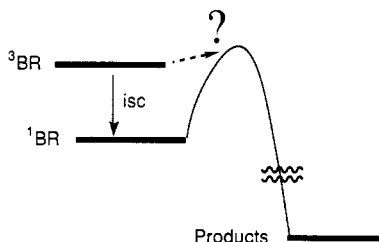


parallels in Table IV suggest such a possibility, and several CIDNP observations have been so interpreted.⁷¹ Why would isc occur during rather than prior to product formation? If isc is not rapid unless the radical centers overlap, movement of the biradical termini along a reaction coordinate would induce isc and also enhance S-T splitting, such that the small activation energies for singlet biradical reaction are transformed into activation entropies for triplet biradical motion. Any additives that affect either isc or product formation then would affect both, as Scaiano has observed.⁶ The question of the separation in time of isc and product formation certainly deserves more attention.



(71) (a) Doubleday, C. *Chem. Phys. Lett.* 1981, 79, 375. (b) Kaptein, R.; DeKanter, F. J. J.; Rist, G. H. *J. Chem. Soc., Chem. Commun.* 1981, 499.

Summary

From a mechanistic standpoint, triplet ketone δ -hydrogen abstraction provides a variety of riches in terms of conformational effects on both triplets and 1,5-biradicals. Rate constants for triplet reaction vary over several orders of magnitude independent of intrinsic C-H reactivity. The probability of the biradicals cyclizing also varies tremendously, depending on environment as well as on any molecular restrictions to free rotation. From a synthetic standpoint, the reaction offers untapped potential but will have to be used with very careful planning because of the relatively large number of competitive reactions that 1,5-biradicals can undergo. Fortunately, irradiation in immobilizing media can minimize some competing triplet reactions.

I thank my various students, especially Michael Meador and Boli Zhou, whose Ph.D. theses describe all of our work on o-alkoxyphenyl and α -o-tolyl ketones, and Brij Giri, who performed the original work on o-tert-butyl ketones; Prof. Ken Houk for a preprint of his unpublished work and stimulating discussions; and Dr. Tito Scaiano at the National Research Council in Ottawa for his enthusiastic cooperation in the measurement of flash kinetics data.

Registry No. H, 1333-74-0.

Comparative Reactivities of Hydrocarbon C-H Bonds with a Transition-Metal Complex

WILLIAM D. JONES* and FRANK J. FEHER†

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received August 15, 1988 (Revised Manuscript Received November 12, 1988)

Alkanes are among the most abundant and unreactive of all organic compounds. Industrial use of these resources often relies upon free-radical activation of carbon-hydrogen bonds, often at high temperatures, thereby limiting the selectivities that can be achieved in any functionalization reaction.¹ Consequently, the selective activation of C-H bonds by homogeneous transition-metal compounds has been a topic that has been of great interest to the organometallic community for many years.²

Bill Jones was born (1953) and raised in suburban Philadelphia. He received his B.S. degree from MIT in 1975, working with Prof. M. S. Wrighton, and continued his graduate studies of vanadium and molybdenum hydrides with Prof. R. G. Bergman at California Institute of Technology and at the University of California at Berkeley, receiving his Ph.D. from the former in 1979. He spent a year at the University of Wisconsin at Madison as an NSF Postdoctoral Fellow studying η^5 - η^1 rearrangements of the cyclopentadienyl ligand with Prof. C. P. Casey, and he joined the faculty at the University of Rochester in 1980, where he began a research program on C-H activation. He is currently a Professor of Chemistry at Rochester and has received Alfred P. Sloan, Camille and Henry Dreyfus, John S. Guggenheim, Fulbright Commission, and Exxon Education Foundation Fellowships.

Frank J. Feher was born in 1958 in Waynesboro, PA. He graduated with his B.S. degree from RPI in 1980 and was the first graduate student to join Jones's group at the University of Rochester, receiving his Ph.D. in 1984 after completing all of the studies in this paper. He undertook one year of postdoctoral study with M. Green at the University of Bristol before taking his current position as an Assistant Professor of Chemistry at the University of California, Irvine, where he now holds a Presidential Young Investigator Award.

Initial observations of oxidative addition to arene C-H bonds in 1965 provided the impetus to look for complexes that would activate the weaker sp^3 -hybridized alkane C-H bonds.³ However, this goal was not achieved until nearly two decades later, encompassing an intermediate period in which much confusion over the thermodynamic feasibility of the reaction took place.⁴ In this Account, mechanistic studies with a series of homogeneous rhodium organometallic complexes are summarized that provide for the first time a comparative evaluation of the relative equilibrium constants and rates of reaction for both alkane and arene hydrocarbon activation (eq 1, 2).

Since Chatt observed the first clear example of simple oxidative addition of the C-H bond of naphthalene to

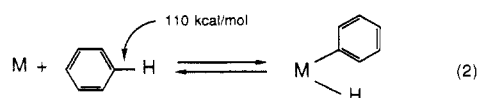
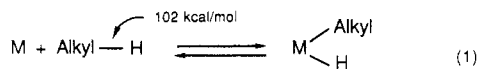
* Current address: Department of Chemistry, University of California, Irvine, CA 92717.

(1) Parshall, G. W. *Homogeneous Catalysis*; John Wiley and Sons: New York, 1980.

(2) For reviews of early reports, see: Parshall, G. W. *CHEMTECH* 1974, 4, 445-447. Shilov, A. E.; Steinman, A. A. *Coord. Chem. Rev.* 1977, 24, 97-143. Parshall, G. W. *Acc. Chem. Res.* 1975, 8, 113-117. Webster, D. E. *Adv. Organomet. Chem.* 1977, 15, 147-188.

(3) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* 1965, 843-855.

(4) Halpern, J. *Inorg. Chim. Acta* 1985, 100, 41-48. Crabtree, R. H. *Chem. Rev.* 1985, 85, 245-269. Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishing Company: Boston, 1984.

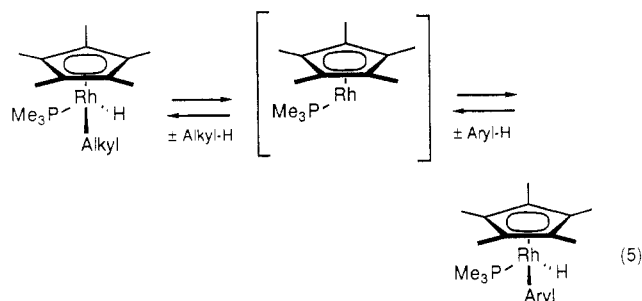
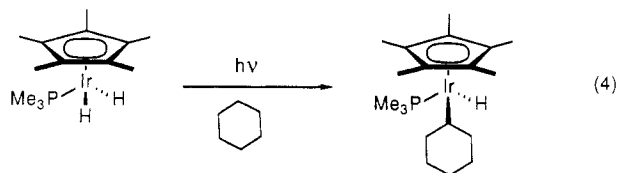
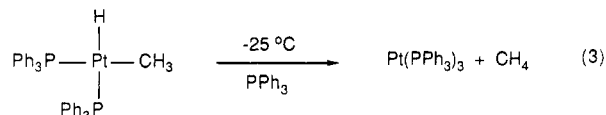


a ruthenium metal center,³ hydrocarbon activation has become the subject of many transition-metal studies. It was rapidly established that many metals activate the strong arene C–H bond (110 kcal/mol) but not the weaker alkane C–H bond (96–102 kcal/mol).⁵ At the same time, examples of *intramolecular* activation of both sp^2 - and sp^3 -hybridized H–C bonds in a variety of ligands appeared.⁶ In examining the dozens of examples of arene oxidative addition, H/D exchange, and intramolecular cyclometalation, one finds that the reactions are scattered over many different transition metals with different ligand systems. The conclusions about thermodynamics that can be drawn from comparisons between these different systems are less than rigorous, since many variables are being changed at the same time.

Nevertheless, two common working hypotheses that surfaced were (1) that arene activation enjoyed a kinetic advantage due to the prior π -coordination of the arene ring and (2) that the equilibrium for alkane oxidative addition was thermodynamically unfavorable. Furthermore, when the complex $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{H}$ was spectroscopically characterized as undergoing irreversible reductive elimination of alkane at -25°C , it was generally assumed that all metal alkyl hydride complexes would be unstable with regard to alkane reductive elimination (eq 3).⁷ This somewhat overstated conclusion stood until an example to the contrary came about, such as Bergman's observation of simple oxidative addition to cyclohexane (eq 4).⁸ The goal of our initial studies begun at Rochester in 1980 was to quantitatively establish the relative thermodynamic and kinetic preferences for both arene and alkane C–H bonds by a *single* metal complex (eq 5). By employment of the same metal–ligand system throughout, extraneous factors in any comparative thermodynamic analysis have been minimized.^{9–14}

Thermodynamics and Kinetics of Intermolecular Arene and Alkane Activation

The complexes chosen for study, $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{R})\text{H}$, possess features commonly found in molecules that were known to activate C–H bonds prior to this work. The choice was based upon the known H/D exchange capabilities of $\text{CpRh}(\text{C}_2\text{H}_4)_2$.¹⁵ The



16-electron intermediate contained a low-valent metal (Rh(I)) and good donor ligands, such as C_5Me_5 and PMe_3 . These ligands also enhance the solubility of the complex in the hydrocarbon that is to be activated. In the first part of the study, preparation of the complexes $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{R})\text{H}$ in which R = aryl or alkyl was undertaken in order to determine the overall stabilities of the compounds involved. It was found that the known compound $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)\text{Cl}_2$ reacts with Grignard or lithium reagents to produce the corresponding derivatives, $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{R})\text{Cl}$, in high yield. These new molecules with R = aryl were found to undergo a dynamic process involving a hindered rotation about the metal–carbon bond. Variation of the aryl, phosphine, halide, and C_5R_5 groups led to the conclusion that electronic effects of the aryl substituent were unimportant and that steric effects (not Rh–aryl π -bonding) dominate the hindered rotation. Over 45 new compounds of this general formula were prepared and characterized by spectroscopic and X-ray techniques.¹⁰

Reduction of the halide derivatives with borohydride (HBR_3^-) or aluminum hydride (H_2AlR_2^-) reagents produced the desired products, $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{R})\text{H}$, for the case in which R = aryl. For the phenyl hydride complex, a reversible reductive elimination of benzene was found to occur at a convenient rate upon heating to $\sim 60^\circ\text{C}$ in C_6D_6 solvent, producing the d_6 product $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$. The reaction followed first-order kinetics over a 46-deg temperature range. An Eyring plot of the first-order rate constants gave the activation parameters for arene loss: $\Delta H^\ddagger = 30.5$ (8) kcal/mol; $\Delta S^\ddagger = 14.9$ (2.5) e.u. The positive value for the entropy of activation is consistent with the formation of an intact, dissociating benzene molecule in the transition state, as will be discussed more fully later. The rate of arene loss is identical in 25:75 benzene/THF, indicating that solvation effects are of little importance in the transition state.^{9,12}

In contrast, the corresponding alkyl complexes such as $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_3)\text{H}$ could only be prepared and examined at low temperature ($< -20^\circ\text{C}$) by first

(5) Castelhan, A. L.; Griller, D. *J. Am. Chem. Soc.* 1982, 104, 3655–3659.

(6) Parshall, G. W. *Acc. Chem. Res.* 1970, 3, 139–144. Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* 1976, 18, 327–352. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 73–86.

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

(8) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1982, 104, 352–354.

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

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

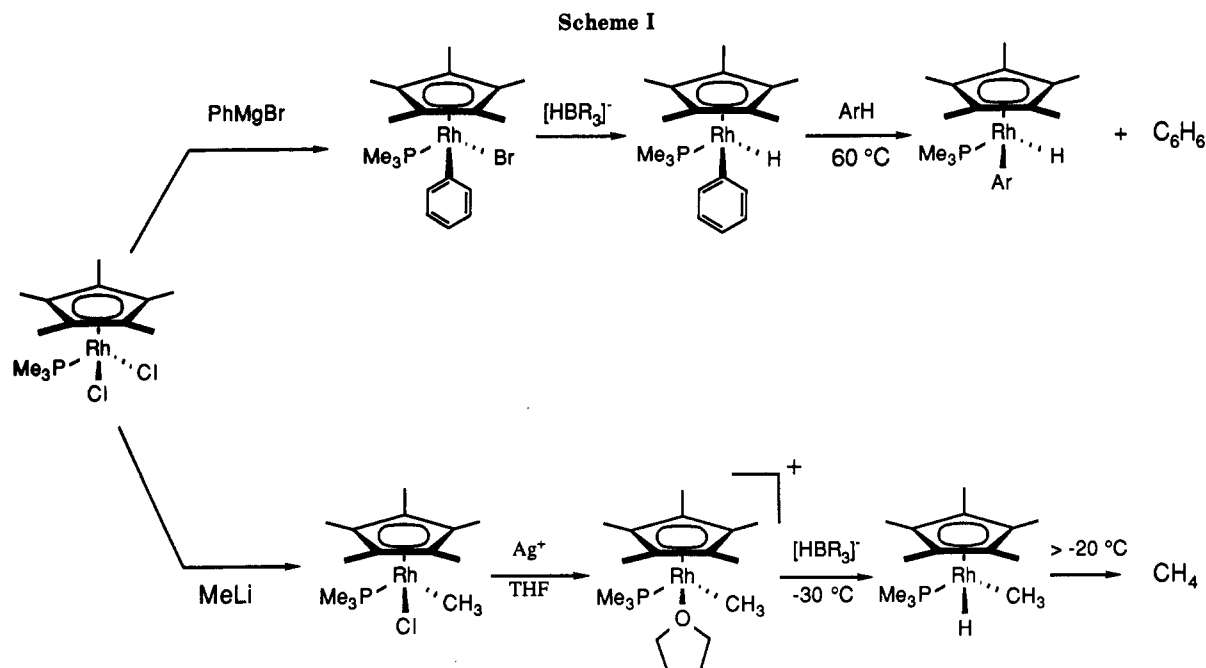
(11) Jones, W. D.; Feher, F. J. *Organometallics* 1983, 2, 562–563.

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

(13) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1985, 107, 620–631.

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

(15) Seiwel, L. P. *J. Am. Chem. Soc.* 1974, 96, 7134–7135.



removing the chloride ligand with silver ion in coordinating tetrahydrofuran solvent and then adding the reducing agent. All alkyl derivatives studied displayed first-order kinetics for irreversible reductive elimination of alkane at or about $-20\text{ }^{\circ}\text{C}$, indicating a much higher lability than for the aryl complexes which did not undergo reductive elimination until about $60\text{ }^{\circ}\text{C}$ (Scheme I). Attempts to measure the temperature dependence of alkane elimination were unsuccessful, as the rates were found to increase dramatically upon warming by only $5\text{ }^{\circ}\text{C}$.^{11,12}

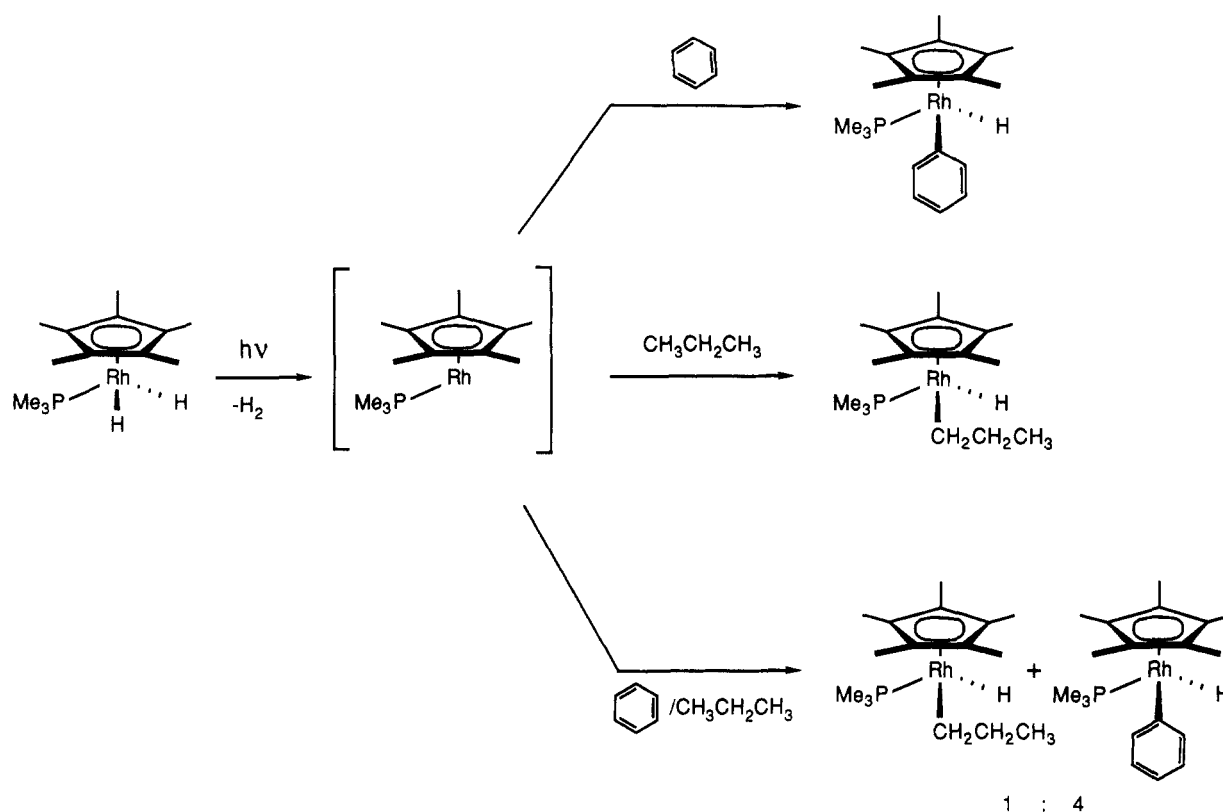
The intermediate responsible for C-H activation is believed to be the 16-electron transient species $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)]$, although this intermediate has not been directly observed yet. The same species can (apparently) be generated at low temperatures by near-UV irradiation of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)\text{H}_2$. Irradiation of this dihydride in benzene solvent results in the efficient formation of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_5)\text{H}$. The dihydride also provided a means for examining alkane activation. As the corresponding alkyl hydride complexes are unstable above $-20\text{ }^{\circ}\text{C}$, the irradiation of the dihydride in liquid propane was carried out at $-55\text{ }^{\circ}\text{C}$, allowing evaporation of the solvent at a temperature at which the product could be isolated ($-40\text{ }^{\circ}\text{C}$). The photolysis produces the *n*-propyl hydride complex $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)\text{H}$, affording one of the first examples of alkane oxidative addition to a transition-metal center. This system was the first to permit examination of both alkane and arene C-H bond activation and elimination by the exact same metal complex and has provided a wealth of kinetic and thermodynamic information. In order to compare the kinetic preference for arene vs alkane C-H bonds, the dihydride was irradiated in a mixed solvent system of propane/benzene at low temperature. Only a slight kinetic preference for benzene (4:1) over propane was observed, despite (what will emerge as) an overwhelming thermodynamic preference for benzene oxidative addition (Scheme II).

These experiments allow the generation of a picture of the thermodynamics of arene and alkane activation

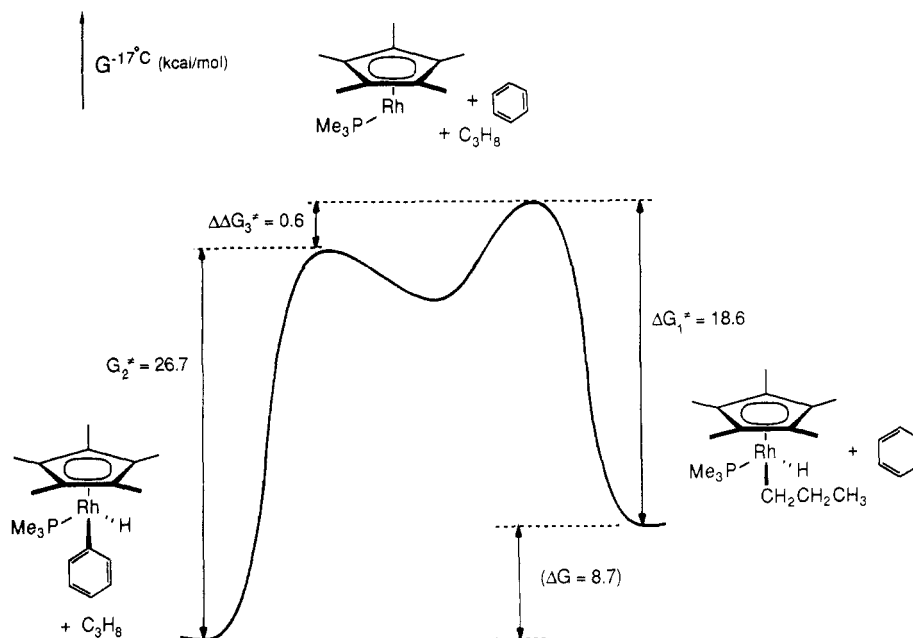
by $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)]$. From the rate at which $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)\text{H}$ loses propane at $-17\text{ }^{\circ}\text{C}$, the activation barrier (ΔG_1^\ddagger) can be calculated. Similarly, the rate of loss of benzene from the phenyl hydride complex at $-17\text{ }^{\circ}\text{C}$ can be calculated from the measured activation parameters for benzene loss (ΔG_2^\ddagger). From the benzene/propane selectivity experiment mentioned above, the difference in free energy of activation of benzene vs propane of 0.6 kcal/mol is calculated ($\Delta\Delta G_3^\ddagger$). As shown in Scheme III, these quantities allow the relation of the three states of the chemical system such that the equilibrium free energy difference between alkane and arene activation can be calculated. The kinetics of the system are used here to determine a thermodynamic quantity (K_{eq}) that could not be measured directly. As can be seen, benzene activation is preferred over propane activation at this temperature ($-17\text{ }^{\circ}\text{C}$) by $\sim 8.7\text{ kcal/mol}$. This value corresponds to an equilibrium constant of 2.4×10^7 , or $\sim 0.000004\%$ propane activation under equilibrium conditions in 1:1 benzene/propane! Even a 1 mM solution of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{Ph})\text{H}$ in propane solvent would contain only 2.8% $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)\text{H}$ at equilibrium at $-17\text{ }^{\circ}\text{C}$. With the stronger temperature dependence of ΔG_1^\ddagger vs ΔG_2^\ddagger , even less propyl hydride complex would be anticipated at $25\text{ }^{\circ}\text{C}$.

In light of the above results, perhaps it is not so surprising that the observation of alkane activation has been so elusive. Under typical laboratory conditions (i.e., room temperature), both benzene and propane would have been activated with comparable ease, but within seconds the alkyl hydride complex would have all but disappeared. Indeed, the earlier observation by Halpern of methane elimination at $-25\text{ }^{\circ}\text{C}$ indicated that only below this temperature is alkane activation feasible, although low temperature may not be a requirement for alkane activation with all metal complexes. With the above experiments, an answer to the question of the direction and magnitude of the equilibria in eq 1 and 2 had been answered. With the question of what, the thermodynamic preferences are

Scheme II



Scheme III



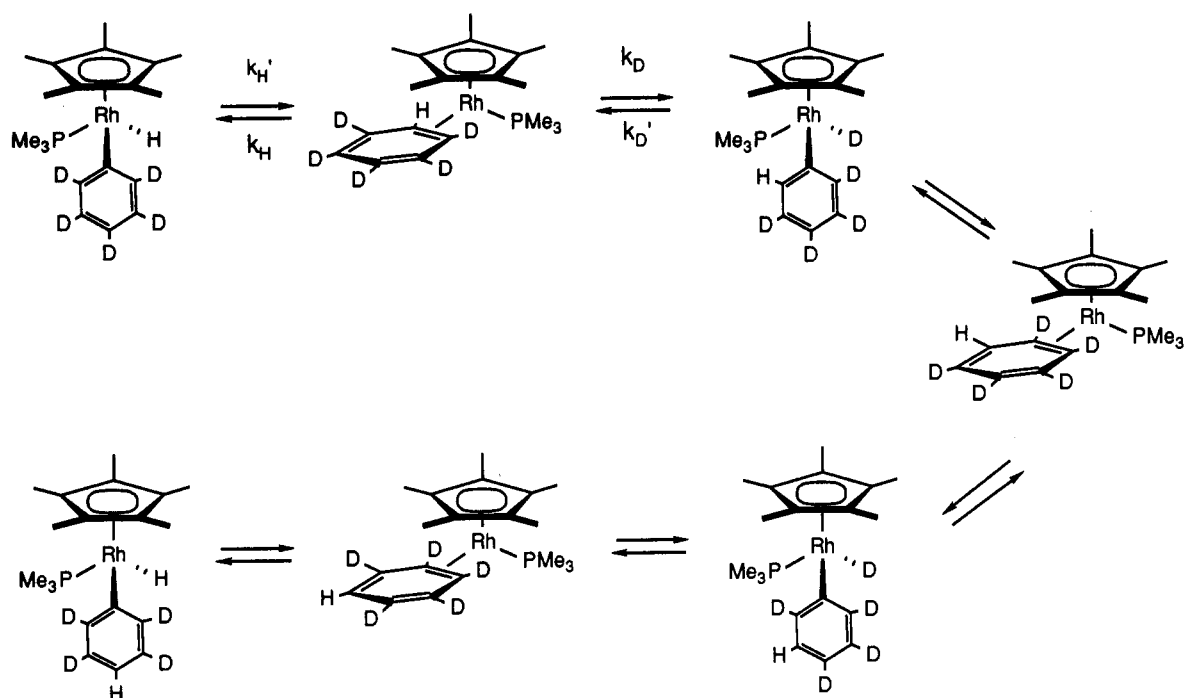
answered; one can now ask why this thermodynamic situation arises.

Intermediates in Arene Activation: η^2 -Arene Complexes

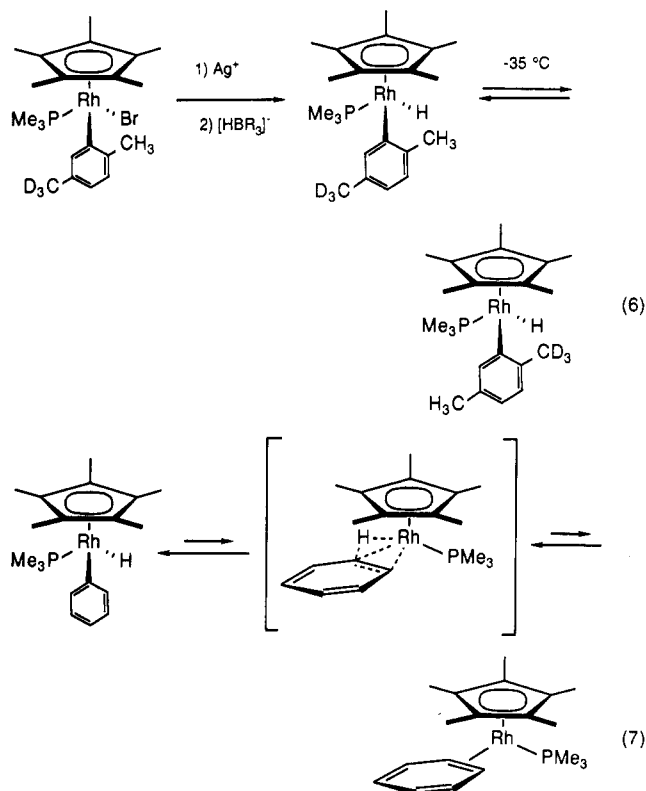
The understanding of the kinetic preference for arene oxidative addition comes from experimental examination of the microscopic reverse process, reductive elimination. It was discovered that the aryl hydride complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ were in rapid equilibrium with the less stable η^2 -arene complexes $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-arene})$. The rearrangement was first observed upon the reduction of $(C_5Me_5)Rh(PMe_3)(p-$

$C_6H_4Me)Br$ with $[HB(s-Bu)_3]^-$. A 2:1 ratio of the *m*-tolyl hydride-*p*-tolyl hydride complexes were obtained. Somehow, M-C and C-H bonds had been exchanged during the course of the preparation. This equilibration process could be studied directly by preparation of the *p*-tolyl hydride complex at low temperature ($-40^\circ C$). Upon warming of the sample to $-10^\circ C$, the growth of the *m*-tolyl hydride species could be observed at the expense of the *p*-tolyl hydride complex over a period of 10–20 min. The equilibration was also studied by the synthesis of a d_3 -labeled *p*-xylyl hydride complex (eq 6) and monitoring of the growth of the hydrogen label in the d_3 site at $-35^\circ C$. At higher temperatures (12–33

Scheme IV



$^{\circ}\text{C}$), the degenerate rearrangement of the d_0 -*p*-xylyl hydride complex was monitored by spin saturation transfer between the inequivalent xylyl methyl groups. From these data over a 68-deg temperature range, activation parameters for the rearrangement were calculated as follows: $\Delta H^{\ddagger} = 16.3$ (2) kcal/mol; $\Delta S^{\ddagger} = -6.3$ (8) eu. The slightly negative entropy of activation suggests an ordered transition state for the rearrangement, as indicated in eq 7.



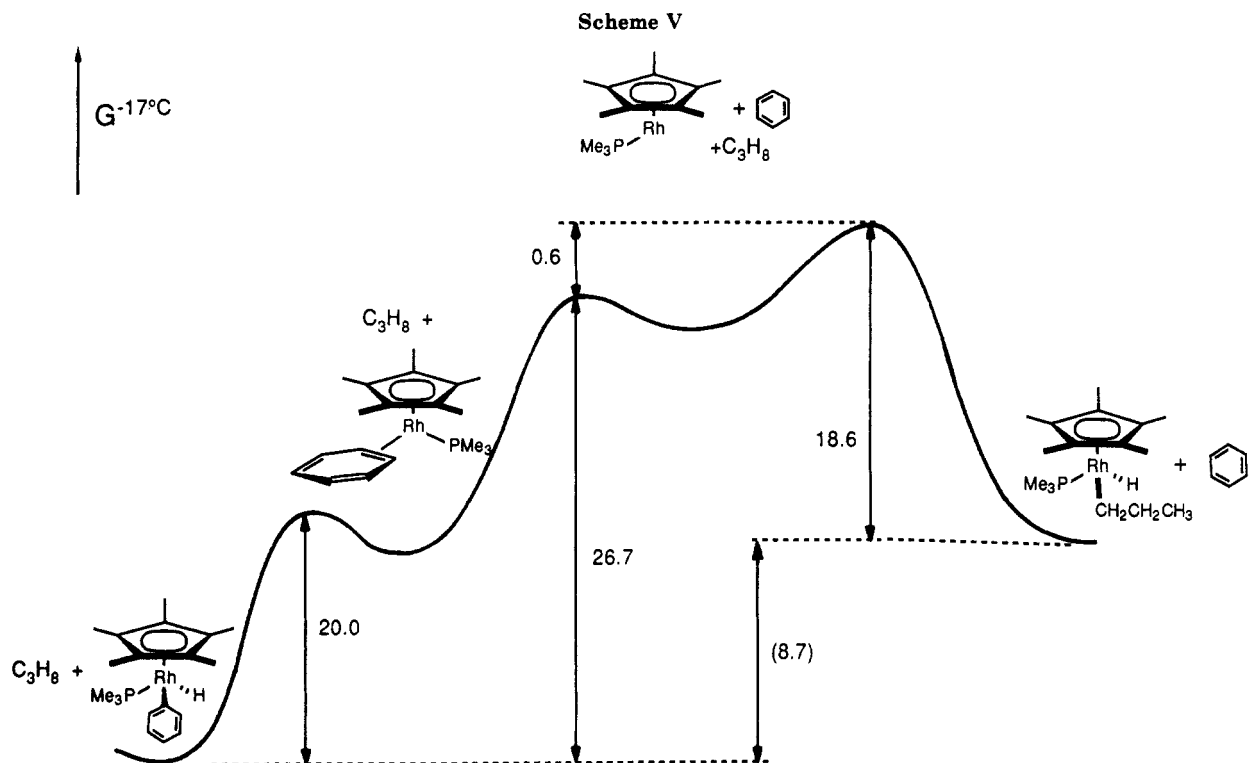
A more informative study about the nature of the rearrangement comes from observations of the isomerization of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{H}$ at -10 $^{\circ}\text{C}$. The

^1H NMR spectrum of this complex provides evidence for a stepwise [1,2] migration of the proton from the metal to the ortho position of the phenyl ring, followed by sequential migration to the meta and para positions. This observation rules out any mechanism in which the aromatic hydrogens become equivalent and is consistent with the intermediacy of $\eta^2\text{-C}_6\text{D}_5\text{H}$ intermediates as shown in Scheme IV.¹²

While other metal complexes having η^2 -arene ligands are known in the literature,¹⁶ direct evidence for η^2 coordination in the present system comes from the generation of the unsaturated intermediate by photolysis of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)\text{H}_2$ in the presence of *p*-di-*tert*-butylbenzene at low temperature. With this arene the η^2 complex can be directly observed by ^1H NMR spectroscopy at -20 $^{\circ}\text{C}$, as activation of the aromatic C-H bond would place the bulky ortho substituent adjacent to the metal center. The two pairs of aromatic hydrogen nuclei appear as a singlet (δ 6.355) and a doublet of doublets (δ 3.879), the latter splitting arising due to rhodium and phosphorus coupling. At -10 $^{\circ}\text{C}$, arene exchange with free *p*-di-*tert*-butylbenzene can be observed by spin saturation transfer from the free arene to the coordinated ligand. The complex is unstable above 0 $^{\circ}\text{C}$, giving no tractable decomposition products.

The above studies differentiate between two distinct steps in the elimination of arene from the metal center. An initial "reductive rearrangement" (i.e., C-H bond formation without arene dissociation) is followed by dissociation of the arene from the rhodium metal center, as shown in the revised free-energy diagram in Scheme V. While all of the experiments mentioned involve reductive elimination, they also provide information about the oxidative addition of arene C-H bonds to a

(16) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, 105, 305-306. Brauer, D. J.; Krüger, C. *Inorg. Chem.* 1977, 16, 884-891. Jones, K. J. *Organomet. Chem.* 1974, 78, 273-279. Muettterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* 1982, 82, 499-525. Heijden, H.; Orpen, G. A.; Pasma, P. *J. Chem. Soc., Chem. Commun.* 1985, 1576-1578. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* 1987, 109, 1883-1885.



metal. By microscopic reversibility, the lowest energy pathway for reductive elimination must also be the lowest energy pathway for oxidative addition. Since these studies show that the highest barrier in the two-step reductive-elimination reaction involves dissociation of arene from the η^2 -arene complex, the rate-determining step in oxidative addition must also involve coordination to the arene π -system. A rapid "oxidative rearrangement" (i.e., C-H bond oxidative addition from the η^2 -arene complex) then occurs once the η^2 -arene complex is formed. This conclusion nicely accounts for many observations in the literature regarding arene activation. These results also explain why the strong aryl-H bond (110 kcal/mol) can be broken competitively with the weaker alkane C-H bond (~ 100 kcal/mol): the arene C-H bond is not involved in the rate-determining step for arene activation! The intermediacy of η^2 -arene complexes also explains the literature-based notion that activation of electron-deficient arenes is kinetically preferred over activation of electron-rich arenes. The more electron deficient π -systems should interact more strongly (as a π -acceptor) with the low-valent coordinatively unsaturated metal intermediate.

In all cases, the elimination of the arene C-H bond from $(C_5Me_5)Rh(PMe_3)(aryl)H$ occurs at $-10^\circ C$, about the same temperature as that for reductive elimination in the alkyl hydride complexes. The greater macroscopic stability of the aryl hydride complexes results from the coordination of the arene in an η^2 fashion in the intermediate formed following the elimination. Additional energy must then be supplied in order to break the η^2 -arene-metal interaction. At room temperature, the aryl hydride complexes are undergoing this reversible intramolecular elimination/readdition about once per second. Their macroscopic stability therefore masks the microscopic lability of the coordination isomers of the arene ligand. X-ray examination of the 3,5-xylyl hydride complex shows only normal

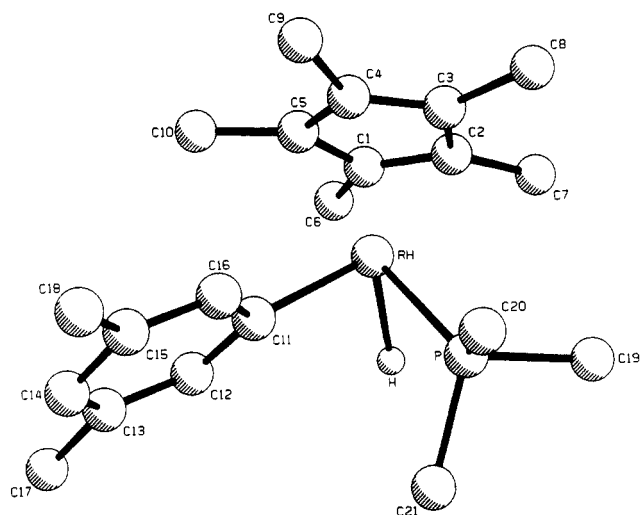


Figure 1. PLUTO diagram of $(C_5Me_5)Rh(PMe_3)(3,5-C_6H_3Me_2)H$.

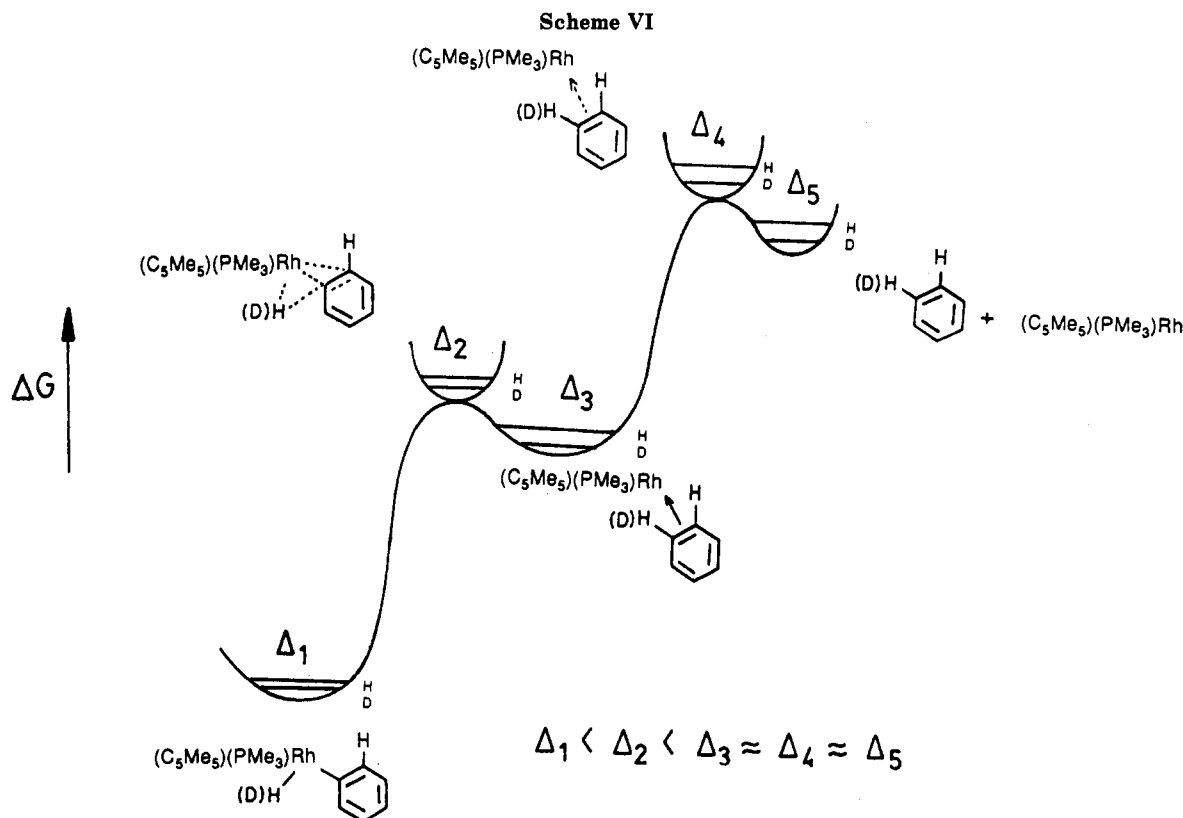
aryl coordination, with no evidence of an incipient η^2 interaction¹⁷ (Figure 1).

While the above picture is aesthetically pleasing in terms of answering *why* arene activation is preferred, we must first determine if the established η^2 -arene complexes lie along the pathway for arene oxidative addition or off to the side, in an unrelated path for aryl group positional isomerization. To do this, isotope effects have been used to examine the nature of the transition states for arene reductive elimination and dissociation.

Isotope Effects in C-H Bond Activation

The kinetic isotope effect studies involve measurement of kinetic isotope effects for both the forward

(17) $(C_5Me_5)Rh(PMe_3)(3,5-C_6H_3Me_2)H$ crystallizes in monoclinic space group $C2/c$ with $Z = 8$, $a = 29.36$ (2) Å, $b = 9.091$ (4) Å, $c = 16.98$ (1) Å, and $\beta = 107.063$ (1)°. The hydride ligand was located in the final difference Fourier map, but was not refined.



(coordination/oxidative addition) and reverse (reductive elimination/dissociation) reactions. Since the activation of benzene C-H bonds by $[(C_5Me_5)Rh(PMe_3)]$ is proposed to occur 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.¹⁴ The diagram proposed in Scheme VI is useful for understanding the magnitude of the observed isotope effects in this system. In this scheme, the Δ_i quantities refer to the zero-point energy differences between the monodeutero and perproto arene complexes, with the C-D bond undergoing oxidative addition to the metal as the reaction proceeds. The residual zero-point energy differences in the saddle-like region of the transition states are also indicated for these isotopically substituted molecules. The highest barrier in the C-H bond activation process in the reaction of $[(C_5Me_5)Rh(PMe_3)]$ with benzene does not involve cleavage of the C-H bond and therefore would be expected to display only 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.¹⁸

The first pair of experiments shows that there must be an intermediate lying along the forward pathway for oxidative addition. Irradiation of a solution of $(C_5Me_5)Rh(PMe_3)H_2$ in a 1:1 mixture of C_6H_6/C_6D_6 produces a 1.05:1 ratio of $(C_5Me_5)Rh(PMe_3)(Ph)H-d_0$ and $-d_6$ products (eq 8). Benzene is not labile in the d_6 and d_0 products 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 $[(C_5Me_5)Rh(PMe_3)]$ occurs.

The next step in the activation process according to Scheme VI, however, does involve cleavage of the C-H (or C-D) bond. Irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ in 1,3,5-trideuterobenzene can produce only one possible η^2 -arene complex, as shown in eq 9. The experiment is performed at low temperature, conditions that ensure that once the oxidative addition has occurred, no isomerization of the kinetically formed product is possible. The ratio k_H/k_D for this reaction therefore reflects only the isotope effect involved in the cleavage of the C-H bond in the second step of the reaction, 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 ($k_H/k_D = 1.4$), as anticipated for a nonlinear transition state.

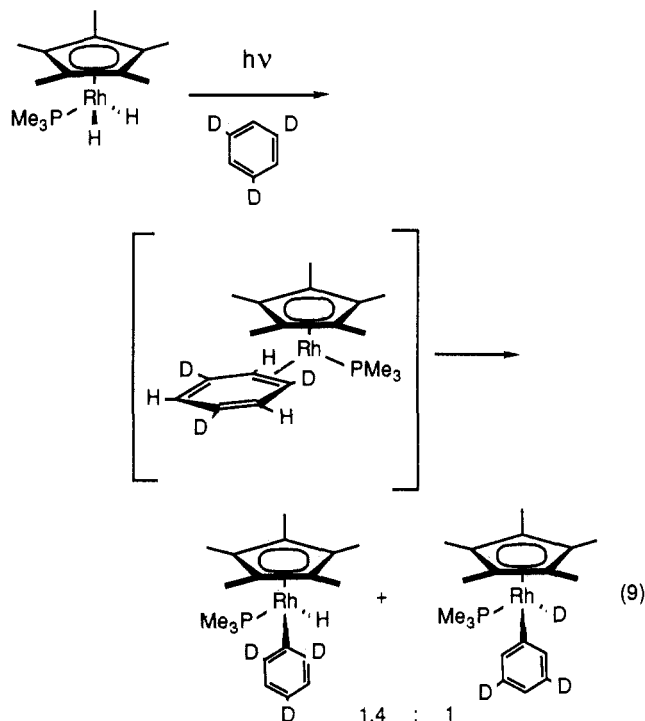
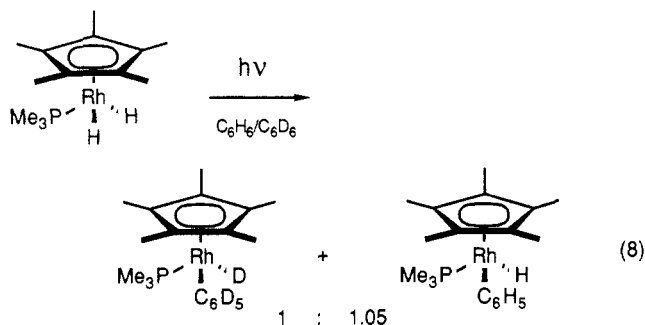
It is important to note that the above two experiments (1) both involve activation of a deuterium-substituted benzene molecule and (2) have different values for k_H/k_D . Since both experiments involve bimolecular activation of the benzene C-H bond ($[(C_5Me_5)Rh(PMe_3)] + \text{benzene}$) and since the kinetic isotope effects are different, an intermediate must be involved along the reaction coordinate. *These observations prove that a direct insertion of $[(C_5Me_5)Rh(PMe_3)]$ into the C-H bond of benzene is not occurring.* Furthermore, the small isotope effect observed with C_6H_6/C_6D_6 is inconsistent with the formulation of the intermediate as a σ complex of the arene C-H bond, as has been postulated by Bergman for alkane activation.^{19,20}

This system also allows measurement of the isotope effects in the reductive elimination sequence (i.e., re-

(18) Melander, L. C. S.; Saunders, W. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

(19) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346-7355.

(20) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 1537-1550.



ductive rearrangement and arene dissociation), the reverse of the η^2 -coordination/oxidative rearrangement process. The rate of loss of xylene from the complexes $(C_5Me_5)Rh(PMe_3)(3,5-C_6H_3Me_2)(H \text{ or } D)$ in C_6D_6 gives a measure of the overall isotope effect for this process. Independent rate measurements of the d_0 and d_1 complexes at 51.2 °C give an *inverse* isotope effect of $k_H'/k_D' = 0.51$. This ratio reflects the zero-point energy differences between the ground state (xylyl hydride complex) and transition state for arene dissociation and, therefore, is consistent with a fully formed C–H (or C–D) bond in the transition state.²¹

The experiment described earlier in which equilibration of the isomers of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ with the hydrogen distributed over the hydride, ortho, meta, and para sites provides verification of the inverse isotope effect. 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 (2.7:2:2:1, hydride:ortho:meta:para). Scheme IV shows the individual steps and rate constants for the equilibration. 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 constants for the reductive elimination involving either a Rh–H

(21) Using equation 2.23 from ref 15, p 27, and assuming typical stretching frequencies $\nu_{C-H} = 3000 \text{ cm}^{-1}$, $\nu_{C-D} = 2120 \text{ cm}^{-1}$, $\nu_{M-H} = 2000 \text{ cm}^{-1}$, and $\nu_{M-D} = 1414 \text{ cm}^{-1}$ (all $\pm 15 \text{ cm}^{-1}$), 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.

or Rh–D bond, respectively. Since the measured value of the equilibrium constant K_{eq} for equilibration of the hydride and ortho isomers is equal to the product of the forward and reverse rate constants, and $k_H/k_D = 1.4$ (determined in the experiment involving 1,3,5- $C_6H_3D_3$), the reductive elimination rate constant ratio k_H'/k_D' can be calculated to be 0.52 from 10, in remarkably good agreement with the inverse rate ratio determined from the xylene exchange experiment.

$$K_{eq} = \frac{\text{ortho H}}{\text{hydride H}} = 0.37 = \frac{k_H'/k_D'}{k_D'/k_H} \quad (10)$$

The agreement between these two experiments is really not surprising in light of the mechanism in Scheme VI. Since the portion of the reaction that involves $[(C_5Me_5)Rh(PMe_3)]$, 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 + $[(C_5Me_5)Rh(PMe_3)] \rightarrow \eta^2$ -arene or η^2 -arene \rightarrow arene + $[(C_5Me_5)Rh(PMe_3)]$). Consequently, virtually all of the isotope effects are associated with the interconversion of $(C_5Me_5)Rh(PMe_3)(Ph)H$ and the η^2 -arene complex.

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. One possible mechanism for this scrambling involves hydridic attack upon a rhodium methylene complex formed by a reversible α -elimination in the methyl cation used in the synthesis.¹⁴ 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 oxidative addition to one of the C–H bonds of the coordinated methane. Bergman has provided strong evidence for the presence of an "alkane complex" by examination of rearrangement of $(C_5Me_5)Rh(PMe_3)(^{13}CH_2CH_3)D$ prior to ethane reductive elimination.²²

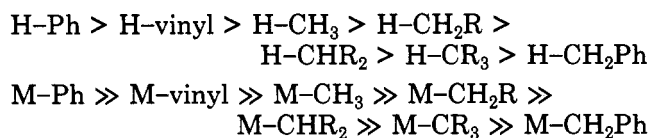
Alkane/Arene Selectivity

As mentioned above, kinetic studies of the arene and alkane elimination reactions permit the calculation of the relative stabilities of the propyl and phenyl hydride complexes. The results indicate that the complex $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ is 8.7 kcal/mol more stable than $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)H$. Notice that if we were to judge the equilibrium based upon only the C–H bond strengths, we would have predicted that propane activation should have been ~ 8 kcal/mol more facile than benzene activation. This reversal of thermodynamic stability can be largely attributed to a much stronger metal–carbon bond for Rh–phenyl compared to Rh–propyl, on the order of 16–17 kcal/mol based upon the thermodynamic data presented here. In other words, *it is the product bond strengths (M–C) that dominate in the determination of the position of the hydrocarbon activation equilibria, not the reactant (C–H) bond strengths.*

This conclusion also accounts for another aspect of C–H bond activation selectivity. With propane, only

(22) Bergman, R. G.; Periana, R. A. *J. Am. Chem. Soc.* 1986, 108, 7332–7346.

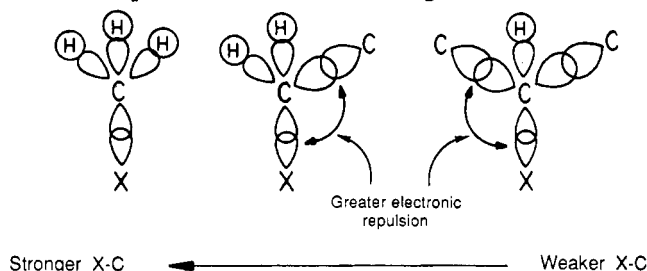
primary C-H bond activation is seen, despite the fact that a weaker (~ 2 kcal/mol) secondary C-H bond is present. This can be accounted for in terms of an even stronger rhodium-*n*-propyl bond compared to a rhodium-isopropyl bond.²³ Similarly, with toluene only aromatic activation is seen even in the presence of the weaker (by >20 kcal/mol) benzylic C-H bond. Again, an extremely weak rhodium-benzyl bond would account for this difference. Both we²⁴ and other workers^{25,26} have noted a general trend in which the stronger C-H bond of methane (104 kcal/mol) is activated in preference to weaker alkane C-H bonds. The strong metal-methyl bond is responsible for this unexpected observation. The general trend among bond strengths that is appearing based upon the recent results with several different metal complexes that are active in C-H bond activation is



Kinetic selectivities are reflected by the thermodynamic selectivities, although to a lesser extent. While some exceptions in the kinetic selectivity have been noted, it is quite general that activation of the stronger C-H bonds is thermodynamically preferred.

One way to account for this trend is in terms of simple steric arguments relating X-C bond strengths. It makes sense, in comparing a series of similar groups X, that the larger X is (i.e., the larger the orbitals on X are), the more spread out a series of X-C bond strengths will be if steric interactions between neighboring groups on X and C are important. As one increases substitution on carbon ($1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$), the series of compounds with a larger X group should display a wider relative range of X-C bond strengths. X = hydrogen, being the least sterically demanding case, should show the most compressed range of bond strengths. With aromatic and vinylic carbon, the substituents (on carbon) are 120° away from the X-C bond and, therefore, are the least sterically demanding of all. Halpern has noted previously the domineering effect of α -substitution on carbon in a homologous series of cobalt-alkyl bond energies.²⁷ The steric effect could involve unfavorable electronic repulsion between the bonding pairs attaching carbon to the α -substituents and the metal-carbon bonding pair, as indicated in the diagram, although repulsive interaction with other lig-

ands bound to the metal cannot be ruled out at this time. While this valence shell electron pair repulsion model is rather simple and ignores important effects such as hybridization upon bond strength, it does provide a simple means of rationalizing the observations.



Concluding Remarks

Several questions arise as a result of these studies. In this system, alkane activation is observed only at low temperatures, while both arene and intramolecular¹³ activation adducts are isolated at room temperature. Extrapolation to other known systems suggests that those that produce aryl hydride products and undergo cyclometalation may exhibit similar chemistry with alkanes at low temperature. Indeed, recent studies with $[\text{Fe}(\text{dmpe})_2]$,²⁸ $[\text{Os}(\text{PMe}_3)_4]$,²⁹ $[\text{PtL}_2]$,³⁰ and $(\text{C}_6\text{H}_6)\text{Os}(\text{CO})_2$ ³¹ indicate that at low temperatures these intermediates all undergo oxidative addition to alkane C-H bonds. It is quite likely that many other metals reversibly add to aliphatic C-H bonds, but that their lability prevents them from being directly observed. In this case, catalytic H/D exchange of the alkane can be a useful way of demonstrating alkane activation.²⁴

Another question that arises concerns the precoordination of arene in an η^2 fashion prior to activation. Is this a general requirement for other metals, or only for the $(\text{C}_5\text{Me}_5)\text{Rh}$ complexes studied in detail here? Parshall had proposed sequential precoordination/oxidative addition equilibria to account for the small range of rate constants observed in the deuteration of various substituted benzenes by Cp_2TaH_3 , $\text{Ir}(\text{PMe}_3)_2\text{H}_5$, and $\text{CpRh}(\text{C}_2\text{H}_4)_2$.³² Werner had postulated the presence of an η^2 -arene species as an intermediate in the conversion of $(\eta^6\text{-C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ to $\text{Os}(\text{PMe}_3)_4(\text{Ph})\text{H}$.³³ Perhaps more significantly, Whitesides has recently published evidence for a similar [1,2] rearrangement in $\text{PtL}_2(\text{C}_6\text{H}_5)\text{D}$ prior to arene elimination.³⁴ In this system the shape of the reaction coordinate for benzene must be similar to that shown in Scheme V. The generality of prior η^2 -arene coordination with other metal complexes remains to be demonstrated.

In comparison, it should be pointed out that olefin C-H bond activation appears not to necessarily occur

(23) It is possible even at the low temperature (-60°C) at which the propane activation experiment was performed that some secondary C-H activation occurred, but that this product is thermally labile at this temperature. We have no evidence to rule out this possibility, although the cyclopentyl hydride complex (which contains Rh-secondary carbon bonds) shows similar stability to the *n*-propyl hydride complex.

(24) Jones, W. D.; Maguire, J. A. *Organometallics* 1986, 5, 590-591.

(25) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* 1982, 104, 3723-3725. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, 105, 7190-7191. (c) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* 1985, 107, 4358-4359. Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* 1986, 108, 4856-4867.

(26) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* 1984, 106, 2214-2216. Watson, P. L. *J. Am. Chem. Soc.* 1983, 105, 6491-6493. Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* 1984, 56, 1-11. Thompson, M. E.; Baxter, S. M.; Bulls, A. Ray; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, 109, 203-219.

(27) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* 1979, 101, 7124-7126. Halpern, J. *Acc. Chem. Res.* 1982, 15, 238-244. Ng, F. T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* 1982, 104, 621-623. Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* 1982, 104, 623-624.

(28) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* 1987, 109, 2825-2826.

(29) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* 1986, 108, 1346-1347. Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* 1986, 108, 7964-7970.

(30) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* 1986, 108, 8094-8095. Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 1449-1462.

(31) Graham, W. A. G. *J. Organomet. Chem.* 1986, 300, 81-91.

(32) Klaubunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* 1972, 94, 9081-9087. Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* 1970, 92, 5234-5233.

(33) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 793-794.

(34) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 1436-1448.

by way of initial π -coordination of the olefin. Evidence with $\text{Re}(\text{PPh}_3)_2\text{H}_7$,³⁵ $\text{CpRe}(\text{PMe}_3)_3$,^{25c,d} and $\text{Fe}(\text{dmpe})_2\text{H}_2$ ³⁶ all indicates that a direct oxidative addition pathway exists in addition to π -coordination. Furthermore, reductive elimination of the vinyl hydride can also lead directly to the π -olefin complex. Consequently, there must be two independent pathways for forming an olefin complex from free olefin and a coordinatively unsaturated metal: (1) direct π -complexation and (2) vinylic oxidative addition followed by intramolecular reductive elimination. It is also interesting to note that the microscopic reverse of this sequence implies that olefin dissociation from the metal also can occur by two pathways, one of which involves intramolecular vinylic activation followed by reductive elimination of free olefin!

Finally, the factors controlling intramolecular activation of the C-H bond of a ligand remains poorly understood in a general sense. It is still not clear why species such as $[\text{Fe}(\text{PMe}_3)_4]$ ³⁷ and $[(\text{C}_5\text{Me}_5)\text{Re}(\text{PMe}_3)_2]$ ^{23c} undergo cyclometalation whereas $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)]$ and $[(\text{C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)]$ do not. It

(35) Faller, J. W.; Felkin, H. *Organometallics* 1985, 4, 1488-1490.

(36) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* 1986, 108, 7433-7434. Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* 1986, 108, 7436-7438.

(37) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* 1977, 110, 2200-2212. Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* 1975, 97, 3272-3273.

is also not clear why $[(\text{C}_5\text{Me}_5)_2\text{W}]$ metalates the C_5Me_5 methyl group³⁸ whereas $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)]$ and $[(\text{C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)]$ do not. It may be that relief of steric compression is the driving force for metalation of the PMe_3 ligand, a force that is not so important in the $[(\text{C}_5\text{Me}_5)\text{M}(\text{PMe}_3)]$ intermediates. The more crowded $[(\text{C}_5\text{Me}_5)\text{Re}(\text{PMe}_3)_2]$ intermediate appears to sit in the middle, with both phosphine metalation and intermolecular hydrocarbon activation in balance. Further elucidation of this important side reaction is warranted.

Acknowledgement is made to the U. S. Department of Energy (DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Alfred P. Sloan and Camille and Henry Dreyfus Foundations for awards.

Registry No. $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_5)\text{H}$, 81971-46-2; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{D}$, 84624-02-2; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_3)\text{H}$, 84624-01-1; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)\text{H}_2$, 84624-03-3; C_6H_6 , 71-43-2; $\text{CH}_3\text{CH}_2\text{CH}_3$, 74-98-6; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)\text{H}$, 84624-04-4; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(p\text{-C}_6\text{H}_4\text{Me})\text{H}$, 81971-48-4; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(m\text{-C}_6\text{H}_4\text{Me})\text{H}$, 81971-47-3; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_3\text{-2-CH}_3\text{-5-CD}_3)\text{H}$, 88704-02-3; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_3\text{-2-CD}_3\text{-5-CD}_3)\text{H}$, 88704-03-4; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_3\text{-2-CH}_3\text{-5-CD}_3)\text{Br}$, 88704-30-7; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{D}_5)\text{H}$, 88704-00-1; *t*-Bu-*p*- C_6H_4 -Bu-*t*, 1012-72-2; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\eta^2\text{-C}_6\text{H}_3\text{-2,5-(Bu-t)}_2)$, 118831-49-5; D_2 , 7782-39-0; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{CH}_3)\text{D}$, 118831-50-8; $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_6\text{H}_3\text{-3,5-Me}_2)\text{H}$, 88704-08-9.

(38) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* 1985, 945-946.

Possible Surface Intermediates in Alkane Reactions on Metallic Catalysts

FRANÇOIS GARIN* and GILBERT MAIRE

Laboratoire de Catalyse et Chimie des Surfaces, UA 423 du CNRS, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg, France

Received September 22, 1987 (Revised Manuscript Received December 19, 1988)

The knowledge of the mechanism of action of most heterogeneous catalysts remains limited. At the most primitive level, the overall product distribution is often known, but the nature of the catalyst-reactant interactions remains unknown. In a few cases, a more detailed proposition of mechanism can be advanced, but these propositions remain modest and ineffective in comparison with mechanistic details that have been developed in molecular organic and organometallic chemistry. It must be recognized, however, that, by

François Garin was born in Saint Germain en Laye, France. He received his "Maîtrise en Chimie Physique" in 1970 and his Doctorat ès Sciences Physiques in 1978 from the University Louis Pasteur in Strasbourg. He is staff member of the CNRS and is interested in the use of surface techniques to investigate more deeply the understanding of catalytic reactions of labeled hydrocarbons performed on supported metallic catalysts.

Gilbert Maire was born in Toulon, France. He received his Doctorat ès Sciences Physiques in 1967 from the University of Caen. After a postdoctoral at Flinders University (Prof. J. R. Anderson), he returned to the University of Caen in 1969 as staff member of the CNRS in collaboration with Prof. F. G. Gault. He joined with F. G. Gault in 1972 the Department of Chemistry at University Louis Pasteur of Strasbourg where he is presently Director of Research (CNRS) and Director of the Laboratory of Catalysis and Surface Science.

comparison with strictly molecular systems, heterogeneous catalysts are intrinsically much more complicated.

Concerning metal catalysis, the making and breaking of C-H and C-C bonds by metal catalysts is a domain where our knowledge appears to be rather good (e.g., hydrogenation of olefins, skeletal rearrangement of hydrocarbons). Although the skeletal rearrangement of hydrocarbons on metals has been known for a long time,^{1,2} the main questions arising are the nature of the intermediate species responsible for the observed kinetics (various mechanisms) and the nature of the sites, correlated, for instance, to particle-size effects.³

A detailed description of the two main classes of reaction mechanisms, cyclic and bond shift, can be made by the use of carbon-13. Metallacyclobutanes, metallacarbenes, and metallacarbynes were proposed as

(1) Anderson, J. R.; Baker, B. G. *Nature (London)* 1960, 187, 937.

(2) Barron, Y.; Maire, G.; Cornet, D.; Muller, J. M.; Gault, F. G. *J. Catal.* 1963, 2, 152.

(3) Bond, G. C. *Surf. Sci.* 1985, 156, 966.