Br	7b	25		98.016 (d, J = 4.5 Hz) 29.051 (td, J = 122.6, 5.7 Hz) 23.183 (tdd, J = 136.0, 22.7, 13.6 Hz) 19.754 (q, J = 124.3 Hz) 15.844 (qd, J = 126.0, 30.2 Hz) 9.360 (q, J = 127.0 Hz)	
Me	c-C_5H_9	Cl	8a	25	4.719 (d, J = 169 Hz)	98.177 (dd, J = 3.5, 3.5 Hz) 37.455 (t, J = 133 Hz) 36.803 (t, J = 133 Hz) 34.83 (br d, J = 159 Hz) 27.152 (t, J = 128 Hz) 26.773 (t, J = 128 Hz) 15.142 (qd, J = 129, 28 Hz) 9.493 (q, J = 127 Hz)	
Me	p-tol	Cl	10a				440, 442 (M^+)
Me	p-tol	Br	10b				484, 486 (M^+)
Me	p-tol	I	10c				532 (M^+)
Me	Ph	Br	11b	−50	5.263 (d, J = 155 Hz)		470, 472 (M^+)
Me	Ph	I	11c				518 (M^+)
Me	C_6D_5	Br	12b				477, 479 (M^+)
Me	p-$C_6H_4CF_3$	Br	13b				539, 541 (M^+)
Me	p-C_6H_4F	Br	14b				488, 490 (M^+)
Me	p-C_6H_4OMe	Br	15b				500, 502 (M^+)
Me	o-tol	Br	17b				484, 486 (M^+)
Me	m-tol	Br	18b				484, 486 (M^+)
Me	2,5-$C_6H_3Me_2$	Br	19b	25	4.861 (d, J = 155 Hz; major) −3.961 (d, J = 158 Hz; minor)		498, 500 (M^+)
Me	3,5-$C_6H_3Me_2$	Br	20b				498, 500 (M^+)
Me	3,4-$C_6H_3Me_2$	Br	21b	25	4.859 (d, J = 155 Hz)		498, 500 (M^+)
Me	$CH{=}CH_2$	Br	28b	25	6.985 (d, J = 153 Hz)[b]	158.53 (ddd, J = 151, 27, 27 Hz) 119.83 (tdd, J = 152, 15, 15 Hz) 98.757 (br s) 15.604 (qd, J = 128, 34 Hz) 9.642 (q, J = 127.7 Hz)	419, 421 (M^+)
Me	$CMe{=}CH_2$	Br	29b				433, 435 (M^+)
Me	$C{=}CH(CH_2)_3$	Br	30b	25	6.738 (d, J = 153 Hz)[b]		460, 462 (M^+)
Et	p-tol	I	32c[c]	−50	35.804 (d, J = 146 Hz)		504 (M^+)
Et	I	I	33c[c]	25	31.341 (d, J = 132 Hz)		

[a] $CDCl_3$ solvent, except as noted. [b] C_6D_6. [c] C_5H_5 derivative.

$(1/T_1)$. The Bloch equations for magnetization along the field (z) axis are given in eq 3–5. If the time evolution of the

$$dM_z^A/dt = -(2k + 1/T_1)A + kB + kC + A_0/T_1 \quad (3)$$

$$dM_z^B/dt = -(2k + 1/T_1)B + kA + kC + B_0/T_1 \quad (4)$$

$$dM_z^C/dt = -(2k + 1/T_1)C + k_A + kB + C_0/T_1 \quad (5)$$

change in the intensities of peaks A, B, and C is monitored by difference NMR spectroscopy, then the relationships in eq 6 and 7 can be used to determine T_1 and k (where M_0^z = initial

$$A + B + C = -2M_0^z e^{-(t/T_1)} \quad (6)$$

$$A - (B + C)/2 = -2M_0^z e^{-(1/T_1 + 3k)t} \quad (7)$$

magnetization of A, B, or C along the z axis). An Eyring plot of the rate constants determined by both SST and CBS analysis is shown in Figure 4. The excellent agreement between these different techniques supports the accuracy of these activation parameter measurements: $\Delta H^\ddagger = 15.7 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -2.8 \pm 0.2$ eu.

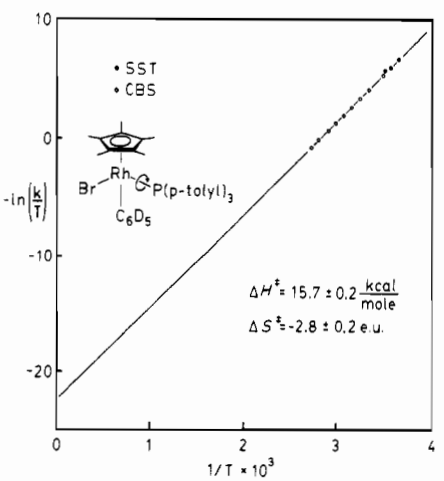

Figure 4. Eyring plot for the dynamic process in $(C_5Me_5)Rh[P(p\text{-tol})_3](C_6D_5)Br$.

Structural Determination of $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ (11b). In order to examine the geometry and steric environment of the aryl group bound to the rhodium center, a single-crystal X-ray determination of the structure of **11b** was

Table III. Activation Parameters for Hindered Rotations

compd	method[a]	T_c, K[b]	$\Delta\nu$, Hz	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
$(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ (**11b**)	CT	308.1	342.5			14.0 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-tol})Br$ (**10b**)	CT	305.9	345.0			13.9 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4CF_3)Br$ (**13b**)	CT	309.1	375.0			14.0 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4F)Br$ (**14b**)	CT	311.2	358.0			14.1 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4OMe)Br$ (**15b**)	CT	307.0	351.0			13.9 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4NMe_2)Br$ (**16b**)	CT	303.9	338.0			13.8 ± 0.1[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-tol})Cl$ (**10a**)	CT	306.0	292.0			14.0 ± 0.1[c]
	CBS	306.0		9.8 ± 0.2	−13.7 ± 0.6	14.0 ± 0.3[c]
$(C_5Me_5)Rh(PMe_3)(p\text{-tol})I$ (**10c**)	CT	291.5	417.0			13.1 ± 0.1[c]
$(C_5Me_5)Rh(PEt_3)(p\text{-tol})Br$ (**27b**)	CT	323.6	353.0			14.7 ± 0.1[c]
$(C_5Me_5)Rh[P(C_6D_5)_3](p\text{-tol})Br$ (**23b**)	CBS	306.0		11.0 ± 0.2	−9.8 ± 0.6	14.0 ± 0.3[c]
$(C_5Me_5)Rh[P(p\text{-tol})_3](C_6D_5)Br$ (**26b**)	CBS, SST	306.0		15.7 ± 0.2	−2.8 ± 0.2	16.6 ± 0.3[d]
$(C_5Me_5)Rh[P(p\text{-tol})_3]Br_2$ (**4b**)	CBS	306.0		14.3 ± 0.3	−1.8 ± 1.1	14.8 ± 0.3[d]

[a] CT = peak separation at coalescence temperature; CBS = complete band shape analysis; SST = spin saturation transfer. [b] ±1.0 K. [c] Rh-C rotation. [d] Rh-P rotation.

Table IV. Selected Distances (Å) and Angles (deg) in $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$

Distances			
Rh-C(11)	2.054 (9)	Rh-P	2.458 (3)
Rh-Br	2.533 (2)		
Angles			
Rh-C(11)-C(16)	121.0 (6)	C(11)-Rh-P	88.0 (3)
Rh-C(11)-C(12)	122.3 (7)	P-Rh-Br	86.3 (1)
C(11)-Rh-Br	94.4 (3)		
Torsional Angles			
Br-Rh-C(11)-C(16)	157.6 (6)	Br-Rh-C(11)-C(12)	29.6 (7)

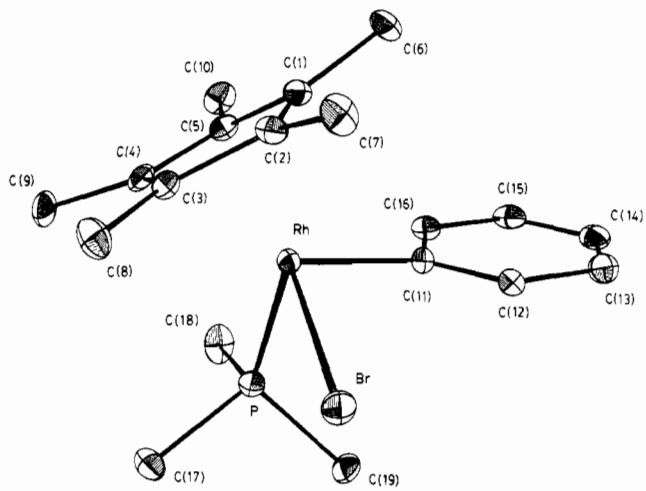

Figure 5. ORTEP plot of $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$. Ellipsoids are shown at 50% probability.

undertaken. Normal data collection, heavy-atom solution, and refinement (R = 4.68%, R_w = 6.15%) produced the ORTEP plot shown in Figure 5. Tables IV and V give selected bond parameters and atomic coordinates.

One notable feature of the structure is that the plane of the phenyl ring is oriented so as to minimize steric hindrance with the permethylcyclopentadienyl ring. Also, the methyl groups of the trimethylphosphine ligand are staggered with respect to the permethylcyclopentadienyl ring, the bromide, and the phenyl ring. The Rh(1)–C(11) bond distance, 2.05 Å, and other distances and angles are all quite normal for this molecule.

Discussion

The temperature-dependent NMR spectra for these complexes can be interpreted in terms of two independent dynamic processes: (1) hindered rotation about the metal–carbon bond and (2) hindered rotation about the metal–phosphorus bond. As these are distinct processes, each will be addressed separately prior to examination for common features.

Table V. Atomic Fractional Coordinates for $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$

atom	x/a	y/b	z/c
Rh	0.15900 (8)	0.23625 (6)	0.13420 (3)
Br	−0.01408 (13)	0.29066 (9)	0.23246 (5)
P	0.32532 (28)	0.19144 (22)	0.21693 (13)
C1	0.1054 (11)	0.2428 (8)	0.0213 (5)
C10	0.3631 (12)	0.1439 (10)	0.0020 (5)
C6	0.1354 (13)	0.3425 (9)	−0.0281 (5)
C8	−0.1149 (12)	0.0404 (10)	0.1346 (6)
C7	−0.1614 (12)	0.2856 (10)	0.0623 (6)
C9	0.2075 (13)	−0.0515 (8)	0.0940 (6)
C2	−0.0215 (11)	0.2147 (8)	0.0585 (5)
C4	0.1432 (11)	0.0656 (7)	0.0769 (5)
C5	0.2168 (9)	0.1546 (8)	0.0365 (4)
C3	0.0009 (10)	0.1029 (8)	0.0908 (4)
C11	0.2548 (11)	0.3986 (7)	0.1285 (4)
C12	0.1808 (11)	0.4966 (8)	0.1454 (4)
C16	0.3984 (10)	0.4140 (8)	0.0987 (4)
C15	0.4505 (12)	0.5250 (10)	0.0881 (5)
C13	0.2361 (14)	0.6082 (8)	0.1343 (5)
C14	0.3748 (14)	0.6225 (9)	0.1048 (5)
C17	0.2649 (11)	0.0755 (9)	0.2743 (5)
C18	0.5088 (12)	0.1423 (9)	0.1879 (7)
C19	0.3793 (13)	0.3044 (9)	0.2781 (6)

The compounds studied here containing metal–carbon bonds can be divided into three classes with regard to the former dynamic process: (a) those whose barrier to rotation is so low (<8 kcal/mol) that rotation cannot be frozen out at low temperatures; (b) those whose barrier to rotation is so high (>18 kcal/mol) that two distinct isomers exist, even at high temperatures; (c) those whose barrier to rotation is moderate enough that the rotation can be frozen out at low temperature or made rapid at elevated temperatures. Of the molecules studied here, only the complex $(C_5H_5)Rh(PEt_3)(p\text{-tol})I$ (**32c**), which lacks a permethylcyclopentadienyl ring, failed to show any evidence for a barrier to rotation at low temperature (−50 °C). If the difference between the tolyl aromatic resonance frequencies in **32c** is assumed to be 300 Hz (cf. Table III), then an upper limit of ~8 kcal/mol can be placed on the barrier to rotation.[10]

At the other extreme, the compound $(C_5Me_5)Rh(PMe_3)(o\text{-tol})Br$ (**17b**) showed a ^1H NMR spectrum containing two singlets for tolyl methyl groups at δ 2.550 and 2.309 in a 3:1 ratio. The spectrum can be interpreted in terms of two nonequilibrating isomers in which the *o*-methyl group on the tolyl ring is adjacent to either the bromine or the PMe_3 ligand, with the former isomer being favored on steric grounds. The NMR spectrum remained invariant at temperatures up to 60 °C,

(10) With use of a peak separation of 300 Hz and rate constant of 10^5 s^{-1} (corresponding to $\Delta G^{\ddagger}$ = 8 kcal/mol at 223 K), a threefold increase in the bandwidth of the ortho resonance would be expected, while the ^1H NMR spectrum of **32c** at −50 °C showed no broadening at the ortho resonance.

which corresponds to a lower limit of 18 kcal/mol for the interconversion process.[11] Another compound that is crowded at the rhodium center and also shows two isomers at room temperature is $(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)Br$ (**19b**). Here, again, the steric interactions of the *o*-methyl group lead to a high rotational barrier. At low temperature (−50 °C), compounds with asymmetric substitution at the meta positions of the aryl ring (**18b**, **21b**) also showed two isomers due to the freezing out of the aryl rotation with the substituent adjacent to either the bromide or the phosphine.

Most of the derivatives prepared showed behavior intermediate to that of the cases discussed above. All of the aryl complexes with PMe_3, PPh_3, or $P(p\text{-tol})_3$ as a ligand showed temperature-dependent NMR spectra that indicated a difference between the halves of the aryl ring at low temperature. This effect is most easily interpreted for the para-substituted phenyl derivatives, in which each hydrogen is coupled significantly only to its neighboring hydrogen, giving rise to AB patterns in the δ 6.5–8.5 region.

The coalescence of these AB patterns with increasing temperature permitted an accurate determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the restricted rotation in two molecules containing *p*-tolyl ligands, **10a** and **23b**. While the steric interaction of the triphenylphosphine ligand with aryl rotation in **23b** might be expected to be greater than the trimethylphosphine interaction in **10a**, there is no difference in their measured rotational barriers ($\Delta G^{\ddagger}$) at 25 °C, although $\Delta H^{\ddagger}$ is larger for **23b**. The planar nature of the phosphine's phenyl groups may present less crowding to the rotating group than one might initially anticipate.

Interestingly, the triethylphosphine derivative $(C_5Me_5)Rh(PEt_3)(p\text{-tol})Br$ (**27b**) shows a 14.7 kcal/mol barrier to rotation at 324 K, significantly higher than the barrier in **10a** (14.3 kcal/mol) or **23b** (14.2 kcal/mol) at the temperature. Apparently, triethylphosphine is sufficiently more crowded than trimethylphosphine or triphenylphosphine that the rotational barrier is affected slightly.

One question that arises concerning the hindered rotation about the rhodium–aryl bond is the contribution of π-back-bonding to the rotational barrier. There are three indications that suggest that π-bonding is unimportant in these rhodium-aryl complexes. First, the structure of **11b** shows a rhodium–carbon distance of 2.05 Å, only slightly shorter than the single-bond distance of 2.10 Å in $(C_5Me_5)Rh(PPh_3)(\eta^2\text{-}CH_2CH_2CH_2CH_2)$.[12] In fact, this shortening can be attributed to the shorter single-bond distance associated with an sp^2-hybridized carbon compared to an sp^3-hybridized carbon. Second, the nature of the para substituent on the phenyl ligand has little effect upon the rotational barrier (Table III), regardless of whether the group is σ-donating (**10b**), σ-withdrawing (**13b**, **14b**), or π-donating (**15b**, **16b**). The free energies of activation (as measured at coalescence temperatures in the range 304–311 K) are spread over a 0.2 kcal/mol range, which is comparable to the estimated limit of error in the $\Delta G^{\ddagger}$ values. Last, these aryl complexes are formally rhodium(III) and are not expected to have sufficient electron density on the metal available for π-back-bonding.

The halide ligand was found to be responsible for a small portion of the rotational barrier, but not in the direction initially expected. While the chloro (**10a**) and bromo (**10b**) derivatives showed activation barriers of 13.9 kcal/mol (306 K), the iodo derivative **10c** showed a lower barrier, 13.1 kcal/mol, at 292 K. Assuming $\Delta S^{\ddagger}$ to be −15 eu for **10c**, $\Delta G^{\ddagger}$ would be raised to only 13.3 kcal/mol at 306 K, still substantially smaller than in the chloro and bromo compounds. The origin of this effect is not obvious, but it may be that since iodide is a softer atom than either chloride or bromide and farther from the metal, the ortho hydrogens on the aryl group encounter a more pliable barrier.

Previously, the complexes $Ni(PR_3)_2(aryl)(C{=}CHCH_2CH_2O)$,[4d] $CpZrR[CH(SiMe_3)_2]$ (R = Cl, H, Me, Pr, Ph),[4b,c] $(CO)_5W[CH(OMe)Ph]$,[4a] $CpFe(CO)(L)(R_f)$ (L = PPh_3, PPh_2Me; R_f = CF_3, CF_2CF_3, $CF(CF_3)_2$, CH_2SiMe_3, $COCH_2SiMe_3$),[4e,f] and $Cp_3U(CHMe_2)$[4g] have been shown to exhibit a barrier to rotation about the metal–carbon σ-bond. The nickel complexes all showed barriers for rotation of the vinyl ether of 10–11 kcal/mol at temperatures of −40 to −80 °C. The tungsten complex with a metal–carbon bond of pure σ character also showed a low barrier to rotation (8.7 kcal/mol at −84 °C). The rotational barriers in the zirconium compounds fall in the range 11.6–15.3 kcal/mol at temperatures of −30 °C. Mesityl rotational barriers are 12.3–14.8 kcal/mol.[4h]

While the barriers to rotation about the Fe–C bonds in the perfluoroalkyliron derivatives were not measured directly, they were estimated to fall in the 5–10 kcal/mol range. The trimethylsilyl derivatives show evidence in the IR spectra for more than one rotamer, although rotation is rapid on the NMR time scale at −80 °C ($\Delta G^{\ddagger} < 9$ kcal/mol). Finally, hindered rotation about the uranium–carbon bond was found to have an activation energy of 10.5 kcal/mol. Consequently, all of the previously measured barriers to metal–carbon single-bond rotation (except in the Zr compound) are substantially lower than those for metal–aryl rotation found here.

The other dynamic process observed in these compounds is hindered rotation about the rhodium–phosphorus bond, which has been observed previously in complexes with bulky alkylphosphines such as tricyclohexylphosphine,[5c] di-*tert*-butylmethylphosphine,[5a,b] dimethylphenylphosphine,[5d] and diphenylmethylphosphine.[5a] The dihalide compounds **3a**–**c** and **4b** possess NMR spectra indicating an inequivalence of the three aryl groups attached to phosphorus that can be attributed to hindered rotation. Compound **26b** with both halide and phenyl ligands also shows hindered phosphine rotation with an activation barrier that is ~2 kcal/mol higher than the barrier in **4b**. This increase in activation energy is undoubtedly attributable to the increased steric demands of the tolyl group compared to those of the bromide.

The only other compound for which activation parameters were measured for phosphine rotation was reported by Bushweller et al.[5a] They found values for $\Delta G^{\ddagger}$ of 8.6–13.7 kcal/mol (25 °C) for the hindered rhodium–phosphorus rotation in *trans*-$RhX(CO)[PR(t\text{-}Bu)_2]_2$ (X = Cl, Br, I; R = Cl, Me, Ph). By comparison, $\Delta G^{\ddagger}(25\ °C)$ = 14.8 kcal/mol for **4b** and 16.5 kcal/mol for **26b**. The larger barriers to Rh–P rotation in **4b** and **26b** are consistent with a more crowded effectively 6-coordinate rhodium center compared to a 4-coordinate square-planar rhodium center.

The rotational barriers about the rhodium–phosphorus bond and the rhodium–carbon bond can be compared in virtually the same molecule by examining the activation parameters for **23b** and **26b**. At 25 °C, $\Delta G^{\ddagger}$ is 13.9 kcal/mol for the latter, indicating that phenyl rotation is about 75 times faster than phosphine rotation. Consequently, a concerted or "cogwheel" rotation of the two ligands does not appear to be occurring here. There is also no evidence for restricted rotation about the rhodium–trimethylphosphine bond as might be expected due to the small size of this ligand.

Conclusion

This paper has presented a number of new organometallic permethylcyclopentadienyl compounds of rhodium and probed

(11) With use of a peak separation of 95 Hz and a rate constant of 10 s^{-1} (corresponding to $\Delta G^{\ddagger}$ = 18 kcal/mol at 333 K), the two exchanging peaks would have been expected to double their bandwidth and halve their intensity.

(12) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zocchi, M. *Inorg. Chem.* **1980**, *19*, 3590–3597.

their conformational potentials. The variety of rotational processes with significant activation energies indicates an important feature of these systems, extreme steric hindrance. Both metal–aryl and metal–phosphine rotations appear to be hindered by only steric interactions, with electronic factors playing a very minor role. There is also no evidence for any contribution to the rotational barrier by rhodium–aryl π-bonding. Interestingly, both trimethylphosphine and triphenylphosphine appear to produce comparable barriers to rhodium–aryl rotation, whereas triethylphosphine induces a noticably higher barrier. On the basis of these studies, it is clear that other bulky ligands (such as secondary or tertiary alkyl) should also exhibit conformational preferences. Further studies of chemical reactions that will capitalize on the conformational barriers discovered here are planned.

Experimental Section

Except for the compounds that contain σ-bonded alkyl ligands, all of the rhodium(III) complexes described in this paper are air stable and can be handled in the air once the reaction mixtures have been properly quenched. Although in most cases the starting materials and products are air stable, crude reaction mixtures containing excess Grignard or alkyllithium reagents are very air sensitive. Otherwise, except where noted, all operations were performed under a nitrogen atmosphere, either in a Vacuum Atmospheres Corp. Dri-Lab or on a high-vacuum line with use of Schlenk techniques.

Rhodium trichloride (42.9% Rh) was obtained as a generous loan for Johnson Matthey, Inc. $[(C_5Me_5)RhCl_2]_2$,[2] $(C_5Me_5)Rh(C_2H_4)_2$,[13] and $(C_5H_5)Rh(C_2H_4)(PEt_3)$[14] were prepared by previously published procedures. Trimethylphosphine and triethylphosphine were purchased from Strem Chemical Co. and were purified by vacuum distillation prior to use (25 °C, 10^{-3} mm). Triphenylphosphine and hexamethyl(Dewar benzene) were purchased from Aldrich Chemical Co. and were used without further purification. All aryl, alkenyl, and alkyl halides were purchased from Aldrich Chemical Co., except for neopentyl bromide and 1-bromo-3,5-dimethylbenzene, which were purchased from Pfaltz and Bauer, Inc. Each was vacuum distilled from a small amount of sodium dispersion (40% in oil) prior to use. 1-Bromocyclopentene was synthesized by using a conventional procedure[15] and purified by preparative gas chromatography prior to use. Lithium wire, lithium powder, sodium dispersion (40% in oil), methyllithium (1.64 M in ether), and vinylmagnesium bromide were purchased from Alfa-Ventron. Magnesium turnings (99.98+%) were obtained from Reade Manufacturing Corp. $P(p\text{-tol})_3$ (tol = tolyl) and $P(C_6D_5)_3$ were prepared according to published procedures.[16] Tetrahydrofuran (THF) and diethyl ether were distilled from dark purple solutions of sodium–benzophenone ketyl under vacuum. Benzene and hexane were vacuum distilled from dark purple solutions of potassium–benzophenone ketyl containing tetraglyme. Before distillation, hexane was 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 anhydrous $CaCl_2$. Methylene chloride (Mallinckrodt, reagent grade) was used without further purification, except when used on the high-vacuum line, in which case it was dried over $CaCl_2$ and freeze–pump–thaw degassed (four cycles) before use.

All alkyllithium and Grignard reagents were standardized immediately prior to use. Except for vinylmagnesium bromide, standardization was accomplished by titrating a 1.00-mL aliquot of the reagent to a 1,10-phenanthroline end point with use of 1.06 M *tert*-butyl alcohol in *p*-xylene.[17] A freshly opened bottle of vinylmagnesium bromide was standardized by quenching an aliquot with distilled water and titrating the solution with standard HCl to a phenolphthalein end point.

Low temperatures were maintained with use of liquid N_2 (−196 °C), acetone/dry ice (−78 °C), $(CH_3OH/H_2O$ (45:55))/liquid N_2 (−40 °C), $(CH_3OH/H_2O$ (30:70))/liquid N_2 (−20 °C), and ice/water (0 °C) baths.

Thick-layer chromatography was performed on precoated Analtech silica gel plates of 2-mm thickness. Filtration chromatography was performed as follows: a hexane slurry of silica gel (Merck catalog no. 7740 silica gel 60 PF-254) was poured into a 30-mL fine-grade sintered-glass funnel. The excess solvent was removed by placing the funnel on a filtering flask and applying a moderate water aspirator vacuum. Just before the silica gel cake could fragment due to lack of solvent, the silica gel was pressed tightly and evenly with use of a glass rod with a flattened tip. After removal of the vacuum, the compound to be purified was evenly applied to the top of the silica gel cake with a minimal amount of solvent. The vacuum was again applied, and the compound was eluted with solvent, with fractions collected in small flasks.[18]

Routine ^1H NMR spectra were recorded on a Varian EM-390 NMR spectrometer. High-field ^1H (400.13 MHz), ^{13}C, (100.62 MHz), and ^{31}P (162.00 MHz) NMR spectra were recorded on a Bruker WH-400 spectrometer. ^1H NMR spectra are reported in units of δ (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). ^{13}C NMR spectra were measured relative to a solvent resonance ($CDCl_3$, δ 77.00; C_6D_6, δ 128.00) and are reported in units of δ (downfield from internal tetramethylsilane). ^{31}P NMR spectra are reported in units of δ (downfield from a coaxially mounted sealed capillary of 30% H_3PO_4). The temperature for dynamic NMR experiments was regulated by a Bruker BVT-1000 temperature control unit (±0.1 °C). Temperatures were calibrated with use of standard methanol (−100 to +60 °C) and ethylene glycol (20–180 °C) calibration samples obtained from Wilmad Glass Co. C_6D_6 and THF-d_8 (Stohler Isotope Co.) were vacuum distilled from sodium–benzophenone ketyl and stored in glass ampules fitted with Teflon stopcocks. $CDCl_3$ (Aldrich) was vacuum distilled from P_2O_5 (25 °C, 10^{-3} mm).

Electron impact mass spectral analyses were conducted on a VG 7035 gas chromatograph/mass spectrometer at 70 or 20 eV. Elemental analyses were performed by Galbraith Laboratories or Mic-Anal Labs. Preparative gas chromatography (50-μL injections) was performed on a 6 ft × $^1/_4$ in. 10% SE-30/Chromosorb WAW column (80 °C, 20 mL/min) with a Varian 90P gas chromatograph.

Preparation of Bromide-Containing Grignard Reagents. For (*p*-tol)MgBr in THF, anhydrous THF (20 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing Mg turnings (400 mg, 16.5 mmol). A small portion of *p*-bromotoluene (100 μL, 0.81 mmol) was introduced by syringe under N_2 at room temperature, followed by 1,2-dibromoethane (50 μL, 0.4 mmol). The mixture was stirred at 25 °C until initiation of the Grignard reaction had occurred as evidenced by a slight corrosion of the shiny metal surface. The remaining *p*-bromotoluene (900 μL, 7.30 mmol) was added dropwise at 0 °C over a period of 20 min. The mixture was stirred for 1 h at 25 °C, transferred to a nitrogen-filled septum-capped bottle via cannula, and then standardized before use. The other bromo Grignard reagents were prepared in an analogous fashion.

Preparation of Chloride-Containing Grignard Reagents.[19] For (*p*-tol)MgCl in THF, anhydrous THF (30 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing Mg turnings (4 g, 0.165 mol). *p*-Chlorotoluene (2.5 mL, 0.021 mol) was introduced by syringe all at once, and 1,2-dichloroethane (2 mL, 0.025 mol) was then added dropwise over a period of 2 h at 25 °C. The mixture was stirred for 4 h before being decanted via a cannula into a septum-capped 40-mL centrifuge tube under N_2. After centrifugation, the clear Grignard solution was transferred to a nitrogen-filled, septum-capped bottle.

Preparation of Cyclopentyllithium in Hexane.[20] Anhydrous hexane (20 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing lithium powder (150 mg, 21.6 mmol). A condenser was attached under a flow of N_2, the mixture brought to reflux, and a small portion of cyclopentyl chloride (100 μL, 0.96 mmol) added. After the reaction had begun (as evidenced by a darkening of the reaction mixture), the remaining cyclopentyl chloride (900 μL, 8.65 mmol) was added dropwise via syringe over 15 min. The mixture was refluxed for an additional 45 min and then allowed to stand undisturbed for 1 h while

(13) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875–2883.
(14) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245–252.
(15) Giacomoni, J. C.; Cambon, A.; Rouvier, E. *Bull. Soc. Chim. Fr.* **1970**, *37*, 3097–3098.
(16) Dodnow, J.; Medox, H. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 907–911.
(17) Watson, S. C.; Eastman, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.
(18) Cf.: Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(19) Lai, Y.-H. *Synthesis* **1981**, 585–601.
(20) Applequist, D. E.; O'Brien, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 743–748.

cooling. The gray solution above the black precipitate was decanted via a cannula into a nitrogen-filled septum-capped bottle. The solution was filtered through a fine-grade frit in the drybox, diluted to 25 mL, with hexane, and titrated before use.

Preparation of Neopentyl- and *n*-Propyllithium in Ether. Diethyl ether solutions (10 mL) of *n*-propyllithium and neopentyllithium were prepared from 1-bromopropane (1.5 mL, 16.5 mmol) and neopentyl bromide (1.4 mL, 11.7 mmol), respectively, and lithium wire (3.0 equiv) according to the procedure of Gilman.[21]

Preparation of $[(C_5Me_5)RhCl_2]_2$ (1a). **1a** was prepared in 91% yield from $RhCl_3 \cdot 3H_2O$ (200 g, 7.6 mmol) and hexamethyl(Dewar benzene) (4 mL, 19.8 mmol) according to the procedure of Kang et al.[2]

Preparation of $[(C_5Me_5)RhBr_2]_2$ (1b). A suspension of **1a** (330 mg, 0.53 mmol) and NaBr (1.0 g, 10 mmol) in acetone (10 mL) was refluxed under nitrogen for 2 h. The acetone was removed (25 °C, 20 mm) and the residue extracted with CH_2Cl_2 (50 mL). Seven milliliters of hexane was added and the solution slowly concentrated under vacuum (20 mm) until crystals appeared. The orange-red product was collected in a fine-fritted funnel, washed with hexane (5 mL), and air-dried to give 416 mg (99%) of pure product.

Preparation of $[(C_5Me_5)RhI_2]_2$ (1c). A suspension of **1a** (500 mg, 0.81 mmol) and NaI (2 g, 13 mmol) in acetone (30 mL) was stirred for 15 min at 25 °C and the solvent then evaporated (25 °C, 20 mm). The product was isolated as dark violet crystals by extracting the residue with CH_2Cl_2 and recrystallizing as for **1b**; yield 765 mg (96%).

Preparation of $(C_5Me_5)Rh(PMe_3)Br_2$ (2b).[22] A 1-L volume of PMe_3 (24.5 mm, 25 °C, 1.32 mmol) was condensed into a flask containing **1b** (500 mg, 0.63 mmol) and CH_2Cl_2 (10 mL) at −196 °C. The mixture was warmed to 25 °C and stirred for 10 min before removing the volatiles (25 °C, 10^{-3} mm). The crude product was recrystallized from CH_2Cl_2/hexane by slow evaporation to give 595 mg (100%) of **2b** as bright orange crystals.

Preparation of $(C_5Me_5)Rh(PEt_3)Br_2$ (5b). PEt_3 (56 μL, 0.38 mmol) was added to a suspension of **1b** (150 mg, 0.19 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 10 min at 25 °C, hexane (5 mL) added, and the product precipitated by concentration under vacuum (20 mm) to 3 mL. The crude product was collected by filtration on a fine-fritted funnel and washed with 5 mL of 1:1 Et_2O/hexane. Recrystallization from CH_2Cl_2/hexane yielded 194 mg (100%) of **5b**.

Preparation of $(C_5Me_5)Rh[P(p\text{-tol})_3]Br_2$ (4b). $P(p\text{-tol})_3$ (42 mg, 0.14 mmol) was added to a solution of **1b** (50 mg, 0.063 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 5 min at 25 °C and the solvent evaporated (25 °C, 20 mm). The crude product was washed with 1:1 Et_2O/hexane and recrystallized from CH_2Cl_2/hexane, yielding 87 mg (98%) of **4b** as bright orange crystals.

Preparation of $(C_5Me_5)Rh(PMe_3)(p\text{-tol})Cl$ (10a). Anhydrous THF (10 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing **1a** (250 mg, 0.40 mmol). The mixture was cooled to −40 °C and (*p*-tol)MgCl (1.00 mL of a 0.69 M solution in THF, 0.69 mmol) added dropwise over 10 min with a syringe. The mixture was stirred 15 min at −40 °C, allowed to warm to 25 °C over 30 min, and then stirred an additional 30 min at 25 °C. The mixture was then quenched with aqueous NH_4Cl (250 μL) and the solvent removed under reduced pressure (25 °C, 20 mm). The residue was extracted with CH_2Cl_2 (50 mL) and concentrated to 5 mL (25 °C, 20 mm). Filtration chromatography (SiO_2, 2% THF/CH_2Cl_2) afforded 267 mg (93%) of analytically pure **10a** after recrystallization from hot hexane.

Preparation of $(C_5Me_5)Rh(PMe_3)(p\text{-tol})Br$ (10b). The preparation of **10b** in 96% yield from **1b** and (*p*-tol)MgBr was the same as for **10a** except for quenching was accomplished with saturated NH_4Br and the eluent for chromatography was CH_2Cl_2. Anal. Calcd for $C_{20}H_{31}BrPRh$: C, 49.50; H, 6.44. Found: C, 49.56; H, 6.48.

General Preparation for the Aryl Derivatives $(C_5Me_5)Rh(PR'_3)RX$. As discussed in the text, care was taken to ensure that all reagents employed contained the same halogen. The reaction was performed on a high-vacuum line in a 10-mL two-necked flask that was fitted with a vacuum stopcock and a 5-mm rubber septum. Anhydrous THF (2 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing the dihalide (**2a–5c**, 10–50 mg). The mixture was cooled to −40 °C and the Grignard reagent (1.05 equiv) added dropwise with a syringe. The mixture was stirred for 15 min at −40 °C, allowed to warm to 25 °C over 30 min, and stirred an additional 30 min at 25 °C. The reaction mixture, which had changed from red to bright orange, was quenched with saturated aqueous NH_4X (25 μL) and the solvent removed (25 °C, 10^{-3} mm). The residue was extracted with CH_2Cl_2 (5 mL), filtered through a cotton plug, and concentrated under reduced pressure (20 mm). The crude products were chromatographed on SiO_2 thick-layer plates with CH_2Cl_2 (except for **16b**, which requires 4% THF/CH_2Cl_2). The products occurred as bright orange bands at R_f 0.4–0.8 and were easily extracted from the SiO_2 with use of 3:1 CH_2Cl_2/Et_2O. Recrystallization generally was accomplished by slowly cooling 3–5-mL hexane solutions (69 °C) of the products to 25 °C and then placing the mixtures in a −40 °C freezer for 1 h. The products were obtained (80% yields) in analytically pure form by decanting the supernatant, washing the crystals with a small amount of cold hexane, and drying under vacuum (25 °C, 10^{-4} mm). A second crop of relatively pure product (5–10%) was obtained by evaporation of the mother liquor. Product **16b** was recrystallized by carefully layering hexane (3 mL) over a THF solution (0.5 mL) of **16b** and allowing the layers to slowly diffuse together and evaporate to 0.5 mL.

Preparation of $(C_5Me_5)Rh(PMe_3)PhI$ (11c) by Halide Exchange. An acetone solution (10 mL) of **11b** (100 mg, 0.21 mmol) and NaI (500 mg, 3.3 mmol) was refluxed under nitrogen. The extent of reaction was monitored by TLC (SiO_2, CH_2Cl_2). After 6 h the starting material (R_f 0.5) had completely reacted and only the desired product (R_f 0.85) could be detected. The acetone was evaporated (25 °C, 20 mm) and the residue extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2 (25 °C, 20 mm) and recrystallization from hexane afforded 106 mg (95%) of **11c**. This same procedure was used to prepare other iodides from the corresponding chlorides.

Preparation of $(C_5Me_5)Rh(PMe_3)(CH{=}CH_2)Br$ (28b). Anhydrous THF (4 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing **2b** (136 mg, 0.29 mmol), the mixture cooled to −40 °C, and $(CH_2{=}CH)MgBr$ (230 μL, of a 1.34 M solution in THF, 0.308 mmol) introduced dropwise via syringe over 5 min. The mixture was allowed to warm to 25 °C over 45 min and then quenched with aqueous NH_4Br (25 μL). The solvent was removed (25 °C, 10^{-3} mm) and the residue extracted with CH_2Cl_2, filtered through a cotton plug, and concentrated (25 °C, 20 mm). Thick-layer chromatography (SiO_2, CH_2Cl) followed by recrystallization from hexane afforded **28b** in 86% yield (106 mg) as orange crystals. Anal. Calcd for $C_{15}H_{27}BrPRh$: C, 42.78; H, 6.46. Found: C, 42.73; H, 6.33.

Preparation of $(C_5Me_5)Rh(PMe_3)(CMe{=}CH_2)Br$ (29b) and $(C_5Me_5)Rh(PMe_3)(C{=}CHCH_2CH_2CH_2)Br$ (30b). **29b** and **30b** were prepared from **2b** and the corresponding Grignard reagents as described in General Preparation for the Aryl Derivatives, in 86% and 67% yields, respectively.

Preparation of $(C_5Me_5)Rh(PMe_3)MeCl$ (6a). Anhydrous THF (5 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing **2a** (76 mg, 0.20 mmol), the mixture cooled to −40 °C, and 310 μL of MeLi (0.69 M in Et_2O, 0.21 mmol) added dropwise with a syringe over 10 min. The mixture was allowed to warm to 25 °C over a period of 25 min and the solvent removed (25 °C, 10^{-3} mm). Thick-layer chromatography (SiO_2, 4% THF/CH_2Cl_2) gave an orange band (R_f 0.5), which was immediately extracted with 3:1 CH_2Cl_2/Et_2O. Evaporation of the solvent (25 °C, 20 mm) and recrystallization of the residue by slow evaporation of a CH_2Cl_2/hexane solution of the product yielded 51 mg (71%) of **6a** as orange-red crystals. Anal. Calcd for $C_{14}H_{27}ClPRh$: C, 46.11; H, 7.46. Found: C, 45.98; H, 7.49.

Preparation of $(C_5Me_5)Rh(PMe_3)(n\text{-}C_3H_7)Br$ (7b), $(C_5Me_5)Rh(PMe_3)(c\text{-}C_5H_9)Cl$ (8a), and $(C_5Me_5)Rh(PMe_3)(CH_2CMe_3)Br$ (9b). **7b**, **8a**, and **9b** were prepared with use of the method for **6a** from either **2a** or **2b** and the appropriate lithium reagent. Unlike **6a**, these alkyl derivatives are unstable toward air or SiO_2 chromatography and were isolated from a small amount of unreacted starting material and LiX by removal of the THF (25 °C, 10^{-3} mm) followed by hexane extraction of the residue. Removal of the hexane (25 °C, 10^{-4} mm) afforded essentially pure products. These compounds are stable under nitrogen in the solid state but slowly decompose in solution (CH_2Cl_2, THF, and C_6H_6).

Preparation of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$. $(C_5Me_5)Rh(C_2H_4)_2$ (25 mg, 0.085 mmol) and PMe_3 (1.1 equiv) were heated in C_6D_6 (1 mL) for 24 h at 80 °C, at which time resonance attributable to the starting material (δ 1.59) had been replaced by resonances attributable to $(C_5Me_5)Rh(PMe_3)(C_2H_4)$. The NMR tube was opened under N_2,

(21) Gilman, H.; Beel, J. A.; Brannen, C. G.; Bullock, M. W.; Dunn, G. E.; Millr, L. S. *J. Am. Chem. Soc.* **1949**, *71*, 1499–1500.
(22) Cf.: Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003–2008.

$$\nu(\upsilon) = \mathrm{Im}\left\{-i(1\quad 1\quad 1)\begin{pmatrix} 2\pi i(\nu-\nu_1)-1/T_2-2k & k & k \\ k & 2\pi i(\nu-\nu_2)-1/T_2-2k & k \\ k & k & 2\pi i(\nu-\nu_3)-1/T_2-2k \end{pmatrix}^{-1}\begin{pmatrix} 1/3 \\ 1/3 \\ 1/3 \end{pmatrix}\right\} \quad (8)$$

$$\nu(\upsilon) = \mathrm{Im}\left\{-i(1\quad 1\quad 1\quad 1)\begin{pmatrix} 2\pi i(\nu-\nu_1)-1/T_2-k & k & 0 & 0 \\ k & 2\pi i(\nu-\nu_2)-1/T_2-k & 0 & 0 \\ 0 & 0 & 2\pi i(\nu-\nu_3)-1/T_2-k & k \\ 0 & 0 & k & 2\pi i(\nu-\nu_4)-1/T_2-k \end{pmatrix}^{-1}\begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}\right\} \quad (9)$$

the tube's contents were transferred to a sublimation apparatus, and the solvent was removed under vacuum (25 °C, 10^{-3} mm). The product was isolated as air-sensitive yellow-orange crystals by sublimation (70 °C, 10^{-4} mm) to a 0 °C probe. NMR (C_6D_6): δ 1.860, d, J = 2.0 Hz, 15 H; δ 0.823, d, J = 8.3 Hz, 9 H.

Preparation of $(C_5Me_5)Rh(PMe_3)(CH_2Ph)Br$ (31b). Anhydrous THF (10 mL) was transferred into a flask containing $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ (11 mg, 0.032 mmol), the solution cooled to −40 °C, and benzyl bromide (4.0 μL, 0.034 mmol) added with a syringe under nitrogen. The solution was allowed to warm to 25 °C over a period of 1 h, the solvent removed under vacuum (25 °C, 10^{-4} mm), and the residue extracted with hexane. Evaporation of the hexane afforded pure **31b** in low yield (13%) as orange microcrystals. The remainder of the residue was a complex mixture of products that consisted of **2b** and a small amount of unreacted $(C_5Me_5)Rh(PMe_3)(C_2H_4)$.

Preparation of $(C_5H_5)Rh(PEt_3)I_2$. Anhydrous THF (5 mL) was vacuum distilled (25 °C, 10^{-3} mm) into a flask containing $CpRh(PEt_3)(C_2H_4)$ (40.8 mg, 0.13 mm). A solution of I_2 (66 mg, 0.26 mmol) in THF (3 mL) was added drropwise and the black ppt. that formed collected by filtration on a fine-fritted funnel. The precipitate was washed with Et_2O (5 mL) and recrystallized from CH_2Cl_2/hexane by slow evaporation; yield 65 mg (93%).

Preparation of $(C_5H_5)Rh(PEt_3)(p\text{-tol})I$ (32c). Complexes **32c** was prepared as orange crystals in 75% yield from $(C_5H_5)Rh(PEt_3)I_2$ and (*p*-tol)MgBr according to General Preparation for the Aryl Derivatives. The eluent for thick-layer chromatography was C_6H_6.

Complete Band Shape Analysis (CBS) of NMR Spectra. The general equation for intensity as a function of frequency was obtained from Sandstrom (p 24).[7] For a system of three exchanging singlets (as in **26b**) of equal population, the intensity $\nu(\upsilon)$ is given by eq 8. T_2 was determined to be 0.12 s by comparison with the spectrum recorded at 286 K. Visual comparison of calculated and observed spectra was used to determine the best value for k (±10%) for the Eyring plot. The same equation was used for CBS analysis of **4b** ($\upsilon_1 = \upsilon_2 = 952.7$ Hz, $\upsilon_3 = 889.9$ Hz) and **26b** ($\upsilon_1 = 971.91$ Hz, $\upsilon_2 = 961.1$ Hz, $\upsilon_3 = 869.1$ Hz).

For a system in which two pairs of coupled doublets are exchanging (A ⇌ A′, B ⇌ B′) with the same rate constant k, the spectra were simulated by calculating the line shapes for two pairs of singlets and then summing in the calculated spectrum offset by the average coupling constant of the doublets (see ref 7, p 25). The intensity for the uncoupled system is given by eq 9.

In addition, one of the ortho resonances (δ 6.138) for compound **26b** showed a temperature-dependent chemical shift of +94 Hz over 150 K. A linear correction to this chemical shift was made in the simulated spectra ($\upsilon = \upsilon_0 + 0.62775(T - 227.2)$) at intermediate temperatures in order to obtain good agreement between the simulated and observed spectra. T_2 was determined from the −46 °C spectrum to be 0.10 s (see ref 7, p 86).

Complex **10a** was treated in an identical fashion except that the ortho resonance at δ 7.637 was found to have a small temperature-dependent chemical shift (19 Hz over 140 K) and a correction was applied ($\upsilon = \upsilon_0 + 0.18344(T - 222.7)$)) at intermediate temperatures. Also the line shape for **10a** was observed to be more narrow at 363 K (T_2 = 0.12 s) than at 210 K (T_2 = 0.08 s). A linear correction to T_2 was made at intermediate temperatures ($T_2 = 0.08 + (T - 222.7)0.000285$) (see ref 7, p 88).

All spectra were computed with use of programs written in BASIC for a PET microcomputer.

Activation Energy Determination by Peak Separation at the Coalescence Temperature. The sample for which $\Delta G^{\ddagger}$ was to be determined was placed in the NMR probe and the temperature varied until the spectrum showed coalescence of the *o*-aryl hydrogens. The separation of the two exchanging resonances was measured at the low-temperature limit and assumed to be the same as at the coalescence temperature. Equation 2 was then used to determine k at T_c. Errors in $\Delta G^{\ddagger}$ can be calculated by using the equation

$$\frac{\Delta\Delta G^{\ddagger}}{\Delta G^{\ddagger}} = \frac{\{(\Delta T_c/T_c)^2[\ln(k_B T_c/hk) + 1]^2 + (\Delta k/k)^2\}^{1/2}}{\ln(k_B T_c/hk)}$$

from ref. 7, p 109. If $\Delta T_c = \pm 2.0$ °C, and if we set $\Delta k = \pm 10$ s^{-1}, T_c = 300 K, and $\Delta G^{\ddagger}$ = 14 kcal/mol, then $\Delta\Delta G^{\ddagger}$ = 0.10 kcal/mol.

Table VI. Summary of Crystal Data and Intensity Collection at 22 °C

compd	$[C_5(CH_3)_5]Rh[P(CH_3)_3](C_6H_5)Br$
fw	471.23
formula	$C_{19}H_{29}BrPRh$
cell parameters	
a	11.459 (12) Å
b	9.008 (6) Å
c	19.298 (13) Å
β	90.03 (2)°
V	1992 Å^3
Z	4
d(calcd)	1.57 g/cm^3
syst abs	$h0l$, l odd; $0k0$, k odd
data collected	$+h,+k,\pm l$
space group	$P2_1/c$
cryst dimens	0.2 mm × 0.2 mm × 0.4 mm
temp	22 °C
radiation	Mo Kα (λ = 0.7107 Å, graphite monochromated)
scan mode	θ–2θ
takeoff angle	1.8°
scan range	1.4–2.0°
scan speed	2°/min
total bkgd time	20 s
2θ range	0–45°
μ	30.3 cm^{-1}
unique data used ($F^2 \geq \sigma(F^2)$)	2009
final no. of parameters varied	199
R	4.68%
R_w	6.15%

X-ray Structural Determination of $(C_5Me_5)Rh(PMe_3)(C_6H_5)Br$ (12b). Data Collection. Well-formed crystals of **11b** were prepared by slowly cooling a saturated hexane solution of **11b** to −20 °C. The same crystal was used for preliminary film work and data collection. Precession photographs seemed to indicate that the crystal belonged to the orthorhomic system ($\alpha = \beta = \gamma = 90°$), but the lack of *mmm* symmetry on the films ruled out this possibility. The single mirror plane in the $hk0$, $hk1$, $0kl$, and $1kl$ photographs and the systematic absences ($h0l$, l odd; $0k0$, k odd) indicated the monoclinic space group $P2_1/c$. Lattice constants at 22 °C were determined from a least-squares refinement of the setting angles for 12 well-resolved reflections ($2\theta > 22°$).[23] The reflections were carefully centered with use of Mo $K\alpha_1$ radiation on a Picker FACS-1 diffractometer equipped with a graphite monochromator. Crystal data and other parameters relevant to the data collection process are listed in Table VI.

Solution and Refinement. The structure was solved with use of a Patterson map to reveal the position of the Rh atom. Two subsequent

(23) The programs for the refinement of the lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corp.
(24) Data reduction was performed with use of modified versions of the programs URFACS, FORDAP, NUCLS, ORFFE, and ORTEP2.
(25) Cromer, D. T.; Mann, B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.
(26) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

difference-Fourier maps revealed all 22 non-hydrogen atoms. Anisotropic least-squares refinement of all atoms followed by a difference-Fourier map revealed all but four of the hydrogen atoms, which were placed at idealized distances (1.00 Å for C–H) and angles (109.6° for H–C–H). Hydrogen atom contributions were included in the final structure factor calculation (B = 6 Å^2), but no refinement of their positional or thermal parameters was permitted. Final positional parameters (Table V) and selected distances and angles (Table IV) are given in the text. Other data have been deposited as supplementary material.

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Supplementary Material Available: Anisotropic thermal parameters (Table VII), calculated and observed structure factors (Table VIII), and bond distances and angles (Table IX) (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511

Nine-Coordinate Hexahydride Complexes of Molybdenum and Tungsten

ROBERT H. CRABTREE* and GREGORY G. HLATKY

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The known complex $WH_6(PMe_2Ph)_3$ is prepared in 53% yield from $WCl_4(PMe_2Ph)_3$ and $NaH_2Al(OCH_2CH_2OMe)_2$ at −80 °C. It reacts with RNC (R = *t*-Bu) to give $[W(RNC)_5(PMe_2Ph)_2]^{2+}$. The corresponding molybdenum complexes MoH_6L_3 (L = PCy_3, PCy_2Ph, $P(i\text{-}Pr)_3$, $P(i\text{-}Pr)_2Ph$) were prepared from $MoCl_4(thf)_2$, L, and $NaAlH_2(OR)_2$ in ~5% yields as unstable oils. They were unambiguously characterized by ^1H NMR and especially $^{31}P\{^1H\}$ NMR spectroscopy. The role of the phosphine in stabilizing these new complexes is discussed. Attempts to prepare MH_9^{3-} (M = Mo, W) were unsuccessful. MoH_6L_3 and the unstable $MoH_5L_4^+$ are the only examples of nine-coordinate mononuclear molybdenum. Evidence for the existence of the latter complex is discussed. The coordination number concept is applied to related organometallic complexes such as $Cp_2MoH_3^+$.

In connection with our studies on C–H activation on alkanes,[1] we set out to make $MH_6(PR_3)_3$ (M = Mo, W). While the tungsten complexes (e.g., PR_3 = PMe_3, PMe_2Ph, or $P(i\text{-}Pr)_3$) can be made[2] from the reaction of $WCl_4(PR_3)_2$ with $NaBH_4$,[2] $LiAlH_4$,[3] or Na/Hg/H_2,[4] the molybdenum analogues were completely unknown.

Results and Discussion

An Improved Preparation of $WH_6(PMe_2Ph)_3$. We felt that a better synthetic route to these complexes might be developed in view of our experience with the corresponding tetrahydrides,[5a] the yields of which were increased from 2–4% (W) or 15–45% (Mo) to 50–70% by using the strongly nucleophilic organic-soluble $LiBEt_3H$ in place of $NaBH_4$. This modification was not useful for the synthesis of $WH_6(PMe_2Ph)_3$ from $WCl_4(PMe_2Ph)_3$. We therefore turned to the readily available aluminum-based reagent $NaH_2Al(OCH_2CH_2OMe)_2$. This gave some improvement, but substantial improvement was only obtained by cooling the reaction mixture to −78 °C. Under these conditions, yields of 50% were obtained[5b] as long as care was taken with the hydrolysis step (see Experimental Section). Similar attempts using other phosphines such as PCy_3 and PCy_2Ph (Cy = cyclohexyl) gave much lower yields (ca. 5%) of the corresponding $WH_6(PR_3)_3$ complexes.

Chemistry of $WH_6(PMe_2Ph)_3$. We were not able to dehydrogenate alkanes with $WH_6(PMe_2Ph)_3$ by heating it with *tert*-butylethylene and cyclopentane.[1,6a] Only $WH_4(PMe_2Ph)_4$ was detected in the products. This was also the case for the reactions with olefins such as cod, nbd, cyclohexadiene, and cyclopentene. Irradiation of $WH_6(PMe_2Ph)_3$ with light at 366 nm gave no photolysis products, and the starting material was recovered.

Table I. NMR Data for the New Molybdenum Hexahydrides

compd	^1H NMR[a] δ[b]	^1H NMR[a] $^2J(P,H)$[c]	$^{31}P\{^1H\}$ NMR,[d] δ
$MoH_6(PCy_3)_3$	−4.42	36.3	62.3
$MoH_6(PCy_2Ph)_3$	−3.71	35	70.32
$MoH_6(P(i\text{-}Pr)_3)_3$	−4.63	35.6	52.54
$MoH_6(P(i\text{-}Pr)_2Ph)_3$	−4.00	35	57.89

[a] Assigned to Mo*H*; C_6D_6 solution. [b] Relative to internal Me_4Si. [c] Hz. [d] Assigned to Mo*P*; C_6D_6 solution; downfield from external 85% H_3PO_4.

In contrast to the corresponding reaction with $ReH_4(PPh_3)_2$,[6b] pyridine and piperidine do not react with the tungsten complex, but PMe_2Ph did react at 80 °C in benzene to give $WH_4(PMe_2Ph)_4$. As Walton[7] et al. have found for the Re complex (eq 1), A related complex $[W(CyNC)_5(dpe)]^{2+}$

$$ReH_4(PPh_3)_2 \xrightarrow{RNC} [Re(RNC)_4(PPh_3)_2]^+ \quad (1)$$

$$WH_6(PMe_2Ph)_3 \xrightarrow{RNC} [W(RNC)_5(PMe_2Ph)_2]^{2+} \quad (2)$$

(dpe = 1,2-bis(diphenylphosphino)ethane) has been obtained from $[W(CyNC)_7]^{2+}$ and dpe.[8] The formation of a cationic

(1) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738; **1982**, *104*, 107. Burk, M. J.; Crabtree, R. H.; Parnell, C. A.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816.
(2) Moss, R. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1910.
(3) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.
(4) Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2492.
(5) (a) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1982**, *21*, 1273. (b) *J. Organomet. Chem.* **1982**, *238*, C21.
(6) (a) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 249; **1982**, 606, 1235; **1983**, 788. (b) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.
(7) Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540.

0020-1669/84/1323-2388$01.50/0