Substituent Effects on Reductive Elimination from Disubstituted Aryl Hydride Complexes: Mechanistic and Thermodynamic Considerations

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The complexes $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)H$ for R = $C(CH_3)_3$, $CH(CH_3)_2$, $Si(CH_3)_3$, CH_3, and CF_3 (**1c**–**g**) have been prepared both by irradiation of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in neat arene and by thermolysis of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1a**) in neat arene. Quenching the hydride species with $CHBr_3$ allowed isolation of the corresponding bromide complexes $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)Br$ (**2c**–**g**). Rates of reductive elimination of arene for the series of disubstituted aryl hydride complexes were measured at various temperatures and activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ obtained and compared with those of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1a**) and $(C_5Me_5)Rh(PMe_3)(tolyl)H$ (**1b**). $\Delta H^\ddagger$ values range from +35 to +18 kcal/mol, and $\Delta S^\ddagger$ values range from +16.4 to −19 cal/mol K. Laser flash photolysis experiments using $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in neat toluene at various temperatures allowed the determination of activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for intramolecular C–H bond oxidative addition of the η^2-arene complex **3b**. Equilibrium measurements allowed determination of ΔG° values for several of the disubstituted aryl hydride complexes versus the parent phenyl hydride complex. A kinetic isotope effect of $k_H/k_D = 1.0 \pm 0.1$ was measured for the reaction of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ with a 1:1 mixture of 5-deuterio-1,3-di-*tert*-butylbenzene and 1,3-di-*tert*-butylbenzene. The equilibrium isotope effect for the same reaction $K_{eq} = 2.27(1)$ favors the aryl hydride and free deuterated arene.

Introduction

Two of the most fundamental steps in organometallic reaction mechanisms are oxidative addition and its microscopic reverse, reductive elimination.[1] Most catalytic and stoichiometric processes that utilize transition metals in the functionalization of hydrocarbon substrates invoke oxidative addition and reductive elimination pathways, and the nature of these steps has been probed in detail. Much work has been done on intramolecular and intermolecular C–H bond activation of alkanes and arenes,[2] yet reductive elimination has received somewhat less attention.[3]

It is now well established that oxidative addition products derived from alkanes are inherently less stable than their aryl counterparts despite the fact that the C–H bond is significantly stronger in arenes than in alkanes. The reason for this apparent discrepancy lies in the much greater range of C–M bond strengths versus C–H bond strengths (for the system $(C_5Me_5)Rh(PMe_3)(R)H$, $D_{Rh-Phenyl} - D_{Rh-Methyl} \approx 13$ kcal/mol and $D_{H-Phenyl} - D_{H-Methyl} \approx 6$ kcal/mol).[4]

Although much work has been done by organic researchers regarding substituent effects on the rates and mechanisms of organic reactions, few studies of this type have been attempted for organometallic systems. Two classic examples of arene substituent effects in organic chemistry are electrophilic aromatic substitution and dissociation constants of benzoic acid derivatives. Strongly electron-donating or -withdrawing substituents dramatically change the rate and stereochemistry of electrophilic attack on benzene derivatives, and K_{eq} values for *para*-substituted benzoic acid derivatives span ~1.5 pK_a units, reflecting a difference of ~2.0 kcal/mol in O–H bond strengths.[5]

The work detailed in this report was undertaken in order to probe (i) electronic effects on the rate of reductive elimination and (ii) η^2-complex stability for a series of disubstituted aryl hydride complexes of the type $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)H$ where R = CF_3, H, CH_3, $Si(CH_3)_3$, $CH(CH_3)_2$, and $C(CH_3)_3$. The *meta*-disubstituted derivatives were chosen rather than *para*-monosubstituted derivatives to avoid the facile equilibration with their *meta*-substituted isomers, which is known to occur in this system.[4] Measurement of rate constants for reductive elimination at various temperatures allowed the determination of activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the series, and flash photochemi-

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(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Application of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987, and references therein. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. (c) Stille, J. K. The Nature and Cleavage of Metal–Carbon Bonds. In The Chemistry of the Metal–Carbon Bond; Hartley, F. R., Patai, S., Eds.; Wiley-Interscience: New York, 1985; Vol. II.

(2) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424. (c) Bergman, R. *Science* **1984**, *223*, 902–908. (d) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (e) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation*; VCH Publishers, Inc.: New York, 1990. (f) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100.

(3) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

(4) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

(5) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981.

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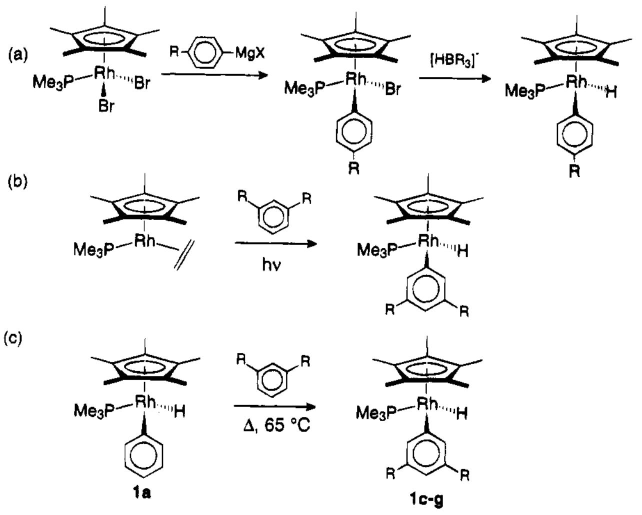
Scheme 1



cal experiments were carried out in order to determine activation parameters for the intramolecular oxidative addition of the η^2-arene complex Cp*Rh(PMe$_3$)(η^2-toluene) to form the corresponding aryl hydride. The kinetic isotope effect for C−H vs C−D bond oxidative addition of di-*tert*-butylbenzene to the fragment [Cp*Rh(PMe$_3$)] was measured. On the basis of these data, mechanistic conclusions are drawn regarding reductive elimination from this series of complexes.

Results

Synthesis of Compounds. Several synthetic routes leading to the 3,5-disubstituted aryl hydride complexes were examined. Earlier work with monosubstituted arenes indicated that reaction of (C_5Me_5)Rh(PMe$_3$)Br$_2$ with aryl Grignard reagents would lead to the aryl bromide complexes, which could then be converted to the desired aryl hydride complexes using LiB(*sec*-butyl)$_3$H (L-selectride).[6] A series of monosubstituted complexes having the general formula (C_5Me_5)Rh(PMe$_3$)(4-C_6H_4R)Br, R = CH_3, CF_3, Si(CH_3)$_3$, and C(CH_3)$_3$ (Scheme 1a), were easily synthesized from (C_5Me_5)Rh(PMe$_3$)Br$_2$ and the corresponding aryl Grignard reagent. However, attempts to use similar techniques for the preparation of the 3,5-disubstituted analogs generally met with failure due to difficulties encountered in preparing the Grignard reagent or the aryl bromide precursor. In addition, attempts to generate (C_5Me_5)Rh(PMe$_3$)[3,5-C_6H_3(CH_3)$_2$]H from the corresponding bromide complex using L-selectride produced a mixture of the desired aryl hydride along with some (C_5Me_5)Rh(PMe$_3$)H$_2$.

A more successful method for preparing the desired complexes took advantage of the photochemical lability of (C_5Me_5)Rh(PMe$_3$)(C_2H_4) to generate the reactive 16-electron intermediate [(C_5Me_5)Rh(PMe$_3$)] (Scheme 1b). Prolonged photolysis of (C_5Me_5)Rh(PMe$_3$)(C_2H_4) in neat 1,3-disubstituted arene (λ > 345 nm) led to loss of ethylene and oxidative addition of the solvent. This procedure was used to prepare the complexes (C_5Me_5)Rh(PMe$_3$)(3,5-$C_6H_3R_2$)H for R = CF_3 (**1g**), CH_3 (**1f**), and C(CH_3)$_3$ (**1c**). Although this procedure worked well for dilute samples [<10 mg of (C_5Me_5)Rh(PMe$_3$)(C_2H_4)], more concentrated solutions darkened considerably and photolysis became ineffective at long reaction times. Maximum yields of 85% were attained, and significant amounts (>5%) of (C_5Me_5)Rh(PMe$_3$)$_2$ were also detected after prolonged photolysis.

A third route to the disubstituted aryl hydride complexes proved to be the most efficient (Scheme 1c). Thermolysis of (C_5Me_5)Rh(PMe$_3$)(Ph)H (**1a**) in neat arene at 67 °C overnight resulted in loss of benzene and generation of the 16e intermediate [(C_5Me_5)Rh(PMe$_3$)], which then reacted rapidly with the arene solvent. The complexes (C_5Me_5)Rh(PMe$_3$)(3,5-$R_2C_6H_3$)H for R = C(CH_3)$_3$, CH(CH_3)$_2$, Si(CH_3)$_3$, CH_3, and CF_3 (**1c**−**g**, Scheme 1) were produced cleanly and in high yield by this method. For 1,3-bis(trifluoromethyl)benzene, *m*-xylene, and 1,3-bis(trimethylsilyl)benzene, the reaction went virtually to completion, whereas reaction with 1,3-diisopropylbenzene and 1,3-di-*tert*-butylbenzene only went to partial completion due to equilibration with the free benzene produced. In the latter two cases, the solvent was removed under high vacuum at room temperature and fresh arene was introduced. Repetition of the thermolysis conditions led to >95% yield (^{31}P NMR) of the desired products. In all cases only a single aryl hydride isomer was formed.

Spectroscopic data for the series of 3,5-disubstituted aryl hydride complexes are typical of other aryl hydride complexes of this type. Single resonances are observed by ^{1}H NMR spectroscopy for the *ortho*-hydrogens of the aromatic ring. Equivalent arene substituent resonances are seen in the ^{1}H NMR spectrum, indicating activation solely at the 5-position of the arene ring and free rotation of the Rh−aryl bond. In addition, resonances attributable to bound (C_5Me_5) and PMe$_3$ ligands are visible, and a hydride resonance is seen in the upfield region with the expected couplings to rhodium and phosphorus. ^{31}P NMR spectroscopy shows a doublet near δ 8−9 ppm with a coupling constant indicative of rhodium in the +3 formal oxidation state ($J_{\text{Rh-P}} \approx 150$ Hz).[7]

The materials were further characterized by conversion to the air-stable aryl bromides by reaction with CHBr$_3$ (eq 1). Addition of several drops of CHBr$_3$ to a

$$(C_5Me_5)Rh(PMe_3)(aryl)H \xrightarrow{CHBr_3} (C_5Me_5)Rh(PMe_3)(aryl)Br \quad (1)$$

benzene solution of (C_5Me_5)Rh(PMe$_3$)(3,5-$C_6H_3R_2$)H produced an immediate color change to bright orange-red. Chromatography on silica plates with 4% THF/CH_2Cl_2 led to the isolation of the complexes (C_5Me_5)Rh(PMe$_3$)(3,5-$C_6H_3R_2$)Br (**2c**−**g**) in moderate yields. Spectroscopic data are given in the Experimental Section.

Kinetic Studies. Thermolysis of these aryl hydride complexes in C_6D_6 led to the reductive elimination of arene and the formation of **1a**-d_6 (eq 2). The rates of

$$(C_5Me_5)Rh(PMe_3)(aryl)H \xrightarrow{C_6D_6} (C_5Me_5)Rh(PMe_3)(C_6D_5)D \quad (2)$$

these reactions were monitored by ^{1}H NMR spectroscopy at various temperatures. Temperature dependent rates were also obtained for the hydride complex (C_5Me_5)Rh-

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(6) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376−2388.

(7) Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450−1462.

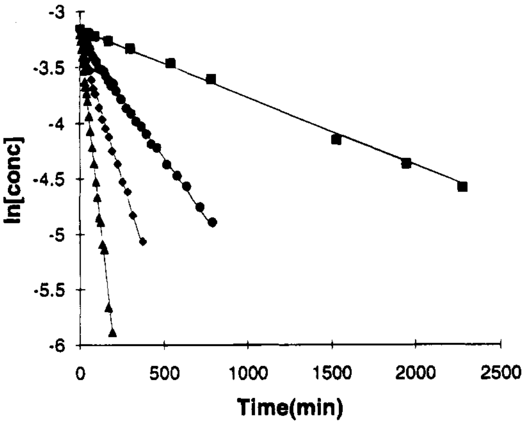

Figure 1. Plot of ln[**1c**] vs time for the elimination of 1,3-$C_6H_4(t\text{-}Bu)_2$ from $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3(t\text{-}Bu)_2)H$ in C_6D_6 at 301 (■), 313 (●), 323 (◆), and 333 K (▲).

(PMe_3)(tolyl)H (**1b**), which is known to exist as a rapidly equilibrating 2:1 mixture of *meta*- and *para*-isomers.[8] Rate constants were determined by a single-exponential fit to eq 3, except for **1g**, which exhibited behavior characteristic of an approach to equilibrium and was therefore fitted to the form of eq 4. Fits were optimized

$$[1] = [1]_0\, e^{-k_{obs}t} \qquad (3)$$

$$[1] = [1]_\infty + ([1]_0 - [1]_\infty)e^{-k_{obs}t} \qquad (4)$$

by varying k_{obs} for **1b**–**g** and also $[Rh(aryl)H]_\infty$ for **1g**. For the reactions of **1b**–**g** first-order behavior was observed (Figure 1) with k_{obs} representing the rate of arene loss; for **1g** the first-order rate constant k_{obs} represents the sum of $k_{forward} + k_{reverse}$. On the basis of the equilibrium constant for this reaction (*vide infra*), the contribution of $k_{reverse}$ to the observed rate constant is 3% or less, which is smaller than the errors (typically 5%–10%) of the measured rate constants. This contribution was therefore disregarded. These results are summarized in Table 1. Details of the kinetic experiments are given in the Experimental Section.

Activation parameters were determined on the basis of the rates listed in Table 1. Eyring plots of $\ln(k_{obs}/T)$ vs $1/T$ over at least a 32 °C temperature range give linear plots with good correlation (Figure 2), yielding enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation as summarized in Table 2. The limited statistical basis for extracting these values introduces large 95% confidence limits on these values. Also, the values for the rate constants for the reaction of **1g** are somewhat suspect due to a competing H/D exchange reaction (*vide infra*). Calculated $\Delta G^{\ddagger}$ values at 298 K are also reported in Table 2 (there is no statistical basis for including confidence limits on these values).

Table 1. Kinetic Data for Reductive Elimination of Arene from the Complexes $(C_5Me_5)Rh(PMe_3)$(aryl)H

aryl	T, K	$k \times 10^5$, s^{-1} [a]
C_6H_5, **1a**[b]	299	0.0622 (0.0035)[b]
	325	3.11 (0.13)[b]
	332	11.1 (1.1)[b]
	345	66.1 (9.8)[b]
$C_6H_4(CH_3)$, **1b**	298	0.189 (0.008)
	313	1.72 (0.11)
	323	6.43 (0.12)
	333	23.3 (0.7)
3,5-$C_6H_3(t\text{-}Bu)_2$, **1c**	301	1.01 (0.02)
	313	3.63 (0.07)
	323	9.00 (0.41)
	333	23.3 (0.5)
3,5-$C_6H_3(i\text{-}Pr)_2$, **1d**	298	0.698 (0.076)
	313	4.16 (0.11)
	323	13.8 (0.33)
	333	37.5 (1.9)
3,5-$C_6H_3(SiMe_3)_2$, **1e**	298	0.127 (0.005)
	313	0.845 (0.020)
	323	3.08 (0.16)
	333	8.93 (0.44)
3,5-$C_6H_3(CH_3)_2$, **1f**	301	1.05 (0.09)
	313	5.06 (0.14)
	324	21.8 (2.3)
	333	51.5 (3.2)
3,5-$C_6H_3(CF_3)_2$, **1g**	325	0.0108 (0.0004)
	343	0.112 (0.004)
	353	0.751 (0.095)
	363	3.56 (0.12)

[a] 95% confidence limits are shown in parentheses. [b] Data from ref 4.

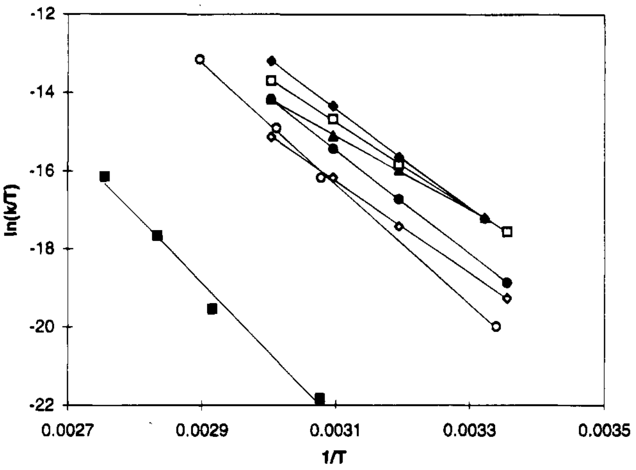

Figure 2. Eyring plots for the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reductive elimination of arene from $(C_5Me_5)Rh(PMe_3)$(aryl)H in benzene, where aryl = C_6H_5 (○), $C_6H_4CH_3$ (●), 3,5-$C_6H_3(t\text{-}Bu)_2$ (▲), 3,5-$C_6H_3(i\text{-}Pr)_2$ (□), 3,5-$C_6H_3(SiMe_3)_2$ (◇), 3,5-$C_6H_3(CH_3)_2$ (◆), and 3,5-$C_6H_3(CF_3)_2$ (■).

Equilibrium measurements were also made in order to determine the difference in $\Delta G°$ values for the various disubstituted arene complexes versus the parent phenyl hydride **1a**. For the cases where equilibrium was reached in the preparation of the aryl hydride from reaction of **1a** in neat arene [R = $C(CH_3)_3$, $CH(CH_3)_2$], equilibrium values were obtained based on ^{31}P NMR integrations of reactant and product resonances. K_{eq} values were calculated on the basis of simple bimolecular equilibrium behavior according to eq 5, and $\Delta G°$ was

$$K_{eq} = \frac{[Rh(Ar)H][PhH]}{[Rh(Ph)H][ArH]} \qquad (5)$$

obtained from the equation $\Delta G° = -RT \ln(K_{eq})$. Equilibrium values for **1g** were obtained by optimizing the least-squares fit of the kinetic data through variation of the final equilibrium value $[Rh(aryl)H]_\infty$. Equilibrium and $\Delta G°$ values are given in Table 3. Equilibrium concentrations were also measured at various temperatures for the complex **1c**, and a van't Hoff plot of $\ln(K_{eq})$ vs $1/T$ allowed determination of $\Delta H°$ and $\Delta S°$ relative to **1a**. These values are listed as well in Table 3.

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(8) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–4242.

Table 2. Activation Parameters for Reductive Elimination of Arene from the Complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$

aryl	$\Delta H^{\ddagger}$, kcal/mol[a]	$\Delta S^{\ddagger}$, cal/mol K[a]	$\Delta G^{\ddagger}_{298}$, kcal/mol	σ_m for aryl substituent
C_6H_5, **1a**	30.6 (2.4)	15.1 (7.4)	26.1	0
$C_6H_4CH_3$, **1b**	26.5 (0.3)	4.1 (1.1)	25.3	−0.07
3,5-C_6H_3(*t*-Bu)$_2$, **1c**	18.8 (0.8)	−19.0 (2.5)	24.5	−0.10
3,5-C_6H_3(*i*-Pr)$_2$, **1d**	21.9 (0.9)	−8.5 (2.8)	24.4	−0.04
3,5-$C_6H_3(SiMe_3)_2$, **1e**	23.5 (1.1)	−6.7 (3.5)	25.5	−0.04
3,5-$C_6H_3(CH_3)_2$, **1f**	24.1 (4.0)	−1.1 (12.7)	24.4	−0.07
3,5-$C_6H_3(CF_3)_2$, **1g**	35.2 (8.3)	17 (24)	30.0	+0.43

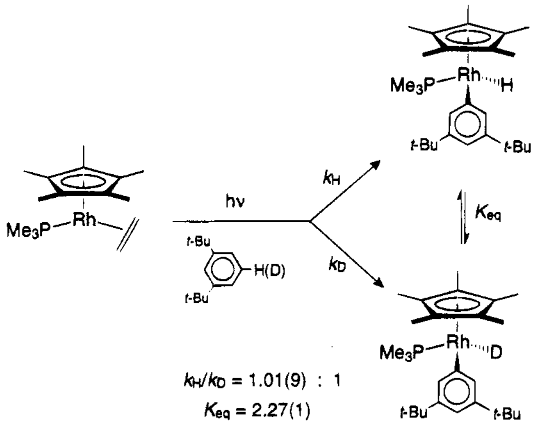
[a] 95% confidence limits for 2 degrees of freedom (n = 4) are shown in parentheses.

Table 3. K_{eq} and $\Delta G°$ Values for the Complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ Equilibrating with C_6H_6

aryl	T, K	K_{eq}	$\Delta G°$, kcal/mol
3,5-$C_6H_3(CF_3)_2$, **1g**	325	40.1	−2.38
$C_6H_4(CH_3)$, **1b**	323	0.37	0.64
3,5-$C_6H_3(CH_3)_2$, **1f**	323	0.083	1.60
3,5-C_6H_3(*i*-Pr)$_2$, **1d**	298	0.132	1.20
3,5-C_6H_3(*t*-Bu)$_2$, **1c**[a]	298	0.0165	2.43
	311	0.0160	2.56
	324	0.0203	2.51
	338	0.0208	2.60
	347	0.0231	2.60

[a] $\Delta H°$ = 1.5(0.6) kcal/mol; $\Delta S°$ = −3(2) cal/mol K.

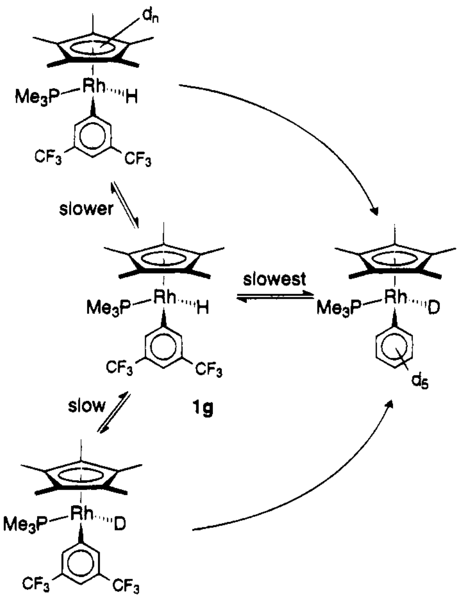
Scheme 2



The kinetic isotope effect for C−H bond activation of 1,3-di-*tert*-butylbenzene was measured (Scheme 2). Photolysis of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in 1,3-di-*tert*-butylbenzene that was 50% enriched at the 5-position at 10 °C produced both **1c** and **1c**-d_1, yielding a kinetic isotope effect of 1.0 ± 0.1 at early reaction times. An equilibrium isotope effect of 2.27(1) (favoring aryl hydride + free deuterated arene) was observed after the sample had equilibrated at room temperature for 10 days (>10 half-lives).

H/D Exchange in 1g. While the loss of arene from **1g** in C_6D_6 was monitored, a competing H/D exchange reaction was observed which deuterates both the hydride and the methyl groups of the (C_5Me_5) ligand (Scheme 3). Although the concentrations of **1g** and **1a** were monitored by ^1H NMR integration of the corresponding PMe_3 resonances, it became readily apparent that the intensities of the (C_5Me_5) resonances for **1g** and **1a** began to broaden and decrease in intensity relative to the PMe_3 resonances. Inspection of the hydride resonance showed that it also diminished in intensity. A ^2H NMR spectrum taken after 2000 h of thermolysis at 54 °C (<2 half-lives; ~60% arene exchange) confirmed deuterium enrichment of both the (C_5Me_5) ligand and of the hydride. ^{31}P NMR spectra also obtained after 2000 h showed a progressive series of resonances with an upfield shift of 35.5 Hz/D for both **1g**-d_n and for **1a**-d_n (Figure 3). These peaks exhibited the expected large coupling to rhodium, but also a smaller 1:1:1 triplet splitting attributable to a rhodium−deuterium coupling. This monotonic upfield shift is attributed to an isotopic perturbation of resonance due to successive deuterium incorporation into the (C_5Me_5) ligand of the starting material. This effect has also been noted in the ^1H NMR spectra in exchange reactions of fluorinated aryl hydrides.[9] Because the kinetic scheme for this reaction is complicated by this H/D exchange process and its associated isotope effects, suspicion must be raised regarding the validity of the measured rate constants and the activation parameters that are derived from them.

Scheme 3



Flash Photolysis Studies. Flash photochemical experiments were carried out in order to examine oxidative addition intermediates with these arenes (Scheme 4). Laser flash photolysis (308 nm, excimer laser) of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in neat toluene produced the transient intermediate $[(C_5Me_5)Rh(PMe_3)]$, which reacted rapidly with the solvent to produce the η^2-arene complex **3b** within the lifetime of the flash. Monitoring the lifetime of the intermediate η^2-complex by UV−vis absorption spectroscopy at various temperatures allowed determination of the first-order rate constants and the activation parameters for intramolecular oxidative addition (Table 4). Similar experiments were described in previous work that established the activation parameters for intramolecular oxidative addition of benzene.[10] The activation parameters for intramolecular oxidative addition of toluene were found to be $\Delta H^{\ddagger}$ = 14.4(2.4) kcal/mol and $\Delta S^{\ddagger}$ = 2.0(0.7) cal/mol K. Attempts to perform similar experiments with other disubstituted arenes were unsuccessful due to

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(9) Selmeczy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, *13*, 385−396.

(10) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 266−269.

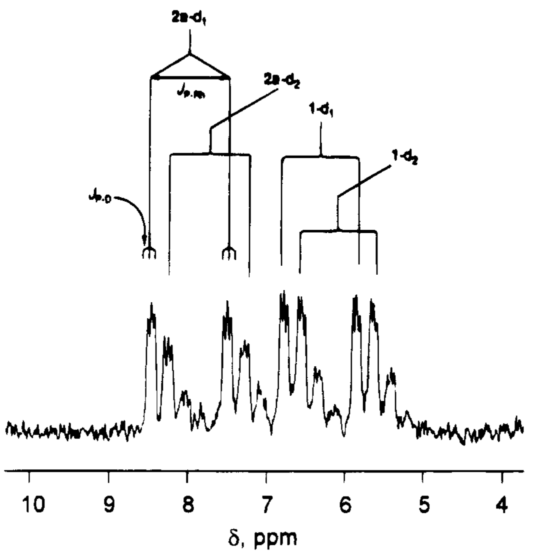


Figure 3. ^{31}P NMR spectrum after heating $(C_5Me_5)Rh(PMe_3)[2,6-C_6H_3(CF_3)_2]H$ at 54 °C in C_6D_6 for 2000 h.

Scheme 4

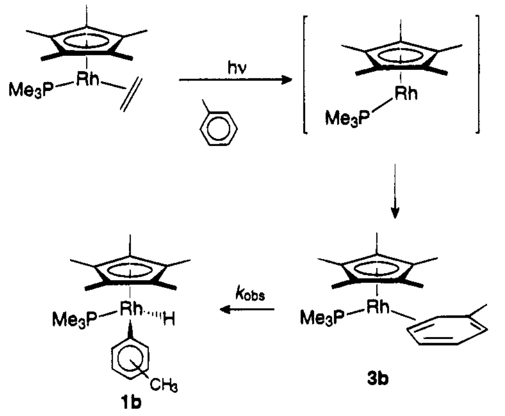


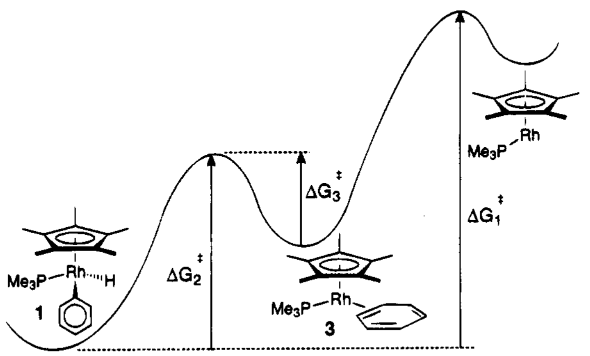
Table 4. Rate Constants for the Conversion of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6H_5CH_3)$ to $(C_5Me_5)Rh(PMe_3)(C_6H_4CH_3)H$ from Flash Photochemical Experiments

T, K	k_{obs}, s^{-1} [a]
295	363 (35)
305	780 (50)
310	983 (80)
310	1030 (45)
323	3610 (260)
333	6180 (550)

[a] 95% confidence limits are shown in parentheses.

substantial UV absorption of the arene at the wavelength of the laser pulse (308 nm).

Scheme 5



Discussion

The mechanism for reductive elimination of benzene from the metal complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ (**1**) has been well studied. Earlier work from our laboratories has provided support for the intermediacy of a stable η^2-arene complex along the oxidative addition/reductive elimination pathways with benzene.[4,11] The free-energy diagram shown in Scheme 5 has been established by self-exchange of C_6H_6 for C_6D_6 ($\Delta G^{\ddagger}{}_1$), spin-saturation transfer ($\Delta G^{\ddagger}{}_2$), and flash photolysis experiments ($\Delta G^{\ddagger}{}_3$). No kinetic isotope effect (KIE) was found for the reaction of the photochemically generated intermediate $[(C_5Me_5)Rh(PMe_3)]$ with a 50/50 mixture of C_6H_6/C_6D_6, but a KIE of 1.40 was observed in the reaction of $[(C_5Me_5)Rh(PMe_3)]$ with 1,3,5-trideuteriobenzene.[12] These results were taken as strong evidence for the existence of an η^2-benzene complex along the reaction coordinate for oxidative addition leading to formation of the phenyl hydride complex **1a**. This η^2-benzene complex was also observed directly in the laser flash experiments of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$.[10] For the reductive elimination of the *m*-xylyl hydride complex **1f**, independent determination of rate constants for loss of *m*-xylene and *m*-xylene-d_1 from the complexes $(C_5Me_5)Rh(PMe_3)[3,5\text{-}C_6H_3(CH_3)_2]H$ and $(C_5Me_5)Rh(PMe_3)[3,5\text{-}C_6H_3(CH_3)_2]D$, respectively, in C_6D_6 showed an inverse kinetic isotope effect $k_H/k_D = 0.51$.[12] The existence of a KIE effect for reductive elimination of Rh(aryl)H vs Rh(aryl)D but not for oxidative addition of aryl–H vs aryl–D is consistent with irreversible formation of an intermediate arene π complex prior to C–H oxidative addition.

The work described in this paper was undertaken in order to examine how electron-donating and electron-withdrawing substituents on the bound arene would affect (i) the rates of reductive elimination of aryl–H and (ii) the stability of the intermediate π-arene complexes. It was anticipated that good σ-donating groups on the aromatic ring would weaken the M–C bond (relative to the parent phenyl hydride **1a**) and would show faster rates of reductive elimination. Conversely, a strong σ-withdrawing aryl substituent should show the opposite behavior through strengthening of the M–C bond, thereby slowing the rate of reductive elimination. A similar trend was anticipated in terms of π-complex stability. Electron withdrawing groups should make the arene a better π-acceptor and stabilize this interaction relative to benzene,[13] while electron-donating substituents make the π-system more electron rich and consequently a poorer π-acceptor than benzene.

The 3,5-disubstituted materials **1c–g** were targeted in order to simplify the experimental rate constant measurements for reductive elimination of aryl–H. Had the monosubstituted series of complexes $(C_5Me_5)Rh(PMe_3)(C_6H_4R)H$ been employed, complications might have arisen due to interconversion of *meta*- and *para*-

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(11) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685–7695.

(12) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819.

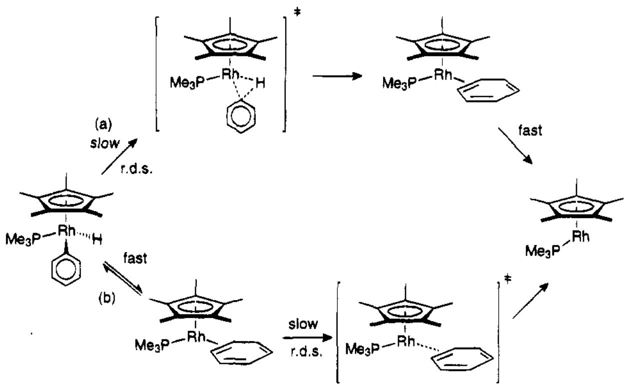
(13) (a) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928–930. (b) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264–266.

isomers. The previously studied tolyl complex **1b** was used since it had been established earlier that equilibration of the *meta*- and *para*-isomers was rapid compared to loss of arene from the intermediate π-complex. Although similar behavior is expected for the monosubstituted series $(C_5Me_5)Rh(PMe_3)(C_6H_4R)H$, this has not yet been confirmed. In addition, two substituent groups should produce a larger inductive effect compared to only one, and the effect on the activation parameters should be more pronounced.

Upon heating the aryl hydride complexes **1b**–**g** in C_6D_6 solvent, first-order loss of arene was observed as **1a**-d_6 formed. The reaction goes to completion with complexes **1b**–**1f**. Only in the case of m-$C_6H_4(CF_3)_2$, a more electron-deficient arene than benzene, did the reaction not go to completion. This observation is somewhat remarkable in that the concentration of liberated m-$C_6H_4(CF_3)_2$ was approximately 1/250th that of the benzene solvent. The large equilibrium constant favoring activation of the fluorinated aromatic accounts for this observation. It is also worth noting that only in the case of **1g** was loss of arene slower than in the parent complex **1a**. All other arenes are lost more rapidly than benzene at a given temperature. The increased lability of **1b**–**f** compared with **1a** can be attributed to a *decrease in the ground-state energy of* the complexes rather than to a lowering of the transition-state energy for arene dissociation (*vide infra*).

Further insight into the way that substituents affect the rate of arene exchange comes from examination of the temperature dependence of these rates. In the series of reactions studied for this report, a trend emerges from the Eyring data shown in Table 2. The notion that electron-withdrawing substituents would slow reductive elimination rates appears correct, in that the barrier for arene loss ($\Delta G^\ddagger$ values) correlates with the electron-withdrawing ability of the substituent. The effect of the electron-donating substituents is similar, as all show a smaller barrier for arene loss than **1a**. Examination of the σ_m values for these substituents accounts roughly for the observed trend and its magnitude.[14] $\Delta H^\ddagger$ follows the same trend (**1g** > **1a** > **1b** > **1f** > **1e** > **1d** > **1c**). This trend was not entirely unexpected, since metal–carbon bond strengths are believed to parallel carbon–hydrogen bond strengths.[15] The range of values is quite large ($\Delta\Delta H^\ddagger \approx 16$ kcal/mol), however, and is certainly far greater than the range of corresponding C–H bond strengths in the arenes (estimated as 3–4 kcal/mol). Previous work in our laboratory has shown that **1a** is thermodynamically favored over the n-propyl complex $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)H$ by ~9 kcal/mol, although the C–H bonds in benzene are approximately 8 kcal/mol stronger than the C–H bonds in propane. This thermodynamic preference translates to a Rh–C_6H_5 bond that is ~17 kcal/mol stronger than a Rh–propyl bond in this series of complexes. Since this difference is roughly twice that for the corresponding H–propyl vs H–phenyl bond enthalpies, a large range of metal–arene bond strengths compared with the H–aryl bond strengths is consistent with these earlier studies, but the magnitude of the range is larger than anticipated.

Scheme 6



Another intriguing feature of the Eyring data is the change in entropy of activation that occurs when the arene substituent is changed from R = CF_3 to R = $C(CH_3)_3$. These values range from what would be considered a dissociative transition state ($\Delta S^\ddagger \approx +16$ cal/mol K) to what would be considered an associative one ($\Delta S^\ddagger \approx -19$ cal/mol K). A dissociative transition state is consistent with the initially proposed reaction mechanism of rapid and reversible reductive elimination/oxidative addition processes interconverting the aryl hydride and the η^2-arene complexes, followed by rate-determining loss of π-bound arene. Earlier work with isotopically labeled materials showed that the degenerate isomerization of $(C_5Me_5)Rh(PMe_3)(p\text{-xylyl})H$ at temperatures below which exchange of bound and free arene occurs yields activation parameters $\Delta H^\ddagger = +16.3$ kcal/mol and $\Delta S^\ddagger = -6.3$ cal/mol K. The slightly negative entropy of activation was interpreted to suggest the ordered transition state for C–H bond formation. The observation of a substantially negative entropy of activation for the complexes where R = $CH(CH_3)_2$ and $C(CH_3)_3$ suggested that a change in the rate-determining step might have occurred. Rate-determining formation of the η^2-arene complex followed by rapid loss of coordinated arene would be consistent with the negative activation entropies for the electron-rich arenes on the basis of the associative three-centered transition state in Scheme 6a. This hypothesis is also supported by the fact that electron-donating substituents on the aromatic ring destabilize the π-complex that is formed, and therefore loss of bound arene might be more favorable.

The notion that C–H bond formation is involved in the rate-determining step led to the prediction of a kinetic isotope effect (KIE) in the *reverse* reaction of the unsaturated intermediate $[(C_5Me_5)Rh(PMe_3)]$ with 5-deuterio-1,3-di-*tert*-butylbenzene (Scheme 2). It had already been shown that irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ in a 50/50 mixture of C_6H_6/C_6D_6 resulted in no measurable KIE ($k_H/k_D = 1.05$), yet the same reaction using 1,3,5-trideuteriobenzene does exhibit a small KIE ($k_H/k_D = 1.40$), since the KIE in the latter reaction reflects the step in which a C–H or C–D bond is broken in the η^2-arene complex. A similar experiment was performed using 1,3-di-*tert*-butylbenzene which had been 50% deuterium-enriched at the 5-position, generating the same unsaturated intermediate via photolysis

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[14] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

[15] Data for substituted arene C–H bond strengths is very limited, but two examples demonstrate the small range of H–Ar enthalpies: for C_6H_6, $D_{C-H} = 110$ kcal/mol, and for C_6F_5H, $D_{C-H} = 114$ kcal/mol. (a) Chamberlain, G. A.; Whittle, E. *Trans. Faraday Soc.* **1971**, *67*, 2077. (b) Choo, K. Y.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1975**, *7*, 713.

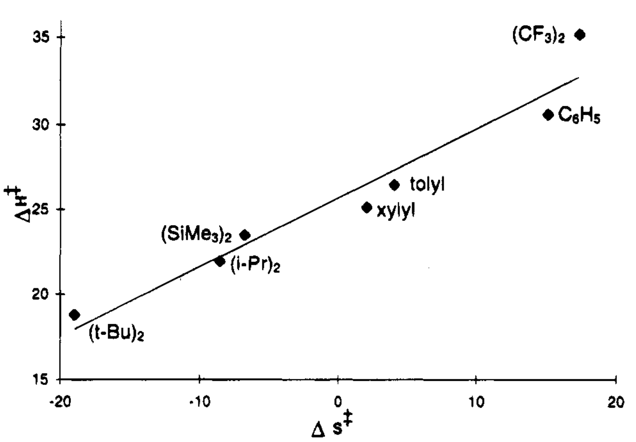

Figure 4. Plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ for the reductive elimination of arene from $(C_5Me_5)Rh(PMe_3)(aryl)H$ in benzene.

of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$. Again no KIE was measured ($k_H/k_D = 1.0$), leading to the conclusion that arene precoordination is still the rate-determining step in all of these C−H bond activation processes (Scheme 6b). Consequently, the negative entropy of activation for **1c** (and **1d** or **1e**) indicates more order in the transition state for dissociation of η^2-1,3-di-*tert*-butylbenzene from the $(C_5Me_5)Rh(PMe_3)$ fragment. Perhaps lack of rotation about the Rh−(η^2-arene) bond with these more hindered arenes accounts for the negative values. The equilibrium isotope effect between **1c** and **1c**-d_1 of 2.27(1) is similar to that seen earlier in **1a**-d_5.[12]

Flash photochemical experiments were performed in order to determine substituent effects on the rate of intramolecular oxidative addition for the η^2-complex **3b**. Irradiation of a solution of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ in neat toluene led to formation of the transient species **3b**. The rate of intramolecular oxidative addition leading to complex **1b** was calculated by monitoring the single-exponential decay of the UV−vis absorbance at 370 nm to a steady-state value. Determination of rate constants over a 38 °C temperature range allowed the calculation of activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for **3b**, $\Delta H^{\ddagger} = 14.4(2.4)$ kcal/mol and $\Delta S^{\ddagger} = 2.0(0.7)$ cal/mol K. Comparison of the lifetimes for the η^2-toluene vs the η^2-benzene complexes reveals that the rate of intramolecular oxidative addition is slower for toluene than for benzene. This was surprising, since it was believed that the less stable π-complex with toluene (worse π-acid) should have reacted more quickly than the corresponding benzene species. The $\Delta H^{\ddagger}$ value for the transformation **3b** → **1b** is roughly 3 kcal/mol higher than that for benzene [for **3a** → **1a**, $\Delta H^{\ddagger} = 11.15(0.31)$ kcal/mol], and the $\Delta S^{\ddagger}$ value is near zero [$\Delta S^{\ddagger} = -4.9(1.1)$ cal/mol K for benzene]. These values indicate a slightly greater degree of bond-breaking and less order in the transition state for the toluene complex compared to the benzene complex, but the differences are small.

Several authors have pointed out that entropy−enthalpy compensation effects can occur when studying a homologous series of reactions. The current data for this series of compounds *appears* to follow such a compensation relationship; as $\Delta H^{\ddagger}$ decreases, $\Delta S^{\ddagger}$ also decreases so as to make $\Delta G^{\ddagger}$ change only slightly. Indeed, a plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ is linear (Figure 4). A systematic relation between the mechanism(s) for arene elimination leads to the principle that there should be a temperature at which all the rates are the same, i.e., an isokinetic temperature. Under such circumstances, the $\ln(k/T)$ vs $1/T$ plots should intersect at a common point. Detailed treatments by Exner,[16] Leffler,[17] and more recently a review by Linert[18] give proper statistical treatments for testing the validity of such a relationship. Examination of the Eyring plots in Figure 2 does not support the presence of an isokinetic relationship, however, *as there is no single point where all lines intersect*, i.e., there is no isokinetic temperature. Peterson has pointed out that a linear $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ plot does not require an isokinetic relationship,[19] and the data here fall into the same category. Using the statistical methods outlined by Exner and Linert, there is no reason to believe that the current trends in activation parameters are consistent with an isokinetic relationship.

At the same time, the underlying physical reason for the large range of enthalpy and entropy values is not clear. Although earlier results have shown that a significant difference between C−M and C−H bond strengths exists, the magnitude of the effect observed in this study seems remarkable. The result from the KIE study is more consistent with C−H bond cleavage not being involved in the rate-determining step, thus arguing against a change in rate-determining step in the mechanism as the cause for the observed entropy values. We tend to believe that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values reflect the tightness of the bound η^2-arene during dissociation from the metal. The larger amount of bond-breaking required for the electron-deficient arenes would be consistent not only with a complex of lower ground-state energy but also with a transition state with relatively more freedom to rotate about the metal−(η^2-arene) bond, and hence a larger $\Delta S^{\ddagger}$. The magnitude of the changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, however, are still larger than one would have anticipated.

Finally, it is tempting to use the equilibrium and rate data presented here to predict kinetic selectivities for oxidative addition of the 16-electron fragment with mixtures of arenes ($\Delta\Delta G^{\ddagger}_{oa} = \Delta G^{\ddagger}_{1g} - \Delta G^{\ddagger}_{1a} + \Delta G^{\circ}$). Unfortunately, the ΔG° values were not measured at the same temperature, and even so, the range of $\Delta\Delta G^{\ddagger}_{oa}$ values calculated is small (~2 kcal/mol). The uncertainty associated with these values renders their use in the prediction of selectivity as less than reliable.

Conclusions

The free-energy barrier to reductive elimination in a series of disubstituted aryl hydride complexes has been shown to increase as the substituents are more electron withdrawing than H and to decrease when the substituents are more electron donating than H. The range of C−Rh enthalpy of activation values is large (~16 kcal/mol), which translates as a large range in Rh−C bond enthalpy values. This range is certainly much greater than the range of corresponding C−H bond enthalpies (estimated between 3 and 4 kcal/mol). Correlated with the large enthalpy change, a dramatic change in the activation entropies suggests that a looser transition

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(16) Exner, O. *Prog. Phys. Org. Chem.* **1973**, *10*, 411−483. Exner, O.; Beranek, V. *Collect. Czech. Chem. Commun.* **1975**, *40*, 781−798.

(17) Leffler, J. E. *J. Org. Chem.* **1955**, *20*, 1202−1231.

(18) Linert, W. *Chem. Soc. Rev.* **1994**, *23*, 429−438.

(19) Peterson, R. C. *J. Org. Chem.* **1964**, *29*, 3133−3135.

state is achieved for electron-poor arenes as compared to the electron-rich arenes.

Experimental Section

General Procedures. All operations and routine manipulations were performed under an atmosphere of nitrogen, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Dri-Lab. Benzene, THF, and hexanes were distilled from dark purple solutions of benzophenone ketyl and stored in glass ampules fitted with Teflon-sealed vacuum line adapters. Alkane solvents were made olefin-free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. *m*-Xylene, 1,3-diisopropylbenzene, and 1,3-bis(trifluoromethyl)benzene were purchased from Aldrich and dried and distilled before use. 1,3-Dichlorobenzene, 1,3,5-tri-*tert*-butylbenzene, $(n\text{-butyl})_3SnD$, 4-*tert*-butylphenylmagnesium bromide, and hexamethylphosphoramide (HMPA) were purchased from Aldrich and used as received. $Si(CH_3)_3Cl$ was purchased from Huls (formerly Petrarch) and used as received.

^1H, ^2H, and ^{31}P spectra were recorded on Bruker AMX400 NMR or Bruker WP200 spectrometers. All chemical shifts are reported in ppm (δ) relative to TMS (tetramethylsilane) and referenced to the residual solvent resonances (benzene, δ 7.15; chloroform, δ 7.24; acetone, δ 2.04). Fits for kinetic data, Eyring and van't Hoff plots, and least-squares analysis were performed using Microsoft Excel. All temperatures for variable temperature NMR spectroscopy were calibrated relative to the chemical shift differences in the NMR spectra of known standards (4% methanol in methanol-d_4). The complexes $(C_5Me_5)Rh(PMe_3)(aryl)Br$ and $(C_5Me_5)Rh(PMe_3)(aryl)H$ for aryl = C_6H_5, 4-$(CH_3)C_6H_4$, 4-$(CF_3)C_6H_4$, and 3,5-$(CH_3)_2C_6H_3$ have been described previously.[4,6] 1,3-Bis(trimethylsilyl)benzene was synthesized using a modified procedure from the one described previously.[20] 1-Bromo-3,5-di-*tert*-butylbenzene was prepared as described.[21] $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ was prepared using a modified procedure of Maitlis[22] (for the triphenylphosphine analog) or using the procedure of Werner.[23]

Preparation of 1,3-Bis(trimethylsilyl)benzene. A 30 g (0.204 mol) amount of *m*-dichlorobenzene was dissolved in 50 mL of HMPA and added slowly to a mixture of 100 mL of HMPA/75 mL (0.585 mol) of $Si(CH_3)_3Cl$/12 g (0.494 mol) of Mg turnings in a 500 mL flask equipped with a reflux condenser. The solution was stirred at 120 °C for 7 days under nitrogen. At this point, an additional 30 mL (0.234 mol) of $Si(CH_3)_3Cl$ was added to the mixture via syringe and the reaction continued for 12 h. The solution was cooled and poured onto 300 g of ice. Extraction of the organic layer with 5 × 200 mL of diethyl ether and removal of volatiles gave a mixture of *m*-chlorophenyltrimethylsilane and 1,3-bis(trimethylsilyl)benzene. Distillation under 0.1 Torr vacuum gave 12 g of a fraction with bp 95–97 °C (26% yield). ^1H NMR (C_6D_6): δ 7.875 (s, 1 H); 7.503 (d, J = 7.6, 2 H); 7.276 (t, J = 7.6 Hz, 1 H); 0.245 (s, 18 H).

Preparation of 5-Deuterio-1,3-di-*tert*-butylbenzene. A 6.0 g (31.6 mmol) amount of 5-bromo-1,3-di-*tert*-butylbenzene was dissolved in 10 g (34.2 mmol) of $(n\text{-butyl})_3SnD$ and heated to 150 °C under a nitrogen atmosphere in a 50 mL flask equipped with a reflux condenser for 6 h. Fractional distillation under 0.1 Torr vacuum gave 4.2 g of a fraction with bp 55 °C. ^1H NMR (acetone-d_6): δ 7.468 (s, 1 H); 7.205 (s, 1 H); 7.198 (s, 1 H); 1.306 (s, 18 H). ^2H NMR (C_6H_6): δ 7.24 (s). GC/MS (70 eV): 191 $(M)^+$, 176 $(M - 15)^+$, 148 $(M - 43)^+$, 116 $(M - 75)^+$, 92 $(M - 99)^+$, 57 $(M - 134)^+$.

Photochemical Preparation of $(C_5Me_5)Rh(PMe_3)$(aryl)H. This method was used for the preparation of aryl hydride complexes where aryl = 1,3-dimethylphenyl, 1,3-bis(trifluoromethyl)phenyl, and 1,3-di-*tert*-butylphenyl. A 25 mg (0.073 mmol) amount of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ was dissolved in 0.7 mL of the neat arene which had been dried and freeze–pump–thaw degassed three times. The solution was placed in a resealable NMR tube and photolyzed using a $\lambda > 345$ nm long-pass filter for 2 days. The solution gradually darkened to a dark red, at which point continued photolysis did not result in further reaction. Typical yields (^{31}P NMR integration) were 80%–85%.

Preparation of $(C_5Me_5)Rh(PMe_3)[4\text{-}(C(CH_3)_3C_6H_4]Br$. A 200 mg (0.421 mmol) amount of $(C_5Me_5)Rh(PMe_3)Br_2$ was dissolved in 25 mL of anhydrous THF. A 0.75 mL amount of 2 M 4-*tert*-butylphenylmagnesium bromide was added under nitrogen. The mixture was stirred for 30 min. The excess Grignard reagent was quenched with 200 μL of saturated aqueous NH_4Br, and the volatiles were removed under vacuum. The red solid was extracted with CH_2Cl_2 and filtered. Chromatography using 4% THF/CH_2Cl_2 on silica gave 120 mg (0.227 mmol, 54%) of $(C_5Me_5)Rh(PMe_3)$(4-*tert*-butylphenyl)Br. ^1H NMR (C_6D_6): δ 8.5 (br s, 2 H), 7.202 (d, J = 7.5 Hz, 2 H), 1.425 (d, J = 1.6 Hz, 15 H), 1.355 (s, 9 H), 1.098 (d, J = 10.3 Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.565 (d, J = 154 Hz).

Preparation of $(C_5Me_5)Rh(PMe_3)[4\text{-}Si(CH_3)_3C_6H_4]Br$. 4-(Trimethylsilyl)phenylmagnesium bromide (0.25 M) was prepared from 4-bromophenyltrimethylsilane and Mg in refluxing THF at 65 °C. A 150 mg (0.316 mmol) amount of $(C_5Me_5)Rh(PMe_3)Br_2$ was dissolved in anhydrous THF, and 10 mL of the 0.25 M 4-(trimethylsilyl)phenyl Grignard reagent was added under nitrogen. The mixture was stirred for 1 h. Addition of 200 μL of saturated aqueous NH_4Br and removal of volatiles gave a red oil. Extraction with CH_2Cl_2 and chromatography using 4% THF/CH_2Cl_2 on silica gave 80 mg of $(C_5Me_5)Rh(PMe_3)$(4-(trimethylsilyl)phenyl)Br (0.147 mmol, 46%). ^1H NMR (C_6D_6): δ 8.6 (br s, 2 H), 7.321 (d, J = 7.8 Hz, 2 H), 1.358 (d, J = 2 Hz, 15 H), 1.027 (d, J = 9.6 Hz, 9 H), 0.276 (s, 9 H).

Reaction of $(C_5Me_5)Rh(PMe_3)[4\text{-}(CH_3)C_6H_4]Br$ with L-Selectride. A 50 mg (0.103 mmol) amount of $(C_5Me_5)Rh(PMe_3)[4\text{-}(CH_3)C_6H_4]Br$ was dissolved in anhydrous THF, and 1.0 mL of 1 M L-selectride (in THF) was added under nitrogen. The volatiles were removed under vacuum, and the remaining gel was reacted for 2 h. The solid lightened to a straw-yellow color. Flash chromatography on silica using a 3:5 hexanes/THF mixture left a dark oil. ^1H and ^{31}P NMR show formation of $(C_5Me_5)Rh(PMe_3)[4\text{-}(CH_3)C_6H_4]H$ and $(C_5Me_5)Rh(PMe_3)H_2$.

Preparation of $(C_5Me_5)Rh(PMe_3)$(aryl)H. This method was used for the preparation of the 3,5-disubstituted aryl hydride complexes $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)H$ for R = CF_3, CH_3, $Si(CH_3)_3$, $CH(CH_3)_2$, and $C(CH_3)_3$. An 80–100 mg amount of $(C_5Me_5)Rh(PMe_3)(Ph)Br$ was converted to $(C_5Me_5)Rh(PMe_3)(Ph)H$ by a previously published procedure.[4] The yellow solid $(C_5Me_5)Rh(PMe_3)(Ph)H$ was then dissolved in 0.7 mL of the 1,3-disubstituted arene, and the mixture was heated at 67 °C for 10–15 h. The reaction went to >95% completion for the complexes where R = CF_3, CH_3, and $Si(CH_3)_3$. An equilibrium mixture was obtained for the complexes where R = $CH(CH_3)_2$ and $C(CH_3)_3$. Removal of the solvent under high vacuum gave dark oils. In the cases where equilibrium mixtures were obtained, fresh arene was introduced into the isolated oil and the reaction conditions were repeated to obtain >95% yield of the desired product.

Spectroscopic Data for Complexes $(C_5Me_5)Rh(PMe_3)$(aryl)H. $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(CF_3)_2C_6H_3]H$. ^1H NMR (C_6D_6): δ 8.088 (s, 2 H), 7.617 (s, 1 H), 1.601 (d, J = 1 Hz, 15 H), 0.735 (d, J = 10 Hz, 9 H), −13.290 (dd, J = 48, 32 Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.717 (d, J = 149 Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(Si(CH_3)_3)_2C_6H_3]H$. ^1H NMR (C_6D_6): δ 7.857 (s,

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[20] Bourgeois, P.; Calas, R. *J. Organomet. Chem.* **1975**, *84*, 165–175.

[21] Bartlett, P. D.; Roha, M.; Stiles, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 2349–2353.

[22] Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393–404.

[23] Werner, H.; Klingert, B. *J. Organomet. Chem.* **1981**, *218*, 395–407.

2 H), 7.548 (s, 1 H), 1.807 (d, $J = 3$ Hz, 15 H), 0.933 (d, $J = 9$ Hz, 9 H), 0.394 (s, 18 H), −13.476 (dd, $J = 49.1, 32.7$ Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.85 (d, $J = 155.2$ Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(CH(CH_3)_2)_2C_6H_3]H$. ^1H NMR (C_6D_6): δ 7.329 (s, 2 H), 6.764 (s, 1 H), 2.876 (sept, $J = 7.4$ Hz, 2 H), 1.833 (s, 15 Hz), 1.365 (dd, $J = 7.4, 3$ Hz, 12 H), 0.956 (d, $J = 10.4$ Hz, 9 H), −13.577 (dd, $J = 50.6, 32$ Hz, 1 H). $^{31}P\{^1H\}$ NMR (1,3-diisopropylbenzene solvent): δ 7.990 (d, $J = 156.6$ Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(C(CH_3)_3)_2C_6H_3]H$. ^1H NMR (C_6D_6): δ 7.498 (s, 2 H), 7.295 (s, 1 H), 1.846 (s, 15 H), 1.461 (s, 18 H), 0.979 (d, $J = 9$ Hz, 9 H), −13.540 (dd, $J = 48.5, 32$ Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 8.520 (d, $J = 157$ Hz).

Preparation of $(C_5Me_5)Rh(PMe_3)$(aryl)Br. To a benzene solution of $(C_5Me_5)Rh(PMe_3)$(aryl)H was added several drops of $CHBr_3$. The solution immediately became red. Chromatography on silica using 4% THF/CH_2Cl_2 allowed isolation of the complexes $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)Br$ for R = CF_3, $Si(CH_3)_3$, $CH(CH_3)_2$, $C(CH_3)_3$.

Spectroscopic Data for Complexes $(C_5Me_5)Rh(PMe_3)$(aryl)Br. $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(CF_3)_2C_6H_3]Br$ ^1H NMR (C_6D_6): δ 9.2 (br s, 1 H), 7.702 (s, 2 H), 1.234 (s, 15 H), 0.905 (d, $J = 10.2$ Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.285 (d, $J = 147.6$ Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(Si(CH_3)_3)_2C_6H_3]Br$ ^1H NMR (C_6D_6): δ 8.7 (br s, 1 H), 7.650 (s, 2 H), 1.430 (d, $J = 2.8$ Hz, 15 H), 1.116 (d, $J = 9.7$ Hz, 9 H), 0.396 (s, 18 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.494 (d, $J = 155.4$ Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(CH(CH_3)_2)_2C_6H_3]Br$ ^1H NMR (C_6D_6): δ 8.28 (br s, 1 H), 6.813 (s, 2 H), 2.89 (br s, 2 H), 1.448 (d, $J = 2.7$ Hz, 15 H), 1.356 (d, $J = 7.6$ Hz, 12 H), 1.129 (d, $J = 10.4$ Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 5.43 (d, $J = 155.2$ Hz). $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(C(CH_3)_3)_2C_6H_3]Br$ ^1H NMR (C_6D_6): δ 8.51 (br s, 1 H), 7.203 (t, $J = 1.8$ Hz, 1 H), 6.975 (br s, 1 H), 1.45 (br s, 18 H), 1.449 (d, $J = 2.8$ Hz, 15 H), 1.140 (d, $J = 10.3$ Hz, 9 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.28 (d, $J = 146$ Hz).

Kinetic Studies. In a typical experiment, 80−100 mg of $(C_5Me_5)Rh(PMe_3)(Ph)Br$ was converted to the phenyl hydride $(C_5Me_5)Rh(PMe_3)(Ph)H$ with L-selectride using a published procedure.[4] The $(C_5Me_5)Rh(PMe_3)(Ph)H$ was converted to the 3,5-disubstituted aryl hydride complex as described above. The dark oil was dissolved in C_6D_6 and diluted to 2.8−3.5 mL with C_6D_6 to yield 4 or 5 NMR samples. The solutions were placed in NMR tubes with vacuum adapters, freeze−pump−thaw degassed and flame-sealed under vacuum and stored at −20 °C until ready to use. For reactions with half-lives of 4 h or less, the NMR probe was heated to the desired temperature and spectra were obtained at 10, 5, or 3 min intervals using the Bruker 2D program KINETICS. For slower reactions, the sample was kept in an equilibrated oil-bath for elevated temperatures or a constant temperature room for room temperature and NMR spectra were obtained at appropriate intervals. Kinetics were monitored for a minimum of 3 half-lives, with one exception being the reaction of $(C_5Me_5)Rh(PMe_3)[3,5\text{-}(CF_3)_2C_6H_3]H$ at 54 °C, which has a half-life of 1600 h. In this case the reaction was followed for 2000 h.

Equilibrium Studies. Equilibrium values were obtained with samples used in the synthesis of the $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3R_2)H$ complexes. For R = $CH(CH_3)_2$ and $C(CH_3)_3$, equilibrium was attained with the C_6H_6 released from $(C_5Me_5)Rh(PMe_3)(Ph)H$. Measurements were made by $^{31}P\{^1H\}$ NMR spectroscopy using inverse-gated decoupling to insure accuracy of the integration. Equilibrium values for R = CF_3 were obtained using final ratios of aryl hydride to phenyl hydride values from the kinetic experiments in C_6D_6, as equilibrium was achieved with the $1,3\text{-}(CF_3)_2C_6H_4$ released.

Kinetic Isotope Effect of $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ with 1,3-Di-*tert*-butylbenzene/5-Deuterio-1,3-di-*tert*-butylbenzene. A sample of composition 50% 5-deuterio-1,3-di-*tert*-butylbenzene was prepared by dilution of >90% 5-deuterio-1,3-di-*tert*-butylbenzene with proteo 1,3-di-*tert*-butylbenzene. The composition was confirmed by GC−MS analysis of the parent ions at 191 and 190 mass units using low ionization voltage. Integration of the phenyl resonances by ^1H NMR spectroscopy quantitatively confirmed the amount of the deuterium enrichment. A 25 mg (0.053 mmol) amount of $(C_5Me_5)Rh(PMe_3)Br_2$ was converted to $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ and sublimed twice onto a liquid nitrogen cold finger. The $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ was dissolved in 0.5 mL of the deuterium-enriched arene and photolyzed at 10 °C with a high-pressure Hg lamp using a $\lambda > 345$ nm long-pass filter. ^{31}P inverse-gated NMR spectra were recorded at 15 min intervals. The relative amounts of aryl hydride and aryl deuteride complexes were determined by integration of the base line-resolved peaks for the two isotopomers.

Flash Photochemical Studies. Flash photolysis experiments were carried out using a flash photochemical apparatus which has been described previously.[10] In a typical experiment, several mg of twice-sublimed $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ was dissolved in high-purity toluene or *m*-xylene which had been distilled and thoroughly dried and degassed. The sample was placed in a flash cell and diluted until the absorbance at 308 nm was between 0.8 and 1.2. The sample was then freeze−pump−thaw degassed three times.

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