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Isotope Effects in Arene C–H Bond Activation by $[(C_5Me_5)Rh(PMe_3)]$

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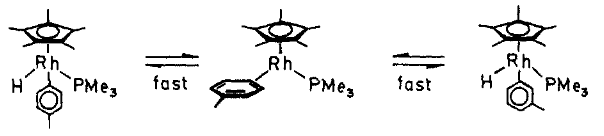
Abstract: The isotope effects involved in the activation of arene C–H bonds by the intermediate $[(C_5Me_5)Rh(PMe_3)]$ have been investigated. The ratio k_H/k_D for coordination to a double bond in benzene (the rate-determining step of arene activation) is found to be 1.05 (6), whereas $k_H/k_D = 1.4$ for the second step in which the C–H bond of the coordinated arene undergoes oxidative addition. The isotope effect $K_{H/D}$ for the equilibrium between the more stable phenyl hydride complex $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ and the complex containing hydrogen in the ortho position of the phenyl ring $(C_5Me_5)Rh(PMe_3)(o\text{-}C_6D_4H)D$ shows a preference for hydrogen (vs. deuterium) on the metal of 2.7. The kinetic isotope effect for reductive elimination and dissociation of *m*-xylene from $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$ vs. $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)D$ is found to be inverse, with $k_H/k_D = 0.51$. Analysis of the data for the deuterated benzene derivatives confirms that the kinetic isotope for the reductive elimination step is inverse. Attempts to prepare the complex $(C_5Me_5)Rh(PMe_3)(CH_3)D$ by reduction of $[(C_5Me_5)Rh(PMe_3)(CH_3)(THF)]^+$ with $[DBEt_3]^-$ resulted in the formation of both $(C_5Me_5)Rh(PMe_3)(CH_3)D$ and $(C_5Me_5)Rh(PMe_3)(CH_2D)H$.

The use of low-valent transition metals to activate aliphatic and aromatic C–H bonds by oxidative addition is an area that has been the subject of intense research over the past few years.[1-11] Insights into the selectivity and generality of these reactions are now fairly well established, with hydrocarbons such as methane, ethane, propane, and cycloalkane becoming common substrates. The relative preference for intramolecular reaction with a coordinated ligand is beginning to be understood, and new metal complexes are appearing with the capability of activating a variety of C–H bonds.

Our initial work has been directed at understanding the competitive activation of the strong C–H bonds of arenes and the weaker C–H bonds of alkanes.[9] In the study of reductive elimination of arene from the aryl hydride complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$, we discovered that a low-energy pathway existed for the interconversion of the carbon attached to the metal. This isomerization was found to occur in a sequential [1,2] fashion, and it can be accommodated by the reversible formation of an η^2-arene complex as shown in eq 1. At higher temperatures the arene can dissociate, thereby permitting intermolecular exchange. A general free energy diagram for this process is shown in Scheme I.



(1)

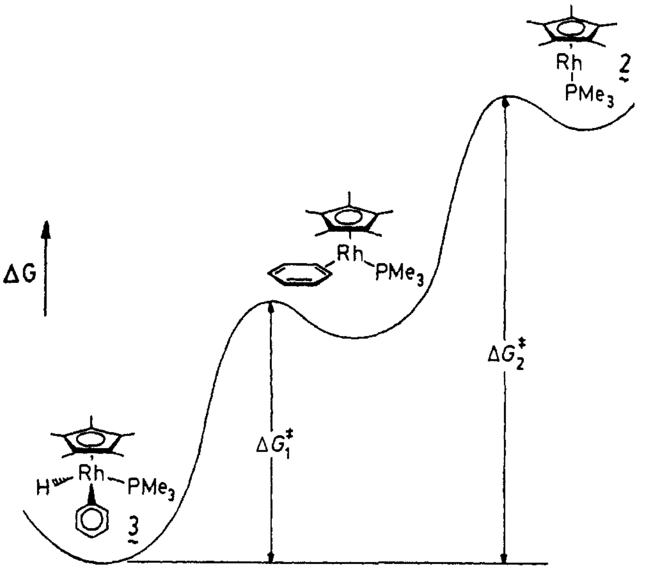
In this paper we report the isotope effects, both kinetic and equilibrium, that confirm the intermediacy of an η^2-arene intermediate. The appearance of a large inverse isotope effect in the reductive elimination of the aryl hydride complex is discussed. The current results are compared and contrasted with earlier reports of isotope effects in reductive elimination and oxidative addition reactions at transition-metal centers.

Results

The photolysis of $(C_5Me_5)Rh(PMe_3)H_2$ (**1**) offers a convenient method for the photoinduced generation of the coordinatively unsaturated intermediate $[(C_5Me_5)Rh(PMe_3)]$ (**2**) by reductive elimination of dihydrogen. This method can be used to study the ability of the reactive species **2** to activate C–H or C–D bonds under conditions of kinetic control as outlined below.

Irradiation of **1** in a 1:1 (v:v) mixture of C_6H_6/C_6D_6 at 10 °C results in the evolution of H_2 and the formation of benzene C–H/C–D activation products $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (**3**) and $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ (**3**-d_6). Quenching of this so-

Scheme I



[†] A. P. Sloan Fellow, 1984–1986. Camille and Henry Dreyfus Teacher-Scholar, 1985–1987.

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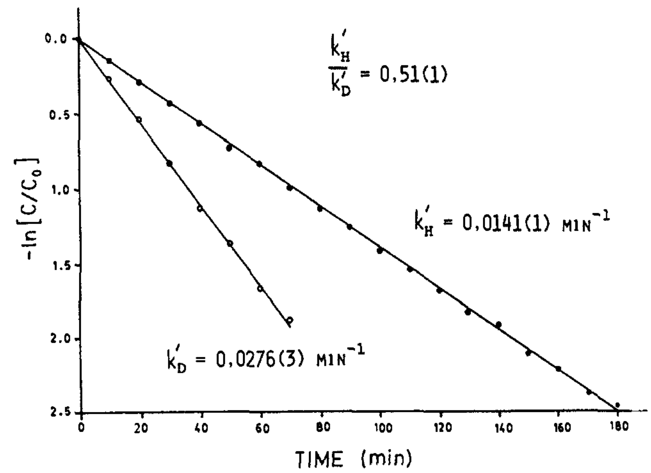
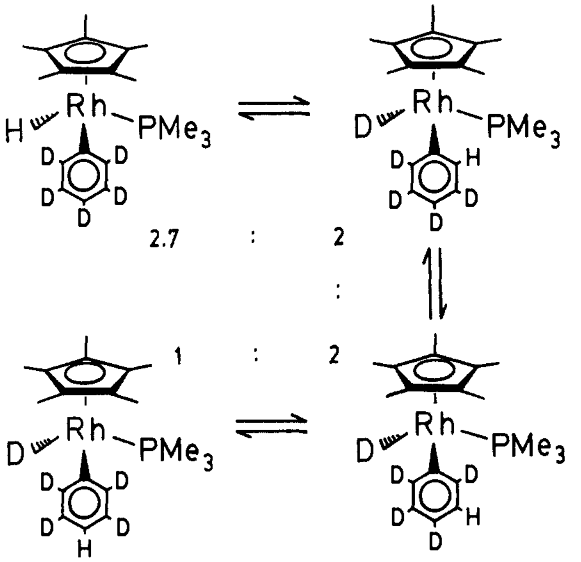
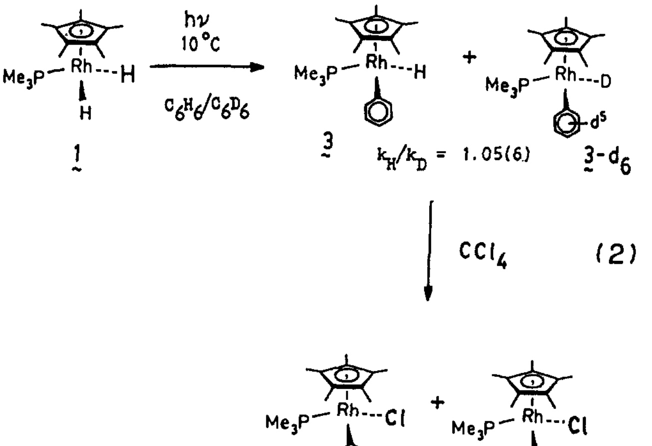


Figure 1. Kinetic data for reductive elimination and dissociation of xylene in $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$ and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)D$ in benzene at 51.2 °C.

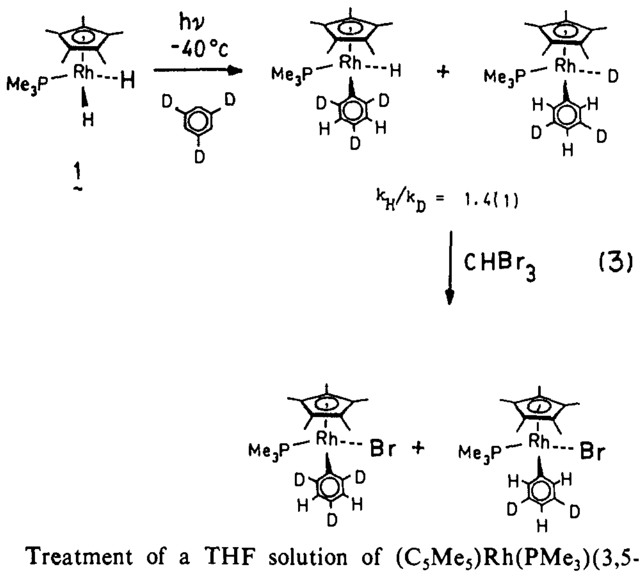
Scheme II



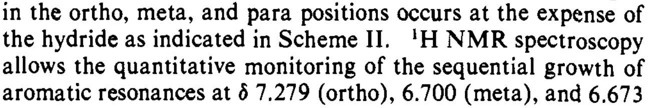
lution with CCl_4 results in the formation of the chloro derivatives $(C_5Me_5)Rh(PMe_3)(C_6H_5)Cl$ and $(C_5Me_5)Rh(PMe_3)(C_6D_5)Cl$ in high yield. Mass spectral analysis of this mixture reveals a 1.05 (6):1 ratio of the products in which C_6H_6 vs. C_6D_6 has been activated (eq 2).



Similarly, irradiation of **1** in a cyclopentane solution of 1,3,5-$C_6H_3D_3$ at −40 °C results in the formation of benzene activation products that can be identified by low-temperature quenching of the reaction with a bromoform/THF solution. ^1H NMR spectral analysis shows $(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2D_3)Br$ and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3D_2)Br$ in a 1.40:1 ratio (eq 3) by integration of the aromatic region of the spectrum (see Experimental Section).



Treatment of a THF solution of $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)Br$ with either $Li^+[HBEt_3]^-$ or $Li^+[DBEt_3]^-$ in THF allows preparation of the corresponding hydride or deuteride derivatives, respectively. The kinetics of arene reductive elimination and dissociation at 51.2 °C can be monitored by ^1H NMR spectroscopy (eq 4) and are found to follow first-order kinetics as indicated in the logarithmic plots in Figure 1. From the slopes of these lines, $k_H = 2.35\ (2) \times 10^{-4}\ s^{-1}$ and $k_D = 4.60\ (5) \times 10^{-4}\ s^{-1}$.



The perdeuterio complex $(C_5Me_5)Rh(PMe_3)(C_6D_5)Br$ reacts with $AgPF_6$ in THF-d_8 solution to give the THF-d_8 complexed cation $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF\text{-}d_8)]^+$, which in turn reacts with $Li^+[HB(\textit{sec}\text{-}Bu)_3]^-$ at −78 °C to give $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ (**3**-d_5). Upon warming this sample to −15 °C, intramolecular equilibration of the isomers containing hydrogen in the ortho, meta, and para positions occurs at the expense of the hydride as indicated in Scheme II. ^1H NMR spectroscopy allows the quantitative monitoring of the sequential growth of aromatic resonances at δ 7.279 (ortho), 6.700 (meta), and 6.673 (para) and the disappearance of the hydride resonance at δ −13.858. At equilibrium at 25 °C, a 2.7:2:2:1 ratio of the areas of the hydride, ortho, meta, and para resonances was observed.

Determination of the rate constant for reductive elimination of CH_3D in the complex $(C_5Me_5)Rh(PMe_3)(CH_3)D$ would allow evaluation of the kinetic isotope effect for reductive elimination of methane. A complication in the synthesis of the complex thwarted attempts to measure this rate constant. Treatment of the cation $[(C_5Me_5)Rh(PMe_3)(CH_3)(THF\text{-}d_8)]^+$ with $Li^+[DBEt_3]^-$ in THF at low temperature resulted in the formation of methyl hydride complex in which some hydrogen appeared in the hydridic position of the molecule, apparently by scrambling from the methyl group (eq 5). A possible origin of this scrambling will be discussed in the following section.

Discussion

Intermolecular exchange of arenes with $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (**3**) occurs readily at temperatures of −60 °C. According to our earlier proposal,[9] arene reductive elimination

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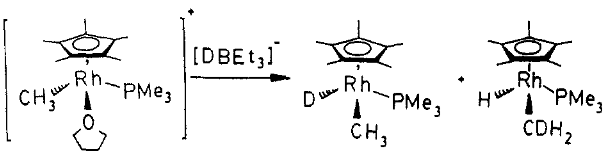

(5)

proceeds intramolecularly and reversibly to give an η^2-arene complex which then undergoes a slower dissociation of arene to generate the unsaturated intermediate **2**. By microscopic reversibility, the reverse of this pathway must be followed when an arene undergoes the process termed "oxidative addition" to the coordinatively unsaturated intermediate **2**. A free energy diagram for this process is shown in Scheme I for the phenyl hydride complex **3**.

Since the activation of benzene C–H bonds by **2** occurs in two discrete steps, the effects of isotopic substitution of deuterium for hydrogen can be used to discern information about the transition state(s) for C–H bond activation. The diagram proposed in Scheme I is useful for understanding the magnitude of the observed isotope effects in this system. The highest barrier in the C–H bond activation process in the reaction of **2** with benzene does not involve cleavage of the C–H bond and therefore would be expected only to display a small secondary isotope effect. The second step of the activation reaction involves oxidative addition of the C–H bond of the η^2-complexed arene and might be expected to display a small isotope effect since a nonlinear transition state should be involved.[12]

The competition experiment in which **2** competes for C_6H_6 or C_6D_6 (described in eq 2 above) produces a ratio of $k_H/k_D = 1.05$ (6). Benzene is not labile in the products **3** and **3**-d_6 under the conditions of the experiment (10 °C) so that this ratio reflects the kinetic isotope effect for arene complexation. This small value of k_H/k_D is consistent with there being little or no C–H bond breaking in the step in which the selection of the arene to be activated by **2** occurs.

The next step in the activation process according to Scheme I, however, does involve cleavage of the C–H (or C–D) bond. The experiment described in eq 3 above is performed at low temperature, conditions that ensure that once the oxidative addition has occurred no isomerization of the kinetically formed product is possible. Complexation of **2** to 1,3,5-trideuteriobenzene can produce only one possible η^2-arene complex, and the ratio k_H/k_D for this reaction therefore reflects only the isotope effect involved in the cleavage of the C–H bond but not in the selection of the arene in which the bond will be cleaved (there is only one arene to choose from!). The magnitude of the effect is small (1.4) as anticipated. One assumption implicit in this interpretation is that the bromoform quench reaction occurs equally well with both substrates, a reasonable assumption since the only difference involved is the reactivity of a Rh–H vs. a Rh–D bond. Also, other photochemical competition reactions with **2** give kinetic selectivities that are different from the thermodynamic selectivities.[9c,d] For example, the reaction of photochemically prepared **2** with toluene shows a kinetic product distribution in which meta, para, ortho, and benzylic C–H bonds are activated, whereas the thermodynamic product distribution shows only *m*- and *p*-tolyl oxidative addition adducts.[9c] It is reasonable that the product ratios in the experiments described here also represent a kinetic selectivity.

It is important to note that the experiments in eq 2 and 3 (1) both involve activation of a deuterium-substituted benzene molecule and (2) have different values for k_H/k_D. Since both experiments involve bimolecular activation of the benzene C–H bond (**2** + benzene) and since the kinetic isotope effects are different, *these observations prove that a direct insertion of* **2** *into the C–H bond of benzene is* **not** *occurring.*[13]

An alternative possibility, that the arene is activated by a direct addition of $[(C_5Me_5)Rh(PMe_3)]$ to the C–H bond and that the η^2-arene complex lies on a separate reaction coordinate that is different from that for the intermolecular C–H bond addition, is inconsistent with the isotope effect experiments described here. The interaction of **2** with *p*-di-*tert*-butylbenzene was previously shown to produce the observable η^2-arene complex $(C_5Me_5)Rh(PMe_3)[\eta^2\text{-}p\text{-}C_6H_4(t\text{-}Bu)_2]$.[9c] The isotope effect studies prove that there is *some* intermediate in the intermolecular activation of benzene by $[(C_5Me_5)Rh(PMe_3)]$, and all evidence points toward the η^2-arene complex as the intermediate.[14] Several reports of η^2-arene complexes have appeared,[15] with a recent one characterized by X-ray structural analysis.[16]

Recent observations by Bergman on the addition of ethylene to $[(C_5Me_5)Ir(PMe_3)]$ indicate that the vinyl hydride complex does not lie along the lowest energy pathway connecting $[(C_5Me_5)Ir(PMe_3)] + C_2H_4$ and the η^2-ethylene complex $(C_5Me_5)Ir(PMe_3)(\eta^2\text{-}C_2H_4)$.[17] In the case of the iridium intermediate, the transition state for oxidative addition of ethylene must closely resemble that for coordination of ethylene so that little selectivity is seen in the reaction of $[(C_5Me_5)Ir(PMe_3)]$ with ethylene. A *separate* lower energy pathway for the interconversion of the vinyl hydride complex to the η^2-ethylene complex was proposed to account for the observations. This conclusion is clearly not the case for the reactions of $[(C_5Me_5)Rh(PMe_3)]$ with arenes. The rhodium complex $(C_5Me_5)Rh(PMe_3)(\overline{C{=}CHCH_2CH_2CH_2})H$ was observed to undergo intramolecular rearrangement to $(C_5Me_5)Rh(PMe_3)(\overline{CH{=}CHCH_2CH_2CH_2})$ at −12 °C, but no report of the kinetic selectivity for the reaction of $[(C_5Me_5)Rh(PMe_3)]$ with ethylene was made for direct comparison with the iridium system.[9c] Two other systems have been reported to show evidence for the preferential activation of olefinic C–H bonds over olefin π coordination. Felkin and Faller have seen exclusive exchange of the *E*-olefinic hydrogen in 3,3-dimethyl-1-butene for deuterium with $Ir[P(i\text{-}Pr)_2H_5]$,[18] and Bergman, Seidler, and Wenzel have seen kinetic ethylene C–H bond activation with $CpRe(PMe_3)_3$.[10] One should keep in mind, however, that in the reactions of olefins with unsaturated metal centers complexation by far dominates C–H insertion and that the above-mentioned systems are quite novel in this regard.

The $(C_5Me_5)Rh(PMe_3)RH$ system also allows measurement of the isotope effects in the reductive elimination and dissociation sequence, the reverse of the η^2-coordination/oxidative addition process. One experiment that gives a measure of the overall isotope effect for this process comes from measurement of the rate of loss of xylene from the complex $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$. Independent rate measurements at 51.2 °C give an *inverse* isotope effect of $k_H/k_D = 0.51$.

A separate experiment provides verification of the inverse isotope effect. Equilibration of the isomers **3**-d_5 in which the hydrogen is distributed over the hydride, ortho, meta, and para sites displays a ratio of areas of 2.7:2:2:1 in the ^1H NMR spectrum as mentioned above. The distribution of hydrogen is statistical with regard to the arene C–H bonds but shows a marked preference for deuterium in the aromatic positions (2.7 × statistical). Equation 6 shows the individual steps and rate constants for the equilibrium according to the mechanism in Scheme I. k_H and k_D are the rate constants for oxidative addition to a C–H or C–D bond in the η^2-benzene complex, and k_H' and k_D' are the rate

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[12] Melander, L. C. S.; Saunders, W. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

[13] For related isotope experiments (a) involving cycloaddition reactions of $H_2C{=}C{=}CD_2$ and (b) involving 1,3,5-$C_6H_3D_3$, see: (a) Dolbier, W. R., Jr.; Dai, S.-H. *J. Am. Chem. Soc.* **1968**, *90*, 5028–5030. Dolbier, W. R., Jr.; Dai, S.-H. *J. Am. Chem. Soc.* **1972**, *94*, 3946–3952. (b) Klaubunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 9081–9087.

[14] Prof. R. Bergman has suggested that this intermediate could be a complex in which the arene bonds to the metal in a σ fashion through one of the C–H bonds. We consider this possibility unlikely in view of the more favorable energetics for arene π coordination and due to the overwhelming evidence for η^2-arene complexes in these and other[15,16] studies.

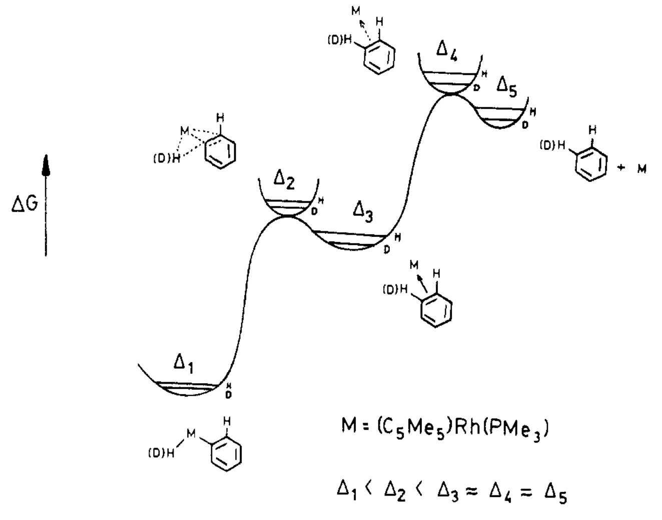
[15] Jonas, K. J. *J. Organomet. Chem.* **1974**, *78*, 273–279. Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1977**, *16*, 884–891. Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499–525. Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1984**, *106*, 305–306.

[16] Heijden, H.; Orpen, G. A.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576–1578.

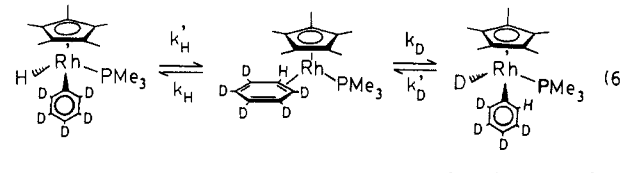
[17] Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582.

[18] Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488–1490.

Scheme III. Reaction Coordinate for Arene Activation by $[(C_5Me_5)Rh(PMe_3)]$ Showing Vibrational Wells and H/D Zero Point Energies



constants for the reductive elimination involving either a Rh–H or a Rh–D bond, respectively.



(6)

Here we have chosen to show k_H' as only forming one of two possible η^2-C_6D_5H complexes (either ortho carbon in **3** could coordinate to the metal in the η^2-arene complex), and therefore the areas of the ortho and meta isomers of **3**-d_5 should be decreased by a factor of 2 to account for this statistical portion of the rate constant k_H'.[19] Therefore, the measured value of the equilibrium constant K_{eq} for equilibration of the hydride and ortho isomers of **3**-d_5 (0.37) is given by eq 7. The kinetic isotope rate ratio for oxidative addition of either a C–H or a C–D bond in an η^2-benzene complex in which the coordinated double bond contains both a C–H and a C–D bond was determined in the previous experiment involving 1,3,5-$C_6H_3D_6$ as $k_H/k_D = 1.4$. Substitution of this ratio into eq 7 allows an independent determination of the reductive elimination rate ratio $k_H'/k_D' = 0.52$, in remarkably good agreement with the inverse rate ratio determined from the xylene exchange experiment.

$$K_{eq} = \frac{[\text{ortho } \mathbf{3}\text{-}d_5]}{[\text{hydride } \mathbf{3}\text{-}d_5]} = 0.37 = \frac{k_H'k_D}{k_D'k_H} \qquad (7)$$

The agreement between these two experiments is really not surprising in light of the mechanism in Scheme I. Since the portion of the reaction that involves **2**, benzene, and the η^2-benzene complex does not involve cleavage of a C–H bond, only a small secondary isotope effect would be expected at most for reaction in either direction (arene + **2** → η^2-arene or η^2-arene → arene + **2**). Consequently, virtually all of the isotope effects are associated with the interconversion of **3** and the η^2-arene complex. The small normal isotope effect observed for the intramolecular oxidative addition reaction was expected on the basis of the bent Rh–H–C geometry of the transition state in which only partial C–H bond breaking has occurred.

The inverse isotope effect for the intramolecular reductive elimination reaction is somewhat unexpected, however. The free energy diagram shown in Scheme III can be used to account for this effect and shows the difference in H/D zero-point vibrational energies of the compounds, the magnitudes of which are based upon M–H(D) and C–H(D) stretching frequencies. Also shown at the transition states is the saddle point nature of this region of the diagram, with the zero-point energies of the combined real C–H or C–D vibrations shown in the saddle.[20] If the magnitude of the residual difference in zero-point energies left in the transition state (Δ_2) is less than that in the η^2-benzene complex (Δ_3) but greater than that in complex **3** (Δ_1), then one expects a normal isotope effect for the intramolecular oxidative addition (i.e., the barrier for breaking the C–H bond is less than that encountered for breaking the C–D bond) and an inverse isotope effect for the reductive elimination.

This situation apparently results because the transition state for oxidative additional occurs early along the reaction coordinate and, according to the Hammond postulate,[21] would exhibit more η^2-arene character than aryl hydride character. Therefore, the transition state of the oxidative addition reaction would have strong C–H or C–D interactions. Since the difference in zero-point energies for C–H/C–D stretching and bending vibrations is greater than that of the corresponding M–H/M–D vibrations, the difference in zero-point energies for the oxidative addition transition state (Δ_2) is actually larger than the difference in ground-state zero-point energies for the metal hydride and deuteride. This leads to the observed isotope effects. If, however, there was a more substantial reduction of the C–H(D) bond order in the transition state (i.e., a later transition state for oxidative addition or earlier transition state for reductive elimination) then Δ_2 would decrease, resulting in a normal isotope effect in both directions provided $\Delta_2 < \Delta_1$.

By assuming that a fully formed C–H or C–D bond is present in the rate-determining transition state for arene loss (represented by Δ_4 in Scheme III), the isotope effect for arene reductive elimination and dissociation from **3** can be calculated.[22] Assuming typical stretching frequencies $\nu_{C-H} = 3000\ cm^{-1}$, $\nu_{C-D} = 2120\ cm^{-1}$, $\nu_{M-H} = 2000\ cm^{-1}$, and $\nu_{M-D} = 1414\ cm^{-1}$ (all $\pm 15\ cm^{-1}$), the kinetic isotope rate ratio is calculated to be $k_H'/k_D' = 0.52 \pm 0.07$, in excellent agreement with the observed rate ratio. An intact C–H bond is therefore present in the rate-determining transition state for arene activation!

Second, this reductive elimination kinetic isotope rate ratio should manifest itself almost entirely in the portion of the reaction coordinate interconverting **3** and the η^2-benzene complex. As the "ring walk" experiment in eq 6 provided a value of $k_H'/k_D' = 0.52$, one must conclude that the transition state represented by Δ_2 in Scheme III also has a virtually intact C–H or C–D bond. Since the kinetic isotope effect for oxidative addition of a C–H vs. a C–D bond is in fact greater than unity ($k_H/k_D = 1.4$, eq 3), however, a small amount of bond breaking is indeed present in the transition state at Δ_2.

Two other systems have recently been reported that display evidence for intramolecular arene isomerization. One example by Rothwell involves the conversion of $Ta[OC_6H_3(t\text{-}Bu)(CMe_2CH_2)][OC_6H_3(t\text{-}Bu)_2](o\text{-tolyl})_2$ to a mixture of meta and para isomers of $Ta[OC_6H_3(t\text{-}Bu)(CMe_2CH_2)]_2(\text{tolyl})$ and was postulated to isomerize by way of a benzyne intermediate in the electrophilically activated intermediate (eq 8).[23] The other system reported by Werner involves the reduction of $Os(PMe_3)_2[P(OMe)_3]_2Cl_2$ in toluene to generate a 1:1.75 ratio of meta:para tolyl isomers of $Os(PMe_3)_2[P(OMe)_3]_2(\text{tolyl})H$.[24] Upon standing the ratio changes to 1:1 after several days. No exchange with C_6D_6 solvent is observed under similar conditions, confirming the

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[19] Scheme II as reported in ref 9c contained erroneous labeling of the rate constants k_H and k_D for interconversion of the ortho and meta isomers. Since only one possible meta isomer can be formed from a given ortho isomer, the rates of interconversion should be k_D, not $2k_D$ as shown in the scheme. The data in ref 9c were in fact actually fit with the correct rate constant k_D.

[20] For a similar treatment, see Hupe, D. J.; Pohl, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 5634–5640 and ref 12, p 22. There are also C–H and C–D vibrational modes with components lying along the reaction coordinate that are excluded in the total residual zero-point energy.

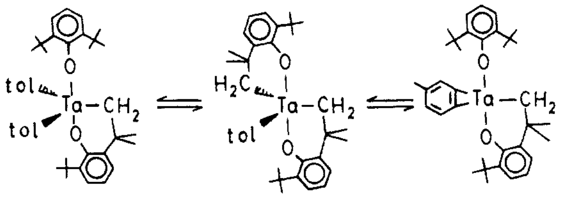
[21] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

[22] See eq 2.23 from ref 12, p 27.

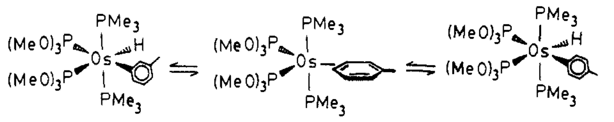
[23] Chamberlain, L. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665–1666.

[24] Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73–93.

intramolecular nature of the rearrangement, possibly by way of an η^2-toluene complex (eq 9).

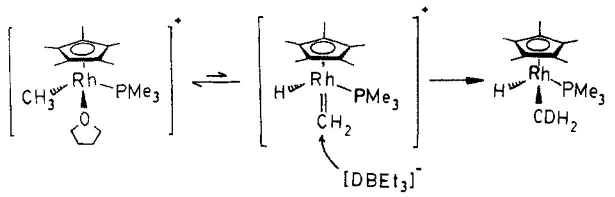


(8)

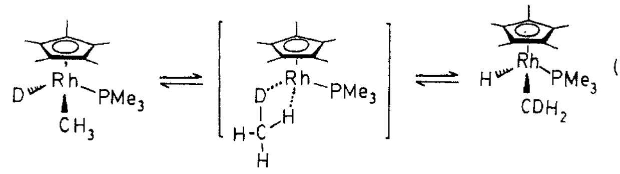


(9)

Attempts to measure the kinetic isotope effect for reductive elimination of methane by measurement of the rate constant for loss of CH_3D in the complex $(C_5Me_5)Rh(PMe_3)(CH_3)D$ were thwarted by scrambling of the methyl hydrogens with the deuteride ligand during the synthesis of the complex (eq 5). One possible mechanism for this scrambling involves hydridic attack upon a rhodium methylene complex formed by a reversible α-elimination in the methyl cation (eq 10).[25] A second mechanism involves a reversible CH_3D reductive elimination of the initially formed product to form a "methane complex" in which dissociation of methane is slower than oxidation addition to one of the C–H bonds of the coordinated methane (eq 11). This possibility was suggested to us on the basis of recent work by Bergman and co-workers with reactions of isotopically labeled $(C_5Me_5)Ir(PMe_3)$(c-hexyl)D.[26] Norton has also seen intermolecular scrambling of deuterium between $Cp_2W(^{13}CH_3)H$ and $Cp_2W(CD_3)H$ so that the origin of the scrambling in the rhodium complexes reported here is ambiguous.[27]



(10)



(11)

Other workers have observed isotope effects during C–H bond making and breaking reactions that complement the studies mentioned here. Highly electrophilic systems such as $(C_5Me_5)_2Lu(CH_3)$[1] and $(C_5Me_5)_2Th(CH_2CMe_3)_2$[3] are believed to activate C–H bonds by a 4-center mechanism and display k_H/k_D values in the region of 5–6. Systems that react intramolecularly by an oxidative addition mechanism generally show smaller isotope effects such as ~3 found for the cyclization of $Pt(PEt_3)_2(CH_2CMe_3)_2$.[28] Bergman reported a k_H/k_D value of only 1.38 for oxidative addition of cyclohexane to $[(C_5Me_5)Ir(PMe_3)]$.[7] With regard to reductive elimination, Halpern's work with $Pt(PPh_3)_2(CH_3)H$ gave a value of 3.3 for k_H/k_D,[29] compared with 2.2 for the related complex $Pt(PPh_3)_2(CH_2CF_3)H$.[30]

With regard to inverse isotope effects in hydrogen atom transfers from a transition metal to a carbon atom, earlier work by Halpern and Orchin has revealed several reactions in which k_H/k_D is less than 1.[31] Similarly, Bergman has seen an inverse isotope effect in the addition of a Mo–H bond to a bridging vinylidene C–H bond.[32] Also, Moore observed a $k_H/k_D = 0.41$ upon hydrogenation of norbornadiene with $[Ir(PPh_3)_2H_2(acetone)_2]^+$.[33] All of these studies involve the transfer of a hydrogen atom from either manganese, cobalt, molybdenum, or iridium to an activated olefin either in or prior to the rate-determining step and can be accounted for in terms of forming a strong C–H or C–D bond from a weaker M–H or M–D bond in the transition state.

Conclusions

The activation of arene C–H bonds by $[(C_5Me_5)Rh(PMe_3)]$ has been definitely found to proceed through an intermediate complex, described by the formulation $[(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6H_6)]$ on the basis of the difference in isotope effects observed during the activation of 1,3,5-$C_6H_3D_3$ vs. a 1:1 mixture of C_6H_6/C_6D_6. The reductive elimination of benzene is found to have a substantial inverse isotope effect and can be accommodated by a transition state for reductive elimination in which substantial C–H bonding is present.

Experimental Section

General. Most of the halide-containing rhodium(III) complexes described here are air-stable and can be handled in air once the reaction mixtures have been properly quenched. All of the rhodium hydride complexes reported are extremely sensitive toward oxygen and halogenated solvents, and operations involving these compounds were performed under a nitrogen atmosphere, either on a high vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corporation dri-lab which was free of halogenated solvents. Rhodium trichloride (42.9%) was obtained as a generous loan from Johnson Matthey, Inc. Pentamethylcyclopentadiene, $Li^+[HBEt_3]^-$ (Super-hydride), $Li^+[DBEt_3]^-$, and $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ were obtained from Aldrich Chemical Co. Pentamethylcyclopentadiene was vacuum distilled from CaH_2 (25 °C, 10^{-3} mmHg) prior to use. Magnesium turnings (99.98+%) were obtained from Reade Manufacturing Corp. 1,3,5-$C_6H_3D_3$ was obtained from MSD Isotopes. Tetrahydrofuran, C_6D_6 (100.0% D), and THF-d_8 were distilled from dark purple solutions of sodium benzophenone ketyl under vacuum. Aliphatic and aromatic hydrocarbon solvents were vacuum distilled from dark purple solutions of potassium benzophenone ketyl containing tetraglyme. Bromoform was purified by fractional crystallization and was freeze-pump-thaw-degassed (3 cycles) before use. All alkyllithium and Grignard reagents were standardized immediately prior to use with 1.06 M *tert*-butyl alcohol/1,10-phenanthroline indicator.

High-field ^1H NMR (400.13 MHz) spectra were recorded on a Bruker WH-400 NMR spectrometer. Temperature for the NMR experiments was regulated by a Bruker BVT-1000 temperature control unit (±0.1 °C). Absolute calibration at ambient temperature (±0.05 °C) was determined by passing dry air through the probe while monitoring the equivalence of both the inlet and outlet stream temperatures with calibrated thermometers. Relative calibration was determined by plotting the separation of the two resonances of standard methanol or ethylene glycol samples vs. the Pt sensor voltage of the BVT-1000 unit.

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(25) For examples of chelating rhodium and iridium alkylidene complexes see: Crocker, C.; Empsall, H. D.; Ernington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217–1224. Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708–6710. Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 498–499.

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The complexes $(C_5Me_5)Rh(PMe_3)Cl_2$, $(C_5Me_5)Rh(PMe_3)H_2$, and $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)Br$ were prepared as previously described.[9]

Equilibration of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$. Details of this reaction were reported earlier.[9c] In summary, a THF-d_8 solution of $(C_5Me_5)Rh(PMe_3)(C_6D_5)Br$ was treated with 1 equiv of $AgPF_6$ to produce the cation $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF\text{-}d_8)]^+$, which was then treated with 1 equiv of $Li^+[HB(sec\text{-}Bu)_3]^-$ in THF at -78 °C. A ^1H NMR spectrum recorded at -40 °C showed only $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ (hydride at δ -13.858, dd), which was observed to equilibrate with isomers containing hydrogen in the ortho (δ 7.279), meta (δ 6.700), and para (δ 6.673) positions upon warming to -14.5 °C. The final area ratio of the hydride:ortho:meta:para peaks was 2.7:2:2:1 at 25 °C.

Competition for C_6D_6 vs. C_6H_6. $(C_5Me_5)Rh(PMe_3)H_2$ (~5 mg, 0.016 mmol) was prepared as previously described[9c] and dissolved in 0.6 mL of 1:1 (v/v) C_6H_6/C_6D_6 (49.8 mol % C_6H_6) in an NMR tube fitted with a rubber septum. The solution was irradiated at 10 °C for ~5 min and then quenched by addition of 10 μL of CCl_4 with a syringe. The solution was transferred to a flask and the solvent removed (25 °C, 10^{-4} mmHg) on a vacuum line. The orange residue was then chromatographed on a thick-layer SiO_2 plate with CH_2Cl_2 was eluent. The isolated product was mass analyzed by its direct inlet mass spectrum (20 eV). The isotopic ratio was determined by taking the average of the ratios of the three large peaks of the parent ion due to $^{35/37}Cl$ and ^{13}C natural abundances in a spectrum that was the sum of 50 individual mass scans. Peak ratios (and their intensities) used for the calculation were observed at 426/431 (100.00/92.20), 427/432 (23.40/21.99), and 428/433 (32.62/33.33).

Competition for C-H vs. C-D in $1,3,5\text{-}C_6H_3D_3$. $(C_5Me_5)Rh(PMe_3)Cl_2$ (13 mg, 0.034 mmol) was converted to the dihydride by using the established procedure. The dihydride was transferred to an NMR tube attached to a ground-glass joint with hexane solvent which was then removed under vacuum (25 °C, 10^{-4} mmHg). $1,3,5\text{-}C_6H_3D_3$ (35 μL) and 200 μL of cyclopentane were then distilled into the tube (25 °C, 10^{-4} mmHg), and the tube was capped with a rubber septum in the dry box. The solution was cooled to -40 ± 5 °C and irradiated for 20 min. A freeze-pump-thaw-degassed (3×) solution of $CHBr_3$ (20 μL) in THF (~10% (v/v)) was then carefully added at -55 °C, ensuring that the added solution had cooled before being allowed to contact the metal-containing solution. The solvent was then removed on the vacuum line and the product purified by chromatography on SiO_2 with CH_2Cl_2 as eluent. The ^1H NMR of the product was recorded at -55 °C, at which temperature rotation about the Rh-C bond is frozen out.[9d] A 1.40:1 ratio of $(C_5Me_5)Rh(PMe_3)(2,4,6\text{-}C_6H_2D_3)Br$ to $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3D_2)Br$ was revealed by integration of the aromatic region of the spectrum, which showed peaks at δ 6.863 and 6.782 for the former compound (average area = 16.6 units) and at δ 7.944, 7.117, and 6.808 for the latter compound (average area = 23.2 units).

Kinetics of the Elimination of *m*-Xylene from $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)H$ and Its Deuteride. In each experiment, 10 mg (0.020 mmol) of the bromide $(C_5Me_5)Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)Br$ was treated with 2.5 equiv of either Super-Hydride or Super-Deuteride and allowed to convert to the hydride or deuteride as described earlier.[9c] Each sample was purified by flash chromatography on SiO_2 with 5:1 hexane:THF. The samples were dissolved in C_6D_6 and sealed under vacuum in NMR tubes. The tubes were heated to 51.2 °C in the probe of the NMR spectrometer, and the rate of disappearance of the starting material was determined quantitatively by integration of the xylyl resonance at δ 2.306 vs. the appearance of the *m*-xylene resonance at δ 2.137. Logarithmic plots of the data are shown in Figure 1.

Attempted Preparation of $(C_5Me_5)Rh(PMe_3)(CH_3)D$. $(C_5Me_5)Rh(PMe_3)(CH_3)Cl$ (15.1 mg) and 10.7 mg of $AgPF_6$ were dissolved in 0.4 mL of a 3:1 mixture of THF-d_8/C_6D_6, and the suspension was filtered through a glass wool plug into a septum capped NMR tube, $Li^+[DBEt_3]^-$ (45 μL) in THF was added to the cooled sample via syringe at -78 °C, and the sample was quickly lowered into the precooled (-40 °C) probe of the NMR spectrometer. An NMR spectrum was recorded immediately, showing a hydride resonance at -14.5 (dd, J = 48, 30 Hz) and a broad multiplet at δ -0.13 in a 1:3 ratio, with a combined area corresponding to ~1 H relative to coordinated PMe_3. This observation corresponds to a statistical scrambling of the three methyl hydrogens over both the methyl and metal hydride locations in the complex $(C_5Me_5)Rh(PMe_3)(CH_3)H\text{-}d_1$, although mixtures of d_0 and d_2 species would give similar results. Some of the dihydride $(C_5Me_5)Rh(PMe_3)H_2$ (43%) was also observed at δ -14.1 (dd, J = 42, 30 Hz).

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Registry No. 1, 84624-03-3; **3**, 81971-46-2; **3**-d_5, 88704-00-1; $(C_5Me_5)Rh(PMe_3)(C_6D_5)Br$, 90624-49-0; $[(C_5Me_5)Rh(PMe_3)(C_6D_5)(THF\text{-}d_8)]^+$, 102808-73-1; $[(C_5Me_5)Rh(PMe_3)(CH_3)(THF\text{-}d_8)]^+$, 84623-99-4; C_6H_6, 71-43-2; D_2, 7782-39-0.